24-28 June 2024, Rome (IT)

Second Symposium for Young Chemists

BOOK OF ABSTRACTS

www.sync2024rome.org

Sapienza
Università di Roma

Endorsements

STVDIVM VRBIS
SAPIENZA
UNIVERSITÀ DI ROMA

ROME
TECHNOPOLE
INNOVATION ECOSYSTEM

Società
Chimica
Italiana

ENEA

SOCIETA ITALIANA
DI AEROSOL
IAS
ITALIAN AEROSOL
SOCIETY

Società
Chimica
Italiana
Gruppo Giovani

aidii
LA CULTURA DELLA PREVENZIONE

UNINDUSTRIA
UNIONE DEGLI INDUSTRIALI E DELLE IMPRESE
ROMA • FROSINONE • LATINA • RIETI • VITERBO

INSTM ®

Consiglio Nazionale
delle Ricerche

INTERREGIONALE - UMBRIA • MOLISE - ROMA - LAZIO • ABRUZZO -
ORDINE
DEI CHIMICI
E DEI FISICI

Sponsors

GOLD SPONSORS

STEROGLASS®

labozeta
la sicurezza nel laboratorio®

SILVER SPONSORS

PerkinElmer®
Science with Purpose

INSTM®

ALFATEST
STRUMENTAZIONE SCIENTIFICA

BRONZE SPONSORS

LS
analytica

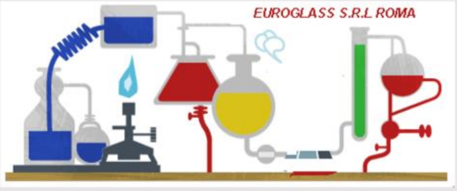


Table of contents

Plenary Lectures 20

Keynote Communications 30

Scientific Committee

Gerardo Palazzo
University of Studi di Bari Aldo Moro,
Italy

Maria Letizia Focarete
Università degli Studi di Bologna,
Italy

Vincenzo Taresco
University of Nottingham,
UK

Luigi Paduano
Università degli studi di Napoli Federico II,
Italy

Stefano Cinti
Università degli studi di Napoli Federico II,
Italy

Camelia Bala
University of Bucharest,
Romania

Viorel Circu
University of Bucharest,
Romania

Luigi Gentile
University of Bari Aldo Moro,
Italy

Cristina Prieto López
Institute of Agrochemistry and Food Technology, Spanish Council for Scientific Research (CSIC),
Spain

Sebastià Puig
Universitat de Girona,
Spain

Marta Fernández-García
Instituto de Ciencia y Tecnología de Polímeros (ICTP), CSIC
Spain

Maria Reis
Universidade Nova de Lisboa,
Portugal

Loris Pietrelli
Scientific Committee – Legambiente,
Italy

Luis Liz-Marzan
CIC biomaGUNE,
Spain

Sergio Moya
CIC biomaGUNE,
Spain

Raffaele Mezzenga
ETH-Zurich,
Switzerland

Juan Jose Nogueira Perez
Universidad Autónoma de Madrid,
Spain

Enrico Bodo
Sapienza University of Rome,
Italy

Marco D'Abramo
Sapienza University of Rome,
Italy

Antonella Cartoni
Sapienza University of Rome,
Italy

Donato Monti
Sapienza University of Rome,
Italy

Federico Marini
Sapienza University of Rome,
Italy

Anna Laura Capriotti
Sapienza University of Rome,
Italy

Giorgio Olivo
Sapienza University of Rome,
Italy

Marianna Villano
Sapienza University of Rome,
Italy

Jeremy Wulff
University of Victoria,
Canada

Andreia F. Sousa
CICECO – Aveiro Institute of Materials,
Portugal

Delia Chillura Martino
University of Palermo,
Italy

Francesca Leonelli
Sapienza University of Rome,
Italy

Isabella Nicotera
University of Calabria,
Italy

Francesca Baldelli Bombelli
Politecnico di Milano,
Italy

Debora Berti
University of Florence,
Italy

Pierandrea Lo Nostro
University of Florence,
Italy

Sergio Murgia
University of Cagliari,
Italy

Thierry Ollevier
Université Laval, Quebec,
Canada

Annemiek ter Heijne
Wageningen University & Research,
Netherlands

Andrea Salis
University of Cagliari,
Italy

Gerardino D'Errico
Università degli studi di Napoli Federico II,
Italy

Mariano Venanzi
University of Rome Tor Vergata,
Italy

Giuseppe Pileio
University of Southampton,
UK

Marco Costantini
Institute of Physical Chemistry – Polish Academy of Sciences,
Poland

Local organizing committee

Luciano Galantini (chair)

Iolanda Francolini (chair)

Marialuisa Astolfi

Matteo Busato

Arcangelo Celeste

Laura Chronopoulou

Chiara Dal Bosco

Alessandra Del Giudice

Fabrizio Di Caprio

Alessandro Franchi

Lorella Gentile

Raffaella Gianferri

Laura Lorini

Giulia Luccisano

Carmela Maria Montone

Camilla Montesano

Piergiorgio Schiavi

Anita Scipioni

Giulia Simonetti

Enrico Taglioni

Alessandro Tofoni

Akiko Tsurumaki

Matteo Tucci (IRSA, CNR)

Fabrizio Vetica

Marco Zeppilli

Rosa Celeste Zumpano

Local advisory board

Plenary Lectures

Point-Of-Care Ultra-Portable Single-Molecule Bioassays for One-Health

Luisa Torsi[1*]

[1]*Università degli Studi di Bari Aldo Moro, Via Orabona 4, 70125 Bari*

*[*luisa.torsi@uniba.it](mailto:luisa.torsi@uniba.it)*

Screening asymptomatic organisms (humans, animals, plants) with a high-diagnostic accuracy using point-of-care-testing (POCT) technologies, though still visionary holds great potential. Convenient surveillance requires easy-to-use, cost-effective, ultra-portable but highly reliable, in-vitro-diagnostic devices that are ready for use wherever they are needed. Currently, there are not yet such devices available on the market, but there are a couple more promising technologies developed at readiness-level 5: the Clustered-Regularly-Interspaced-Short-Palindromic-Repeats (CRISPR) lateral-flow-strip tests and the Single-Molecule-with-a-large-Transistor (SiMoT) bioelectronic palmar devices. They both hold key features delineated by the World-Health-Organization for POCT systems and an occurrence of false-positive and false-negative errors <1-5% resulting in diagnostic-selectivity and sensitivity >95-99%, while limit-of-detections are of few markers. CRISPR-strip is a molecular assay that, can detect down to few copies of DNA/RNA markers in blood while SiMoT immunometric and molecular test can detect down to a single oligonucleotide, protein marker, or pathogens in 0.1mL of blood, saliva, and olive-sap. These technologies can prospectively enable the systematic and reliable surveillance of asymptomatic ones prior to worsening/proliferation of illnesses allowing for timely diagnosis and swift prognosis. This could establish a proactive healthcare ecosystem that results in effective treatments for all living organisms generating diffuse and well-being at efficient costs. [1-5]

References

[1] E. Genco, et al. Adv. Mater. 2023, DOI: 10.1002/adma.202304102
[2] E. Macchia et al. Sci. Adv. 2022, DOI: 10.1126/sciadv.abo0881
[3] E. Macchia et al. Chem. Rev. 2022, DOI: 10.1021/acs.chemrev.1c00290
[4] E. Macchia et al. Adv. Mat. 2023, DOI: 10.1002/adma.202309705
[5] F. Torricelli, et al. Nature Reviews Methods Primers 2021 DOI: 10.1038/s43586-021-00065-8

Engineered protein-nanomaterial composites: versatile tools for biocatalysis, bioelectronics, sensing, imaging, and therapy

Aitziber L. Cortajarena[1,2*]

1Center for Cooperative Research in Biomaterials (CIC biomaGUNE), Basque Research and Technology Alliance (BRTA), Donostia-San Sebastián 20014, Spain

2Ikerbasque, Basque Foundation for Science, 48009 Bilbao, Spain.

*alcortajarena@cicbiomagune.es

Inspired by nature, we explore biomolecules and their derivatives as novel biomedical and technological tools. Among biomolecules, proteins rise huge interest due to their high structural and functional versatility, biocompatibility, and biodegradability. In particular, we mainly focus on a class of engineered repeat proteins, due to their stability and robustness as a base scaffold that can be easily tailored to endow desired functions to the protein and to encode defined supramolecular assembly properties. For example, the introduction of metal-binding residues (e.g., histidines, cysteines) drives the coordination of metal ions and the subsequent formation of tailored nanomaterials, with luminescence, magnetic, or catalytic properties.[1,2] Additionally, new binding capabilities can be encoded within the CTPR unit or this can be conjugated with other peptides/proteins.[2] These properties allow the development of protein-nanomaterial composites.[3,4] Generally, the fusion of two distinct materials exploits the best properties of each, however, in protein-nanomaterial composites, the fusion takes on a new dimension as new properties arise.

These composites have ushered the use of protein-based nanomaterials as biopharmaceuticals beyond their original therapeutic scope and paved the way for their use as theranostic agents, as demonstrated in our pioneering in vitro and in vivo examples.[3,4] In addition, these protein hybrids can be also implemented in technological applications, towards protein-based biocatalytic and bioelectronic materials. [5]

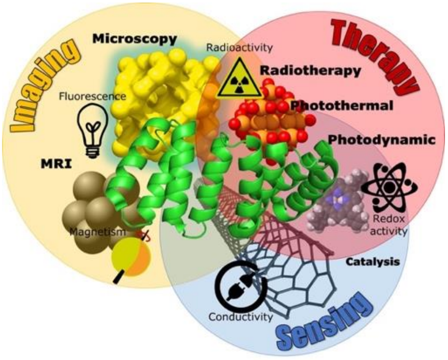


Figure 1. Scheme of engineered protein-based composites and potential applications.

References

[1] Z. Yang, H. Gu, D. Fu, P. Gao, J. K. Lam and B. Xu, Adv. Mater. 16 (2004) 1440.
[2] C. Muller, A. Ontani, A. Bigo--Simon, P. Schaaf, L. Jierry, Adv. Colloid Interf. Sci. 304 (2022) 102660.
[3] J. Rodon Fores, M. Criado-Gonzalez, A. Chaumont, A. Carvalho, C. Blanck, M. Schmutz, C.A. Serra, F. Boulmedais, P. Schaaf, L. Jierry, Angew. Chem. Int. Ed. 58 (2019) 18817.
[4] J. Rodon Fores, M. Criado-Gonzalez, A. Chaumont, A. Carvalho, C. Blanck, M. Schmutz, F. Boulmedais, P. Schaaf, L. Jierry, Angew. Chem. Int. Ed. 59 (2020) 14558.
[5] J.-Y. Runser, M. Criado-Gonzalez, F. Fneich, M. Rabineau, P. Weiss, B. Senger, L. Jierry, P. Schaaf, J. Colloid Interf. Sci. 620 (2022), 234.
[6] J.-Y. Runser, F. Fneich, B. Senger, P. Weiss, L. Jierry, P. Schaaf, J. Colloid Interf. Sci. 633 (2023), 876.

Quantitative and qualitative comparison of field-based analytical technologies for petroleum hydrocarbons determination in soils

Frederic Coulon[1*]

[1]*Cranfield University, School of Water, Energy and Environment, Cranfield, MK43 0AL, UK*

**f.coulon@cranfield.ac.uk*

Over the past decade, a range of commercial and R&D field-based analytical technologies have been made available for soil analysis. This has allowed the determination of hydrocarbons (HCs) in soil to be expedited, increase the number of samples that can be processed at lower cost and enhance spatial resolution of soil data at impacted sites. There are to date, however, aspects that have not been fully studied, such as the performance and accuracy of analytical field technologies for different soil types, levels of contamination and fuel type contamination. In this study, the performance of seven field-based analytical technologies were evaluated for a range of gasoline and diesel spiked soils and contaminated soils from field sites. Performance of the field technologies were compared to an established reference gas chromatography coupled to mass spectrometry (GC-MS) method (spiked soils) and accredited commercial laboratory analysis (real soils).

The field-based technologies included 3 portable solvent-based technologies (one portable GC-MS, one portable nondispersive infrared (NDIR) spectrophotometer, one portable ultraviolet fluorescence (UVF) spectrometer), and 4 handheld solvent free technologies (one handheld visible and near-infrared reflectance (vis-NIR) spectrometer, two handheld Fourier-transform infra-red (FTIR) spectrometers, and one handheld photoionization detector (PID)) were evaluated. Three soils (sandy loam, silty clay loam, and clay loam) were spiked with gasoline or diesel fuel on w/w basis to achieve 100, 1000 and 10,000 mg/kg spike levels. All samples were analysed for Total Petroleum Hydrocarbons (TPH), Volatile Organic Compounds (VOCs), Gasoline Range organic (GRO) and Diesel Range organic (DRO) and speciated HC compounds when the chosen technology allowed to do so. All solvent-based field technologies performed well independently of soil types with RSD values within 15% and bias within 30% for all spiked soils with gasoline and diesel. They can provide GC comparable TPH recoveries and meet the performance requirements for regulatory standards. Further to this, the UFV field technology was able to provide simultaneously determination for total BTEX, GRO C5-C9, DRO C10-C40, TPH C5-C40, and total aromatics C10-C35 within roughly 5 min. This offers time saving for individual soil sample analysis compared to GC-MS methods. In contrast, solvent free, non-invasive technologies showed higher variability and lower accuracy for the low-level diesel spikes (100 mg/kg) and when the levels of soil organic carbon or clay content were high. The IR technologies can however be useful to classify accurately field samples into low, medium, and high concentrations applying a threshold of 1000 mg kg^{-1}. For TPH determination below 500 mg kg^{-1} an alternative technology should be then considered. Overall, this study is the first overview and comparison of multiple field-based analytical technologies along with bench marking to established laboratory methods and provides guidance to practioners on the selection and use of these technologies for petroleum hydrocarbons determination in soils.

Synergies between Chemistry and Nanotechnology: possible solutions to impossible challenges

Maurizio Prato[1,2*]

[1]Department of Chemical and Pharmaceutical Sciences, University of Trieste, Italy
[2]CIC BiomaGUNE, San Sebastián, Spain

**prato@units.it, mprato@cicbiomagune.es*

How strange it is to completely ignore all the restrictions we experienced during the pandemic! It now feels as though those years never existed! However, if the situation has returned to normal, we owe it to the vaccines that were rapidly developed using highly innovative technologies. In fact, especially over the last few decades, science has accustomed us to the rapid resolution of even complex problems, such as the broad diffusion of COVID-19. Solving particularly difficult problems requires considerable efforts from the scientific community, employing multidisciplinary approaches and modern tools—the result of years of research and development. However, problems are not always solved, and some are not always solvable by science. Think of wars, world hunger, human rights, and poverty. Yet, certain issues, particularly those concerning health and the environment, can and must be addressed and solved by scientific research. During this talk, we will discuss how Chemistry can play a fundamental role in our society. In particular, we will describe an original approach to the treatment of nerve injury repair. We have used carbon nanotubes in combination with moldable polymers in order to reconnect interrupted nerves. Although our research has not yet led to a solution, it has opened up interesting new horizons on possible solutions. We will also discuss energy. The exploitation of fossil fuels has caused significant damage to our planet, and these resources are not infinite. Already, there are attempts to address the problem of energy supply with alternative sources, such as photovoltaics. One promising alternative is the production of hydrogen from water, a process known as water splitting. However, this process is currently very expensive in terms of production costs. To tackle this challenge, we have developed a new catalytic system based on the combination of perylene bisimides and polyoxometalates. These components are arranged in a hierarchical supramolecular assembly driven by electrostatic forces, offering new opportunities for the biomimetic splitting of water.

Acknowledgments

Part of the work described in this talk is financially supported by the European Commission - Horizon Europe through the EIC Pathfinder OPEN 2022 project: PLANKT-ON / 101099192.

Light-driven processes in biology: what we can learn from an atomistic modeling

Benedetta Mennucci[1*]

[1]*Department of Chemistry, University of Pisa, via G. Moruzzi 13, 56126 Pisa, Italy*

**benedetta.mennucci@unipi.it, Web:molecolab.dcci.unipi.it*

Organisms of very different life domains possess the capability to detect, utilize, and react to light thanks to specific light-sensitive proteins. While the molecular strategies employed are varied, the most common starting event is an electronic excitation occurring within a chromophoric unit that is embedded in the protein. This initial excitation propagates through space, transforming into different energy forms, and ultimately contributes to the organism's biological function. The entire process encompasses a broad spectrum of spatial and temporal scales: starting from the ultrafast electronic processes at the subnanoscale level within the chromophoric unit and culminating in large conformational changes of the protein that occur over microseconds to milliseconds.

The theoretical investigation of this cascade of processes at an atomistic level necessitates the development of models and computational approaches capable of capturing dynamics across these diverse scales. Achieving this is a formidable challenge, as the interactions and dynamics at each scale are governed by distinct principles, ranging from quantum laws at the smallest scales to classical mechanics at larger scales. An effective strategy is to couple quantum chemistry and classical models and integrate the resulting multiscale approach into molecular dynamics.

Here, we provide an overview of this strategy and its application to specific light-driven processes, while also addressing the challenges that must be overcome to enhance its efficacy and scalability for more complex and larger systems.

Enzyme-Assisted Self-Assembly of Peptide Nanofibers: From Nanostructure Resolution to Supramolecular Hydrogel Applications

Loïc Jierry[1,2]*

[1]*Institut Charles Sadron (UPR22-CNRS), Strasbourg, France*
[2]*Ecole Européenne de Chimie Polymère et Matériaux, Université de Strasbourg, France*

**ljierry@unistra.fr*

Nature controls many biological mechanisms through localized self-assembly processes. Cellular adhesion is, for example, initiated by focal adhesions which result in the formation of actin fibers that play an essential role in cell motility. Yet, developing localized molecular self-assembly processes leading to the growth of nanostructures exclusively near a surface, or at an interface, and with a precise control over its structure and resulting properties is not an easy task. In 2004, a new way to initiate the self-assembly of low molecular weight hydrogelators (LMWH) has been reported: an enzyme is used as a trigger able to transform a precursor compound into an efficient LMWH.[1] In the last seven years, we have spatially localized different enzymes on various kind of materials to control the self-assembly process in a spatiotemporal way (Fig. 1a and 1b).[2] Based on this approach, we have designed original flow reactors allowing the production of enantiopure chemicals using a catalytically-active hydrogel supported on polymer foams.[3] Supramolecular hydrogel able to self-sustain its own growth through an autocatalytic way was demonstrated as well.[4] In addition, this presentation will also focus on our recent developments about the near-atomic nanostructure resolution of a tripeptide and the impact of the peptide self-assembly in host enzyme-embedded materials (Fig. 1c).[5,7]

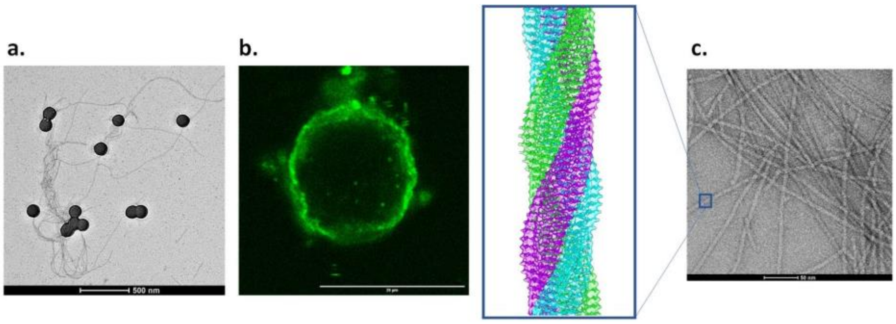


Figure 1: (a) TEM image of self-assembled peptides nanofibers grew from enzyme-coated silica nanoparticles; (b) Confocal laser scanning microscopy image of a unilamellar vesicle modified with a phosphatase in presence of both a phosphorylated peptide hydrogelator and Thioflavine T (Scale bar = 20 µm); (c) Peptide assembly resolved from cryo-TEM images reconstruction.

References

[1] Z. Yang, H. Gu, D. Fu, P. Gao, J. K. Lam and B. Xu, Adv. Mater. 16 (2004) 1440
[2] C. Muller, A. Ontani, A. Bigo--Simon, P. Schaaf, L. Jierry, Adv. Colloid Interf. Sci. 304 (2022) 102660.
[3] J. Rodon Fores, M. Criado-Gonzalez, A. Chaumont, A. Carvalho, C. Blanck, M. Schmutz, C.A. Serra, F. Boulmedais, P. Schaaf, L. Jierry, Angew. Chem. Int. Ed. 58 (2019) 18817.
[4] J. Rodon Fores, M. Criado-Gonzalez, A. Chaumont, A. Carvalho, C. Blanck, M. Schmutz, F. Boulmedais, P. Schaaf, L. Jierry, Angew. Chem. Int. Ed. 59 (2020) 14558.
[5] J.-Y. Runser, M. Criado-Gonzalez, F. Fneich, M. Rabineau, P. Weiss, B. Senger, L. Jierry, P. Schaaf, J. Colloid Interf. Sci. 620 (2022), 234.
[6] J.-Y. Runser, F. Fneich, B. Senger, P. Weiss, L. Jierry, P. Schaaf, J. Colloid Interf. Sci. 633 (2023), 876.

Clean and Green - new approaches to the polymers society needs

Steve M. Howdle[1*]

[1]*School of Chemistry, University of Nottingham, United Kingdom*

**steve.howdle@nottingham.ac.uk*

We will report on the development of new monomers and polymers derived from renewable resources. We have utilized a number of different sources to create a wide range of monomers and polymers. These sources include terpenes, sorbitol, lactide, ε-caprolactone and fatty acids that are derived directly from nature, including from tree bark and oils from waste seeds.

Our group has developed significant expertise in utilizing supercritical carbon dioxide (scCO2). In particular, we have exploited the low viscosity and high diffusivity of scCO2 to create a highly efficient and reversible plasticizer. This in-situ plasticization allows us to perform polymerisation reactions at temperatures as low as 40°C; much lower than is possible under conventional operating conditions which has opened up the opportunity to use enzymatic catalysts to yield new polymeric materials from renewable monomers. We will also demonstrate new applications and opportunities in 3-D printing.

Data does NOT speak for itself: why it is important to communicate science

Matteo Capone[1]*, Chiara Biagini[1]*

[1] *Divulgatori scientifici di Il Chimico sulla Tavola*

**ilchimicosullatavola@gmail.com, web: https://www.ilchimicosullatavola.it*

A 2021 European survey showed that, when it comes to science, 45% of Europeans and 60% of Italians agree with the phrase “Science is so complicated that I don't understand anything about it”. Of course, not everyone needs to become a science expert. Yet, having a basic understanding of science - the so-called “scientific literacy” - is essential for everyone to take informed positions about small and big matters alike: from which bottle of wine to buy at the supermarket, to which energy sources our Country should use.

As people who deal with science every day, we have a role in this, and we can use our experience to support people around us to approach the most complex aspects of science. Because data doesn’t speak for itself, but with the right spokesperson they can be explained to everyone: from children, to our families, to a larger audience of a festival - we just need the right strategies and instruments. And, maybe, we could find out that the same strategies that help us explain climate change to our grandmother can help us also present our paper to a scientific congress.

Bio:

“Il Chimico sulla Tavola” is a scientific dissemination duo founded by Dr. Matteo Capone and Dr. Chiara Biagini. Matteo, PhD in Mathematical Models at Università degli Studi dell’Aquila, is a research fellow in computational biochemistry at the CNR-NANO institute of Modena; Chiara, PhD in Organic Chemistry at Sapienza University of Roma, has a specialization in communication and works in corporate sustainability.

Communicate wisely: a guide for combating “washing” practices in science

Sharon Spizzichino[1]*, Carlotta Micaela Jarach[1]*, Shirley Genah[1]*

[1]*Divulgatori scientifici di Mada Advances*

**madaadvances@gmail.com, web: https://www.madaadvances.com*

In scientific and chemical fields, where information has the power to shape politics, public health, and environmental outcomes, effective communication is crucial. However, the rise of "washing" tactics, prevalent on social media and in marketing, poses a significant threat to the integrity of scientific dialogue. Greenwashing, in particular — the misleading portrayal of a company's environmental practices by promoting baseless claims of sustainability — can lead to environmental degradation and reputational damage, promoting distrust within the community and conspiratorial attitudes towards science.

What can we do as scientists to prevent it? Recognizing greenwashing and promoting accurate communication should be the first steps to drive positive change in society. This presentation will examine cases of greenwashing and explore ethical communication strategies that go beyond mere profit-driven promotion, fostering genuine sustainability.

Bio:

Mada Advances is a scientific communication project started in 2020 by a group of young researchers with the shared goal of disseminating and explaining the latest advancements in the scientific field to a broad audience. Currently, Mada Advances is managed by Sharon Spizzichino, Carlotta Jarach, Shirley Genah, and Nicole Pavoncello.

Shirley Genah, PhD, is a molecular biologist and scientific communicator for Mada Advances. She currently holds a position as an AIRC post-doctoral researcher at Bambino Gesù Children′s Hospital in Rome.

Sharon Spizzichino, PhD, is a structural biologist, biochemist, and scientific communicator for Mada Advances. She is currently a post-doctoral researcher at the Sapienza University of Rome.

Carlotta Micaela Jarach, PhD Candidate, is a biostatistician, epidemiologist, and scientific communicator for Mada Advances. She currently holds a position as a researcher at Mario Negri Institute for Pharmaceutical Research in Milan.

Nicole Pavoncello, PhD candidate, is a neurobiologist and communicator for Mada Advances. She currently holds a position as a doctoral researcher at Technion Institute in Haifa.

Keynote Communications

Flow Chemistry as Enabling Technology in Organic Chemistry

Dr. Jesus Sanjosé-Orduna[1]*, Prof. Timothy Noël[1]

[1]Flow Chemistry Group, Van't Hoff Institute for Molecular Sciences (HIMS), University of Amsterdam.
Science Park 904, 1098 XH, Amsterdam (The Netherlands)

**j.sanjoseorduna@uva.nl*

Flow chemistry has emerged as a transformative tool in the realm of organic chemistry. Compared to conventional batch processing, often carried out in round-bottom flasks, it offers several advantages. These include enhanced mass and heat transfer, improved safety, increased reaction efficiency, reduced waste, better scalability, and improved reproducibility offering unprecedented advantages for reaction control, efficiency, and scalability.[1] These benefits have led to the increasing adoption of flow chemistry in academia and various industries for pharmaceuticals, fine chemicals, and materials science.

On one side, flow photochemistry has witnessed remarkable growth in recent years, enabling precise control of photon irradiation and reaction kinetics. This results in higher yields and selectivity compared to traditional batch processes, allowing to explore previously inaccessible photochemical transformations.[2]

Moreover, flow chemistry has enabled the incorporation of gaseous reagents into the organic chemist synthetic toolbox.[3] By harnessing the advantages of gas-liquid interactions within microreactors, reactions involving hazardous or volatile gases can be conducted safely and with superior efficiency, opening the doors to the synthesis of challenging molecules that were previously deemed impractical or hazardous.

Furthermore, automation is a cornerstone of modern flow chemistry, offering a paradigm shift in experimental design and execution.[4] The seamless integration of robotic platforms and advanced control systems has led to increased productivity and reproducibility. Researchers can now perform a wide range of reactions with unparalleled precision, freeing up valuable human resources for creative problem-solving and innovation.

The following presentation will underscore the different benefits of applying flow chemistry in organic synthesis, particularly in the domains of photochemistry,[5a] use of gaseous reagents[5b] and in the digitalization and automation of chemistry.[5c]

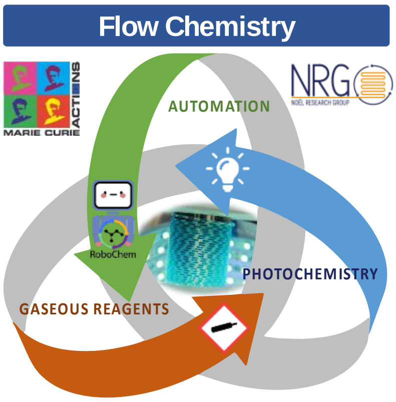


Figure 1. Application of continuous-flow technologies for organic synthesis

References

[1] Buglioni, L.; Raymenants, F.; Slattery, A.; Zondag, S. D. A.; Noël, T. *Chem. Rev*. 2022, **122**, 2752.
[2] Rehm, T. H. *Chem. Eur. J.* 2020, **26**, 16952
[3] Pulcinella, A.; Mazzarella, D.; Noël, T. *Chem. Commun*. 2021, **57**, 996
[4] Hardwick, T.; Ahmed, N. *Chem. Sci.* 2020, 11, 11973.
[5] (a) Sanjosé-Orduna, J.; Silva, R. C.; Raymenants, F.; Reus, B.; Thaens, J.; de Oliveira, K. T.; Noël, T. *Chem. Sci*. 2022, **13**, 12527. (b) Raymenants, F.; Masson, T.; Sanjosé-Orduna, J.; Noël, T. *Angew. Chem. Int. Ed.* 2023, **62**, e202308563. (c) Slattery, A.; Wen, Z.; Tenblad, P.; Sanjosé-Orduna, J.; Pintossi, D.; den Hartog, T.; Noël, T. *Science* 2024, **383**, eadj1817

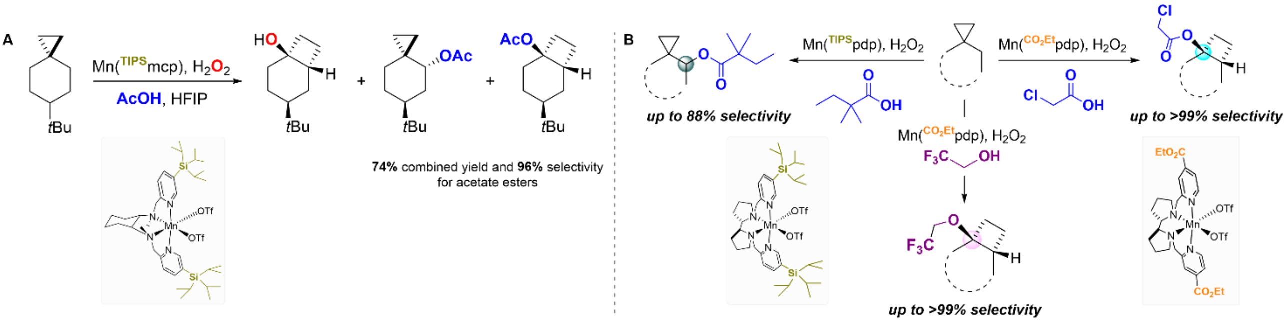
Catalyst and Medium Control Over Rebound Pathways in Manganese-Catalyzed Methylenic C-H Oxidation

Marco Galeotti[1*], Massimo Bietti[2], Miquel Costas[1]

[1] *QBIS Research Group, Institut de Química Computacional i Catàlisi (IQCC) and Departament de Química, Universitat de Girona, Campus Montilivi, Girona E-17071, Catalonia, Spain*
[2] *Dipartimento di Scienze e Tecnologie Chimiche, Università "Tor Vergata", Via della Ricerca Scientifica, 1 I-00133 Rome, Italy.*

**marcogaleotti94@gmail.com*

The ubiquity of oxidized aliphatic frameworks in molecules of biological and pharmaceutical interest makes the conversion of C(sp^3)-H into C(sp^3)-O bonds a preferential modification in modern synthetic organic chemistry.[1] Among the numerous methodologies, C-H bond oxygenation executed by enzymes and bioinspired catalysts represents an efficient way to perform these transformations and proceeds through a well-established HAT/OH rebound radical mechanism.[2] C-H functionalization products derived from competitive ligand transfer pathways are seldom observed and when they operate, the canonical hydroxylation reaction typically prevails.[3] Very recently, we have carried out a detailed mechanistic study on the oxidation of 6-tert-butylspiro[2.5]octane with hydrogen peroxide catalyzed by manganese catalysts. By using AcOH as co-ligand and HFIP as the solvent, high yield and outstanding selectivities for the formation of acetate esters were observed, pointing toward carboxylate transfer as the main rebound pathway (**Scheme 1A**).[4] Taking 6-*tert*-butylspiro[2.5]octane as reference substrate, a new set of unrearranged and rearranged functionalized products has been obtained, by carefully modulating catalyst electronics and reaction conditions (fluorinated alcohol solvent and carboxylic acid co-ligand), with unprecedented control over chemoselectivity (**Scheme 1B**).[5] The scope of the reaction has been then extended to other cyclopropyl derivatives. The results obtained through this study will be discussed.



Scheme 1. Control over rebound pathways in aliphatic C-H oxidation.

References

[1] Chambers, R. K., Weaver, J. D., Kim, J., Hoar, J. L., Krska, S. W., White, M. C. *Proc. Natl. Acad. Sci. U.S.A.* 2023, **120**, e2300315120.
[2] Guo, M., Corona, T., Ray, K., Nam, W. *ACS Cent. Sci.* 2019, **5**, 13-28.
[3] Ottenbacher, R. V., Bryliakova, A. A., Shashkov, M. V., Talsi, E. P., Bryliakov, K. P. *ACS Catal.* 2021, **11**, 5517-5524.
[4] Galeotti, M., Vicens, L., Salamone, M., Costas, M., Bietti, M. *J. Am. Chem. Soc.* 2022, **144**, 7391-7401.
[5] Galeotti, M., Bietti, M., Costas, M. *J. Am. Chem. Soc.* 2024, **146**, 8904-8914.

Epoxide and Isocyanate Free Synthesis of Polyurethane Foam from Glycerol and CO_2

Young In Jo[1*], Jun Ho Jang[1], Geun Woong Ryoo[1], Min Sang Kwon[1], Ki Tae Nam[1]

[1]*Department of Materials Science and Engineering, Seoul National University, Seoul, Republic of Korea*

**yicho98@snu.ac.kr*

Utilizing carbon dioxide as a foundational element in polymer production represents an innovative approach towards carbon sequestration and reducing dependence on fossil fuel-derived chemicals. Among the various options, non-isocyanate polyurethane (NIPU) emerges as a promising polymer derived from CO_2, poised to replace traditional isocyanate-based polyurethanes. Enhancing the sustainability of NIPU synthesis involves leveraging biomass-derived materials, with glycerol as a desirable candidate due to its surplus from bio-diesel production.

The surplus of glycerol, resulting from the increasing production of bio-diesel, far surpasses current demand, necessitating the exploration of new industrial applications. Our study explores a novel synthesis route for glycerol and CO_2-based NIPU, aiming to replace the conventional method involving glycerol-derived epoxide and gaseous CO_2 with a process utilizing glycerol-derived halohydrin and captured CO_2.

Recent research has demonstrated the synthesis of cyclic carbonate esters by reacting organic bicarbonate with halohydrins.[1] Our group has further shown that cyclic carbonate esters can be produced from simple inorganic bicarbonates, such as sodium bicarbonate and halohydrins.[2] This approach capitalizes on captured CO_2 in bicarbonate form, eliminating the energy-intensive release process required for gaseous CO_2.

Our study proposes a novel synthesis strategy for flexible NIPU foam utilizing glycerol and captured CO_2. This involves the synthesis of brominated cyclic carbonate ester by reacting activated di-brominated glycerol with captured CO_2, specifically sodium bicarbonate. Subsequently, flexible NIPU foam is synthesized through a multi-cyclic carbonate ester reaction, obtained via selective substitution reactions with multi-thiol, diamine, and water. The resulting NIPU foam exhibits excellent compressibility and resilience comparable to commercial polyurethane foam. Our strategy presents a new avenue for CO_2 utilization in polymer synthesis without needing epoxides by utilizing captured CO_2. This approach can be extended to synthesizing NIPU based on biomass-derived sugar alcohols, offering a promising pathway towards sustainable polymer production.

Acknowledgements: This work was supported by the National Research Foundation of Korea(NRF) grant funded by the Korea government(MSIT) (No. RS-2023-00259920)

References

[1] Marcileia Zanatta, Eduardo Garcia-Verdugo, Victor Sans, *ACS Sustainable Chem. Eng.*, 2023, **11**, 9613

[2] Jun Ho Jang, Changsoo Kim, Onkar S. Naya, Jia Bin Yeo, Gyu Ri Kim, Jinju Kim, Young In Jo, Ung Lee, Ming Sang Kwon, Ki Tae Nam, *Nature Synthesis*, 2024, **Accepted.**

Glycerol-based Sustainably Sourced Resin for Volumetric Printing

Vincenzo Taresco[1*]

[1]*School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD*

**vincenzo.taresco@nottingham.ac.uk*

Volumetric Additive Manufacturing (VAM) represents a revolutionary advancement in the field of Additive Manufacturing, as it allows for the creation of objects in a single, cohesive process, rather than in a layer-by-layer approach. This innovative technique offers unparalleled design freedom and significantly reduces printing times. A current limitation of VAM is the availability of suitable resins with the required photoreactive chemistry and from sustainable sources. To support the application of this technology, we have developed a sustainable resin based on polyglycerol, a bioderived (e.g., vegetable origin), colourless, and easily functionisable oligomer produced from glycerol.[1] To transform polyglycerol-6 into an acrylate photo-printable resin we adopted a simple, one-step, and scalable synthesis route. Polyglycerol-6-acrylate (Figure 1) fulfils all the necessary criteria for volumetric printing (transparency, photo-reactivity, viscosity) and was successfully used to print a variety of models with intricate geometries and good resolution. The waste resin was found to be reusable with minimal performance issues, improving resin utilisation and minimising waste material. Furthermore, by incorporating dopants such as poly(glycerol) adipate acrylate (PGA-A) and 10,12-pentacosadyinoic acid (PCDA), we demonstrated the ability to print objects with a diverse range of functionalities, including temperature sensing probes and a polyester excipient, highlighting the potential applications of these new resins.

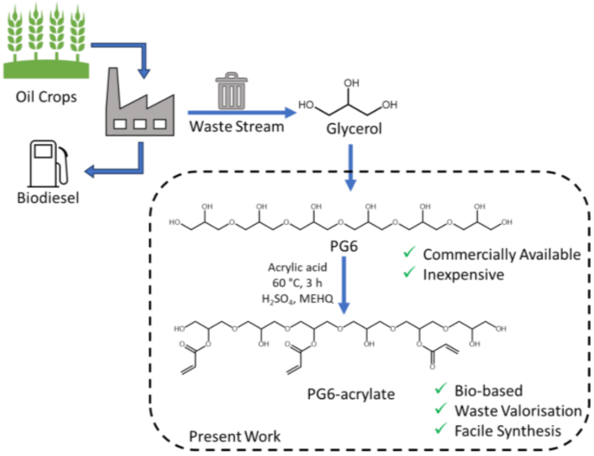


Figure 1. Synthesis route towards PG6-acrylate.

References

[1] E. Krumins, Joachim C. Lentz, B. Sutcliffe, A. Sohaib, P.L. Jacob, B. Brugnoli, V. Cuzzucoli Crucitti, R. Cavanagh, R. Owen, C. Moloney, L. Ruiz-Cantu, I. Francolini, S.M. Howdle, M. Shusteff, F. R.A. J. Rose, R.D. Wildman, Y. He and V. Taresco, *Green Chem.*, 2024, **26**, 1345-1355.

Liposomes for the delivery of antimicrobial peptides (AMPs)

Beatrice Simonis[1*], Federica Toma[2], Antonia Volpe[2], Barbara Salierno[2], Fabiana Pandolfi[1], Damiano Squitieri[4], Stefano Borocci[1,3], Francesca Ceccacci[1], Simona Sennato[6], Federica Massaro[3], Fernando Porcelli[3], Francesco Buonocore[3], Maura Di Vito[4], Maurizio Sanguinetti[4,5], Francesca Bugli[4,5], Cecilia Bombelli[1]

[1]CNR-Institute for Biological Systems (ISB), Secondary Office of Rome-Reaction Mechanisms c/o Department of Chemistry, Sapienza University, P. le A. Moro 5, Rome, 00185, Italy
[2]Department of Chemistry, Sapienza, University of Rome, P. le A. Moro 5, Rome, 00185, Italy Italy
[3]Department for Innovation in Biological, Agrofood and Forest Systems, University of Tuscia, Viterbo, 01100, Italy
[4]Department of Basic Biotechnology Sciences, Clinical Intensivology and Perioperative, UCSC, Rome, 00168, Italy
[5]Department of Laboratory and Infectious Sciences, Fondazione Policlinico Universitario A, Gemelli IRCCS, Rome, 00168, Italy
[6]CNR-Institute for Complex Systems (ISC) c/o Department of Physics, Sapienza, University of Rome, 00185, Italy

**beatrice.simonis@cnr.it*

The emergence of multi drug resistance (MDR) has caused conventional antibiotics to be ineffective, requiring the development of new drugs to address the issue. In this context, antimicrobial peptides (AMPs) are among the most promising biomolecules to fight MDR pathogens and biofilm-associated infections. However, their use is still limited by low cell permeability and oral bioavailability, limited stability, and some toxicity. Therefore, the inclusion of AMPs in liposomes could protect them from degradation, increasing their bioavailability and reducing their toxicity. In this work, we developed liposome formulations for the inclusion of two AMPs (2-Myr and 3a-Pep) derived from a natural antimicrobial peptide Chionodracin isolated from an Antarctic fish. [1] The antimicrobial activity of these AMPs against ESKAPE pathogenic bacteria and different *Candida* species had already been demonstrated [2,3]. With the final aim of achieving suitable AMP-loaded liposomes, the lipid/AMP molar ratio were modulated, and different preparation protocols were investigated. For all formulations colloidal stability over time in terms of size, PDI and ζ potential was evaluated by Dynamic Light Scattering and electrophoretic mobility measurements, while the morphological characterization was carried out by Transmission Electron Microscopy. The peptide entrapment efficacy (EE%) inside liposomes was evaluated by UV-vis spectroscopy measurements and the secondary structure of AMP included in the liposome bilayer was investigated by Circular Dichroism experiments. The cytotoxic effect of the formulations was investigated *in vitro* on a primary line of human fibroblasts and *in vivo* on *Galleria mellonella* larvae. The antimicrobial activity was evaluated on two *Candida* strains: *C. albicans* and *C. tropicalis* and two strains of the pathogen *Acinetobacter baumannii*, while Live and Death assay was carried out to assess the antibiofilm activity.

Acknowledgements:
This work was supported by the project "One Health Basic and Translation Research Actions addressing unmet Needs on Emerging Infectious Diseases, INF-ACT" NRRP Next Generation EU project (Project code PE00000007) and by PRIN project 2022 "Fish-inspired antimicrobial peptide delivered by specific nanosystems to fight ESKAPE bacteria: a powerful weapon against antibiotic resistance" -FIDEANT (project n. 2022FKLKSY) funded by the European Union – Next Generation EU.

References

[1] Buonocore, F., et al. *Fish & Shellfish Immunol.*, 2012, **33**, 1183–1191.
[2] Olivieri, C., et al. *RSC Advances*, 2018, **8**, 41331-41346
[3] Bugli, F., et al.. *Int.J Mol. Sci*, 2022, **23**, 2164.

The sequential relaxations of poly(L-lactide) from glass to crystal

Valerio Di Lisio[1*], Lorenzo Augusto Rocchi[2], Elisa Sturabotti[3], Andrea Martinelli[2], Daniele Cangialosi[1,4]

[1] Donostia International Physics Center, Paseo M. Lardizabal 4, 20018 San Sebastian, Spain
[2] Department of Chemistry, Sapienza University of Rome, P.le aldo Moro 5, 00185 Rome, Italy
[3] CIC biomaGUNE, Paseo Miramòn 194, 20014 San Sebastian, Spain
[4] Materials Physics Center, Paseo M. Lardizabal 5, 20018 San Sebastian, Spain
**valerio.dilisio@dipc.org*

The reorganization of polymer disordered phases into crystals is a multifaceted phenomenon, characterized by dramatic thermodynamic and dynamic property changes, that profoundly impact the applicability and processing strategies of polymers across various technological fields [1]. For instance, poly(L-lactide), PLLA, is a valuable bio-based alternative to fossil fuels derived plastics, thanks to its toughness, transparency, degradability, and biocompatibility. To endow PLLA with new and/or enhanced physical properties, a precise control over nuclei formation and crystal phases must be taken in consideration. Many strategies can be pursued to this aim, including the thermal treatment of PLLA amorphous phase prior to the crystallization [2]. Indeed, an extensive understanding about transformations of polymeric amorphous phases is crucial to widen the application spectrum of materials and, so, facilitating the transition to sustainable polymers.

In this study, new insights into the transformation kinetics of the amorphous phase of PLLA to crystals are presented. Quenched PLLA (rapidly cooled from the melt to avoid nucleation) is isothermally treated over a wide temperature interval (55-105 °C), comprising the glassy phase and the supercooled liquid. The thermal properties and the conformational behaviour are investigated combining Fast Scanning Calorimetry and Time Resolved Infrared Spectroscopy. Surprisingly, among the physical aging of the glass and the nucleation process, a significant additional event has been uncovered, involving the relaxation of the liquid state [3] that loses enthalpy up to 0.6 J g^{-1}. The nucleation process takes place as soon as the liquid ends its transformation. Infrared analysis allowed to associate the liquid relaxation to a localized conformational rearrangement of PLLA disordered chains, without provoking the formation of long-range ordered structures (10_3 helices), which are the building blocks of the crystal phase. Kinetically speaking, a clear sequential path of relaxation mechanisms emerges, introducing for the first time the liquid rearrangement as a trigger of the nuclei development. The sequence comprises, in order, the physical aging of the glass up to reach the supercooled liquid, the conformational rearrangement of the liquid, nucleation, crystallization. The rearrangement of liquid phases in crystallizable polymers, overlooked in the state of the art, uncovers new tools for understanding and controlling polymer nucleation processes.

References

[1] Zheng Y., Pan P., *Progress in Polymer Science*, 2020, **109**, 101291.
[2] Simmons H., Tiwary P., Colwell, J.E., Kontopoulou, M., *Polymer degradation and stability*, 2019, **166**, 248-257.
[3] Di Lisio V., Sturabotti E., Francolini I., Piozzi A., Martinelli A., *Journal of Polymer Science Part B: Polymer Physics*, 2019, **57**, 174-181.

Electrospun PCL Filtration Membranes Enhanced with an Electrosprayed Lignin Coating to Control Wettability and Anti-Bacterial Properties

Sara Bergamasco[1*], Noemi Fiaschini[1], Luis Alexander Hein[1], Marco Brecciaroli[2], Roberta Vitali[3], Manuela Romagnoli[4], Antonio Rinaldi[3]

[1]*NANOFABER S.r.l., Via Anguillarese 301, 00123 Rome*
[2]*Simitecno srl, 00173 Rome, Italy*
[3]*Italian National Agency for New Technologies, Energy and Sustainable Development (ENEA), Casaccia Research Center, 00123 Rome, Italy*
[4]*Department for Innovation in Biological, Agro-Food and Forest Systems (DIBAF), University of Tuscia, ViaSan Camillo de Lellis snc, 01100 Viterbo, Italy*

**sara.bergamasco@nanofaber.com*

This study reports on the two-step manufacturing process of a filtration media obtained by first electrospinning a layer of polycaprolactone (PCL) non-woven fibers onto a paper filter backing and subsequently coating it by electrospraying with a second layer made of pure acidolysis lignin. The manufacturing of pure lignin coatings by solution electrospraying represents a novel development that requires fine control of the underlying electrodynamic processing. The effect of increasing deposition time on the lignin coating was investigated for electrospray time from 2.5 min to 120 min. Microstructural and physical characterization included SEM, surface roughness analysis, porosity tests, permeability tests by a Gurley densometer, ATR-FTIR analysis, and contact angle measurements vs. both water and oil. The results indicate that, from a functional viewpoint, such a natural coating endowed the membrane with an amphiphilic behavior that enabled modulating the nature of the bare PCL non-woven substrate. Accordingly, the intrinsic hydrophobic behavior of bare PCL electrospun fibers could be reduced, with a marked decrease already for a thin coating of less than 50 nm. Instead, the wettability of PCL vs. apolar liquids was altered in a less predictable manner, i.e., producing an initial increase of the oil contact angles (OCA) for thin lignin coating, followed by a steady decrease in OCA for higher densities of deposited lignin. To highlight the effect of the lignin type on the results, two grades of oak (AL-OA) of *the Quercus cerris L*. species and eucalyptus (AL-EU) of the *Eucalyptus camaldulensis* Dehnh species were compared throughout the investigation. All grades of lignin yielded coatings with measurable antibacterial properties, which were investigated against *Staphylococcus aureus* and *Escherichia coli*, yielding superior results for AL-EU. Remarkably, the lignin coatings did not change overall porosity but smoothed the surface roughness and allowed modulating air permeability, which is relevant for filtration applications. The findings are relevant for applications of this abundant biopolymer not only for filtration but also in biotechnology, health, packaging, and circular economy applications in general, where the reuse of such natural byproducts also bring a fundamental demanufacturing advantage.

Modelling absorption and emission spectra of firefly's light emitter

Isabelle Navizet*,1, Etienne Mangaud[1], Houda Moumène[1], Cristina Garcia Iriepa[1], Madjid Zemmouche[1], Romain Berraud-Pache[1]

[1]*Univ Gustave Eiffel, Univ Paris Est Creteil, CNRS, UMR 8208, MSME, F-77454 Marne-la-Vallée, France*

**isabelle.navizet@univ-eiffel.fr*

The emitting light in fireflies or other bioluminescent species arises from the electronic relaxation of oxyluciferin, an organic compound resulting from the oxidation of the D-luciferin substrate inside an enzyme called luciferase. These systems are already used in applications such as cell cancer detection. One of the challenges of the modelling of such systems is to reproduce the experimental absorption, fluorescence and emission spectra in order to better interpret the experimental results.

Here will be presented the methodologies that can be used to study the spectroscopic proprieties of bioluminescent systems using quantum mechanics, molecular dynamics and hybrid (QM/MM) methods[1]. The experimental emission and absorption spectra are accurately reproduced when the dynamic of the system is taking into account [2]. Information on the nature of the transition can be taken from the modelling and insight of the influence of the protein environment can be highlighted.

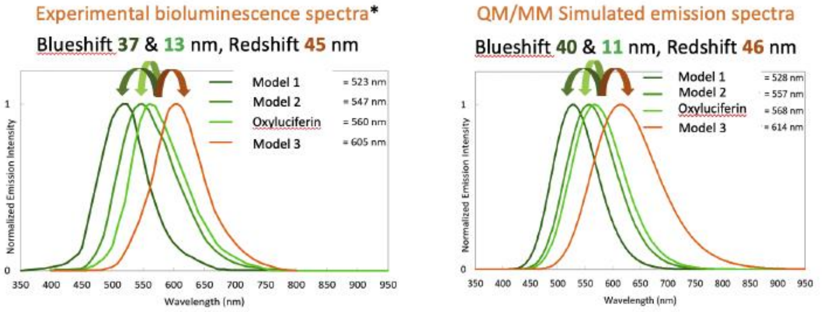


Figure 1. *Comparison of experimental and theoretical spectra for oxyluciferin and analogues [3]*

References

Navizet, I.; Liu, Y.-J.; Ferré, N.; Xiao, H.-Y.; Fang, W.-H.; Lindh, R. Color-Tuning Mechanism of Firefly Investigated by Multi-Configurational Perturbation Method. *J. Am. Chem. Soc.* 2010, **132** (2), 706–712. https://doi.org/10.1021/ja908051h.

García-Iriepa C; Gosset P; Berraud-Pache R; Zemmouche M; Taupier G; Dorkenoo K D; Didier P; Léonard J; Ferré N and Navizet I, Simulation and analysis of the spectroscopic properties of oxyluciferin and its analogues in water, JCTC 2018, **14,** 2117-2126 https://doi.org/10.1021/acs.jctc.7b01240

Zemmouche, M., C. Garcia-Iriepa, I. Navizet, Emission's colour modulation of oxyluciferin synthetic analogues by QM and QM/MM approaches Physical Chemistry Chemical Physics, 2020, **22**, 82 – 91 https://doi.org/10.1039/C9CP04687A

A Coarse-Grained membrane probe to monitor tension changes in flat and curved membranes

J. Alba[1*], T. Mandal[2], V. Zoni[13], S. Vanni[1]

[1]Dept. of Biology – University of Fribourg, Switzerland
[2]Dept. of Physics - Indian Institute of Technology, Kanpur
[3]Dept. of Biology – University of Vigo, Spain

**e-mail josephine.alba@unifr.ch*

Lipid membrane organization and composition confers high versatility to cell membranes to handle stress conditions, and to regulate important cell processes such as endocytosis and cell division. These tasks are initialized by membrane tension changes acting remodelling membrane shape and lipid organization. Understanding how membrane tension variations are involved in cell processes is, then, a challenge.

Here we present a computational membrane tension Coarse-Grained (CG) probe inspired by the widely used fluorescence probe FlipTR, developed for in vitro assays. FlipTR can monitor changes in membrane tension by changing its fluorescence lifetime as a function of the twist between its fluorescent groups [1]. Our CG probe, designed on the cholesterol model of Martini force field, was built as a “toy-model” to sense membrane tension changes at different lipid compositions (Figure 1). As FliptR, our CG probe monitors membrane changes changing the twist of two bulky groups, mimicking the FlipTR lifetime (Figure 1).

To test the CG probe, about 4 CG molecular dynamics (MD) simulations lasting 4μs were performed with different lipid composition representing the liquid-disorder (l_d) and the liquid-order (l_0) phases, in flat membranes. Following, two systems representing the l_d and l_0 were selected and used to investigate the CG probe behaviour after applying an external tension (from 5mN/m to 17mN/m).

In addition, to investigate the CG probe behaviours in curvature systems membrane vesicles and tubules with different diameters and lipid compositions were modelled and simulated. In this work, where a total of 27 CG MD simulations were performed to test the CG probe in flat bilayer (with and without applying a tension), in vesicles and tubules membrane, it was demonstrated that: i) the lifetime of the CG probe in l_0 phase increases in flat bilayer, ii) decreases after applying a tension and iii) decrease increasing membrane curvature. These results are in line with the experimental data [1].

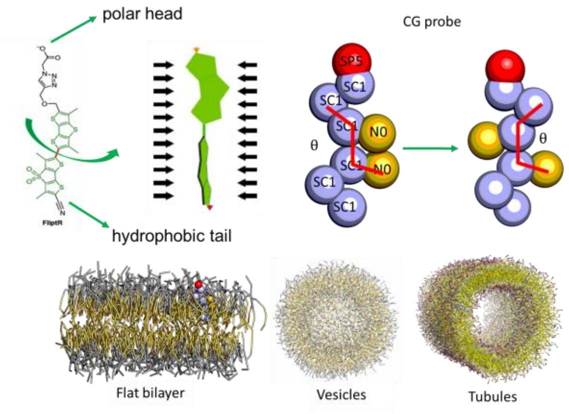


Figure1. **CG probe and tested systems.** Upper left, FlipTR molecule; upper right the CG probe designed. The line in red represents the variation of the dihedral angle computed to measure the lifetime of the CG probe. In bottom, a representation of the systems modelled and simulated.

References

[1] Colom A. et al, Nat Chem, 2018, **10**:1118–1125

Transient spectroscopy simulations from first principles: decoding ultrafast TRPES signals in acetylacetone

Flavia Aleotti*,[1], Stefano Severino[2], Francesco Segatta[1], Lorenzo Mai[2], Aurora Corego[3,4], Fabio Medeghini[2], Fabio Frassetto[5], Luca Poletto[5], Matteo Lucchini[2,4], Maurizio Battista Reduzzi[2], Rocío Borrego-Varillas[4], Mauro Nisoli[2,4], and Artur Nenov[1]

[1] Department of Industrial Chemistry “Toso Montanari”, Università di Bologna, Bologna, Italy
[2] Department of Physics, Politecnico di Milano, Milano, Italy
[3] Departamento de Física Aplicada, Universidad de Salamanca, Salamanca, Spain
[4] Institute for Photonics and Nanotechnologies, IFN-CNR, Milano, Italy
[5] Institute for Photonics and Nanotechnologies, IFN-CNR, Padova, Italy

* *flavia.aleotti@unibo.it*

The recent joint advancements in experimental time-resolved spectroscopic techniques (improving temporal resolution) and computational simulation tools (improving the accuracy of electronic structure methods) have allowed to close the gap between experiment and theory and to gain a deep understanding of the coupled electronic–nuclear dynamics behind photoinduced molecular motion.[1] In the present study, we show how surface hopping nonadiabatic dynamics simulations performed with multiconfigurational wavefunction theory (CASSCF/CASPT2) for photoexcited acetylacetone are able to faithfully reproduce highly resolved transient photoelectron spectroscopy (TRPES) experiments recently performed (by the group of Prof. Mauro Nisoli) with unprecedented temporal resolution (sub-20 fs). With over 100 nuclear trajectories, our simulations track the sub-50 fs intramolecular H-atom transfer driving the $S_2 \rightarrow S_1$ internal conversion immediately after excitation[2] (see decay of initial TRPES signal in Fig. 1) and allow to quantitatively reproduce the experimental evidence both in terms of binding energy and time-evolution of the associated signals. The protocol for TRPES simulation (along with protocols for transient UV/Vis and X-ray spectroscopies) is fully integrated in the COBRAMM package[3] and makes use of wavefunction overlap (i.e. Dyson norm) between valence and ionic excited states along the nuclear trajectories to reproduce the experimental cross-section.

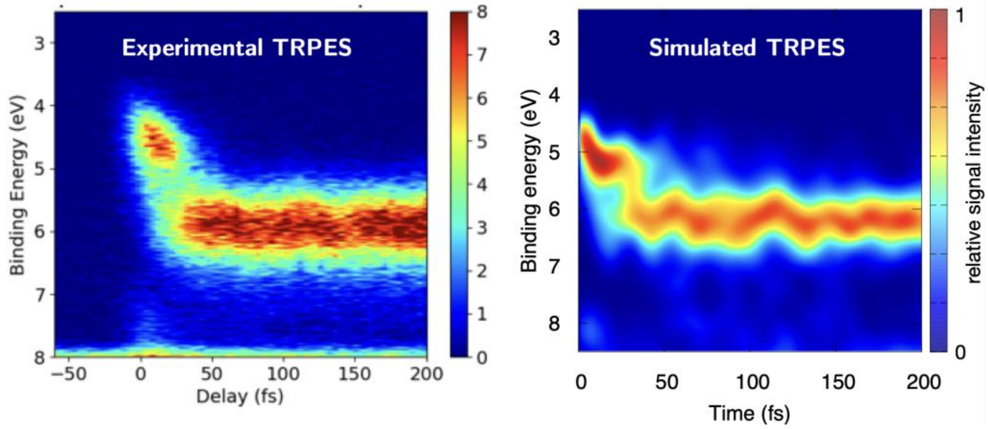


Figure 1 – Experimental vs simulated (COBRAMM, CASPT2) TRPES spectrum of acetylacetone.

References

[1] Conti I., Cerullo G., Nenov A. and Garavelli M. *JACS*, 2020, **142**, 16117.
[2] Poisson L., Roubin P., Coussan S., Soep B. and Mestdagh J. *JACS*, 2008, **130**, 2974.
[3] Cobramm is Optimized in Bologna to Run Ab-initio and Molecular Mechanics (COBRAMM), available at https://gitlab.com/cobrammgroup/cobramm/

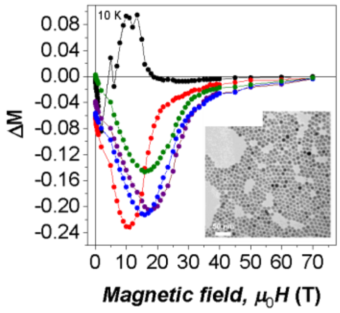
Neutron Scattering to Understand the Complex Magnetic Properties in Co-Mn Ferrite Nanoparticles

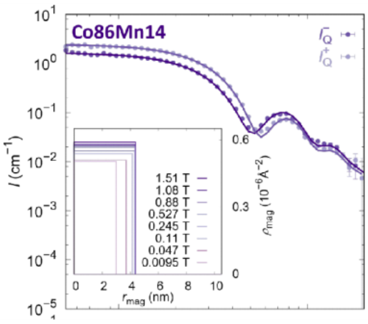
Sanna Angotzi,[a] V. Mameli,[a] M. Gerina,[b] D. Zákutná,[b] and C. Cannas[a]

[a]Department of Chemical and Geological Sciences, University of Cagliari, SP8 km 0,700, 09042, Monserrato, Italy
[b]Department of Inorganic Chemistry, Charles University, Hlavova 8, 12800, Prague, Czech Republic

**sannamarco91@gmail.com*

Cobalt-substituted mixed spinel ferrites, used in various applications, have adjustable magnetic properties influenced by cation type and structural features. The theoretical framework for these materials assumes homogeneously magnetized, single-domain, non-interacting particles. However, recent studies reveal that nanoparticle systems are more complex, even with highly crystalline, monodisperse, non-interacting ensembles. Factors like spin disorder and dipolar interactions can significantly affect the material's magnetic properties. In this study, we delve into the evolution of magnetic and structural properties within a series of oleate-capped manganese-substituted cobalt ferrites (denoted as $Mn_xCo_{1-x}Fe_2O_4$) with varying Co/Mn molar ratios.[1] The results can be interpreted solely based on their actual composition, independent of other parameters, thanks to the single-phase nanoparticles with similar crystallite and particle sizes (about 10 nm), size dispersity (14%), and weight percentage of capping oleate molecules (17%).[2] The temperature and magnetic field dependences of the magnetization revealed the magnetic anisotropy to be the key parameter affecting the magnetic parameters, including T_{max}, T_{diff}, T_b, H_c, HK, and Mr/Ms, caused by the different cobalt content. Deviations from the ideal scenario of non-interacting NPs become evident in all samples when employing IRM-DCD protocols, showing negative ΔM peaks in Mn-rich samples (with a correlation between cobalt content and magnetic anisotropy), while positive ΔM is observed in the Co-enriched sample, possibly due to strong dipole-dipole interactions or surface spin phenomena. Small-Angle Polarized Neutron Scattering (SANSPOL) was then employed to study the quantitative distribution of magnetization within NPs, to reveal the presence of surface spin disorder, to access the surface anisotropy constant, and therefore to isolate the magnetocrystalline anisotropy and correlate it with the Mn content.





References

[1] M. Sanna Angotzi et al., J. Nanosci. Nanotechnol., 2019, 19, 8, 5008–5013
[2] M. Sanna Angotzi, et al., J. Phys. Chem. C, 2021, 125, 37, 20626–20638Name A., Name B., Name C. *Journal Title*, 2000, **35**, 3523.

A universal paper-based origami device towards multi-fold analyte preconcentration

Panagiota Kalligosfyri[1*] and Stefano Cinti[1,2]

[1]*Department of Pharmacy, University of Naples Federico II, Naples, Italy*
[2]*BAT Center – Interuniversity Center of Studies on Bioinspired Agro-Environmental Technology, University of Naples Federico II, Naples, Italy*

**pkalligosfyri@gmail.com*

In the field of analytical chemistry, preconcentration plays a pivotal role in refining detection accuracy. However traditional preconcentration methods like electrodeposition, coprecipitation, liquid-liquid extraction, solid phase extraction etc, pose challenges such as complexity, assay cost and time consumption.[1] Recent efforts have focused on miniaturizing these systems and combining them with paper-based materials as sustainable alternatives.[2] In this context, our study introduces, for the first time, a universal origami device for multi-fold analyte preconcentration by exploiting the advantages of the paper-based substrates[3], including their porosity and versatility. The proposed paper-based origami system, due to its three-dimensional architecture, enables preconcentration without prolonging assay time. Our system was optimized by considering several important parameters (i.e. device length, preconcentration area size, unfolding time, volume of reagents) and successfully applied for efficient preconcentration and detection of trace analytes in real matrices. The final optimized device was integrated with electrochemical assays for the detection of mercury in drinking water and glucose in sweat, resulting in sensitivity improvement up to 400%. This innovative tool overcomes traditional methods limitations by enhancing sensitivity without costly and lengthy procedures. Moreover this paper-based origami preconcentration device is designed to be adaptable to various analytical systems and applications, serving as a universal tool for diagnostic, environmental, and agri-food fields.

Acknowledgements:

The research leading to these results received funding from AIRC under MFAG 2022—ID. 27586 project—P.I. Stefano Cinti. Panagiota Kalligosfyri acknowledges AIRC for funding her postdoctoral Fellowship.

References

[1] Sharma R.K., Pant P. *J Hazard Mater*, 2009, **163** (1), 295–301.
[2] Giordano B.C., Burgi D.S., Hart S. J. *Anal Chim Acta*, 2012, ***718***, 11–24.
[3] Kalligosfyri P.M., Cinti S. *ACS Mater Lett*, 2024, 1184–1198.

Optimization of water-based extraction of Chamomile (*Matricaria Chamomilla* L.) by Analytical and Chemometric Approach

M. Foschi[1*], C. Scappaticci[1], L. Marsili[1], A.A. D'Archivio[1], F. Ruggieri[1], A. Biancolillo[1]

[1]*Department of Physical and Chemical Sciences, University of L'Aquila, Via Vetoio, 67100, Coppito, L'Aquila, Italy*

**martina.foschi@univaq.it*

Chamomile (Matricaria Chamomilla L.) is a medicinal plant recognized for its wide range of beneficial properties, such as anti-inflammatory, antiseptic, analgesic, antimicrobial, antispasmodic, and sedative effects, and is reported in the pharmacopeias of 26 countries worldwide, including Italy. A significant component of chamomile's phytochemical composition is its content of polyphenols [1]. Specifically, *M. chamomilla* infusions primarily consist of phenolic acids and flavonoids, water-soluble bioactive compounds that, demonstrating significant antioxidant activity, help reduce oxidative stress and inflammation in the human body. The current study seeks to optimize a cold-water extraction method for chamomile flower heads to obtain an aqueous extract with antioxidant properties. As a result, an easy, economical, safe, and environmentally friendly extraction method was developed by employing appropriate analytical and chemometric approaches, addressing the demand for effective and sustainable extraction techniques for high-value bioactive compounds from natural sources like chamomile. The Design of Experiments (DOE) was employed to systematically plan the experiments [2]. The characterization of the extract was conducted using High-Performance Liquid Chromatography with Diode-Array Detection (HPLC-DAD) and Ultraviolet-Visible (UV-Vis) spectrophotometry. The optimization process took into account the antioxidant activity test, which was assessed based on the percentage of DPPH (2,2-diphenyl-1-picrylhydrazyl) scavenging activity. Eventually, the effects of the process variables (extraction time and Temperature) on the UV-Vis spectra were evaluated using Anova-Simultaneous-Component-Analysis (ASCA). In this context, the interpretation of the impact of extraction temperature and time, supported by HPLC analysis, and their correlation with antioxidant activity were proposed. The described approach offers a comprehensive understanding of the extraction process and its influence on the antioxidant properties of the extract.

References

[1] Singh, O., Khanam, Z., Misra, N.; Srivastava, M. K. *Pharmacognosy Reviews*, 2011**, 5**, 82–95.
[2] Leardi, R.; Armanino, C.; Lanteri, S.; Alberotanza, L. *J Chemom*, 2000**, 14**, 187–195.

Multifunctional biosurfactants: Self-aggregation and antioxidant activity of rhamnolipids

Matilde Tancredi[1,2*], Irene Russo Krauss[1,2], Luigi Gentile[2,3], Alessandro Cangiano[1,2],
Luigi Paduano[1,2], Gerardino D'Errico[1,2]

[1] University of Naples Federico II, Department of Chemical Sciences, Italy,
[2] CSGI (Consorzio per lo Sviluppo dei Sistemi a Grande Interfase), Italy
[3] University of Bari Aldo Moro, Department of Chemistry, Ital.

**mat.tancredi@studenti.unina.it*

There is a growing interest in industrial formulations based on natural ingredients that have a low environmental impact [1]. In this perspective, the use of biosurfactants derived from fungi, yeasts or bacteria is a key strategy to obtain products that are biocompatible and biodegradable. In particular, rhamnolipids appear to be suitable candidates for replacing synthetic surfactants [2]. They are biotechnologically produced from industrial waste oils, are safe, biocompatible, biodegradable and available at low cost [3]. Although the micellization of rhamnolipids in dilute solutions is well known, their self-aggregation in concentrated mixtures remains largely unexplored.

In this contribution, Electron Paramagnetic Resonance (EPR) spectroscopy is used to study the local structure and dynamics of concentrated aqueous rhamnolipid mixtures using paramagnetic molecular probes. A detailed computational analysis of the EPR spectral components clearly shows a dramatic molecular reorganization of the mixture starting from 80 wt% rhamnolipid, as the microviscosity and polarity parameters indicate the formation of more compact lipid aggregates. These observations suggest a phase transition that is currently being investigated by SAXS for meso-morphological characterization of aggregates. Preliminary results indicate the presence of unstructured ordered phases [4]. The concentrated rhamnolipid mixtures are currently also being studied by rheology, as viscoelastic properties are fundamental for a variety of practical applications [5]. Concentrated samples exhibit shear thinning at 45 °C, suggesting a non-isotropic solution. Notably, as the temperature decreases, shear thinning is not observed at 70%, while it remains present at high concentration.

Interestingly, the presence of endogenous free radicals in the samples is revealed by EPR and correlated with the antioxidant activity of the rhamnolipids. The persistent signal registered even in the absence of spin probes suggests the formation of meso structures capable of stabilizing radical species, thus acting as "redox buffers".

Our results highlight rhamnolipids as promising multifunctional components for eco-sustainable formulations where, in addition to the typical role of surfactants (e.g. foaming or emulsifying agents), they can also act as pro- or anti-oxidants depending on the external conditions.

Acknowledgements: We acknowledge financial support under the National Recovery and Resilience Plan (NRRP), Mission 4, Component 2, Investment 1.1, Call for tender No. 1409 published on 14.9.2022 by the Italian MUR, funded by the European Union – NextGenerationEU – Project Title: Structure and flow dynamics of Concentrated AMphiphilic BIOmolecules (CAmBio) – CUP E53D23015540001 – Project Number P202229ME2 - Grant Assignment Decree No. 1386 adopted on 01/09/2023 by the Italian MUR

References

[1] Hayes G. D., Smith A. G., *AOCS Press*, 2019, 3-38.
[2] Sarubbo A. L. et al., *Biochemical Engineering Journal*, 2022, **181**, 108-377.
[3] Esposito R. et al., *International Journal of Molecular Sciences*, 2023, **24 (6)**, 5395.
[4] Baccile N. et al., *Langmuir*, 2023, **39 (27)**, 9273-9289.
[5] Khan M. B. et al., *JCIS Open*, 2022, **8**, 100067

Designing bioinspired eumelanin-like hybrid nanomaterials for regenerative medicine

Giuseppe Vitiello[1,2,*]

[1]*Department of Chemical, Materials and Production Engineering (DICMaPI), University of Naples Federico II, Piazzale Tecchio 80, 80125 Naples, Italy.*
[2]*CSGI - Center for Colloid and Surface Science, via della Lastruccia 3, 50019 Sesto Fiorentino (FI), Italy.*

**giuseppe.vitiello@unina.it*

The design and engineering of nanomaterials with high biocompatibility and bioactivity and/or of nano-biointerfaces reproducing the microenvironment in which the cells can properly acquire a specific fate is a decisive step towards the effective exploitation of regenerative medicine.

In this context, colloidal chemistry represents an intriguing way to project and create through bottom-up approaches a huge set of new multifunctional nanomaterials and nanointerfaces with a structural hierarchy and with a large spectrum of known and as yet unknown properties. In particular, organo-inorganic nanomaterials can be created starting by the molecular precursors of both phases, thus leading to hybrid nanoplatforms exerting peculiar functionalities for technological applications.

Among the plethora of available sources to design bioinspired materials, eumelanins are increasingly emerging as valuable candidates for bioelectronics and regenerative medicine [1]. They represent a heterogeneous group of phenolic biopolymers found widespread in nature, from fungi and bacteria to plants, molluscs, and mammals, up to humans. These hydrophobic natural pigments have been emerging as a powerful organic component for developing biologically active nanomaterials because of their several biological functions, such as photo-protection and photosensitization, free radical quenching, metal ion chelation and even intrinsic red-ox behaviour.

In the last years, a versatile synthetic strategy has been defined to efficiently combine at a molecular level the eumelanin pigments with different colloidal inorganic nanoparticles, such as titanium [2,3], silica, zinc or cerium [4] oxides as well as nanohydroxyapatite [5]. The ability of such colloidal nanoparticles is to act as polymerization nuclei for the eumelanin precursors and, consequently, to catalyse the formation of both hybrid and/or coated nanoplatforms with advanced antimicrobial and antioxidant activities as well as relevant bioactivity and cells adhesion ability, thus proposing as valuable candidates to realize biocompatible nano-interfaces applied in the biomedical field.

Here, an overview of functional eumelanin-like hybrid nanomaterials with advanced physicochemical properties and biological activity as prepared through colloidal chemistry routes is proposed. The obtained results confirm the potentialities that these multifunctional nanomaterials could play in regenerative medicine, from stem cells growth and differentiation to radical homeostasis regulation and wound healing applications.

References

[1] Cavallini C., Vitiello G., et al. *Nanomaterials* 2020, **10**, 1518.
[2] Pota G., […], Vitiello, G. *Colloids and Surfaces B: Biointerfaces*, 2021, **202**, 111671.
[3] Amantea F., […], Vitiello G. *Applied Surface Science* 2023, **633**, 157608.
[4] Pota G., Silvestri B., Vitiello G., et al. *Biomaterials Advances* 2023, **153**, 213558.
[5] Furlani F., Pota G., […], Vitiello G. *Colloids and Surfaces B: Biointerfaces* 2024, **235**, 113756.

Delivery of hydrophilic molecule via intranasal route using nanotechnology- a novel approach for optimizing antipsychotic-like activity while minimizing peripheral exposure

Reham Abu Ghoush,[1] Anna Morshin, [1] Jonathan Jurevitz, [2] Yoel Shor, [2] Avigail Zucher, [2] Ori Shalev, [3] Amit Lotan, [2] Katy Margulis [1] **

[1]*The Institute for Drug Research, the School of Pharmacy, the Faculty of Medicine, The Hebrew University of Jerusalem, Jerusalem 9112192.*
[2]*Department of Psychiatry, Hadassah Medical Center, the Faculty of Medicine, The Hebrew University of Jerusalem, Jerusalem 9112192.*
[3]*Metabolomics Center, Core Research Facility, the Faculty of Medicine, The Hebrew University of Jerusalem, Jerusalem.*

Schizophrenia is a devastating mental disorder. Novel treatments are crucially needed due to common medication resistance. We identified a promising hydrophilic drug that effectively mitigates psychotic symptoms in various pharmacological mouse models of psychosis. This molecule can permeate the blood-brain barrier; however, its systematic exposure is undesired. To overcome this, we developed an intranasal nanoformulation tailored for direct brain delivery. Leveraging nanotechnology, our formulation, with its nanometric inner domains and permeation-enhancing agents, facilitates targeted drug transport to the brain. Using desorption electrospray ionization mass spectrometer imaging (DESI-MSI), we assess the spatial brain distribution of the drug and the unique metabolomics signature it elicits post-intranasal delivery compared to intraperitoneal administration. This work offers a novel therapeutic approach for optimizing brain-specific drug delivery while minimizing peripheral exposure, thus offering hope for enhanced schizophrenia treatment.

Revolutionizing Sustainability in Biobased Furan Polymers through Enzymatic Polymerization

Dina Maniar [1*]

[1] *Macromolecular Chemistry and New Polymeric Materials, Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands.*

**d.maniar@rug.nl*

Environmental issues due to plastic waste accumulation and climate change are two prevalent problems faced by modern society. Tremendous efforts to develop sustainable polymer alternatives from renewable resources have become an urgent necessity. Biomass-derived molecules have emerged as key components in the development of biobased chemical platforms for polymer synthesis. Among these, furan derivatives and furan chemistry are especially appealing. The structural similarity between furan and phenyl rings presents an opportunity for a biobased alternative for phenyl-based polymers. However, current research involving furan polymers is predominantly at the stage of material development and faces some limitations e.g. due to poor thermal stability. Achieving sustainable and effective synthetic processes of furan polymers remains a formidable challenge. Moreover, simply relying on renewable resources is insufficient for developing truly ˈgreenˈ approaches. Within this contribution, insight into integrating enzymatic catalysis for the synthesis of novel furan polymers will be discussed. The focus of this presentation will be on enzymatic polycondensation of a series of furan (co)polymers. The fundamental impact of enzymatic catalysis in furan polymer synthesis and its potential scalability for an environmentally friendly synthetic approach are highlighted.

Acknowledgements:
Contributions from various coworkers and PhD students are acknowledged.

References

[1] D. Maniar, Y. Jiang, A. J. J. Woortman, J. van Dijken, K. Loos, ChemSusChem 2019, **12**, 990.
[2] Loos, K.; Zhang, R.; Pereira, I.; Agostinho, B.; Hu, H.; Maniar, D.; Sbirrazzuoli, N.; Silvestre, A. J. D.; Guigo, N.; Sousa, A. F. *Frontiers in Chemistry*, 2020, **8** (585).
[3] Post, C.; Maniar, D.; Voet, V. S. D.; Folkersma, R.; Loos, K. *ACS Omega, 2023,* **8 (10)**, 8991-9003. DOI: 10.1021/acsomega.2c07629.
[4] F. Silvianti, D. Maniar, B. Agostinho, T. C. de Leeuw, T. Pelras, L. Dijkstra, A. J. J. Woortman, J. van Dijken, S. Thiyagarajan, A. F. Sousa, K. Loos, Adv. Sustainable Syst. 2024, 2300542. https://doi.org/10.1002/adsu.202300542.

Ammonium recovery from pig slurry storage pits using modular submerged microbial electrolysis cells

M. Cerrillo[1*], F. Alcalde[1], N. Ruiz[1], M. Moreno[1], L. Burgos[1], V. Riau[1] and A. Bonmatí[1]

[1]*Sustainability in Biosystems, Institute of Agrifood Research and Technology (IRTA), Torre Marimon, E-08140 Caldes de Montbui, Barcelona (Spain)*

**miriam.cerrillo@irta.cat*

The open-air farm's storage of livestock manure poses a significant challenge due to emissions of greenhouse gases and ammonia into the atmosphere. Bioelectrochemical systems have been widely studied for ammonium recovery from wastewater [1], prompting this project to explore the application of a submerged Microbial Electrolysis Cell (MEC) within livestock manure storage pits to mitigate ammonia emissions. The objective of this study is to design, construct, and operate a new configuration MEC that can be submerged in a livestock manure storage pit to recover ammonium. Furthermore, the potential impact of ammonium extraction and recovery by the MEC on atmospheric emissions from slurry storage pits will be assessed.

A tubular submerged MEC has been developed, comprising a NAFION^{TM} membrane bag housing the cathode compartment (1.2 L) internally. Carbon felt wraps around the membrane exterior as the anode. A modular design with 4 MEC units has been constructed and submerged in an outdoor tank with 600 L of raw pig slurry. The cathode compartments have been filled with a NaCl solution (0.1 g/L) which is continuously recirculated with a peristaltic pump. The MECs' electrodes are connected in parallel with a power source. A second tank, without MEC, is used as control.

During the first 68 days of operation of the submerged module, 25 g of N have been recovered in the catholyte, representing an average of 1.12 $gN/m^2/d$. From day 67, a second module has been submerged in the tank, to increase ammonia recovery and evaluate the influence of ammonium reduction on pig slurry ammonia emissions into the atmosphere, currently in progress.

The new design of modular submerged MEC is an initial step towards the upscaling of this technology for the application in the recovery of ammonium from outdoor storage of livestock manure and the reduction of emissions into the atmosphere. The recovered ammonia solution can be reused as fertilizer in order to close the nutrient cycle.

Acknowledgements:

This research was funded by the Spanish Ministry of Economy and Competitiveness (PID2020-118830RR-I0). The support of the CERCA Program and of the Consolidated Research Group of Sustainability in Biosystems (ref. 2021 SGR 01568), both from the Generalitat de Catalunya, is also acknowledged.

References

[1] Cerrillo, M., Riau, V., Bonmatí, A. Recent Advances in Bioelectrochemical Systems for Nitrogen and Phosphorus Recovery Using Membranes. Membranes, 2023, **13**, 186. Name A., Name B., Name C. *Journal Title*, 2000, **35**, 3523.

Closing the loop on battery manufacturing, the use of recycled material for advanced Li-ion and Na-ion batteries

Darjazi H[1,2], Piovano A.[1,2], Porporato S. [1,2], Gastaldi M. [1,2], Meligrana G. [1,2], Elia G. A.[1,2], Gerbaldi C.[1,2]

[1]*GAME Lab, Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi, 24, 10129, Torino, Italy*
[2]*National Reference Center for Electrochemical Energy Storage (GISEL) - INSTM, Via G. Giusti 9, Firenze 50121, Italy*
hamideh.darjazi@polito.it

Electrochemical energy storage and conversion systems are integral to our daily lives and hold significant importance for the future, addressing environmental concerns and the energy crisis. The pursuit of greener, more affordable, and safer rechargeable batteries is currently recognized as a strategically important goal in advancing energy storage technology. Li-ion batteries (LIBs) and Na-ion batteries (NIBs) play a crucial role as energy storage devices for electric vehicles and smart grids. It's widely recognized that a detailed analysis of an electrode reveals that each component—such as the active material, conductive carbon, current collector, and binder—contributes to the overall battery performance. It has been discovered that the binder, despite its relatively low content—typically a few percent (up to 5 wt%, but usually 2 wt%) in relation to the total electrode composition—plays a decisive role in determining electrode performance. This is noteworthy considering its chemical and electrochemical inactivity. Besides, an essential role is played by electrolytes and separators, which are deepened in this work. Indeed, many factors must be considered while selecting the best separator, including electronic insulation, low ionic resistance, mechanical stability, chemical resistance to degradation, wettability and uniform thickness [1]. In this context, we prepared polyurethane-based membranes starting from polyvinyl butyral (PVB) and diisocyanate, by means of a coagulation bath [2]. In addition, particular attention is paid to understanding the impact of PVB as a binder on the properties and behavior of electrodes based on hard carbon, and especially the effects given by the different physical structures of the electrodes toward the electrochemical response in LIBs and NIBs. The choice of PVB as the polymer is related to the European project SUNRISE, which aims to find different recycling pathways for this material, normally used as polymeric interlayer into laminated glasses for construction and automotive. At the moment, the PVB fraction collected after disposal, which lacks optical and mechanical requirements for its original purpose, is incinerated or landfilled, causing tons of losses every year, even though it could find a second life within the energy storage panorama [3]. The goal of our group is to exploit new strategies for the reuse in energy storage application of the fraction of PVB, which does not fulfill the requirements for the re-integration in the original glass manufacturing process. PVB-based membranes were characterized from the physico-chemical and they were tested as separating membranes inside both lithium- and sodium-metal cells. We have made a research of the electrochemical performances of hard carbon with PVB, polyacrylic acid (PAA) and poly(vinylidene fluoride) (PVDF) binders for LIBs and NIBs. Preliminary results are highly encouraging and pave the way to the development of more sustainable separators and binders from waste products for safe, low-cost energy storage devices.

Acknowledgements:

The SUNRISE project (https://sunrise-project.eu/) has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 958243.

References

[1] Arora, P. et al., Chem. Rev., **2004**, 104, 4419–4462
[2] Lian, F. et al., J Memb. Sci., **2014**, 456, 42–48
[3] F. Duffner et al., Renewable Sustainable Energy Rev., **2020**, 127, 10987

Combining the acid and the redox function to design mesostructured catalysts for DME production from CO_2

Fausto Secci[1,2*], Valentina Mameli[1,2], Marco Sanna Angotzi[1,2], Lorenza Piroddi[3], Nicola Pinna[4], Mauro Mureddu[3], Carla Cannas[1,2]

[1]Department of Chemical and Geological Sciences, University of Cagliari, Monserrato (CA), Italy
[2]National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence, Italy
[3]Sotacarbo S.p.A., Carbonia, (SU), Italy
[4]Institut für Chemie and IRIS Adlershof, Humboldt-Universität zu Berlin, Berlin, Germany
**fausto.secci@unica.it*

Due to the increasing attention toward global warming, current research is focusing on green fuels obtained by the reduction of captured CO_2 (e-fuels). One of the most promising e-fuels is dimethyl ether (DME), a replacement or additive for diesel fuel. DME is obtained from CO_2 through two subsequent reactions. The first one, promoted by Cu-based redox catalysts, is the reduction of CO_2 to methanol; the second one, promoted by solid acidic catalysts, is the dehydration of methanol to DME[1]. Particularly, when the two catalytic phases are present into the same system, the one-step CO_2-to-DME conversion can be performed; this process, compared with the two-step route, presents several advantages[1]. The redox and the acidic catalysts can be combined by physically mixing them together[2,3] or by obtaining supported composite materials (here referred as "chemical mixtures") with a more intimate contact between the two phases, through chemical routes. The effect of the different contact (physical vs. chemical) on the catalytic performance is still object of debate.

In order to assess this effect and determine the proper combination between the redox and the acid phase to maximize catalytic performances, a direct comparison between physical and chemical mixtures has been performed. First, a redox catalyst (CZZ, consisting of $CuO/ZnO/ZrO_2$) was synthesized using a self-combustion approach and subsequently mixed with different mesostructured acidic aluminosilicates (Al-MCM-41; Al-SBA-15; Al-SBA-16), synthesized by sol-gel routes[3], to obtain physical mixtures. Along with the physical mixtures, three nanocomposite catalysts (chemical mixtures) were obtained by using the mesostructured acidic aluminosilicates as supports, impregnating them with the same CZZ redox catalyst, performing the self-combustion reaction in the presence of the support. The catalysts were characterized with different techniques, showing that, in the case of chemical mixtures, the redox phase is homogeneously distributed throughout the mesostructure of the support in the form of either small nanoparticles or as a nanolayer. Both physical and chemical mixtures were subsequently tested for the one-step CO_2 conversion to DME in a bench-scale plant equipped with a fixed-bed reactor, and their catalytic performances were compared, to assess the effect of the interface between the redox and the acidic phase. The catalytic tests point out that, in all cases, nanocomposite catalysts feature higher values of CO_2 conversion compared with the corresponding physical mixtures, presumably due to the higher dispersion of the redox phase in chemical mixtures. However, physical mixtures, compared with chemical mixtures, show higher DME yield, due to their significantly higher values of selectivity to DME. This fact can be ascribed to the partial coverage of the acid sites of the supports, responsible for methanol dehydration to DME, due to the impregnation process. Physical mixtures, thus, showed better overall performances than nanocomposites (chemical mixtures) for the one-pot DME synthesis from CO_2.

References

[1] E. Catizzone, C. Freda et al, Journal of Energy Chemistry 2021, 58, 55 – 57.
[2] C. Cara, F. Secci et al, Journal of CO_2 Utilization 2022, 62, 102066
[3] F. Secci, V. Mameli et al, Journal of Environmental Chemical Engineering 2023, 11, 110018

Sustainable adhesives: exploring boronic ester vitrimer composites containing lignin microparticles

Martina Nardi*, Luca Ceseracciu[2], Marco Contardi, Vincenzo Scribano, Arkadius Zych, Athanassia Athanassiou[n]

[1] Istituto Italiano di Tecnologia, Via Morego 30, Genova 16163, Italy
[2]Materials Characterization Facility, Istituto Italiano di Tecnologia, Via Morego 30, Genova 16163, Italy
[3]Department of Earth and Environmental Sciences (DISAT), Piazza della Scienza, 20126, Milan, Italy

**martina.nardi@iit.it*

The production of adhesive materials has been continuously growing in recent years since they are key components in several industries, such as automotive, aerospace, construction, and electronics.[1-4]The attention is focused on formulations that combine lightweight materials with outstanding properties in terms of high bonding strength, durability, and insulation.[4] Despite these great advantages, many commercial formulations have drawbacks related to the presence of permanent and non-processable crosslinking bonds, and the petroleum-based origin of the monomers involved in the crosslinking process, raising concerns about their potential harm to the environment and human health. In this regard, the United Nations asked for a decisive change towards the production of bio-based materials that could be evenly reprocessed, recycled, and biodegraded.

In this contribution, a series of bio-based vitrimer composites, made from two renewable feedstocks, namely epoxidized linseed oil and commercial Kraft lignin, were prepared and used as alternative sustainable adhesives on several substrates, such as aluminium, stainless steel and ash tree wood. Specifically, lignin microparticles were added in 20 to 50 wt% to the vitrimeric matrix formed by epoxidized linseed oil and a dithiol boronic acid without any previous chemical modification or the assistance of additional solvents. The lignin/vitrimer composites showed lap shear strengths in the range of 9-17 MPa and good to excellent rewelding abilities depending on the filler amount in the matrix. The presence of a vitrimeric matrix allowed the processability and recyclability of the materials at temperatures above 160 °C, while the inclusion of a pulp industry waste product positively influences the thermal and mechanical properties, improving the rewelding abilities of the adhesive and enhancing the biodegradability in seawater and soil. The reported materials want to pave the way for a new class of bio-based, biodegradable, and highly processable and recyclable adhesives.

Acknowledgements:

Fondazione CARIPLO (Grant n° 2021-0757).

References

[1] Banea, M.D., et al., Multi-material adhesive joints for automotive industry. Composites Part B: Engineering, 2018, **151**, 71.
[2] Novák, I. and Š. Florián, Pressure-sensitive adhesives for electronic applications. Journal of Materials Science Letters, 2003, **22**(18), 1237.
[3] Gadhave, R.V.I. and C.R. Gadhave, Adhesives for the paper packaging industry: an overview. Open Journal of Polymer Chemistry, 2022, **12**(2), 55.
[4] Marques, A.C., et al., Review on Adhesives and Surface Treatments for Structural Applications: Recent Developments on Sustainability and Implementation for Metal and Composite Substrates. Materials, 2020, **13**(24), 5590.

HMF: A Responsive Bio-Based Building Block for Diels-Alder Reaction

Arianna Sinibaldi[1*], Irene Rosa Gallo[1], Lucrezia Margherita Comparini[1], Felicia D’Andrea[1], Christian Silvio Pomelli[1], Andrea Mezzetta[1], Mauro Pineschi[1], Lorenzo Guazzelli[1].

[1]*Pharmacy Department, University of Pisa, Pisa, Italy*

**arianna.sinibaldi@farm.unipi.it*

5-Hydroxymethylfurfural (HMF) is an organic molecule mainly derived from demolition processes of renewable carbohydrate-based sources (such as fructose, glucose, sucrose or cellulose).[1] Considering the high bioavailability of the precursors, HMF gained a particular interest in the chemical industry over the past decade, showing great potential in terms of conversion and valorisation, therefore, inspiring numerous innovative green transformations in different areas of organic chemistry, biofuels, polymers, and pharmaceuticals.[2]

In this context, the synergistic use of new generation organic-green solvents, such as bio-based solvent or deep eutectic solvents (DES), can further expand the potential for HMF utilization, targeting a more sustainable chemistry.[3] Within the framework of our research program on the valorisation of this versatile building block, we present preliminary data on the HMF conversion and functionalization, highlighting its reactivity in conventional organic solvents, green organic solvents and DES. Specifically, we will examine the influence of these solvents on inducing exo/endo isomerism in the Diels-Alder reaction employing HMF as a diene.

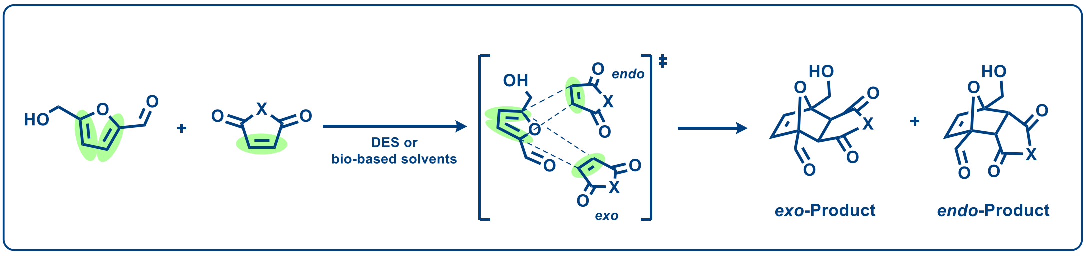


Figure 1: General scheme for Diels-Alder reaction performed with non-conventional solvents.

Acknowledgements:

This work has been funded by European Union – Next Generation EU in the framework of the PRIN 2022 SEED4GREEN - Code 20223W4RT9.

References

[1] Kucherov F.A., Romashov L.V., Galkin K. I., Ananikov V.P. *ACS Sustainable Chem. Eng.* 2018, **6**, 8064.
[2] Konga Q.-S., Lia X.-L., Xub H.-J., Fua Y. *Fuel Processing Technology* 2020, **209**, 106528.
[3] Wang H., Cui J., Zhao Y., Li Z., Wang *J. Green Chemistry* 2021, **23**, 405.

Univocal determination of the binding sites of a cytotoxic dinuclear Cu(II) complex to nucleotides by IR ion spectroscopy and calculations

Davide Corinti,[1*] Marco Giampà,[2] Alessandro Maccelli,[1] Simonetta Fornarini,[1] Giel Berden,[3] Jos Oomens,[3] Sabrina Schwarzbich,[4] Thorsten Glaser,[4] Maria Elisa Crestoni[1]

[1] Dipartimento di Chimica e Tecnologie del Farmaco, Sapienza – Università di Roma, Italy
[2]Department of Clinical and Molecular Medicine, Norwegian University of Science and Technology, Norway
[3]Institute for Molecules and Materials, FELIX Laboratory, Radboud University, the Netherlands
[4]Lehrstuhl für Anorganische Chemie I, Fakultät für Chemie, Universität Bielefeld, Germany

**davide.corinti@uniroma1.it*

Metallodrugs play a vital role in anticancer therapy and remain pivotal in treating various solid tumors. Notably, cisplatin and other Pt(II)-based drugs serve as frontline therapeutics for lung, prostate, and neck cancers.

In the quest for safer and more potent metallodrugs, the dinuclear copper complex bis(acetato)-(μ-2,7-bis({bis[(6-methylpyridin-2-yl)methyl]amino}methyl)naphthalene-1,8-diolato)-di-copper(II), designated as $[(HtomMe)\{Cu(OAc)\}_2]^+$, has been designed and synthesized (Figure 1). Its mode of action diverges from that of cisplatin, being specifically tailored to interact with DNA phosphates, thereby inducing genetic damage. This study presents an investigation utilizing high-resolution mass spectrometry (MS), tandem MS, and infrared multiple photon dissociation (IRMPD) spectroscopy within the 600-1800 cm^{-1} spectral range to analyze complexes formed by the reaction of $[(HtomMe)\{Cu(OAc)\}_2]^+$ with H_3PO_4, 1,2-ethylenediphosphonic acid (1,2-POH_2), 1,4-butanediphosphonic acid (1,4-POH_2), deoxyadenosine monophosphate (dAMP), and deoxyguanosine monophosphate (dGMP).[1] By juxtaposing the structural insights unveiled by IRMPD spectroscopy with linear IR spectra of the energetically favored structures, distinctive signatures of the binding modes between the dinuclear copper(II) complex and phosphate groups can be discerned. These findings imply that the predominant interaction of $[(HtomMe)\{Cu(OAc)\}_2]^+$ with DNA phosphate groups may underpin its observed anticancer efficacy.

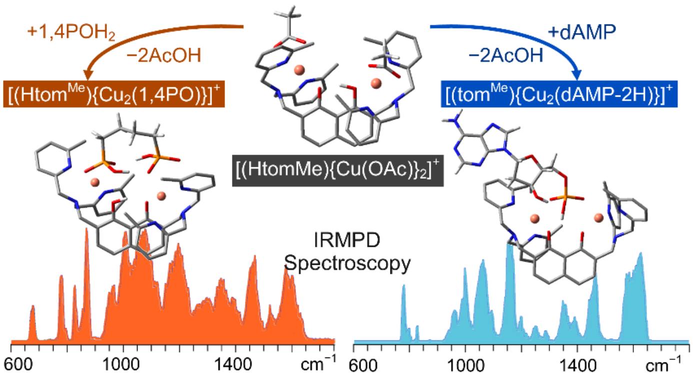


Figure 1: Scheme of the reaction of $[(Htom^{Me})\{Cu(OAc)\}_2]^+$ with 1,4POH_2 and dAMP. The IRMPD spectra of the products $[(Htom^{Me})\{Cu_2(1,4PO)\}]^+$and $[(tom^{Me})\{Cu_2(dAMP\text{-}2H)\}]^+$ are reported together with their attributed structures. The structure of the starting ion $[(Htom^{Me})\{Cu(OAc)\}_2]^+$is also shown.

References

[1] M. Giampà, D. Corinti, A. Maccelli, S. Fornarini, G. Berden, J. Oomens, S. Schwarzbich, T. Glaser, M.E. Crestoni, *Inorg. Chem.*, 2023, **62**, 1341.

Reduction of bacterial adhesion on wrinkled surfaces under fluid shear

Luca Pellegrino[1*], Giovanni Savorana[2], Eleonora Secchi[2], & Roberto Rusconi[1,3]

[1] *Department of Biomedical Sciences, Humanitas University, Via Rita Levi Montalcini 4, 20072 Pieve Emanuele, Italy*
[2] *Institute of Environmental Engineering, ETH Zürich, Zürich, 8093, Switzerland*
[3] *IRCCS Humanitas Research Hospital, Via Manzoni 56, 20089 Rozzano, Italy*

**luca.pellegrino@humanitasresearch.it*

Surface properties and fluid dynamics within confined spaces are pivotal factors influencing bacterial adhesion – a critical step in surface colonization and biofilm formation. This phenomenon gains exceptional significance in the context of implantable devices, where biofilm-related infections present daunting clinical challenges due to their resilience against mechanical stresses and antibiotics. Yet, the interplay between surface topography and fluid shear in microbial attachment remains inadequately understood. Here, we employ surface fabrication techniques[1] coupled with microfluidics to investigate the adhesion of both motile and non-motile Pseudomonas aeruginosa bacterial strains on sinusoidal patterns and in the presence of flow, across varying shear rates (ranging from 0.4 to 200 s^{-1}). Our findings revealed that the presence of a patterned surface topography – having a length scale comparable to the bacterium size– significantly impacts the local shear rate field, creating stress concentration points that hinder bacterial spatial arrangement, particularly for non-motile species. In turn, as shear rates increase, we observed a 'shear-detachment' effect that contrasts with what has been found in the case of flat surfaces[2]. Moreover, when patterns are aligned perpendicular to the flow direction, detachment increases, especially under moderate shear rates. These results provide valuable insights into the interplay between prescribed surface topography and fluid shear forces, shedding light on strategies to delay and frustrate the early stages of biofilm formation. Such insights hold promising implications for the development of innovative strategies to mitigate biofouling and device-associated infections.

Acknowledgements: This work was supported by project MSCA IF - MOBILE - GA101110029 – HUNIMED of the HORIZON EUROPE EU Framework Programme for Research and Innovation.

References

[1] Caldara, M., Belgiovine, C., Secchi, E., & Rusconi, R. (2022). *Clinical microbiology reviews, 35*(2), e00221-20.
[2] Pellegrino, L., Tan, A., & Cabral, J. T. (2022), *Physical Review Letters*, *128*(5), 058001.
[3] Rusconi, R., Guasto, J. S., & Stocker, R. (2014). *Nature physics, 10*(3), 212-217.

Block Copolymer Nanocarriers Made by PISA for Controlled Drug Delivery: From *In Situ* Encapsulation to Stimuli-Responsive Release and Degradation

Hien Phan [1,2], Robert Cavanagh [3], Philippa Jacob [2], Clémence Le Cœur[1], Damien Destouches [4], Benedetta Brugnoli [2,5], Steve Howdle [2], Vincenzo Taresco [2] and Benoit Couturaud [1*]

[1]*Institut de Chimie et des Matériaux Paris-Est (ICMPE), CNRS, University Paris Est Créteil, UMR 7182,*
[2]*School of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, UK*
[3]*School of Medicine, University of Nottingham, University Park, Nottingham NG7 2RD, UK*
[4]*TRePCa, University Paris Est Créteil, 94010 Créteil, France*
[5]*Department of Chemistry, Sapienza University of Rome, Piazzale Aldo Moro 5, 00185 Rome, Italy*

**Benoit.couturaud@cnrs.fr*

The applications of block copolymer nanoparticles (NPs) synthesized via polymerization-induced self-assembly (PISA) hold immense potential in the field of drug delivery systems. These nanoparticles offer a versatile platform for encapsulating therapeutic agents, enabling targeted delivery and controlled release. In our research, we focus on exploring the synthesis and functionalization of block copolymer NPs to address key challenges in drug delivery.

We begin by describing the synthesis of block copolymers containing poly((ethylene glycol) methacrylate)-*co*-poly(pentafluorophenyl methacrylate)-*b*-poly(hydroxypropyl methacrylate) (P((PEGMA-*co*-PFBMA)-*b*-PHPMA)). Our investigation involves two approaches: in situ encapsulation of Doxorubicin (DOX) during PISA and surface functionalization of PISA-made vesicles with drug therapies.

In addition to in situ encapsulation, we investigated stimuli-responsive block copolymer NPs. H_2O_2-sensitive NPs composed of P((PEGMA-*c*o-PEGMAOH)-*b*-PMTEAM) were synthesized via PISA, displaying morphological transitions in response to H_2O_2, enabling controlled drug release.

Lastly, semi-degradable nanoparticles synthesized via photo-PISA using pH-sensitive poly(ether-*co*-ether carbonate) copolymers displayed versatile behaviours under alkaline conditions. The hydrolysis of carbonate linkages induced a transition from steric to electrostatic stabilization, impacting nanoparticle morphology and stability.

In conclusion, our findings highlight the potential of PISA-derived block copolymer NPs for versatile drug delivery applications. These NPs offer tunable properties for *in situ* encapsulation, surface functionalization, and stimuli-responsive release or degradation, holding promise for future biomedical applications.

References

[1] Phan H., Cavanagh R., Jacob P.L., Destouches D., Vacherot F., Brugnoli B., Howdle S., Taresco V. and Couturaud B.*, *Polymers*, 2023, 15(14), 3070.
[2] Phan H., Cavanagh R., Destouches D., Vacherot F., Brissault B., Taresco V., Penelle J., Couturaud B.*, *ACS Applied Polymer Materials*, 2022, 4, 10, 7778–7789.
[3] Phan H., Cossutta M., Houppe C., Le Cœur C., Prevost S., Cascone I., Courty J., Penelle J., Couturaud B.* *Journal of Colloid and Interface Science*, 2022, 618, 173-184.

Supramolecular Chromophores: From Assembly to Photocatalysis

Luka Đorđević [1,*]

[1]*Department of Chemistry, University of Padova, Padova, Italy, 35131*

**luka.dordevic@unipd.it*

In the field of artificial photosynthesis, self-assembly is an attractive strategy that utilizes noncovalent interactions to mimic the alignment and organization of light-harvesting machinery found in plants. Although recently there has been much progress in the chemistry of supramolecular polymers for harvesting sunlight, most systems are limited to the aqueous photocatalytic production of hydrogen. Therefore, efforts are still needed to develop artificial photosynthetic systems for the great challenge of CO_2 reduction (especially with nonabundant metals) and/or production of liquid fuels.

To obtain supramolecular materials for production of solar fuels, the design of monomers is crucial. The monomers utilized are chromophore amphiphiles that, on one hand, encode the light-harvesting ability to drive photocatalytic reactions and, on the other hand, spontaneously self-assemble in aqueous solutions. This talk will describe two separate strategies to use self-assembled materials to photocatalytically produce either (*i*) carbon monoxide and methane starting from carbon dioxide or (*ii*) hydrogen peroxide from water and oxygen.

References

[1] Cappelletti, Barbieri, Aliprandi, Maggini, Đorđević *Nanoscale* **2024**, 10.1039/D4NR00383G
[2] Đorđević, L.;† Dumele, O.;† (eq. contr.); Sai, H.; Cotey, T.; Sangji H. M.; Kohei, S.; Dannenhoffer, A.; Stupp, S.; Photocatalytic Aqueous CO_2 Reduction to CO and CH_4 Sensitized by Ullazine Supramolecular Polymers. *J. Am. Chem. Soc.* **2022**, *144* (7) 3127–3136.
[3] Đorđević, L.; Sai, H.; Yang, Y.; Sather, N. A.; Palmer, L. C.; Stupp, S. I.; Heterocyclic Chromophore Amphiphiles and their Supramolecular Polymerization. *Angew. Chem. Int. Ed.* **2023**, *62* (17), e202214997.

Organic Energy Materials towards a Sustainable Society

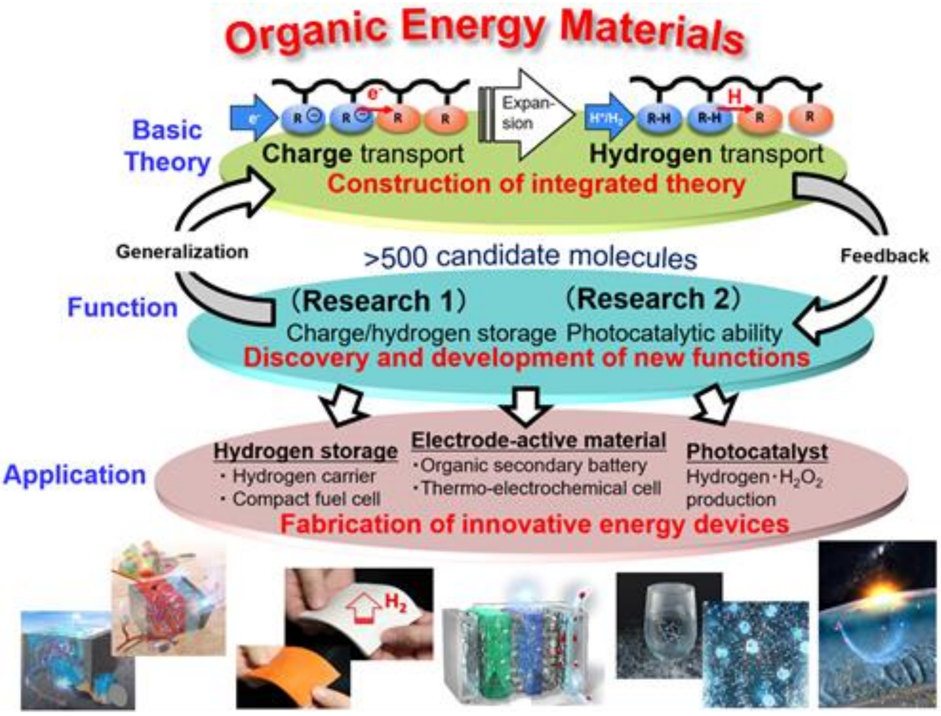
[1]Kouki Oka*

[1]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Miyagi, Japan*

**oka@tohoku.ac.jp*

Toward the realization of a sustainable society, the development of innovative organic energy materials, which are composed of earth-abundant elements and which play a role in energy conversion and storage, is highly required. In this lecture, I will describe several examples of organic energy materials (organic polymeric materials) with the following energy-related functions (1)−(5) (**Figure**). (1) Charge storage and transport. (2) Proton storage and transport. (3) Hydrogen gas production and storage. (4) gas selective adsorption and storage. (5) Photocatalysis and clean energy production. The latest efforts towards designing materials with both robust functionality and material decomposition will be also introduced.

In addition, this lecture will also cover the prototyping of applications or devices using these organic energy materials (**Figure** below). For example, ① Organic secondary batteries which are composed of organic electrode-active materials. ② Compact fuel cells which use organic electrode-active materials as an anode. ③ Hydrogen carrier materials (Polymeric hydrogen storage materials) which chemically fix and release hydrogen gas (H_2) even under mild conditions. ④ CO_2 storage material. ⑤ On-site clean energy (e.g., H_2 and H_2O_2) production which uses organic energy materials as a photo(electro)catalyst or electrocatalyst.



Acknowledgements:

This work was partially supported by Grants-in-Aids for Scientific Research (23K17945, 23H03827, 24K01552) from MEXT and the Environment Research and Technology Development Fund (JPMEERF20241RA4) of the Environmental Restoration and Conservation Agency, Japan.

Oral Communications

Theme A - Advances in Organic Chemistry

Photochemical Late-stage Functionalization of Peptides in Batch and in Flow

Francesca Arrighi[1][a][b]*, Nikolaos Kaplaneris [b], Merve Akdeniz[b], Méritxell Fillols[b], Gana Sanil[b] [c], Daniel T. Gryko[c], and Timothy Noël[b].

[1]*Department of Chemistry and Technology of Drugs, "Sapienza University of Rome", Rome, Italy*
[2] *[a]Department of Chemistry and Technology of Drugs, "Sapienza University of Rome", P.le Aldo Moro 5, 00185, Rome, Italy*
[b] Flow Chemistry Group, Van't Hoff Institute for Molecular Sciences (HIMS) University of Amsterdam Science Park 904, 1098 XH, Amsterdam (The Netherlands)
[c]Institute of Organic Chemistry, Polish Academy of Sciences Kasprzaka 44/52, 01-224 Warsaw (Poland)

**francesca.arrighi@uniroma1.it*

Unnatural amino acids, and their synthesis via the late-stage functionalization (LSF) of peptides, play a crucial role in areas such as drug design and discovery [1]. Historically, the LSF of biomolecules has predominantly utilized traditional synthetic methodologies that exploit nucleophilic residues, such as cysteine, lysine, or tyrosine [2]. In this study, we present a photocatalytic hydroarylation process targeting the electrophilic residue dehydroalanine (Dha). This residue possesses an α, β-unsaturated moiety and can be combined with various arylthianthrenium salts, both in batch and flow reactors. In our methodology, we utilized DIPEA as the stechiometric reductant and eosin Y as the photocatalyst, harnessing visible light irradiation at 456 nm wavelength. Expanding on the established optimal conditions for the photocatalytic arylation of Dha , both in batch and flow setups, we aimed to assess the versatility and applicability of our methodology. Notably, the flow setup proved instrumental for efficient scale-up, paving the way for the synthesis of unnatural amino acids and peptides in substantial quantities. Our photocatalytic approach, being inherently mild, permits the diversification of peptides even when they contain sensitive functional groups. In addition, the readily available arylthianthrenium salts facilitate the seamless integration of Dha-infused peptides with a wide range of arenes, drug blueprints, and natural products, culminating in the creation of unconventional phenylalanine derivatives.In summary, our method enables the synthesis of numerous unnatural amino acids in both batch and flow setups, facilitating easy scalability. Notably, our approach demonstrates exceptional compatibility with diverse functional groups, accommodating sensitive structural elements present in both reactants. The precision in targeting specific sites and functional groups in peptide hydroarylation is evidenced by its ability to preserve delicate residues within various amino acids. This mild photochemical technique holds promise for advancing late-stage functionalization of sizable peptides and proteins.

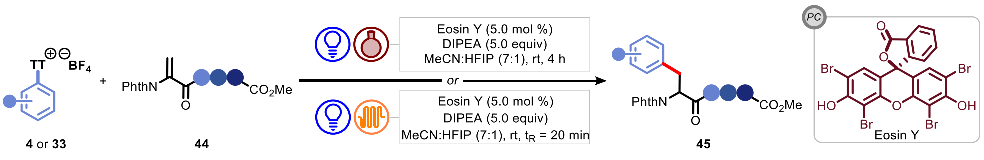


Figure 1. LSF of Dha-containing peptides leading to conjugation and ligation.

References

[1] M. T. Taylor, J. E. Nelson, M. G. Suero, M. J. Gaunt, *Nature* **2018**, 562, 563-568;
[2] R. A. Aycock, D. B. Vogt, N. T. Jui, *Chem. Sci.* **2017**, *8*, 7998-8003

Chiral carbon dots from L-proline: electrochemical synthesis and application as recyclable nano-organocatalysts

Martina Bortolami[1*], Fabrizio Vetica[2], Marta Feroci[1]

[1]Department of Basic and Applied Sciences for Engineering (SBAI), Sapienza University of Rome, Via Castro Laurenziano 7, I-00161, Rome, Italy
[2]Department of Chemistry, Sapienza University of Rome, Piazzale Aldo Moro 5, 00185, Rome, Italy

**martina.bortolami@uniroma1.it*

Carbon dots (CDs) are quasi-spherical carbon-based nanomaterials with excellent photoluminescence properties, together with low-toxicity and generally high biocompatibility. These nanoparticles are characterized by a carbon core and a surface functionalized with different chemical groups. Among the various synthetic procedures, electrochemistry has proved to be a green, practical, and efficient method for CDs preparation. [1] Due to their characteristics, CDs have been employed in many fields, such as in chemical and electrochemical sensors, in photovoltaics, as well as in organocatalysis.

Since CDs have found efficient applications as catalytic materials in organic synthesis, chiral CDs (obtained either by late-stage surface modifications or by one-pot preparations starting from chiral molecules) could represent new recyclable heterogeneous organocatalysts to promote stereoselective reactions. [2]

In this context, we have studied the possibility of electrochemically synthesizing chiral CDs to be used as sustainable, green and biocompatible nano-organocatalysts to promote stereoselective reactions. We have developed an efficient and cost-effective electrochemical synthetic methodology for the synthesis of chiral CDs, using L-proline as starting material or passivating agent. We have systematically screened different electrochemical set-ups and their influence on the performance of chiral CDs as catalytic materials (Figure 1). [3] The obtained CDs have been successfully employed to catalyze an asymmetric aldol reaction, showing excellent results in terms of yield, diastereo- and enantioselectivity, [3] and in a Mannich reaction, giving good yields when carried out in water. [4] Moreover, the sustainable nature of the CDs was demonstrated by recycling the catalysts for up to three cycles without any loss of reactivity or stereoselectivity.

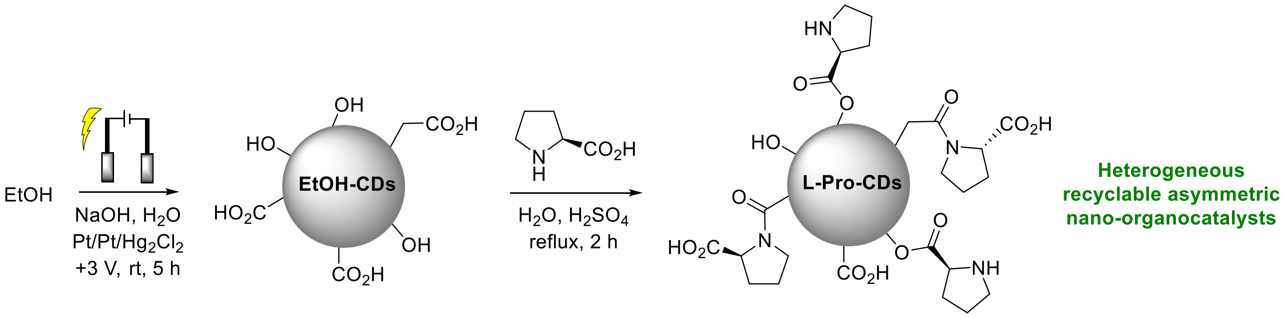


Figure 1. Optimized procedure for L-Pro-CDs preparation.

References

[1] Rocco D., Moldoveanu V.G., Feroci M., Bortolami M., Vetica F. *ChemElectroChem*, 2023, **10**, e202201104.
[2] Rosso C., Filippini G., Prato M., *ACS Catal.*, 2020, **10**, 8090–8105.
[3] Bortolami M., Bogles I.I., Bombelli C., Pandolfi F., Feroci M., Vetica F., *Molecules*, 2022, **27**, 5150.
[4] Bortolami M., Rocco D., Simonis B., Feroci M., Vetica F., *Synth. Commun.*, 2023, **53**, 1647–1663.

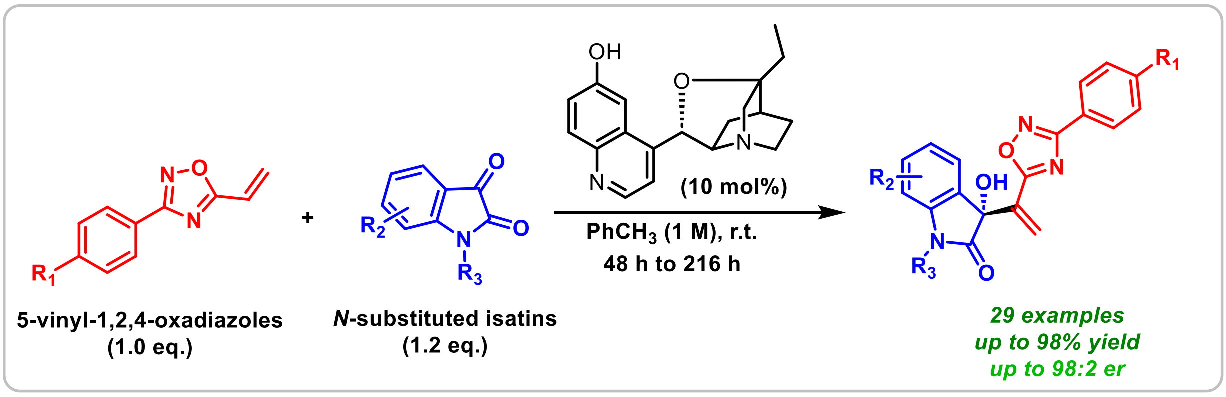
Asymmetric organocatalyzed Morita-Baylis-Hillman reaction of isatins with 5-vinyl-1,2,4-oxadiazoles

Thaynan A. B. Chagas[1*], Fábio S. Fernandes[1], Bruno A. Piscelli[2], Rodrigo A. Cormanich[2] and Fernando Coelho[1]

[1]Laboratory of Synthesis of Natural Products and Drugs, Institute of Chemistry, University of Campinas – UNICAMP, Campinas, São Paulo, Brazil, 13083-970
[2]Laboratory of Experimental and Theoretical Organic Chemistry, Institute of Chemistry, University of Campinas – UNICAMP, Campinas, São Paulo, Brazil, 13083-970

**thaynan.abchagas@gmail.com*

Recently, our research group reported 5-vinyl-1,2,4-oxadiazoles as new nucleophilic partners in the Morita-Baylis-Hillman (MBH) reaction[1] and it was discovered that some of the MBH adducts containing this heterocycle motif have good antiparasitic activity.[2] Until now, there is no report on the use of vinyl heterocycles in asymmetric MBH reactions. Therefore, in this work we developed a new methodology for asymmetric MBH reaction of isatins with 5-vinyl-1,2,4-oxadiazoles. During reaction optimization, we evaluated nine organocatalysts, twelve solvents and ten additives. We also evaluated different temperatures, solvent concentration, equivalence of substrates and catalytic amount. The best condition is shown in Scheme 1. A broad scope of compounds was obtained with good yields and good enantiomeric ratios using this new and efficient methodology. Theoretical studies are being conducted in order to understand the factors that influence the enantiomeric ratios.



Scheme 1. New asymmetric methodology of MBH reaction.

Acknowledgements:

We thank FAPESP (grants 2018/03910-1, 2021/13544-5, 2022/10156-7 and 2023/18007-3), CNPq (grants 301330/2018-2, 151763/2022-4 and 407960/2023-2), CAPES (grant 88887.937775/2024-00) and FAEPEX for scholarships and financial support.

References

[1] Fernandes F.S., Rodrigues Jr. M.T., Zeoly L.A., Conti C., Angolini C.F.F., Eberlin M.N., Coelho F. *Journal of Organic Chemistry*, 2018, **83**, 15118.
[2] Fernandes F.S., Santos H., Lima S.R., Conti C., Rodrigues Jr. M.T., Zeoly L.A., Ferreira L.L.G., Krogh R., Andricopulo A.D., Coelho F. *European Journal of Medicinal Chemistry*, 2020, **201**, 112418.

Low Environmental Impact Synthesis of γ-Lactones through Photoinduced Baeyer-Villiger Oxidation of Cyclic Ketones

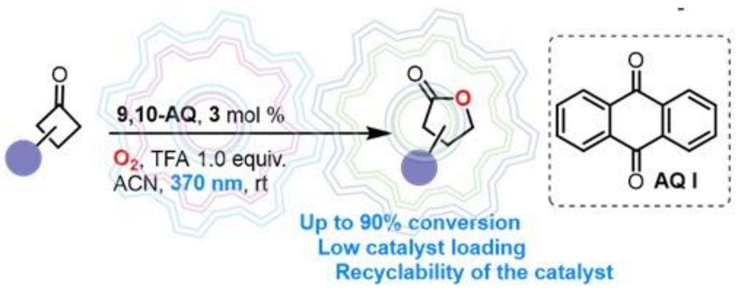
M. C. Cabua[1*], D. Moi[1], F. Secci[1]

[1] *Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Cagliari, 09042, Monserrato (CA)*

* *m.cabua@studenti.uniss.it*

γ-lactones are five-membered cyclic esters that constitute a key structural motif widespread in many biologically active compounds.[1] A great variety of methods have been developed to achieve the synthesis of this moiety, amongst them the oxidation of cyclic ketones through the Baeyer-Villiger (BV) reaction still shines for its efficiency and wide applicability.[2]

This project consisted in the development of a new chemo- and regioselective protocol that allows to obtain γ-lactones in good to excellent yields through the atom-efficient photo-oxidation of functionalized cyclobutanones[3] in the presence of TFA, and generating the reactive oxygen species *in situ* using anthraquinone and molecular oxygen under visible light irradiation. 2- and 3-substituted cyclobutanones have been used to study the scope of the reaction, furthermore the reaction of enantiopure ketones provided the oxidation products with full preservation of their stereochemical identity. In the majority of studied cases the desired compounds have been obtained with high purity after simple filtration of the catalyst, thus allowing to significantly reduce the production of solvent waste.



References

[1] S. Schulz, S. Hötling, Nat. Prod. Rep. 2015, **32**, 1042-1066.
[2] G.-J. Ten Brink, I. W. C. E. Arends, R. A. Sheldon, Chem. Rev. 2004, **104**, 4105-4124.
[3] A. Frongia, C. Girard, J. Ollivier, P. P. Piras, F. Secci, Synlett 2008, **18**, 2823-2825.

Mechanochemical Synthesis of Agrochemicals

Andrea Casagrande[1,2*], Riina Aav[3], Dzimitry Kananovich[3], Allan Niidu[2], Evelina Colacino[1]

[1] Institut Charles Gerhardt (ICGM), University of Montpellier, Montpellier, France
[2] Virumaa College, Tallinn University of Technology, Tallinn, Estonia
[3] Department of Chemistry and Biotechnology, Tallinn University of Technology, Tallinn, Estonia

**andrea.casagrande@etu.umontpellier.fr, ancasa@taltech.ee*

The herein presented work aims to illustrate alternative, greener protocols, that can represent an alternative to deliver the synthesis of industry valuable agrochemicals through the use of mechanochemical protocols. The necessity of greener protocols to deliver this reaction stems from the necessity of reduce the environmental impact in targets that have high production volumes, also addressing hazard concerns to the operators, by developing routes that have also simplified setups and less hazardous chemicals. Various protocols were explored to provide a more sustainable alternative to classical solution-based methodologies as mechanochemistry makes use of transmission of mechanical energy in a solvent-less environment, resulting mainly in less waste production, resource use and energy efficiency, in compliance with green chemistry principles[1]. Reactions were performed by milling in a vibrating ball mill (VBM) or planetary mill (PBM) for upscale purposes, exploring the effects that different jar and ball material have on the product output. The reactions were performed either completely solventless or with catalytic amounts of solvents, by taking advantage of a technique called liquid assisted grinding[2] (LAG). Moreover, a greenness assessment was made with the use of toolkits useful to confront green metrics and to assess the adherence to green chemistry principles, that show quantitatively and semi-quantitatively the overall better performance and greenness of the mechanochemical methods against the solution-based commercial routes[3]. In conclusion, it was shown that greener possibilities to perform alternative solid-state syntheses to already established solution-based protocols are possible, and grace to the simple setup and workup procedures, along with the repurposing of already in-use instruments in the industry (e.g. ball millers), the proposed protocol can be readily implemented in real world industrial scenarios.

References

[1] P. Anastas, J. Warner, Green Chemistry: Theory and Practice, Oxford University Press, New York, 1998.
[2] G. A. Bowmaker, Chem. Commun. 2013, 49, 334–348.
[3] N. Fantozzi, J.-N. Volle, A. Porcheddu, D. Virieux, F. García, E. Colacino, Chem Soc Rev 2023, 52, 6680–6714.

Total synthesis of kinamycin F and its analogues through transition metal-catalyzed domino reaction

Lorenzo Celio[1*], A. Ingvarsson[2], P. Dunås[2], S. E. Lewis[3], N. Kann[2]

[1]*Department of Chemistry, Sapienza University of Rome, Rome, Italy*
[2]*Department of Chemistry and Chemical Engineering, Chalmers University of Technology, Göteborg, Sweden*
[3]*Department of Chemistry, University of Bath, Bath, United Kingdom*

**lorenzo.celio@uniroma1.it*

Kinamycins are bacterial secondary metabolites that belong to the tetrahydrofluorenone class of natural products. They contain a [6-5-6] ring scaffold and possess a broad range of biological properties. In particular, kinamycin F (**Fig.1**) shows marked anti-cancer activity and may be obtained directly from bacteria. However, this method provides access only to small amounts of compound, thus not enough to carry out in-depth studies on the development of kinamycin F and its possible derivatives displaying cytotoxic behaviour.[1] Hence, this project aims to develop a robust and diversity-oriented synthetic route to kinamycin F in order to also access different analogues for biological screening purposes and applications. The proposed total synthesis revolves around a Pd-catalyzed domino cyclization reaction developed in a previous work on similar substrates.[2] In addition to this reaction, key steps in this sequence involve enzymatic arene oxidation, selective reduction of an amide directing group to a methyl, as well as the installment of two additional hydroxy-substituents via epoxidation and hydrolysis.

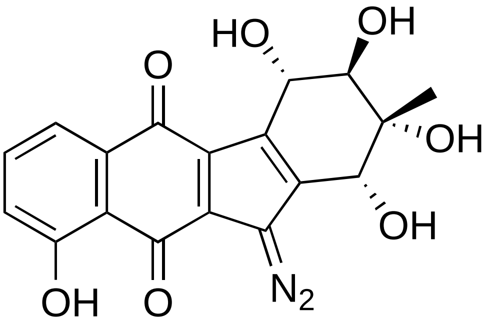


Figure 1. Kinamycin F

Acknowledgements:

Thanks to the Department of Chemistry of Sapienza University of Rome and Chalmers University of Technology for the given opportunity to work on this project. The Swedish Research Council (Grant no. 2023-04342) is gratefully acknowledged for fundings.

References

[1] Herzon, S. B. The Kinamycins. In Total Synthesis of Natural Products: At the Frontiers of Organic Chemistry, Li, J. J., Corey, E. J. Eds.; *Springer Berlin Heidelberg*, 2012; pp 39-65.
[2] P. Dunås, A. J. Paterson, G. Kociok-Köhn, M. Rahm, S. E. Lewis, N. Kann, *Chem. Commun.* 2021, **57**, 6518–6521.

Enantioselective α-Alkylation of Aldehydes by Photoexcitation of Carbon Dots

Antonio Di Sabato[1]*, Marta Santoni[1], Vyali Georgian Moldoveanu[1], Francesca Leonelli[1], Fabrizio Vetica[1]

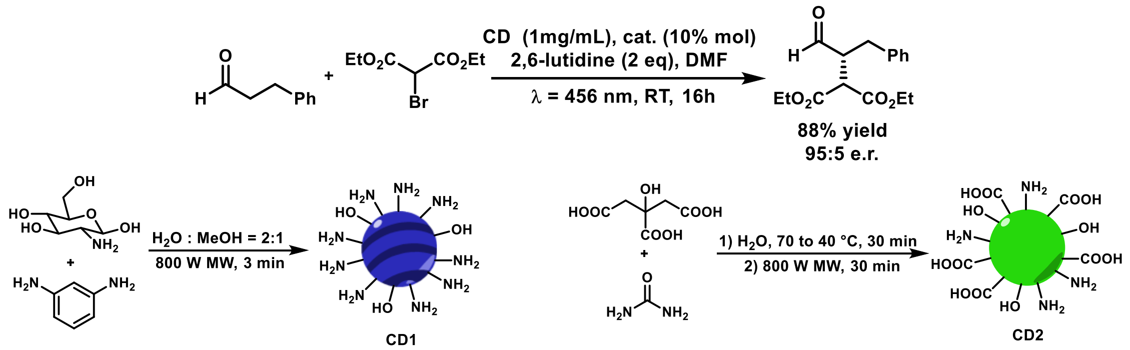
[1]*Department of Chemistry, Sapienza University of Rome, Piazzale Aldo Moro 5, 00185 Rome, Italy*

**antonio.disabato@uniroma1.it*

In the last few years, Carbon Dots (CDs) are emerging as a novel class of photoluminescent nanomaterials. They can be easily prepared with both bottom-up and top-down approaches from readily available feedstock materials or waste biomasses[1]. Given their biocompatibility, efficient and modulable light absorption, great electron-transfer ability, and chemical stability, they have been used in a wide range of applications, such as drug delivery, bioimaging, photocatalysis for water splitting and in optoelectronics. These proprieties suggest the possible use of CDs as a photocatalyst in organic transformations, as a cheap and sustainable alternative to Iridium and Ruthenium pyridyl complexes. While CDs have been successfully employed in photoinduced aldol condensation[2], cross-coupling[3] and Knoevenagel reaction[4], stereoselective transformations are still unexplored.

In this work we disclose the potential of CDs as photocatalysts in the enantioselective alpha alkylation of hydrocinnamaldehyde with diethyl bromomalonate. The CDs used in this study show excellent photocatalytic activity at loadings down to 0.1 mg/mL, with very high yield (up to 88%) and enantioselectivity (up to e.r. = 95:5). These results are in line with those known in the literature for the same substrates, proving the viability of CDs as a new, cheap, and green alternative to transition metal-based photocatalysts[5][6].

Moreover, we investigated the role of the various components of the reaction, coupled with extensive spectroscopic studies, to picture a possible reaction mechanism.



References

[1] Đorđević L., Arcudi F., Cacioppo M., Prato M., *Nat. Nanotechnol.*, 2022, **17**, 112.
[2] Han Y., Huang H., Zhang H., Liu Y., Han X., Liu R., Li H., Kang Z., *ACS Catal.*, 2014, **4**, 781.
[3] Zhao Z., Pieber B., Delbianco M., *ACS Catal.*, 2022, **12**, 13831.
[4] Pei X., Xiong D., Wang H., Gao S., Zhang X., Zhang S., Wang J., *Angew. Chem. Int. Ed.*, 2018, **57**, 3687.
[5] Nicewicz D. A., MacMillan D. W. C., *Science*, 2008, **322**, 77.
[6] Gualandi A., Marchini M., Mengozzi L., Kidanu H. T., Franc A., Ceroni P., Cozzi P. G., *Eur. J. Org. Chem.*, 2020, **10,** 1486.

Proximity Effects on the Reactivity of Nonheme Fe(IV)=O complex in C-H Oxidation

Alessandro Fagnano*,[a§] Federico Frateloreto,[a§] Roberta Paoloni,[a] Carla Sappino,[a] Osvaldo Lanzalunga,[a] Miquel Costas,[b]* Stefano Di Stefano[a] * and Giorgio Olivo[a]*

[a] *Dipartimento di Chimica and Istituto CNR per i Sistemi Biologici (ISB-CNR); Sezione Meccanismi di Reazione, Università di Roma "La Sapienza", P.le A. Moro, 5, 00185 Rome, Italy.*
[b]*QBIS-Cat, Institut de Química Computacional i Catàlisi (IQCC), Departament de Quimica, Universitat de Girona, Campus Montilivi, 17071 Girona, Catalonia, Spain.*

**alessandro.fagnano@uniroma1.it*

Precise control of substrate positioning and orientation (its proximity to the reactive unit) is often invoked to rationalize the superior enzymatic reaction rates and selectivities when compared to synthetic models. Artificial nonheme Fe(IV)=O complexes react with C(sp^3)-H bonds via a biomimetic Hydrogen Atom Transfer/Hydroxyl Rebound mechanism,[1] but rates, site-selectivity and even hydroxyl rebound efficiency (ligand rebound versus substrate radical diffusion) are smaller than in oxygenases.[2,3] Herein, we quantitatively analyze how substrate binding modulates nonheme Fe(IV)=O reactivity by comparing rates and outcomes of C-H oxidation by a pair of Fe(IV)=O complexes that share the same first coordination sphere but only one contains a crown ether receptor that recognizes the substrate (Figure 1). Substrate binding makes the reaction intramolecular, exhibiting Michaelis-Menten kinetics and increased reaction rates. In addition, C-H oxidation occurs with high site selectivity for remote sites. Analysis of Effective Molarity reveals that the system operates at its maximal theoretical capability for the oxidation of these remote sites. Remarkably, substrate positioning also affects Hydroxyl Rebound, whose efficiency increases only on the sites placed in proximity by recognition. Overall, these observations provide evidence that control of substrate positioning via weak interactions is an effective tool to modulate the reactivity of oxygenases and its models.

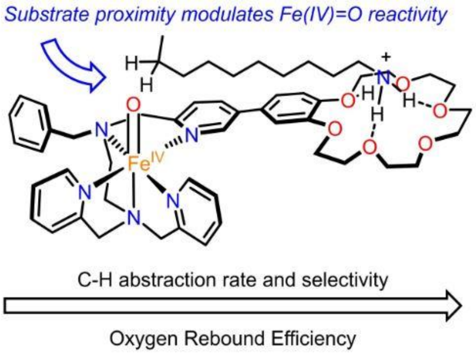


Figure 1: representation of a supramolecularly guided C-H oxidation by a Fe(IV)=O complex. Crown ether receptor interact with primary ammonium function of oxidable substrate.

[1] A. J. Jasniewski, L. J. Que, *Chem. Rev.* 2018, **118**, 2554–2592.
[2] S. D. Wong, M. Srnec, M. L. Matthews, L. V. Liu, Y. Kwak, K. Park, C. B. Bell, E. E. Alp, J. Zhao, Y. Yoda, et al., *Nature* 2013, **499**, 320–323.
[3] K. Bin Cho, H. Hirao, S. Shaik, W. Nam, *Chem. Soc. Rev.* 2016, **45**, 1197–1210.

Enzyme adsorption on hydroxyapatite to enable continuous flow biocatalysis

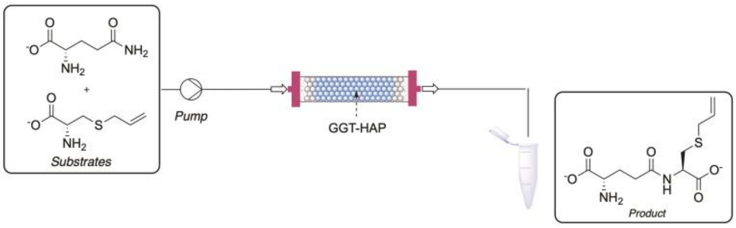
L. Gelati[1,2*], F. Medici[1], A. Gervasini[1], M. Benaglia[1], G. Speranza[1], C. F. Morelli[1]

[1]*Department of Chemistry, University of Milan, Milan, Italy*
[2]*Department of Architecture and Industrial Design, University of Campania Luigi Vanvitelli, Aversa, Italy*

**leonardo.gelati@unimi.it*

Biocatalysis has emerged in the last time as an interesting tool for organic synthesis: in fact, the use of enzymes provides high efficiency and selectivity, mild operational conditions, and lower hazards thanks to their non-toxicity.[1] However, the high cost of these catalysts often hampers their application at an industrial level. To tackle this issue, their recoverability and reusability must be granted, and this can be achieved through enzyme immobilization on a solid support.[2] Compared to free enzymes in solution, the immobilized ones are more robust, possess higher operational and storage stability as well as higher tolerance to organic solvents, and can be integrated in continuous flow reactors to achieve process intensification.[3] Among the possible carriers for enzyme immobilization, hydroxyapatite (HAP), the inorganic component of bones, is emerging for its many favourable features, such as non-toxicity, high structural stability, large surface area, and ease in surface modification.[4] Moreover, it can be obtained from waste such as ashes from waste-to-energy plants, the fish supply chain, the avian supply chain, etc., in agreement with circular economy principles.

γ-Glutamyl transferase from *Escherichia coli* (EcGGT) was chosen as the model enzyme to study the immobilization process on HAP. Enzyme immobilization was carried out by adsorption, simply by mixing an enzyme solution and a hydroxyapatite suspension under controlled conditions (pH, temperature). Different particle sizes and experimental set-up were investigated and, after assessing that the enzyme did not desorb under reaction conditions, the supported GGT was tested as biocatalysts in the enzymatic synthesis of γ-glutamyl-*S*-allyl-L-cysteine, a natural compound with flavor-enhancing properties. The enzyme reusability was tested and its storage stability was verified. After assessing the applicability of the HAP-adsorbed GGT in batch conditions, the same enzyme was adsorbed in continuous flow conditions in a packed-bed reactor made of HAP. Different residence times were studied and the obtained reactor was used in the same model reaction (Scheme 1).



Scheme 1 In flow γ-glutamylation of *S*-allyl-L-cysteine

Acknowledgements:

Project realized within the MUSA – Multilayered Urban Sustainability Action – project funded by the European Union – NextGenerationEU, under the National Recovery and Resilience Plan (NRRP) Mission 4 Component 2 Investment Line 1.5: Strengthening of research structures and creation of R&D “innovation ecosystem”, set up of “territorial leaders in R&D”

References

[1] Sheldon R. A., *Catal Today*, 2024, **431**, 114571.
[2] Aggarwal S., Chakravarty A., Ikram S., *Int J Biol Macromol*, 2021, **167**, 962.
[3] Benítez-Mateos A. I., Paradisi F., *Methods in Molecular Biology*, 2022, Chapter 14, pp. 263-276, Humana Press Inc., USA, New York
[4] Gelati L., Rabufetti M., Benaglia M., Campisi S., Gervasini A., Speranza G., Morelli C. F., *ChemPlusChem*, accepted for publication, DOI: 10.1002/cplu.202400204

Stereoselective Synthesis of Crucial Fragments for the Total Synthesis of Voratin C

Vyali Georgian Moldoveanu[1*], Francesca Leonelli[1], Fabrizio Vetica[1]

[1]*Departmen of chemistry, Sapienza University of Rome, Rome, Italy*

**vyaligeorgian.moldoveanu@uniroma1.it*

For centuries, natural products have fueled the imagination of chemists due to their complex structures and potential medical benefits. However, harvesting these compounds from nature on a large scale proves impractical and incompatible with human needs.

In recent years, dinoflagellates, especially certain algae species[1], have emerged as promising sources of bioactive compounds with medicinal potential. While challenges persist in cultivating these microorganisms in labs, synthetic chemistry offers a hopeful path for replicating these compounds. This approach holds potential for industrial-scale production. Notably, asymmetric synthesis plays a crucial role in tackling the inherent chemical complexities of these natural products. Among these discoveries are the Voratins (A-C)[2], a novel class of natural compounds showing promise in treating benign prostatic hyperplasia, a widespread condition.

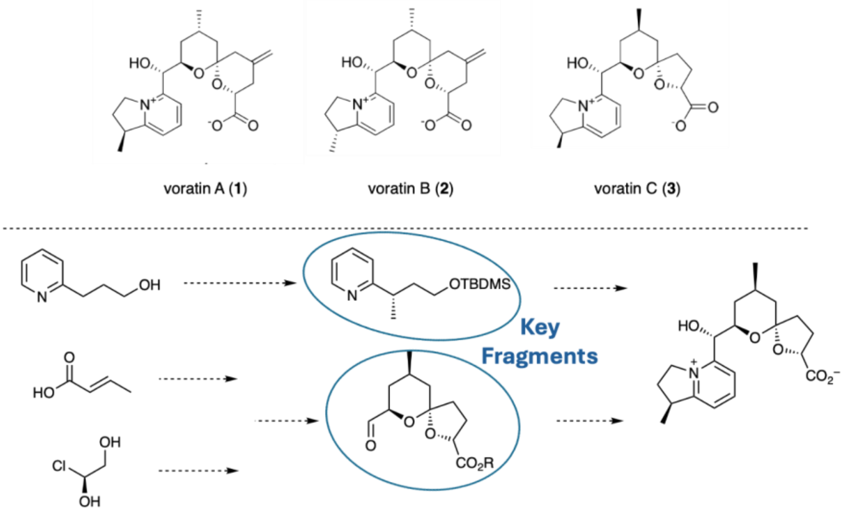

voratin A (**1**) voratin B (**2**) voratin C (**3**)

Figure 1. – *Voratins (A-C) molecules; scheme of voratin C synthesis*

Voratin C (**3**) exhibits stronger anti-tumor action than A and B justifying its selection as the target molecule for this total synthesis. The strategy aims to streamline synthesis, maximizing efficiency and minimizing waste by breaking down the process into manageable pathways. Convergent retrosynthesis optimizes resource utilization, reduces waste generation, and allows precise control over reaction conditions. Crucially, the molecule's complex structure, with numerous chiral centers, necessitates a strong emphasis on asymmetric procedures. By leveraging asymmetric catalysis or chiral auxiliaries, this approach ensures the synthesis proceeds with high efficiency and precision. Overall, this convergent retrosynthetic approach offers a streamlined and eco-friendly route to Voratin C synthesis, maximizing efficiency while minimizing environmental footprint.

References

[1] Clardy J.,Walsh C. *Nature*, 2004, **432**, 829.
[2] Lee H., Moon J.,Yoo Y.,Jeong E., Rho J. *J. Nat. Prod.* 2022, **85**, 1495.

Transition-metal free one-pot synthesis of 1-aryl-1,2,4-triazoles via arylazo sulfones under visible light irradiation

L. Nicchio[1,2*], L. Di Terlizzi[1], L. Neuville[2], M. Fagnoni[1], G. Masson[2], S. Protti[1]

[1] *PhotoGreen Lab, Department of Chemistry, University of Pavia, V. Le Taramelli 12, Pavia 27100, Italy*
[2] *Institut de Chimie des Substances Naturelles, Université Paris Saclay, UPR2301- CNRS, Avenue de la Terrasse, 91198 Gif-sur-Yvette Cedex, France*
**luca.nicchio01@universitadiapvia.it*

The 1,2,4-triazole core is present in several bioactive molecules and therapeutically significant drugs including alprazolam and fluconazole. The growing interest for this scaffold and the drawbacks of traditional approaches have raised the demand for mild and sustainable synthetic routes.[1] Photochemical approaches utilizing visible light to achieve this target remain underexplored. In the view of this, we exploited arylazo sulfones as photoactive substrates for the synthesis of the 1,2,4-triazole ring. The dyed auxiliary group (N_2SO_2R) in arylazo sulfones is responsible for visible light absorption and photoreactivity, allowing the formation of radical species.[2] Indeed they have been recently employed as photoactive reagents in the visible-light-mediated metal and (photo)catalyst-free preparation of α-sulfonyl arylhydrazones.[3]

We present herein a one-pot, 100% atom economy, mild and transition-metal-free photochemical route to *N*-aryl-1,2,4-triazoles, by irradiation of variously substituted arylazo sulfones **1** in the presence of different *N*-alkenyl amides **2** (Figure 1). The desired products **3** have been isolated in moderate to satisfactory yields via cyclization of the key intermediate **I** and the developed protocol showed an excellent group tolerance. Post-transformations on compounds **3** and their preparation under flow conditions have been also performed.

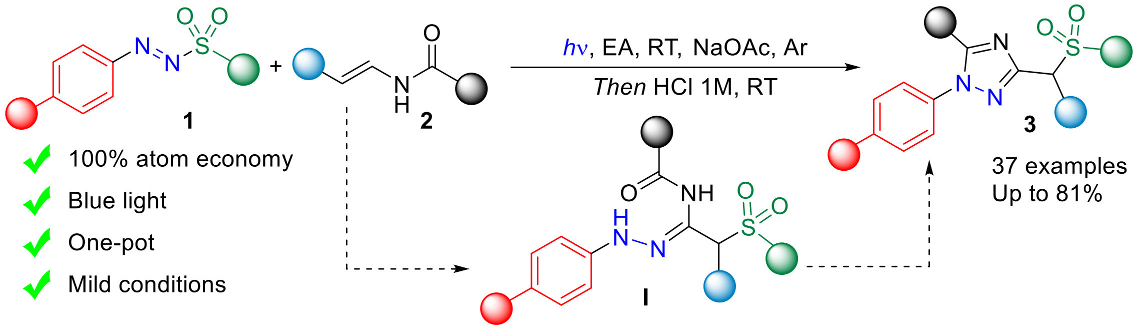


Figure 1: General scheme of the proposed photochemical approach to 1-aryl-1,2,4-triazoles.

Acknowledgements:

LN is grateful to the support of the IDEX Paris-Saclay, “ADI 2022” ANR-11-IDEX-0003-02 for the doctoral fellowships.

References

[1] Gonnet L., Baron M., Baltas M. *Molecules*, 2021, **26**, 5667.
[2] Qiu D., Lian C., Mao J., Fagnoni M., Protti S. *J. Org. Chem.*, 2020, **85**, 12813.
[3] Di Terlizzi L., Nicchio L., Callegari C., Scaringi S., Neuville L., Fagnoni M., Protti S., Masson G. *Org. Lett.*, 2023, **25**, 9047.

The role of catalysis in the conversion of carbohydrates

Fabrizio Olivito[1*], Goldie Oza[2], Pravin Jagdale[3], Giovanni Golemme[1]

[1]Department of Environmental Engineering, University of Calabria, Cosenza, Italy
[2] Centro de Investigación y Desarrollo Tecnológico en Electroquímica (CIDETEQ), Parque Tecnológico, Querétaro CP 76703, Mexico
[3] Center for Sustainable Future Technologies (IIT@PoliTO), Italian Institute of Technology (IIT), 10144 Torino, Italy

**fabrizio.olivito@unical.it*

The conversion of naturally-occurring organic compounds, in the form of waste or natural abundant sources, is one of the main purposes of the current research on sustainable chemistry. Catalysis represents a crucial point towards the evolution of processes in terms of yield, efficiency, time and costs. Carbohydrates and related polymers continue to be a theme with many opportunities in terms of discoveries and applications [1]. Platform molecules, such as furan compounds, can be obtained from biomass by green methodologies and mild conditions [2]. These renewable chemicals, produced from biomass-derived carbohydrates have a huge number of applications, such as polymer chemistry and biofuels [3,4]. In this work, we will demonstrate how, by varying the type of catalyst, based on certain experimental conditions, it is possible to direct the synthesis into one of the products shown in Figure 1A. For example, fructose can be converted in the same experimental conditions, but varying the catalyst, into three different reaction products (Figure 1B), due to the different reaction mechanisms. Some practical applications of the products obtained will also be discussed.

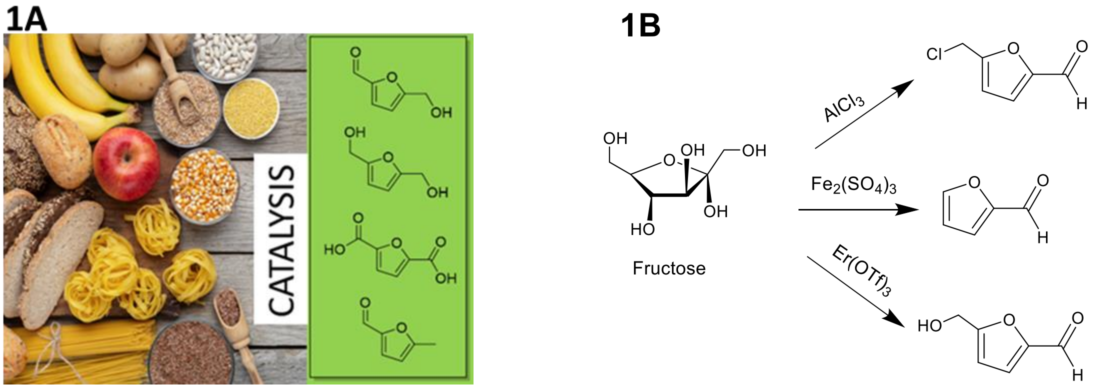


Figure 1. Some carbohydrate-rich foods and their derived furan compounds (1A). Different products obtainable from fructose with the choice of the right catalyst (1B).

References

[1] Tursi A., Olivito F., *Advances in Bioenergy and Microfluidic Applications*, 2021, Chapter 1, Pages 3-39, Elsevier.
[2] Olivito F., Jagdale P., and Oza G., *ACS Sustainable Chemistry & Engineering*, 2023, **11**, 17595.
[3] Olivito F., Jagdale P., Oza G. *Toxics*, 2023, **11**, 698.
[4] Romeo I., Olivito F., Tursi A., Algieri V., Beneduci A., Chidichimo G., Maiuolo L., Sicilia E., De Nino A., *RSC Adv.*, 2020,**10**, 34738.

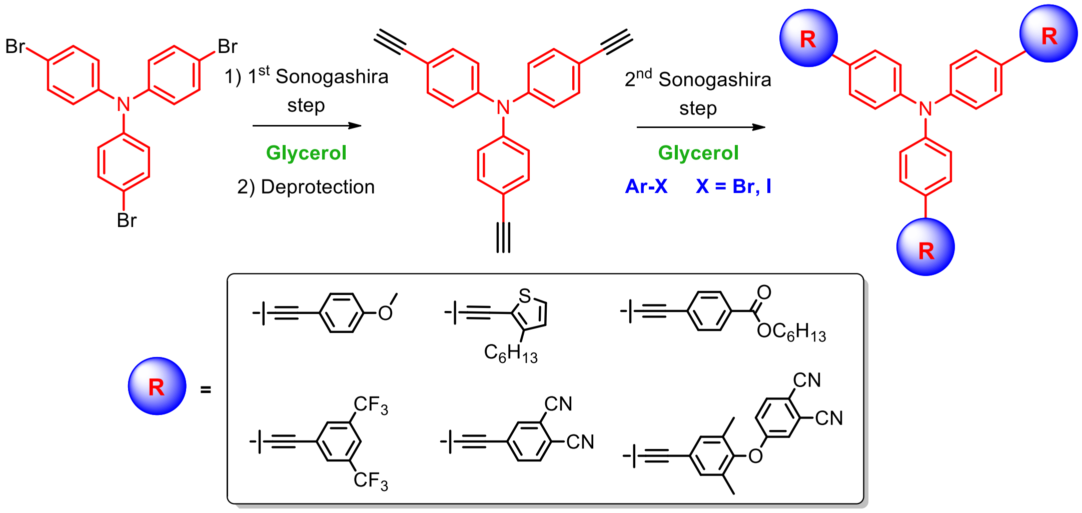
Greener Light: Triarylamine-Based Materials for Sustainable Optoelectronics

V. Raglione[1*], F. Palmeri[1,2], G. Zanotti[1]

[1] Consiglio Nazionale delle Ricerche, Istituto di Struttura della Materia (CNR-ISM), Via Salaria km 29300, 00015 Monterotondo, Italy
[2] Department of Chemistry, Sapienza University of Rome, Ple Aldo Moro, 5, 00185 Rome, Italy

* *venanzio.raglione@mlib.ism.cnr.it*

The ever-growing drive for cleaner and more efficient chemical processes has fueled significant exploration within the scientific community for the development of greener synthetic methods. These methods prioritize the elimination or substantial minimization of hazardous and expensive chemicals, while simultaneously striving to maintain high reaction efficiency. Glycerol, a non-toxic and readily available byproduct generated during biodiesel production, is emerging as a highly valuable resource for sustainable organic synthesis. By offering a convincing alternative to traditional organic solvents, glycerol could potentially enhance the green and efficient nature of organic synthesis[1]. In this contribution, we present a sustainable approach to the Sonogashira reaction, which harness glycerol as the reaction solvent. This alternative strategy was successfully employed in the synthesis of a series of novel triarylamine-based derivatives. These derivatives incorporate either electron-donating or electron-withdrawing substituents, allowing for an extensive investigation into the structure-reactivity relationship of the starting aromatic halides. Furthermore, a thorough optical and physicochemical characterization of the obtained compounds, revealed their suitability for cutting-edge optoelectronic applications. For example, steady-state or time-resolved fluorescence spectroscopy as well as pump probe spectroscopy were used in order to study electronic dynamics. All their optical characteristics make them particularly suitable for application as hole transport materials (HTMs)[2] in wide-band gap perovskite solar cells (PSCs) and luminophores in Luminescent Solar Concentrators (LSCs)[3].



References

[1] Yanlong G. and Jerome F. *Green Chemistry*, 2010, **12**, 1127.
[2] Rodríguez-Seco C., Cabau L., Vidal-Ferran A., Palomares E. *Acc. Chem. Res.* 2018, **51**, 869.
[3] J. Roncali *Adv. Energy Mater.* 2020, **10**, 2001907.

Radical strain-release photocatalysis for the synthesis of azetidines

L. Rizzo[1], R. I. Rodríguez[1], V. Corti[1], S. Visentini[1], M. Bortolus [1], A. Amati[2], M. Natali[2], G. Pelosi[3], P. Costa[1], L. Dell'Amico[1]

[1] Department of Chemical Sciences, University of Padova, Via Francesco Marzolo 11 Padova, Italy.
[2] Department of Chemical, Pharmaceutical and Agricultural Sciences, University of Ferrara, Via Luigi Borsari 46, Ferrara, Italy
[3] Department of Chemistry, Life Sciences and Environmental Sustainability, University of Parma, Parco Area delle Scienze 17,Parma, Italy.

**lorenzo.rizzo@phd.unipd.it*

The renascent interest on four-member rings has vastly widen the range of research and applications in medicinal chemistry discovery programs, guiding the scientific community to upgrade, rethink, and reinvent obsolete strategies for their crafting[1]. Such scenario has enlarged the tactical repertoire of drug hunters, particularly awakening the almost-forgotten concept of strain-release[2]. However, in contrast to the tens of well-described strategies that access small carbocyclic derivatives, azetidines remain severely unexplored in both polar and radical realms[3,4]. Here is reported a general solution by introducing azabicyclo[1.1.0]butanes (ABBs) to the field of strain-release photocatalysis, showing that can be transformed directly to sulfonylazetidines through a one-step difunctionalization protocol[5]. Successful implementation requires the unprecedented addition of a transient sulfonyl radical to the nitrogen atom of ABB, followed by a carbon- and nitrogen-centred radical recombination. The chemistry is orchestrated by a novel organic photosensitiser (PS), which governs the key energy transfer process with various types of sulfonyl imine precursors. The radical intermediates are intercepted by the ABB via a radical strain-release process, providing access to azetidines in high chemical yields and in a single operation.

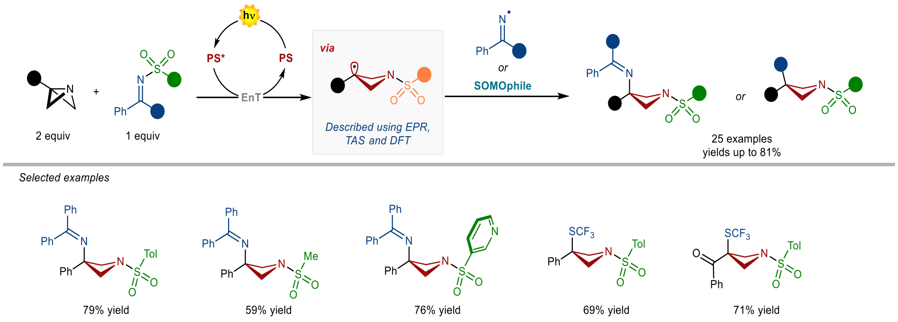


Figure 1. Photocatalysis in action for crafting azetidines.

References

[1] M. R. Bauer, P. Di Fruscia, S. C. C. Lucas, I. N. Michaelides, J. E. Nelson, R. I. Storer, B. C. Whitehurst, *RSC Med. Chem.*, **2021**, *12*, 448-471.
[2] J. Turkowska, J. Durka, D. Gryko, *Chem. Commun.*, **2020**, *56*, 5718-5734.
[3] M. Andresini, L. Degennaro, R. Luisi, *Org. Biomol. Chem.*, **2020**, *18*, 5798-5810.
[4] P. Belloti, F. Glorius, *J. Am. Chem. Soc.*, **2023**, *145*, 20716-20732.
[5] R. I. Rodríguez, V. Corti, L. Rizzo, S. Visentini, M. Bortolus , A. Amati, M. Natali, G. Pelosi, P. Costa, L. Dell' Amico, **2024**, ChemRxiv preprint DOI: 10.26434/chemrxiv-2024-f5g9p

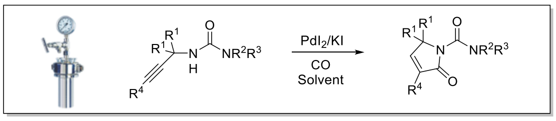
Palladium-Catalysed Additive Carbonylation of Propargyl Urea Enables Modular Synthesis of α,β-Unsaturated-γ-Lactams

Debora Schiroli *[1], A. Voronov[1], F. Pancrazzi[1], L. Capaldo[1], N. Della Ca'[1]

[1]*SynCatLab, Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale (SCVSA)*
Parco Area delle Scienze 17/A, University of Parma, 43124 – Parma

**e-mail address: debora.schiroli@unipr.it*

In the realm of sustainable chemistry, harnessing carbon monoxide as a versatile reagent for carbonylation and carbonyl insertion represents a contemporary challenge. Hence, achieving clean, low-carbon valuable liquid fuels and chemicals through CO/CO_2 conversion is of paramount importance and the topic of much research, both in industry and academia. Our method focuses on the Palladium-catalyzed synthesis of α,β-unsaturated-γ-lactams, employing a straightforward, ligand-free catalytic system which allows the insertion of carbon monoxide on the propargylic moiety. The process originates from readily accessible propargyl ureas, effortlessly stocked and stable at ambient temperatures. This feature streamlines synthesis without complicating procedures, contributing to its practical applicability. Notably, this approach exhibits good selectivity, delivering remarkable yields without any post-reaction interventions. Under the optimized conditions, the scope of this additive cyclocarbonylation reaction was expanded to a wide variety of acetylenic ureas. The formation of a 5-carbon ring with an α-β unsaturated amide position, provides a versatile platform for diverse functionalization strategies. Furthermore, the stability of the resulting products with free NH_2 or glycine derivatives enables extended functionalization pathways, including the reactivity with amino acids or isocyanates, facilitating the synthesis of different compounds with high molecular complexity. Additionally, the molecule demonstrates promising activity against HIV integrase in preliminary tests validated by a significant SI index (SI = CC50/IC50), suggesting potential therapeutic applications. These findings stimulate further investigations to fully understand the potential of these molecules and their implications in biomedical research. Remarkably, the reaction demonstrates exceptional atom economy, relying solely on PdI_2/KI in the reaction system, emphasizing its sustainability: this method is indeed a good example of re-evaluating and utilizing carbon monoxide for sustainable chemistry, adaptable even on a larger scale, up to 2.5 mmol. This project showcases the combination of sustainable practices and advancements in organic synthesis. It demonstrates how pursuing sustainability can align with synthetic development, paving the way for ethical and environmentally conscious approaches in innovative discovery.



References

[1] 1. A. Bonardi, M. Costa, B. Gabriele, G. Salerno, G.P. Chiusoli, *Tetrahedron Lett.* **1995**, *36*, 7495.
[2] 2. A. Bacchi, G. P. Chiusoli, M. Costa, C. Sani, B. Gabriele, G. Salerno, *J. Organomet. Chem.* **1998**, *562*, 35.
[3] 3. Italian Patent: "Uso di derivati 2-oxo-2H-pirrol-1(H)-carbossamidici come agenti anti-HIV e processo per la loro produzione" 102016000022765 (UA2016A001346), 04-03-2016.

Theme B - Biomaterials

Sustainable self-surfactant Poly-hydroxyalkanoates (PHAs) systems for hydrophobic drug encapsulation

Sara Alfano[1*], Benedetta Brugnoli[1],Lorenzo Ceparano[1], Iolanda Francolini[1], Andrea Martinelli[1]

[1]*Department of Chemistry, University of Rome La Sapienza, Rome, Italy*

**sara.alfano@uniroma1.it*

Polymer nanoparticles (NPs) have gained interest in various fields for environmental, sensing and biomedical applications. As far as the latter, nanostructured systems can encapsulate and vehiculate drugs or bio-active molecules that are toxic in systemic administration or not soluble in physiological fluids, such as hydrophobic ones (i.e. corticosteroids, steroids and cortisone) [1].

In the design of a drug delivery system, biocompatibility is a key factor that drives the choice of materials, chemicals and processing to avoid or reduce possible harm to the body. Bio-polyesters, including polyhydroxyalkanoates (PHAs), are a class of polymers very appealing in this field due to their biodegradability in nontoxic products. However, there are many drawbacks related to their high hydrophobicity which favours nano-particle aggregation and reduces the compatibility towards living systems.Surfactants are essential excipients in nanoparticle preparation since they increase the wettability of hydrophobic matrices, ensure dimensional stability and dispersion and play a key role in cellular interaction. Recently, biosurfactants gained a lot of interest due to safety and environmental concerns. In this work, the polyester poly-3hydroxybutirate-co-3hexanoate (PHBHHx) belonging to the PHAs family, has been chemically modified using the ionic liquid choline taurinate ([Ch][Tau]) as a non-cytotoxic and eco-friendly reagent [2]. More in detail, PHBHHx chains have been cleaved and functionalized through aminolysis by exploiting the amino group of [Ch][Tau] as a nucleophilic agent with the scope to obtain amphiphilic molecules with a self-surfactant behaviour (Fig. 1).

Sulfonated chains with different hydrophobic tail lengths were obtained in non toxic ethyl acetate/ethanol medium by varying the molar ratio between PHBHHx repeating units and [Ch][Tau]. Nanoparticles were then obtained through the preparation of an oil-in-water emulsion and subsequent solvent evaporation method.

The safety of the chemicals and solvents used has made it possible to eliminate the time-consuming and complex purification process. The aminolysis reaction product were characterized by GPC and infrared spectroscopy (FTIR) and the nanoparticles by dynamic Light Scattering (DLS) and Scanning Electron Microscopy (SEM). The nanoparticle were loaded by usnic acid and the drug uptake was evaluated by UV-vis spectroscopy. The study of in vitro biological activity is currently under investigation.

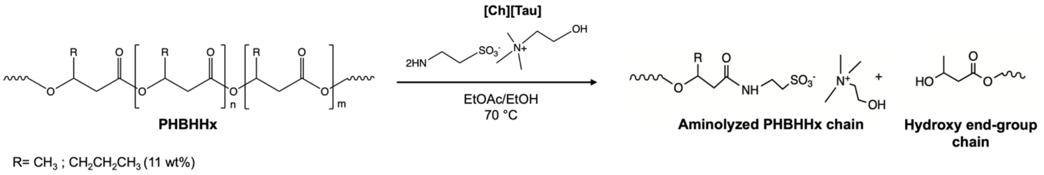


Figure 2 PHBHHx aminolysis reaction scheme

References

[1] Brugnoli B., Perna G., Alfano S., et al., *Polymers*, 2024, **16**, 427.
[2] De Felice A.C., Di Lisio V., Francolini I. et al., *Pharmaceutics*, 2022, **14**, 158.

Glycerol- and diglycerol-based polyesters: Evaluation of backbone alterations upon nano-formulation performance

Eleni Axioti[a], Emily G. Dixon [a], Philippa L Jacob [a], Robert J. Cavanagh,[b] Steven M Howdle [a],
Veeren M Chauhan [b], and Vincenzo Taresco[a]

[a] *School of Chemistry, University Park, Nottingham NG7 2RD, United Kingdom*
[b] *School of Pharmacy, University of Nottingham, Boots Sciences Building, University Park, Nottingham NG7 2RD, United Kingdom*
*eleni.axioti@nottingham.ac.uk

Despite the success of polyethylene glycol-based (PEGylated) polyesters in the drug delivery and biomedical fields, concerns have arisen regarding PEG's immunogenicity and limited biodegradability. In addition, inherent limitations, including limited chemical handles as well as highly hydrophobic nature, can restrict their effectiveness in physiological conditions of the polyester counterpart. To address these matters, an increasing amount of research has been focused towards identifying alternatives to PEG. One promising strategy involves the use of bio-derived polyols, such as glycerol. In particular, glycerol is a hydrophilic, non-toxic, untapped waste resource and as other polyols, can be incorporated into polyesters via enzymatic catalysis routes. In the present study, a systematic screening is conducted focusing on the incorporation of 1,6-hexanediol (Hex) (hydrophobic diol) into both poly(glycerol adipate) (PGA) and poly(diglycerol adipate) (PDGA) at different (di)glycerol:hex ratios (30:70; 50:50 and 70:30 mol/mol) and its effect on purification upon NPs formation. By varying the amphiphilicity of the backbone, we demonstrated that minor adjustments influence the NPs formation, NPs stability, drug encapsulation, and degradation of these polymers, despite the high chemical similarity. Moreover, the best performing materials have shown good biocompatibility in both in vitro and in vivo (whole organism) tests. As preliminary result, the sample containing diglycerol and Hex in a 70:30 ratio, named as PDGA-Hex 30%, has shown to be the most promising candidate in this small library analysed. It demonstrated comparable stability to the glycerol-based samples in various media but exhibited superior encapsulation efficiency of a model hydrophobic dye. This in-depth investigation provides new insights into the design and modification of biodegradable (di)glycerol-based polyesters, potentially paving the way for more effective and sustainable PEG-free drug delivery nano-systems in the pharmaceutical and biomedical fields.

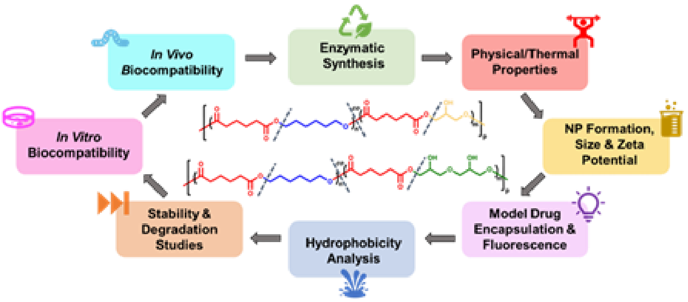


Figure 3: Graphical Abstract

References

[1] E. Axioti, et al., Colloids and Surfaces B: Biointerfaces, 2024, 236.
[2] V. Taresco, et al., Polymer, 2016, 89, 41-49.
[3] P. L. Jacob et al., J Colloid Interface Sci, 2023, 641, 1043-1057.

Chitosan-sodium usnate nanosystems: Preparation, characterization, and biocompatibility

Benedetta Brugnoli[1*], Alessia Mariano[2], Beatrice Simonis[1,3], Cecilia Bombelli[3], Simona Sennato[4], Antonella Piozzi[1], Vincenzo Taresco[5], Veeren M. Chauhan[6], Steven M. Howdle[5], Anna Scotto d'Abusco[2], Iolanda Francolini[1]

[1]Department of Chemistry, Sapienza University of Rome, Rome, Italy
[2]Department of Biomedical Sciences, Sapienza University of Rome, Rome, Italy
[3]CNR-Institute for Biological Systems (ISB), Secondary Office of Rome-Reaction Mechanisms
c/o Chemistry Department, Sapienza University, Rome, Italy
[4]CNR-Institute of Complex Systems (ISC) and Physics Department, Sapienza University, Rome, Italy
[5]Department of Chemistry, University of Nottingham, Nottingham, NG7 2RD, UK
[6]School of Pharmacy, Boots Science Building, University of Nottingham, Nottingham, NG7 2RD, UK

**benedetta.brugnoli@uniroma1.it*

Nanostructured drug delivery systems have an outstanding position in the pharmaceutical and medical fields since they can enable the release of the active pharmaceutical ingredients (APIs) at desired therapeutic doses, improve drug solubility, protect drugs from degradation, and reduce toxic effects [1]. Polymers are among the most studied materials as drug carriers, due to their tunable chemical structure and ability to self-assemble to give different types of nanostructures. In this study, chitosan nanoparticles (CS NPs) were investigated as carriers for the anticancer drug sodium usnate (NaU) for the treatment of osteosarcoma (OS), which is the most prevalent primary malignant bone sarcoma in pediatric and adolescent patients [2]. CS self-assembly was induced by electrostatic interactions with the drug and the anionic cross-linker tripolyphosphate, thus obtaining stable nanosystems and a high drug encapsulation efficiency. Compared to free NaU, a significant reduction in NaU cytotoxicity versus hepatocytes when encapsulated in CS NPs was evidenced, suggesting a potential CS protective role against liver damage. NaU-loaded CS NPs (CSNaU$_{5x}$) at 0.312 mg/mL concentration decreased osteosarcoma 143B cells viability after 48 h and 72 h treatment at 0.312 mg/mL concentration, higher than free drug. Interestingly, this system also stimulated in 143B cells Maspin production, an agent known for its tumor suppressor properties. Relevant synergistic activity between CS and NaU in promoting Maspin stimulation was found, suggesting the potential of the systems to reduce invasiveness of OS cancer [3].

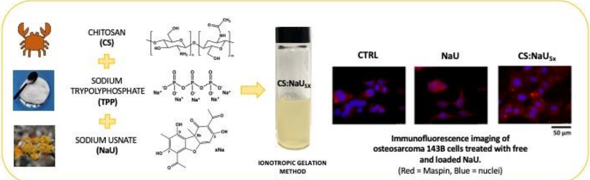


Figure 4. Preparation and immunofluorescence imaging of CSNaU$_{5x}$ against osteosarcoma 143B cells

References

[1] Adepu S., Ramakrishna S. *Molecules*, 2021, **26(19)**, 5905.
[2] Li S., et al. Targeted therapy for osteosarcoma: a review. *J Cancer Res Clin*, 2023, **149**, 6785-6797.
[3] Brugnoli, B., et al. Self-assembled chitosan-sodium usnate drug delivery nanosystems: Synthesis, characterization, stability studies, in vitro cytotoxicity and in vivo biocompatibility against 143 B cells. *Carbohydr. Polym. Technol. Appl.* 2023, **6**, 100373

In Situ Labeling of the Aqueous Compartment of Extracellular Vesicles with Luminescent Gold Nanoclusters

Ester Butera[1,2*], Regina Maria Chiechio[3], Giuseppe Maccarrone[1] , Annalinda Contino[1], P. Even-Hernandez[2] , Célia Ravel[4,5] , Valerie Marchi[2] .

[1] *Dipartimento di Scienze Chimiche, University of Catania, Catania, Italy*
[2] *Institut des Sciences Chimiques de Rennes, University of Rennes, Rennes, France*
[3] *Dipartimento di Fisica e Astronomia "Ettore Majorana", University of Catania, Catania, Italy*
[4] *Service de Biologie de la Reproduction-CECOS, CHU Rennes, Rennes, France*
[5] *Institut de Recherche en Santé, Environnement et Travail, Inserm, EHESP, University of Rennes, Rennes, France*
**ester.butera@phd.unict.it*

Extracellular vesicles (EVs), membrane-limited particles secreted by both healthy and cancerous cells, can be isolated also in human follicular and seminal fluid and they are involved in cell communication, besides to be considered biomarkers for early cancer diagnosis.[1] Thus, the topic of their isolation and characterization is continously arising. To this aim, gold nanoclusters (AuNCs) could be used, since they are non-toxic bright fluorophores with ultrasmall size, large fluorescence lifetime, and good biocompatibility, making them attractive for biological labeling and bioimaging.[2-5] Their small size facilitates clearance when injected into the body and allows them to be encapsulated into liposomes without damaging compartment integrity. Their direct electrostatic interaction with extracellular vesicles results in membrane labeling or multilamellar structure disruption.[6] In this work, the encapsulation of ultra-small red emitting Au NCs into liposomes with different sizes and chemical compositions has been investigated. Cell-like-sized vesicles (LUVs) encapsulating red Au NCs were successfully obtained by an innovative method using emulsion phase transfer. Through complementary investigations carried out by using cryo-TEM, SAXS, and confocal imaging techniques, the structural and morphological characteristics of the AuNCs enclosing vesicles were linked to the encapsulation process efficiency. Finally, exosome-like-sized vesicles (LUVs) containing Au NCs were obtained with an encapsulation yield of 40%, as estimated from ICP-MS.[7] The study explores the interactions between the as synthesized liposomes with fusogenic characteristics and EVs from human seminal fluids. The membrane composition was optimized to enhance fusion properties. These interactions, thanks to lipid exchange, give rise to fused hybridosomes with an increased size, as shown by FRET experiments and cryo-TEM.[8] The resulting fused vesicles, which exhibit typical AuNCs fluorescence and increased size, could serve as drug or macromolecule carriers or nanosensors in living organisms. Their potential applications could also include EVs content analysis since this innovative technique use non-disruptive interactions.

References

[1] A.S. Neyroud, R. M. Chiechio, M. Yefimova, J.M. Lo Faro, N. Dejucq-Rainsford, S. Jaillard, P. Even-Hernandez, V. Marchi, C. Ravel. *Basic and Clinical Andrology*. 2021, **31**, 25.

[2] R. M. Chiechio, R. Le Guevél, S. Ducarre, H. Solhi, S. Dutertre, X. Pinson, J.P. Bazureau, O. Mignen, P. Even-Hernandez, P. Musumeci, C. Ravel, M. J. Lo Faro, V. Marchi. *ACS Appl. Nano Mater*. 2023, 6, **10**, 8971–8980.

[3] J. Wang, J. Ye, H. Jiang, S. Gao, W. Ge, Y. Chen, C. Liu, C. Amatore, X. Wang. *RSC Adv*. 2014, 4, **71**, 37790–37795.

[4] Nonappa. *Beilstein J. Nanotechnol*. 2020, **11**, 533–54.

[5] H. Cui, Z.S. Shao, Z. Song, Y.B. Wang, H.S. Wang. *J. Mater. Chem*. C, 2020, **8**, 14312—14333.

[6] R. M. Chiechio, S. Ducarre, G. Moulin, A. Dupont, C. Marets, P. Even-Hernandez, F. Artzner, P. Musumeci, G. Franzò, C. Ravel, M. J. Lo Faro, V. Marchi. *J. Phys. Chem. Lett*. 2022, 13, **30**, 6935–6943

[7] R. M. Chiechio, S. Ducarre, C. Marets, A. Dupont, P. Even-Hernandez, X. Pinson, S. Dutertre, F. Artzner, P. Musumeci, G. Franzò, C. Ravel, M. J. Lo Faro, V. Marchi. *Nanomaterials*. 2022,12, **21**, 3875.

[8] E. Butera, A. Dupont, A. Aimé, S. Ducarre, R. M. Chiechio, P. Even-Hernandez, A. Contino, G. Maccarrone, C. Ravel, V. Marchi. *ACS Appl. Mater. Interfaces.* 2024

Biomaterials-based cryogels for bone tissue engineering

Carriero V.C.[1*]; Di Muzio L.[1]; Sergi C.[2]; Bigi B.[1]; Tirillò J.[2]; Petralito S. [1]; Paolicelli P. [1]; Casadei M.A.[1]
[1]*Departmen of Drug Chemistry and Technologies, Sapienza University of Rome, Italy*
[2]*Department of Chemical Engineering Materials Environment, Sapienza University of Rome, Italy*
**vitocosimo.carriero@uniroma1.it*

Introduction

Gelatin (Gel) and chondroitin sulfate (CS) produce highly porous cryogels suitable for tissue engineering[1,2]. Despite they mimic the extracellular matrix of the bone tissue, they lack of osteoinductive properties. The addition of hydroxyapatite (HA) to these matrices might improve the mechanical behaviour of these systems and it may impart osteoinductive properties[3]. Based on this rationale, Gel and CS cryogels were enriched by HA and it was investigated the influence of such a mineral on the mechanical and physical properties of these biomaterials-based systems.

Materials and methods

The cryogels were produced via radical crosslinking of Gel and CS methacryloyl derivatives[4,5] (GelMA and CSMA) at -12°C. Plain and HA-enriched scaffolds were characterized by swelling ratio in phosphate buffer (PBS), response to mechanical compression and scanning election microscopy (SEM).

Results and discussion

HA inclusion into the cryogels did not affect the swelling ratios which range between 19 and 21(fig 1 A). The systems remain able to adsorb large amounts of PBS. This outcome suggests that the crystals do not interfere with the scaffold porosity, as confirmed by SEM micrographs (fig 1 B), and with the ability to host cells and their physiological exchange. Contrary, mechanical tests highlighted that HA contributes to increase the resistance of the systems to compression stresses (fig 1 C).

Conclusions

The addition of HA to suitable systems for bone regeneration leads to highly porous cryogels with promising influence on the cryogels stiffness. Future long-term in vivo studies will provide insights into the effective osteoinductive performances of such scaffolds.

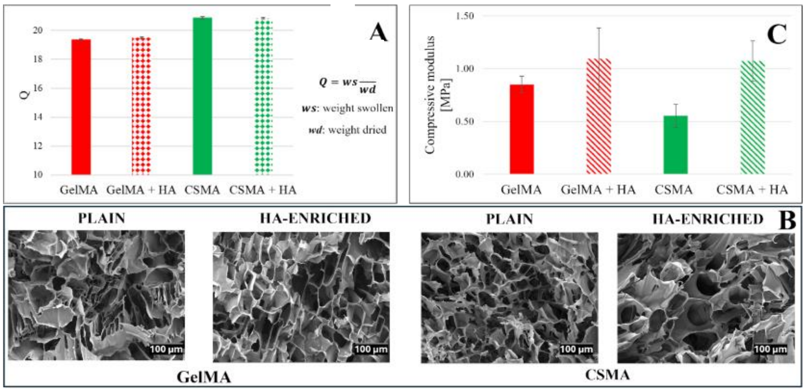


Figure 1 A) swelling degree of plain and HA-enriched GelMA and CSMA cryogels; **B)** compressive modulus of plain and HA-enriches GelMA and CSMA cryogels; **C)** SEM micrographs of plain and HA-enriched cryogels.

References

(1) Di Muzio L. et al. *Reactive and Functional Polymers* **2023**, *189*.
(2) Demirci S. et al. *Gels* **2021**, *7* (3). https://doi.org/10.3390/gels7030127.
(3) Carriero, V. C. et al. *Gels* **2023**, *9* (12), 979.
(4) Di Muzio, L. et al. *European Polymer Journal* **2021**, *154*, 110538.
(5) Di Muzio, L. et al. *Carbohydrate Polymers* **2022**, *296*, 119916.

3,4 Hydroxycinnamic acid-containing antimicrobial dressings based on functionalized chitosan for applications in tissue regeneration

Clarissa Ciarlantini[1*], Elisabetta Lacolla[1], Iolanda Francolini[1], Marta Fernández-García[2],
Carolina Muñoz-Núñez[2], Alexandra Muñoz-Bonilla[2], Antonella Piozzi[1]

[1] *Chemistry Department, University La Sapienza, Piazzale Aldo Moro 5, 00185 Rome, Italy*
[2] *Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC), C/ Juan de la Cierva 3, 28006 Madrid, Spain*

**Clarissa.ciarlantinini@uniroma1.it*

The development of systems able to heal a high percentage of wounds quickly, completely and sustainably is of paramount importance in daily clinical practice. This need has led researchers to develop bioactive membranes, i.e., systems capable of encapsulating components that could have a positive action on the healing process, thus limiting inflammatory phenomena. In the manufacturing of these devices, polymers of natural origin are widely used thanks to their biocompatibility, absence of toxicity, and biodegradability [1]. In the present work, innovative dressings based on modified chitosan (CS) were developed using the solvent casting technique. In particular, CS, characterized by good antimicrobial activity [2] but poor dimensional stability in physiological environment, was first modified with glycidylmethacrylate (GMA) and glycerol (GLY) and then with ethylene glycol dimethacrylate (EGDMA). GMA was introduced into the polysaccharide to have a functionality (double bond) to be exploited in the subsequent crosslinking reaction with EGDMA, while GLY was taken into consideration as a plasticizer to provide the polymer films with adequate elastic properties. To evaluate the effect of GLY on the mechanical properties of the developed matrices, the films were obtained by varying glycerol concentration (10, 20 and 30% w/v). For all samples, at each concentration of GLY, an increase in elongation at break and dimensional stability in an aqueous environment was observed, with however a considerable decrease in elastic modulus. In particular, the matrix containing 30% GLY was too fragile and therefore not suitable for applications in tissue regeneration, while the one with 20% GLY ensured the greatest elongation at break. Then, this matrix was subjected to a cross-linking process. To obtain membranes with different elasticity, three different concentrations of EGDMA (0.05–0.1–0.5 mM) and same reaction time (5 min) were used. The cross-linked matrices showed a significant increase in the elastic modulus value for all concentrations. However, EGDMA concentration that allowed the maintenance of suitable elongation at break and hydrophilicity values ($\theta° = 86.5 \pm 0.6$) as well as an appropriate water vapour transmission rate (WVTR = 450 ± 10) was 0.05 mM. To avoid possible inflammatory reactions during the healing phase, the films were functionalized with 3,4 hydroxycinnamic acid (HCAF), an antioxidant capable of limiting the phenomenon of oxidative stress [3]. The introduction of HCAF into the films was carried out both by imbibition and covalent bonding between CS amino groups and catechol OH, using laccase as catalyst. In both cases, the introduction of HCAF molecules increased the antioxidant and adhesive properties of the membranes. Finally, antimicrobial tests in broth showed the effectiveness of the membrane containing the physically bound antioxidant.

References

[1] Sahana T.G., Rekha P.D. *Mol Biol Rep*, 2018, 45, 2857.
[2] C. Goy R., De Britto D., B. G. Assis O., *Polímeros: Ciência e Tecnologia*, 2009, 19, 241.
[3] Hussain T., Tan B., Yin Y., Blachier F., C. B. Tossou M., Rahu N., O*xidative Medicine and Cellular Longevity*, 2016, 2016, 1.

Resveratrol-based liposomes as model to study drug delivery across Blood Brain Barrier

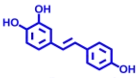
Mariangela Clemente[1*], Beatrice Simonis[1], Enrica Donati[2], Domenico Vignone[3], Odalys Gonzalez Paz[3], Annalise Di Marco[3], Luciano Galantini[4], Simona Sennato[5], Francesca Santangeli[4], Sara Marcoccia[6], Giovanna Mancini[2], Cecilia Bombelli[1], Francesca Ceccacci[1].

[1]CNR-ISB- Secondary office of Rome, Reaction Mechanisms c/o Chemistry Department, Sapienza University, 00185, Rome, Italy
[2] CNR-ISB, Rome 1 Resarch Area, 00015, Montelibretti (RM), Italy
[3]Experimental Pharmacology, IRBM SpA, via Pontina Km 30.600, 00071 Pomezia (RM), Italy
[4]Chemistry Department, Sapienza University, 00185, Rome, Italy
[5]CNR-ISC- Secondary office of Rome c/o Physics Department, Sapienza University,
[6] Department of Physiology and Pharmacology, Sapienza University00185, Rome, Italy - IRCCS Santa Lucia Foundation, 00179, Rome Italy

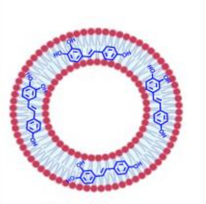
**mariangela.clemente@cnr.it*

The role of the Blood Brain Barrier (BBB) in controlling the flow of substances between blood and brain cells is a double-edged sword that on the one hand allows an effective modulation between what can enter (nutrients) and what must be rejected (harmful substances), but on the other hand excludes many of the clinically approved drugs from access to the Central Nervous System (CNS). Organic nanocarriers, such as liposomes, represent one of the most successful and promising strategies adopted to facilitate drug permeation in CNS. The architecture of liposomes, their biocompatibility, low toxicity, and ease of functionalization have made them very attractive tools as brain-targeted drug delivery systems. [1].

Our research work is aimed at developing cationic liposomes formulated with a phosphocoline (DPPC or DOPC) and cholesterol in mixture with gemini and/or glycosylated amphiphiles. The presence of these synthetic amphiphiles should promote the transport across BBB *via* adsorptive-mediated-transcytosis or carrier-mediated transport [2]. To evaluate the ability of formulations to cross an *in vitro* human model of BBB, *trans*-Resveratrol (a phenolic molecule with interesting biological properties but low bioavailability) was loaded in liposomes and employed as a probe. Results showed that the permeability of formulations was affected both by the type of phosphocholine used (DOPC or DPPC) and by the functionalization of the liposomes.



trans-Resveratrol



Cationic liposome

Acknowledgements: this work was supported by Regione Lazio -through the projects LIPOBARR (Prot. n°. 85-2017-15057), and LIMONE (Prot. n°. A0375-2020-36730)- within the call “Progetti Gruppi di Ricerca 2020” and by Ministero dell’Università e della Ricerca through the project ‘‘CNCCS-Centre for rare, neglected and poverty related diseases”.

References

[1] Wu, D., et al. *Signal transduction and targeted therapy*, 2023, **8**, 217.
[2] Simonis, B., et al. *Journal of Colloid Interface Science*, 2022, **627**, 283.

Bacterial cellulose from kombucha tea as a promising green material

Federica Daus[1*], Martina Bruschi[2], Anna Liguori[1], Maria Letizia Focarete[1]

[1]Department of Chemistry "Giacomo Ciamician", University of Bologna, Bologna, Italy
2Bioniks s.r.l., Verona, Italy

**federica.daus2@unibo.it*

Cellulose is the most abundant, inexpensive and readily available bio-polymer on Earth[1], and it is becoming increasingly popular due to its biocompatibility and its remarkable mechanical and physical properties. It is traditionally extracted from plants and plant-based materials, but it can also be produced by some bacterial strains. Bacterial cellulose (BC) is a linear homopolysaccharide of β-1,4-linked anhydro-D-glucose units with molecular formula $(C_6H_{10}O_5)_n$. It is secreted in the form of ribbons, composed of nanochains arranged in elementary fibrils further aggregated in bundles of microfibrils, interacting with each other through inter- and intra-chain hydrogen bonds and Van der Waals interactions, resulting in a highly organized structure[2]. This 3D network of microfibrils stabilized by hydrogen bonds provides BC with outstanding mechanical properties, hydrophilicity, great capacity for holding water[3] and insolubility in water and in common organic solvents. Considering its biocompatibility and non-toxicity, nowadays bacterial cellulose is mainly employed in the biomedical area as wound dressing, drug delivery systems, artificial cartilage and artificial skin. One of the many substrates from which BC can be obtained is Kombucha tea, a slightly alcoholic sugared beverage produced by the fermentation of tea leaves and sugar, during which a gelatinous cellulose-based biofilm is formed at the air-liquid interface called Scoby ("Symbiotic Culture of Bacteria and Yeasts")[4]. In this work, a preliminary characterization was carried out on the so-obtained raw material and on the purified BC membrane by means of thermogravimetric (TGA), field-emission scanning electron microscopy (FE-SEM), X-ray diffraction, ATR-FTIR, and mechanical analyses. The obtained results showed that, after the purification process, the biofilm maintained its crystalline structure and morphology while its thermal degradation temperature slightly increased, meaning that the removal of bacteria and other impurities enhanced its thermal stability. The above-mentioned analyses suggested that bacterial cellulose obtained from Kombucha Scoby is a promising material that can be valuably used for many different applications.

References

[1] JDP. de Amorim, KC. de Souza, *Environ Chem Lett.*, 2020, **18(3)**, 851-69.
[2] C. Chen, W. Ding, *Carbohydrate Polymers*, 2022, 278.
[3] D. Klemm, B. Heublein. *Angew Chem Int Ed*, 2005, **44(22)**, 3358–3393.
[4] AS. Amarasekara, D. Wang. *SN Appl Sci.*, 2020, **2(2)**, 1-7.

Tailoring toughness: frontal polymerization of hydrogels with controlled mechanical properties

Luana Di Lisa[1*], Mariangela Rea[1], Daniele Nuvoli[2], Cristiano Albonetti[3], Alberto Mariani[2], Maria Letizia Focarete[1]

[1]Department of Chemistry ''Giacomo Ciamician'', University of Bologna, Bologna, Italy
[2]Department of Chemistry and Pharmacy, University of Sassari, and INSTM, Sassari, Italy
3CNR-ISMN, Bologna, Italy

**luana.dilisa2@unibo.it*

Hydrogels have gained significant attention in biomaterial science due to their tunable properties and wide-ranging applications in tissue engineering, drug delivery, and soft robotics. This study presents the synthesis and characterization of hydrogels containing Gelatin Methacryloyl (GelMa) via frontal polymerization (FP)[1]. FP is a self-sustaining synthesis triggered by thermal or photo stimuli, resulting in the formation of a "polymerization front", with no need for continuous external heating. This offers advantages in time, energy, and cost efficiencies over conventional polymerization methods. Employing GelMa with varying degrees of methacrylation (30 and 75 mol%), we fabricated copolymers of GelMa with bis-acrylamide and semi-IPNs, introducing a secondary gelatin network. We demonstrated GelMa superior biocompatibility and efficient crosslinking, compared to bis-acrylamide, requiring significantly lower methacrylic group concentrations for hydrogel formation. Physical interactions, alongside chemical crosslinking, enhanced mechanical properties. Furthermore, varying the GelMa substitution degree influenced hydrogel properties markedly. The introduction of gelatin as a secondary network in semi-IPNs added additional physical crosslinking trough hydrogen bonding, affecting rheological and mechanical properties. Increasing gelatin concentrations augmented hydrogel modulus and stiffness, attributed to enhanced physical interactions within the network. Compression tests highlighted the influence of gelatin content on hydrogel mechanical behavior, with significant increases in modulus observed. Finally, dynamic rheological shear strain tests and cyclic loading compression tests demonstrated exceptional recovery capabilities in all hydrogel formulations, highlighting their potential for resilient, mechanically robust applications. Overall, our study unveils a versatile platform for tailoring hydrogel properties through gelatin incorporation, opening avenues for diverse biomedical and materials applications.

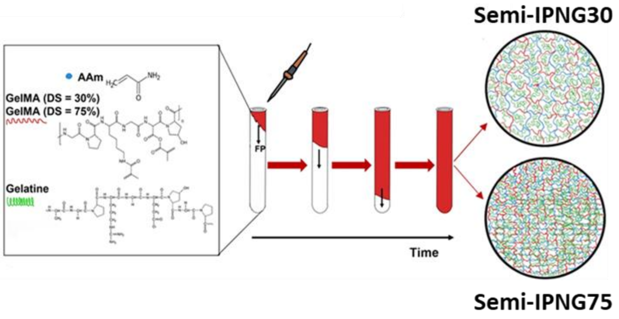


Figure1. Scheme of frontal polymerization synthesis of Semi-IPN.

References

[1] LI, Qing, et al. Advances in frontal polymerization strategy: From fundamentals to applications. Progress in Polymer Science, 2022, 127: 101514.

Gelatin methacryloyl in tissue engineering: from an innovative synthesis to its use for 3D scaffolds fabrication

Di Muzio L.[1*], Carriero V.C.[1], Sergi C.[2], Bigi B.[1], Tirillò J.[2], Petralito S.[1], Paolicelli P.[1], Casadei M.A.[1]

[1] *Department of Drug Chemistry and Technologies, Sapienza University of Rome,Italy*
[2] *Department of Chemical Engineering Materials Environment, Sapienza University of Rome, Italy*
**laura.dimuzio@uniroma1.it*

INTRODUCTION

Methacrylic gelatin (GelMA) is a widely used biomaterial to produce 3D scaffolds for biomedical applications[1], but the low reproducibility of the derivatization degree and its gelation temperature still remain a challenge to overcome to further expand its use. Thus, the first aim of this work was to optimize a new single-phase synthetic procedure suitable for producing GelMA with different and appropriate rheological properties. The obtained product was then successfully employed to produce GelMA-based scaffolds suitable for tissue engineering applications via cryogelation technique (cryogels)[2] but also pneumatic extrusion 3D-bioprinting technology.

MATERIALS AND METHODS

Synthesis of GelMA: GelMA was synthesized following a two-phase protocol (GelMAdp), as already reported[3], and a single-phase procedure (GelMAsp). In this case, type A Gel was solubilized in anhydrous DMSO (5%w/v) for 3h at 50°C, then MAA was added and the reaction was carried out for 3h. The mixture was dialyzed and freeze-dried.

Cryogels and bioinks preparation: GelMA-based cryogels were synthesized by free radical crosslinking method at -12°C, using ammonium persulfate and N,N,N′,N′-tetramethyl ethylenediamine. GelMA-based bioinks were prepared using different concentrations of GelMA.

RESULTS AND CONCLUSION

The innovative single-phase synthesis allowed producing GelMAsp derivatives characterized by high reproducibility of the methacrylation degree and a significant decrease in sol-gel transition temperature (Fig. 1A-B). These derivatives were successfully employed for the preparation of cryogels, macroporous and sponge-like polymeric structures, by a finely regulated radical crosslinking process carried out under frozen conditions (cryotropic gelation) (Fig. 1C). Moreover, GelMAsp was used to produce an high-printability biomaterial ink used for the fabrication of 3D scaffolds bearing great shape fidelity (Fig. 1E). Contrary, using GelMAdp only collapsed cryogels and low resolution 3D-printed structure were obtained (Fig. 1D-F) confirming the effect of GelMA rheological properties. Thus the proposed single-phase synthesis proves to be an real step toward expanding GelMA use for 3D scaffolds fabrication.

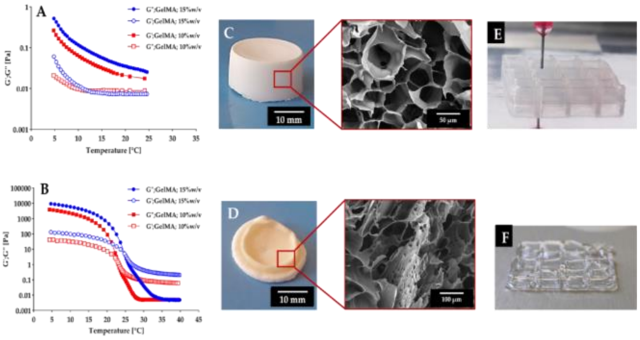


Figure 1. *(A-B) Temperature ramps of GelMA$_{sp}$ and GelMA$_{dp}$. (C) Cryogel prepared using GelMA$_{sp}$ and (D) GelMA$_{sp}$ and SEM micrograph. 3D-printed scaffolds using (E) GelMA$_{sp}$ and (F) GelMA$_{dp}$*

References

[1] Mohanto S. et al. *Int J Biol Macromol* 2023, **253**, 127143.
[2] Di Muzio L. et al. *Eur Polym J*, 2021, **154**, 110538.
[3] Di Muzio L. et al. *React Funct Polym*, **189**, 105607.

Novel hydrogel dressings based on bacterial cellulose and FucoPol for advanced wound treatment

Asiyah Esmail[1,2*], Ana Teresa Serra[3,4] , Filomena Freitas[1,2]

[1] *Associate Laboratory i4HB - Institute for Health and Bioeconomy, School of Science and Technology, NOVA University Lisbon, 2829-516, Caparica, Portugal*
[2] *UCIBIO – Applied Molecular Biosciences Unit, Department of Chemistry, School of Science and Technology, NOVA University Lisbon, 2829-516, Caparica, Portugal*
[3] *ITQB NOVA, Instituto de Tecnologia Química e Biológica António Xavier, Universidade Nova de Lisboa, Avenida da República, 2780-157 Oeiras, Portugal*
[4]*iBET, Instituto de Biologia Experimental e Tecnológica, Avenida da República, Quinta-do-Marquês, Estação Agronómica Nacional, Apartado 12, 2780-157 Oeiras, Portugal*

**a.esmail@campus.fct.unl.pt*

Chronic wounds pose significant challenges, impacting patients and healthcare systems with high costs, exacerbated by factors like obesity, diabetes, and aging populations. Effective wound care relies on dressings to protect against infection and promote healing [1]. The demand for affordable solutions drives research into advanced therapeutic dressings. Bacterial cellulose (BC) is a glucose homopolymer, known for its mechanical strength and biocompatibility, and is utilized in wound dressings due to its moisture retention and absorption properties [2]. However, BC lacks the bio-functional activity necessary for wound healing, which can be resolved by functionalization with other compounds. FucoPol (FP), a polyanionic fucose-rich exopolysaccharide, exhibits wound-healing abilities, as well as adhesive, photoprotective and bioactive properties [3,4].

In this work, BC and FP are combined to create a composite hydrogel tailored for wound dressing purposes, leveraging the unique properties of each polymer. BC was impregnated with FP through agitation, followed by gelation using Fe^{3+} (0.26, 1.0, 2.5 and 5 g/L) as a crosslinking agent. Rheological studies determined that 2.5 g/L of Fe^{3+} ensured the consolidation of both materials, while also improving gel strength when compared to BC alone. Different FP impregnation concentrations (0.5, 1.0, 1.5 and 2.0 wt.%) were tested, revealing that increasing FP concentration improved the mechanical strength of the composite. Moreover, the obtained hydrogels were demonstrated to be non-toxic (cell viability >80%), and exhibit wound-healing capacity, towards HaCaT cells (human skin keratinocytes), and NCTC clone L929 (mouse fibroblasts) cell lines, thus validating its suitability for wound dressing applications.

Acknowledgements: This work was financed by national funds from FCT/MCTES - Fundação para a Ciência e a Tecnologia, I.P., Ministério da Ciência, Tecnologia e Ensino Superior, in the scope of the projects UIDP/04378/2020 and UIDB/04378/2020 of the Research Unit on Applied Molecular Biosciences – UCIBIO, project LA/P/0140/202019 of the Associate Laboratory Institute for Health and Bioeconomy - i4HB. AE acknowledges FCT I.P. for PhD Grant 2021.05014.BD.

References

[1] Man, E.; Hoskins, C. Towards advanced wound regeneration. Eur. J. Pharm. Sci. 2020, 149,
[2] Portela, R., Leal, C. R., Almeida, P. L. & Sobral, R. G. Bacterial cellulose: a versatile biopolymer for wound dressing applications. Microb. Biotechnol, 2019, 12, 586-610.
[3] Reis, P., Pereira, C., Batista, M., Sevrin, C., Grandfils, C., Marques, A., Fortunato, E., Gaspar, F., Matias, A., Freitas, F. & Reis, M. Silver nanocomposites based on the bacterial fucose-rich polysaccharide secreted by Enterobacter A47 for wound dressing applications: Synthesis, characterization and in vitro bioactivity. Int. J. Biol. Macromol, 2020, 163, 959-969.
[4] Guerreiro, B. M., Freitas, F., Lima, J. C., Silva, J. C. & Reis, M. A. M. Photoprotective effect of the fucose-containing polysaccharide FucoPol. Carbohydr. Polym, 2021, 259, 117761.

Advances in scalable manufacturing of niosomes using microfluidic technique

Jacopo Forte[1*], Maria Gioia Fabiano[1], Eleonora D'Intino[1], Federica Rinaldi[1], Carlotta Marianecci[1], Maria Carafa[1]

[1]*Sapienza University of Rome, Department of Drug Chemistry and Technology, Rome, 00185, Piazzale Aldo Moro, Italy.*

**e-mail address of the presenting author: jacopo.forte@uniroma1.it*

Progresses in the field of nanotechnologies applied to therapy and diagnostics have led to the birth of a new branch of science defined as nanomedicine, in which several types of nanocarriers have been discovered and successfully used, such as: niosomes, liposomes, nanoemulsions. In recent years, niosomes acquired growing scientific attention as an alternative potential drug delivery system to conventional pharmaceutical forms. These surfactant vesicles have several advantages such as greater stability, thus lesser care in handling and storage and lower cost. In addition, niosomes are able to encapsulate both hydrophilic and lipophilic drugs, minimizing their degradation and inactivation after administration, preventing unwanted side effects, increasing the bioavailability of the drug and targeting it to the disease area by exploiting specific characteristics (e.g., thermosensitivity or pH sensitivity). [1]. One of the problems preventing innovative formulations from being widely used in therapy lies in the production by conventional methods, which are associated with long production times, high consumption of reagents, difficult industrial scale up and costs. The need to switch to fast, safe and efficient production, has led to the emergence of a new production technique, called microfluidics. This new technology allows many advantages, including: processes reproducibility, speed of execution and elimination of toxic and/or harmful solvents for humans or the environment, ease in industrial scaling up [2]. The main aim of this research project was to design, prepare and characterize a niosomal formulation, consisting of Tween21 and Cholesterol, using two different preparation methods: "Thin layer Evaporation" (TLE) and microfluidic technique (MT) and to investigate how these two methods could influence the chemical-physical characteristics of the same nanocarrier. Firstly, a deep characterization of the prepared niosomes was carried out evaluating size, ζ-potential, polydispersity index. Furthermore, to have information about the niosomal bilayer and to verify the influence of the different preparation methods, different lipophilic probes (pyrene and DPH) were used, to evaluate bilayer fluidity, polarity and microviscosity. The obtained results showed that the two preparation methods do not cause any changes in bilayer features. Finally, two probes, Calcein and Nile Red, were used to evaluate the entrapment efficiency (E.E.) of niosomes. The results showed a significant increase in E.E. when using MT. Specifically, for Nile Red, we achieved an E.E. of 100% with MT, compared to 50% with TLE. For Calcein, an E.E. of 90% was obtained with MT, while 30% was achieved with TLE. Considering these satisfactory results, it has been decided to deliver Amphotericin B, formulating niosomes using MT, to attempt to counteract Leishmaniasis, a commonly neglected disease which is caused by different Leishmania species, preparing an effective nanocarrier for targeted drug delivery to the affected site, thus contributing to the reduction of drug toxicity.

Acknowledgements: "Sapienza-Rome Technopole per Attrazione di early-career researchers MSCA Fellowships" - Progetto di ricerca: "Green approach for deliver old and new antibiotics.

References

[1] Liu, Zhongbing, et al. Current Pharmaceutical Biotechnology, 2019, 20.11: 934-944.
[2] Machado, N. D. et al. Chemical Engineering Research and Design, 2020, 162: 162-171.

Synthesis and characterization of cyclodextrin/Chitosan systems containing curcumin for biomedical applications.

Elisabetta Lacolla[1*], Clarissa Ciarlantini[1], Iolanda Francolini[1], Antonella Piozzi[1]

[1]*Chemisry Department, Sapienza University, Rome, Italy*

**elisabetta.lacolla@uniroma1.it*

Cyclodextrins (CDs) are cyclic oligosaccharides possessing a toroid-like structure with a hydrophobic internal cavity. This characteristic allows them to form *host-guest* inclusion complexes with suitable polarity and dimension molecules. As a consequence, CDs can enhance solubility and stability of poorly water-soluble compounds and improve the bioavailability of some drugs [1]. The thermodynamic equilibrium among associated and dissociated species is however unstable. Therefore, it can easily shift towards the dissociated form resulting in uncontrolled drug release. Many studies have shown the ability of CDs to cooperate when they are close together. In fact, systems in which cyclodextrins have a limited mobility can provide diffusion-controlled kinetics and, more importantly, affinity release kinetics [2]. In this work, systems based on β-CD-functionalized chitosan (CS) were prepared for curcumin (CUR) release. CUR, selected as a model drug for its antibacterial, antioxidant and anti-cancer properties [3], is a rather hydrophobic molecule therefore, its delivery within the human body is very difficult.

To obtain carboxyl groups on cyclodextrin to react with the amine groups of CS, β-CD was functionalized with succinic anhydride (S) and maleic anhydride (M). The obtained systems were named CD_S_CS and CD_M_CS, respectively. FTIR spectroscopy confirmed chemical functionalization while ^{1}HNMR analysis was used to determine the functionalization degree. Then, the functionalized CDs were conjugated to CS by the EDC/NHS reagent pair. After incorporation of CUR into the obtained systems, the samples were freeze-dried to manufacture solid matrices (CD_S_CS_CUR and CD_M_CS_CUR scaffolds). The amount of encapsulated CUR, determined by UV-vis analysis, and expressed in terms of inclusion ratio (ratio between the CUR content used initially and that present within the matrix after encapsulation) was of about 80%. Since CS does not have dimensional stability in aqueous environment, a cross-linking process of the systems was also performed. Specifically, a physical cross-linking reaction with tripolyphosphate (TPP) was used for both scaffolds, while a chemical crosslinking with ethylene glycol dimethyl acrylate (EGDMA) was employed for the CD_M_CS_CUR system, exploiting the double bond provided by maleic anhydride. The scaffolds were then characterized by thermal analysis (TGA and DSC) and swelling measurements in phosphate buffer (PBS, pH=7.4). Also, the CUR kinetic release from the systems as well as their antioxidant properties were studied.

References

[1] M. E. Davis, M. E. Brewster, *Nat. Rev. Drug Discovery*, 2004, 3, 1023-1035.
[2] Concheiro A., Alvarez-Lorenzo C., *Advanced Drug Delivery Reviews,* 2013, 65, 1188-1203
[3] R. Jamwal, *Journal of Integrative Medicine*, 2018, 16, 367-374

Synthesis and evaluation of Polyglycerol-based polymers as an alternative to PEG-based coatings

Federico Luchi[1*], Ander Eguskiza Bilbao[1], Riccardo Ossanna[1], Giulia Climani[1], Roberto Fiammengo[1]

[1]*Department of Biotechnology,University of Verona,Verona, Italy*

**federico.luchi@univr.it*

In recent years nanoparticles (NPs) have emerged as an important player in biomedicine, with applications in drug delivery, disease diagnosis, and specific treatments.1,2Furthermore, when NPs are introduced into a biological medium interact with the present biomolecules, in particular with proteins,leadingtotheformationoftheso-calledproteincorona.Thepresenceofproteincoronamay alter the characteristics of the NPs and consequently influence their cellular uptake.3Therefore, to mitigate protein absorption, NPs are functionalized with polymers. This allows tuning of the hydrophilicity of nanoparticle coatings, conferring them antiadhesive and stealth properties. In this work, we focus on the synthesis of different hydrophilic polymers and on understanding how they influence cellular internalization and the impact they have on protein adsorption.

The synthesized polymeric coatings are thiols with a C11 long alkyl chain and a hydrophilic part of polyethyleneglycol (PEG) or polyglycerol (PG) units with a neutral or negative charge (Figure 1a). While in literature several studies deal with PEG-based coatings4, thereis scarceinformation about PG-based coatings. Starting from the synthesized polymers, we functionalized 13 nm gold nanoparticles (AuNPs) by the formation of self-assembled monolayers (SAMs) of these ligands on their surface. These designed libraries ofdifferently passivated gold nanoparticles were used to investigate by ICP-MS the impact of a progressive and gradual variation of the coating composition on the uptake of AuNPs by immune system cells (Figure 1b). We further prepared the same SAMs on gold flat surfaces to estimate by QCM-D the protein adsorption to the different coatings (Figure 1c). These analyses evidenced that PG-based coatings are a valuable alternative to PEG. Indeed, they have similar levels of cellular internalization, and, moreover, the mixed layers present a reversible protein absorption. These formulations show properties that can be exploited in therapeutic and diagnostic application fields.

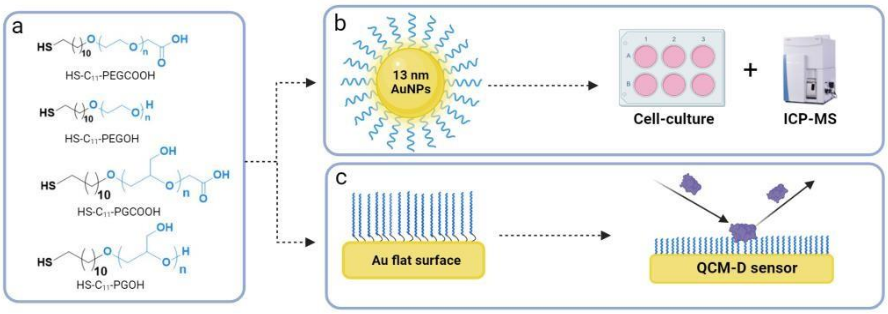


Figure1. a) Synthesis of different amphiphilicpolymers; b) Evaluation of the internalization levels of differently coated AuNPs and c) of the protein adsorption on gold flat surface.

References

[1] Peer, D.; Karp, J. M.; Hong, S.; Farokhzad, O. C.; Margalit, R.; Langer, R. Nanocarriers as an Emerging Platform for Cancer Therapy.*Nat. Nanotechnol.***2007**,*2*(12), 751–760.

[2] Mitchell,M.J.;Billingsley,M.M.;Haley,R.M.;Wechsler,M.E.;Peppas,N.A.;Langer,R.Engineering Precision Nanoparticles for Drug Delivery.*Nat. Rev. Drug Discov.***2021**,*20*(2), 101–124.

[3] Mishra,R.K.;Ahmad,A.;Vyawahare,A.;Alam,P.;Khan,T.H.;Khan,R.BiologicalEffectsof Formation of Protein Corona onto Nanoparticles.*Int. J. Biol. Macromol.***2021**,*175*, 1–18.

[4] Maus, L.; Dick, O.; Bading, H.; Spatz, J. P.; Fiammengo, R. Conjugation of Peptides to the Passivation Shell of Gold Nanoparticles for Targeting of Cell-Surface Receptors. *ACS Nano* **2010**, *4* (11), 6617–6628.

Innovative antimicrobials from facial steroidal surfactants

Claudia Marconi [1*], Angela Cirigliano [2], Teresa Rinaldi [2], Giovanna Serino [2],
Alessandra del Giudice [1], Sergio Moya [3], Marco Fornasier [4], Karin Schillén [4], Anita Scipioni [1],
Luciano Galantini [1]

[1] *Dep. of Chemistry, Sapienza University of Rome, P.le Aldo Moro 5, 00185 Rome, Italy*
[2] *Dep. of Biology and Biotechnology, Sapienza University of Rome, P.le Aldo Moro 5, 00185 Rome, Italy*
[3] *Soft Matter Nanotechnology Group, CIC biomaGUNE, Paseo Miramón 182 C, 20009 San Sebastián, Guipúzcoa, Spain*
[4] *Dep. of Chemistry, Lund University, P.O. Box 124, SE-221 00 Lund, Sweden*

**claudia.marconi@uniroma1.it*

Antimicrobial resistance represents an increasing threat to public health and makes urgent the need for new-generation antimicrobials.

Natural antimicrobial peptides (AMPs) have been widely regarded as a promising solution for fighting multi-drug resistant bacteria, due to their broad-spectral bactericidal activity, rapid killing rate, and a membrane targeted mechanism of action that gives them low susceptibility for developing resistance. Indeed, AMPs adopt a facial amphiphilic structure when in contact with bacterial membranes, by winding into α-helix or β-sheet structures with positive charges and lipophilic groups arranged on opposite sides. This facial amphiphilicity allows AMPs to efficiently bind to negatively charged bacterial membranes and penetrate inside them leading to cell death [1].

In the fight against antimicrobial resistance, the development of new antimicrobials able to reproduce the main structural feature of AMPs, such as peptide amphiphiles (PAs), is a major strategy.

In this work we present the synthesis, physical-chemical properties, antimicrobial activity and cytotoxicity studies of a new class of antimicrobials obtained by joining the facial amphiphilic skeletons of bile acids [2] to cationic peptides. The influence of structure, net charge, and self-assembly behavior on the antimicrobial activity of these unconventional PAs was investigated through multiple experimental techniques, such as Dynamic and Static Light Scattering, Electrophoretic Mobility, Small-Angle X-ray Scattering, Nuclear Magnetic Resonance, Circular Dichroism, Fluorescence Spectroscopy, Atomic Force Microscopy, cryo-Transmission Electron Microscopy, Electrochemical Impedance Spectroscopy and Quartz Crystal Microbalance with Dissipation measurements. The antimicrobial activity was tested against model bacteria such as Gram-positive *Staphylococcus aureus* and Gram-negative *Pseudomonas aeruginosa*, and the pathogenic yeast *Candida albicans,* while cytotoxicity tests were performed both *in vitro,* treating human cells cultures, and *in vivo,* challenging the nematode worms *Caenorhabditis elegans* to our antimicrobial PAs, with very promising results.

References

[1] M. Pasupuleti, A. Schmidtchen and M. Malmsten, *Crit. Rev. Biotechnol.*, **2012**, 32, 143-171.
[2] M. C. di Gregorio, L. Travaglini, A. del Giudice, J. Cautela, N. V. Pavel and L. Galantini, *Langmuir*, **2019**, 35, 6803-6821.

Biopolymers from waste-deriving α-OH fatty acids for marble coating

Camillo Morano[1*], Stefano Gazzotti[2], Sara Casati[3], Roberta Bergamaschi[3], Marco Ortenzi[2],
Gabriella Roda[1], Marco Pallavicini[1], Cristiano Bolchi[1]

[1]Department of Pharmaceutical Sciences, University of Milan, Milan, Italy
[2]Department of Biomedical, Surgical and Dental Sciences, University of Milan, Milan, Italy
[3]Department of Chemistry, University of Milan, Milan, Italy

**camillo.morano@unimi.it*

Lanolin, grease deriving from sheep wool scouring, could represent a renewable waste biomass, unique in properly said fatty acids (FAs) and, above all, alpha-hydroxy fatty acids (α-HFAs) richness. α-HFAs can be exploited in the production of biodegradable polymers. The aim of this work was to i) recover FAs from waste lanolin and ii) chemically convert them to α-HFAs, using a green chemistry procedure, and iii) exploit them as substrates for the synthesis of new biopolymers to be used as coating material for the protection of marble manufactures.
Acid components of lanolin were recovered by saponification with KOH; then, FAs were separated from α-HFAs as depicted in Figure 1A. Composition of the different portions (A-E) were assessed through ^{1}H-NMR and GC-MS [1]. After that, fractions B and E were thoroughly mixed and subjected to alpha-hydroxylation, as previously proposed by Bertolini et al. [2], applying few changes to the procedure (Figure 1B). Biopolymers were attained by modifying the hydroxyl group in polyglicerolsebacate (PGS) with either a mixture of linoleic acid and α-HFAs or linoleic acid, α-HFAs and cinnamic acid (Figure 1C). Polymeric films over Botticino marble samples were prepared by adding 1.3% (w/w) of 1-hydroxycyclohexyl phenyl ketone as radical initiator and curing for 48h under UV. Resulting coating materials were tested by themselves and added with silica nanoparticles (2-4%); in either case, they increased hydrophobicity (+40%/80%) and reduced the capillarity absorption of water (-20%/40%) while maintaining the passage of water vapour unaltered.

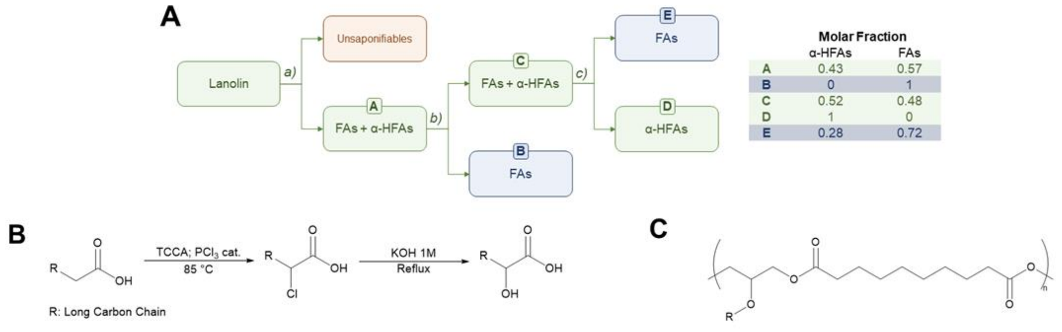


Figure 1A Schematic representation of lanolin acid components fractionation, along with molar fraction composition. a) KOH 10% (w/v), reflux, 48h; b) Methanol, rt, 2h; c) Cyclohexane, rt, o.n. **1B** Reaction scheme for alpha-hydroxylation of fatty acids. **1C** Chemical structure of modified PGS (R: Sebacic acid, Linoleic acid, Cinnamic acid or α-HFAs)

References

[1] C. Morano et al., *Molecules*, 2023, **28(4)**, 1635.
[2] V. Bertolini et al., *ACS Omega*, 2021, **6**, 31901–31906

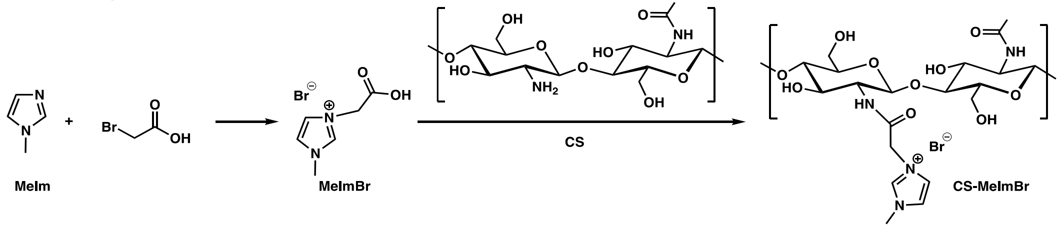
Antimicrobial and antioxidant scaffolds obtained from chemically modified chitosan with imidazole groups

Carolina Muñoz-Núñez, [1,2*], Arantza Barco-Martín[1,2], Alexandra Muñoz-Bonilla [1,2], Marta Fernández-García[1,2]

[1] *Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC), Madrid, Spain*
[2] *Interdisciplinary Platform for Sustainable Plastics towards a Circular Economy (SusPlast-CSIC)*

**carolinamunoz@ictp.csic.es*

Tissue engineering aims to find regenerative solutions for damaged or lost tissues, where biomaterials as chitosan (CS) have a crucial role by providing scaffolds for cell growth. Chitosan, derived from deacetylation of chitin, a biopolymer found in crustacean exoskeletons, is biocompatible and biodegradable, with moderate antimicrobial properties and high susceptibility to chemical modification. In this work, CS was modified using N-acylation with bromide 3-(carboxymethyl)-1-methylimidazol-3-ium (MeImBr) (Scheme 1)[1]. This synthesized CS derivative (CS-MeIm) exhibited enhanced antimicrobial and antioxidant properties. Based on these findings, CS-MeImBr was integrated into a scaffold based on CS matrix with glycerol as a plasticizer for applications in tissue engineering. Despite the positive properties of CS, its inherent fragility and inconsistent structure present significant challenges. To solve this issue, chitin nanowhiskers (Nw) were introduced to reinforce the scaffold, aiming to improve its mechanical properties, stability, and provide a better pore structure. Finally, the resulting scaffolds were chemically crosslinked with genipin , resulting in a characteristic blue colour [2].



Scheme 1: Synthesis of MeImBr and chemical modification of CS

CS-MeImBr were characterized by nuclear magnetic resonance (NMR) and Fourier transform infrared spectroscopy (FTIR). Moreover, the thermal behavior was analyzed by differential scanning calorimetry (DSC), while the thermal degradation study in inert atmosphere was performed by thermogravimetric analysis (TGA). The antioxidant evaluation in comparison with CS was tested using DPPH radical test and, the antimicrobial activity against gram-positive and gram-negative bacteria was done following the dynamic contact method. Finally, the viability and cell proliferation test were performed with fibroblast cell line.

Acknowledgements:

This work was funded by the MICINN (PID2022-136516OB-I00). C. Muñoz-Núñez acknowledges MICINN for his FPI fellowship: PRE2020-093596.

References

[1] Lin, J., Peng, Y., Liu, Q., Li, K., Lv, G., Seimbille, Y., Qiu, L. *Chemical Biology & Drug Design,* (2021) 97(1), 121-133.

[2] Yan, L. P., Wang, Y. J., Ren, L., Wu, G., Caridade, S. G., Fan, J. B., ... & Reis, R. L. Journal of Biomedical Materials Research Part A, (2010) 95(2), 465-47

Hybrid biomaterial for in situ oxygen generation against hypoxia-reperfusion injury

Pierro C. I.[1*], Albanese P.[2] , Lavecchia A.M.[3], Xinaris C.[3], Mavelli F.[1], Altamura E.[1]

[1] *Department of Chemistry, University of Bari "Aldo Moro", Bari, Italy*
[2] *Department of Earth, Environmental and Physical Sciences, University of Siena,Siena,Italy*
[3] *Department of Molecular Medicine, Institute Mario Negri, Bergamo,Italy.*
*carmela.pierro@uniba.it

Understanding hypoxia-reperfusion injury is crucial in medical research, as researchers and clinicians work to develop strategies to minimize damage during reperfusion and improve outcomes in conditions like ischemic stroke or myocardial infarction.

This work aims to develop a smart soft biomaterial, capable to photo-produce O_2 under continuous irradiation to counteracting the effects of the absence of oxygen on cell tissues. It consists of thylakoids (1), photosynthetic membranes extracted from chloroplast of *Spinacia oleracea* leaves, embedded in a thermogel matrix composed of a triblock copolymer: the poloxamer Kolliphor© P407 (2).

The thylakoid dispersion in the poloxamer solutions (Fig. 1) does not influence the polymer physico-chemical properties always exhibiting a sol-gel transition at gelation temperatures that slightly decrease as the thylakoid content increases, as confirmed by rheological analysis. On the other hand, the incorporated thylakoids are not perturbed by the sol-gel transition and appear homogeneously dispersed in the gel phase, as evidenced by the fluorescent confocal microscopic analysis. The photoactivity of the photosynthetic apparatus, specifically photosystem II (PSII), embedded in the gel phase has been also tested by the Hill assay (5). PSII absorbs photon energy by catalysing the water molecule oxidation with the production of molecular O_2 (the water-splitting reaction) and, therefore, donates electrons to an external electron acceptor, the Hill's reagent (2,6-dichlorophenol indophenol, DPIP). The O_2 photoproduction of thylakoid was quantified through oxygraphy resulting in about 700 nmol/mL under continuous lighting for about 1 hour.

The O_2 photoproduction was first tested in a thylakoid bulk dispersion then, then *in vitro* on cardiomyocytes of the left ventricle (AC16) in hypoxia condition. The human cells were kept in hypoxic condition (6) for one hour and a half, subsequently are treated with thylakoids in the following hour. Preliminary results showed that the mortality of AC16 treated with thylakoids, is quantitatively reduced (65%) compared to the untreated sample (90%).

For these reasons, poloxamer gels embedding thylakoids could be considered as new smart soft biomaterials capable of photo-producing molecular oxygen and thus can be proposed as suitable tools in alternative therapies for in situ recovery of cells in hypoxia condition.

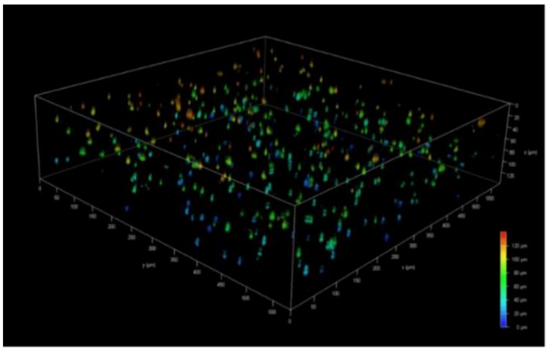


Figure 1. 3D representation of thylakoids embedded in P407 gel, obtained by the convolution of 141 confocal images.

References

1. Johnson M. P., *Essays in Biochemistry*, 60 (**2016**), 225-273.
2. Dumortier G., et al., *Pharmaceutical Research*, 23 (**2006**), 2709-2728.
3. Miller T.E., et al., *Science*, 368 (**2020**), 649-654.
4. Liu T. and Chu B., *Journal of Applied Crystallography*, 33 (**2000**), 727-730.
5. Hill R., *Nature*, 139 (**1937**), 881.
6. Pittman R. N., *San Rafael (CA): Morgan & Claypool Life Sciences*, (**2011**). PMID: 21634070

Characterization of BSA coated- and uncoated hemoglobin nanoparticles (HbNPs) prepared by Co-precipiation-crosslink-dissolution method (CCD) in different concentration of glutaraldehyde (GA)

Siwanut Pummarin[1*], Alejandro Fábrega Puentes[2], Paolo Di Gianvincenzo[2] and Sergio Moya[2]

[1] Medical Science program, Chulalongkorn University, Bangkok, Thailand
[2] Soft Matter Nanotechnology, Center for Cooperative Research in Biomaterials (CICbiomaGUNE), Donostia-San Sebastian, Spain

**p.siwanut@gmail.com*

Hemoglobin (Hb) is a fundamental protein, which is present in red blood cells, and responsible of carrying oxygen in the body. Synthetic hemoglobin-based oxygen carriers (HBOCs) have gained increasing attention as blood substitutes. In this work, Hb has been used to develop nanoparticles capable of carrying oxygen aiming at applications in cancer therapy. Albumin was used for coating the Hemoglobin nanoparticles (HbNPs) for particle stability and to enhance circulation . Nanoparticles were prepared applying the Co-precipitation-crosslinking-dissolution (CCD) method . In this method Hb is entrapped via the precipitation of of $MnCl_2$ with Na_2CO_3 (forming a $MnCO_3$ template). Then, a crosslinking step is performed with glutaraldehyde (GA) to crosslink amino groups from the proteins and give stability to the nanoparticles. Different GA concentrations were used for the crosslinking (0.01% - 0.08%). After crosslinking, $MnCO_3$ template was dissolved by using EDTA. The particles were characterized by dynamic light scattering, zeta potential, and circular dichroism. The results show that the size of particles was not affected by the GA concentration in both BSA coated and pure HbMPs,. All particles showed negative zeta potential between -5 to -45 mV. Zeta potential decreased with increasing GA concentration. Circular dichroism shows that the majority of Hb and BSA are alpha-helixes. On the other hand, alpha-helix of Hb and BSA in particles decreased 17%–34%, while β-strand and random coil increased 10%-15% and 8%-20% respectively. The change in conformation of proteins does not affect their capacity to carry oxygen.

References

[1] Yu Xiong., Axel Steffen., Hans Baumler. *Biomacromolecules*, 2012, **13**, 10, 3292-3300.
[2] Sarany CHaiwaree., Ausanai Prapan., Hans Haumler. Pharnaceutics, 2020, **12(3)**, 224.

Enhanced antibacterial activity of Vancomycin loaded on functionalized polyketones

Rampazzo Rachele[1,2*], Andrea Vavasori[1], Lucio Ronchin[1], Pietro Riello[1], Martina Marchiori[1], Gloria Saorin[1], Valentina Beghetto[1,3,4]

[1] *Department of Molecular Sciences and Nanosystems, Ca' Foscari University Venice, Mestre-Venezia, Italy.*
[2] *Department of Architecture and Industrial Design, University of Campania "Luigi Vanvitelli", Aversa, Italy*
[3]*Crossing S.r.l., Viale della Repubblica 193/b, 31100 Treviso, Italy*
[4]*Consorzio Interuniversitario per le Reattività Chimiche e la Catalisi (CIRCC), via C. Ulpiani 27, 70126 Bari, Italy.*

**rachele.rampazzo@unive.it*

Today polymeric Drug Delivery Systems (DDS) appear as an interesting solution against bacterial resistance, having great advantages such as low toxicity, biocompatibility, and biodegradability[1]. In this work, two polyketones (PK) have been post-functionalized with taurinate (PKT) or sulfanilate (PKSK) and employed as biocompatible carriers for Vancomycin against bacterial infections. Modified PK were easily prepared by Paal-Knorr reaction and loaded with Vancomycin at variable pH[2,3]. All polymers were characterised by FT-IR, DSC, TGA, SEM and elemental analysis. Antimicrobial activity was tested against Gram positive Staphylococcus aureus ATCC 25923 and correlated to the different pH used for its loading (between 2.3 and 8.8). In fact, minimum inhibitory concentrations achieved with both PKT and PKSK loaded with Vancomycin are similar, 0.23µg/mL and 0.24µg/mL respectively, i.e. six times lower that Vancomycin alone. The use of post-functionalized aliphatic polyketones has thus been demonstrated to be a promising way to obtain efficient polymeric DDS.

Figure 5: Use of polymers for biomedical application is increasing due to their interesting features, allowing the development of antibacterial delivery systems. In this work, post-functionalized aliphatic polyketones have been synthesized, by Paal-Knorr reaction in the presence of two different amines, and Vancomycin loaded at different pH (2.3,5.0,8.8). These polymer drug delivery systems gave MIC values six times lower than Vancomycin alone.

References

[1] A. Morandini, E. Spadati, B. Leonetti, R. Sole, V. Gatto, F. Rizzolio, V. Beghetto, RSC Adv., 2021, **11**, 28092-28096.
[2] E. Agostinelli, F. Belli, G. Tempera, A. Mura, G. Floris, L. Toniolo, A. Vavasori, S. Fabris, F. Momo, R. Stevanato, J. Biotechnol. 2007, **127**, 670–678.
[3] J. C. Ruiz, C. Alvarez-Lorenzo, P. Taboada, G. Burillo, E. Bucio, K. De Prijck, H. J. Nelis, T. Coenye, A. Concheiro, Eur J Pharm Biopharm, 2008, **70**, 467–477.

Active starch-based films for food packaging applications: choline chloride plasticizer and self-polymerized polydopamine with antioxidant and UV barrier properties

Susanna Romano[1*], Serena De Santis[1], Clarissa Ciarlantini[2], Antonella Piozzi[2], Giovanni Sotgiu[1], Monica Orsini[1]

[1]Department of Industrial, Electronic and Mechanical Engineering, Roma Tre University, Rome, Italy
[2]Department of Chemistry, University of Rome "La Sapienza", Rome, Italy

**susanna.romano@uniroma3.it*

Plastic packaging has revolutionized multiple aspects of food preservation, transportation, and consumption, offering workability and flexibility in design and customization, and playing a crucial role in preserving food quality and extending its shelf life [1]. However, the widespread use petroleum-derived plastics has a massive impact leading to serious environmental concerns.

In such context, the request for sustainable alternatives derived from renewable resources such as plants, algae, and microorganisms has intensified [2], with flexible starch-based materials emerging as a promising eco-friendly opportunity. However, the starch nature entails some drawbacks which prevent its usage as packaging material. The main limitations of starch film can be effectively overcome by practicing chemical or physical modifications of the starch itself, such as esterification, blending with other polymers or addition of some plasticizers [3], which can also lead to the development of active biodegradable packaging systems.

Choline chloride (Cho) is a safe, biodegradable, and easily accessible ionic compound that has emerged as an interesting plasticizer for starch film production, and small amounts of polydopamine (pDA) were introduced by self-polymerization of dopamine to obtain antioxidant and UV shielding food packaging systems.

In this work, active biodegradable films for food packaging applications were produced from arrowroot starch. The effect of self-polymerized dopamine and starch acetylation on film properties was investigated by FT-IR spectroscopy analysis, mechanical tests, contact angle measurements, and the UV barrier properties were tested.

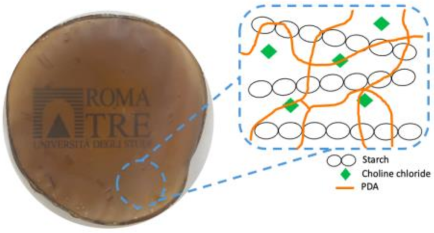


Figure 6. PDA/Starch network

References

[1] R. Porta, The Plastics Sunset and the Bio-Plastics Sunrise, Coatings, 2019, 9, 526

[2] Faizan Muneer; Nadeem, H.; Arif, A.; Zaheer, W. Bioplastics from Biopolymers: An Eco-Friendly and Sustainable Solution of Plastic Pollution. *Polymer Science, Series C* **2021**, *63*, 47–63, doi:10.1134/S1811238221010057.

[3] Masina, N.; Choonara, Y.E.; Kumar, P.; du Toit, L.C.; Govender, M.; Indermun, S.; Pillay, V. A Review of the Chemical Modification Techniques of Starch. *Carbohydr Polym* 2017, *157*, 1226–1236.

Linking biopolymers production with Microbial Electrochemical Technologies

Gaia Salvatori[1,2*], Marianna Villano[1], Bernardino Virdis[2]

[1]*Department of Chemistry, Sapienza University of Rome, Rome, Italy*
[2]*Australian Centre for Water and Environmental Biotechnology, The University of Queensland, Brisbane, Australia*

**Gaia.salvatori@uniroma1.it*

The possibility of linking microbial biopolymer production with Microbial Electrochemical Technologies (MET) has been very recently investigated with the perspective of using MET as a strategy to manipulate both biopolymer yield and composition [1][2][3].

Among biopolymers, polyhydroxyalkanoates (PHAs) are particularly interesting, since they are a family of polyesters synthesized by over 300 species of microorganisms and completely biodegradable. Typically, PHA production is achieved through aerobic bioprocesses, involving either pure microbial strains or Mixed Microbial Cultures (MMC), with the latter also allowing the use of renewable carbon sources, such as wastewaters or food wastes and by-products, as feedstock. Commonly, the PHA-MMC production process involves three main stages represented by the combination of the acidogenic fermentation (AF) step, the microbial selection of PHA-storing microorganisms starting from activated sludge, and the polymer accumulation stage.

Notwithstanding the research efforts to reduce production costs – mainly associated with polymer downstream steps and the continuous aeration to supply at the bioreactors - PHA production stalls at the pilot scale. In this context, the employment of MET potentially represents a game-changing strategy to reduce the oxygen demand and enhance biopolymer production.

Here, preliminary results regarding PHA storage in the absence of aeration, by exploiting the capability of electro-active bacteria to store electrons during the oxidation of the carbon source (i.e., acetate), are presented. PHA storage capacity was assessed at different values applied to the anodic potential (i.e., +0.40 V; +0.20 V; and 0 V, with respect to the Standard Hydrogen electrode, SHE) and two feeding strategies (i.e., carbon and nitrogen-coupled and -uncoupled feeding). The obtained results show that under uncoupled feeding conditions, and when the anode was polarized at 0 V *vs.* SHE, MMC enriched (from an activated sludge) in genus *Geobacter* was able to store polyhydroxybutyrate (PHB). In the same conditions a maximum polymer storage yield (0.13±0.02 mol-C PHB/mol-C acetate) was detected, confirming that the adopted operational and feeding strategy conditions were successful. These results are interesting because the capacity for PHA storage in organisms belonging to the genus *Geobacter* (a well-known electroactive strain) has been limited so far. This opens new opportunities for controlling the MMC-PHA production process through the exploitation of MET.

References

[1]Nishio K., Kimoto Y., Song J., Konno T., Ishihara K., Kato S., Hashimoto K., Nakanishi S., *Environ. Sci. Technol. Lett.* 2013, ***1***, 40–43.
[2] Ter Heijne A., Pereira M. A., Pereira J., Sleutels T., *Trends Biotechnol.* 2021, ***39***, 34–42.
[3] Pereira J., Neves P., Nemanic V., Pereira M. A., Sleutels T., Hamelers B., Ter Heijne A., *Water Res.* 2023, ***242***, 120278.

Microfluidic production of amiodarone loaded nanoparticles and application in drug repositioning in ovarian cancer

Gloria Saorin[1*], Asia Saorin [1], Fahriye Duzagac[2], Pietro Parisse[3], Ni Cao[1], Corona Giuseppe[4],
Enrico Amedeo Cavarzerani[1], Beghetto Valentina[1,5], Flavio Rizzolio[1,6].

[1] *Department of Molecular Sciences and Nanosystems, Ca'Foscari University of Venice, Venezia-Mestre, Italy.*
[2] *Department of Clinical Cancer Prevention, The University of Texas MD Anderson Cancer Center, Houston, TX, USA.*
[3] *Elettra-Sincrotrone Trieste S.C.p.A., Area Science Park, Strada Statale 14 km 163.5, 34149 Basovizza, Trieste, Italy.*
[4]*Immunopathology and Cancer Biomarkers Unit, Centro di Riferimento Oncologico di Aviano (CRO), IRCCS, Aviano, Italy.*
[5]*Crossing S.r.l., Viale della Repubblica 193/b, 31100 Treviso, Italy.*
[6] *Pathology Unit, Centro di Riferimento Oncologico di Aviano (C.R.O.) IRCCS, 33081, Aviano, Italy.*

**gloria.saorin@unive.it*

Repositioning amiodarone for cancer treatment holds promise; however, its potential is limited by toxicity concerns. Recent studies have explored its application in ovarian cancer (OC), a type notorious for peritoneal metastasis. OC is characterized by heightened fatty acid oxidation, driven by the overexpression of CPT1A, a key transporter protein. Amiodarone, known to inhibit CPT1A, presents an intriguing avenue for investigation in OC therapy[1]. To overcome toxicity issue, relate to amiodarone administration for cancer treatment, drug delivery systems (DDS) can be applied. Among the different possible DDSs liposomes are considered ideal systems. Liposomes are characterized by high biocompatibility and are particularly advantageous for cancer treatment, as they can accumulate via the Enhanced Permeability and Retention effect or through surface modifications targeting specific receptors, thereby enhancing the pharmacokinetics of the encapsulated drug[2]. Various methods have been developed for liposome production, the choice of production method significantly impacts the characteristics of the resulting vesicles. Traditionally used methods often necessitate post-production steps for homogenization and purification to achieve liposomes suitable for clinical applications. In recent years, microfluidics has emerged as a promising approach for liposome production. Its precision enables the regulation of parameters, facilitating control over factors such as lamellarity, average size, and size distribution of the vesicles[3]. Microfluidic amiodarone encapsulation into liposomes was achieved together with simultaneous production of amiodarone lipidic particles. Optimization of microfluidics parameters, including temperature and flow rate ratio, allowed the successful production of stable particles. Bothe theses lipidic DDSs were fully characterized and proved their efficacy over ovarian cancer models[4].

Acknowledgements:

The authors are thankful to Dr. Loredana Casalis for the availability of AFM. Fahriye Duzagac and Ni Cao received support by AIRC (F.R.: I.G.23566). Research at CNR-IOM has been funded by the European Union—NextGenerationEU under the Italian Ministry of University and Research (MUR) National Innovation Ecosystem grant ECS00000041—VITALITY. P.P. acknowledges Università degli Studi di Perugia, CNR and MUR for support within the project Vitality.

References

[1] Sawyer B.T., Qamar L., Yamamoto T.M., McMellen A., Watson Z. L., Richer, J. K., Behbakht K., Schlaepfer I.R., Bitler B. G. 2020, Molecular Cancer Research, **18**, 1088.

[2] Bitounis D., Fanciullino R., Iliadis A., Ciccolini J. 2012, ISRN Pharmaceutics, 2012, **1**, 11.

[3] Carugo D., Bottaro E., Owen J., Stride E., Nastruzzi, C. 2016, Scientific Reports, **6**, 25876.

[4] Saorin A., Saorin G., Duzagac F., Parisse P., Cao N., Corona G., Cavarzerani E., Rizzolio F. 2024, Scientific Reports, **14**, 6280.

From molecularly docked aptamer design to detection: E-aptasensor for okadaic acid (OA)

Margherita Vit[a]*, Sondes Ben-Aissa[a,b], and Sabina Susmel[a]

[a] *Department of Agri-Food, Environment and Animal Sciences (Di4A), University of Study of Udine, Italy*
[b] *Chemistry Department, Imperial College London, UK*

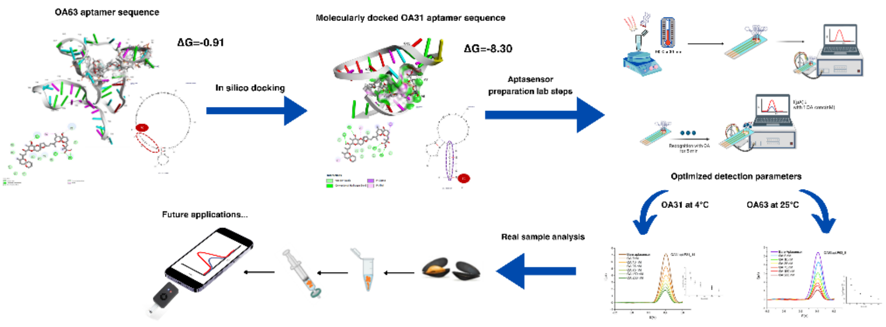
* *margherita.vit@uniud.it*

Harmful algal blooms (HABs) produce various toxins, notably Okadaic Acid (**OA**), which pose a significant health hazard when ingested through contaminated shellfish, leading to diarrheic poisoning (DSP). The European Union has established stringent OA limits in bivalves at 180 nM (EC Regulation 2004). Current detection techniques, such as chromatography, are often time-consuming, impeding swift responses during HABs occurrences. There is a growing interest in rapid and cost-effective technologies, with aptamers, short DNA or RNA sequences, showing promise due to their stability and customizable synthesis. This research focuses on optimizing an Electrochemical Aptamer-Based Sensor (**E-aptasensor**) for OA detection, comparing two aptamers of different lengths, **OA63** and **OA31**, both tagged with ferrocene for electrochemical OA detection via Differential Pulsed Voltammetry (DPV). Starting with OA63[1], OA31 was molecularly docked, and four thiol-modified capture probes (**P**) of various lengths (P_{63}_8, P_{63}_16, P_{31}_6, P_{31}_14), complementary to the aptamers, were designed. Thiol chemistry was selected to chemisorb onto a gold-modified (AuNPs) screen-printed electrode. The study investigated several variables, including electrode pre-treatment, hybridization protocol, combinations of aptamers and capture probes, as well as OA detection times and temperatures. The most effective outcomes in terms of repeatability, signal intensity, and OA recognition were observed for **OA31-P_{31}_14** at 4°C and **OA63-P_{63}_8** at 25°C, both with a 5-minute incubation period. With these conditions, OA was detected in a range of 5-200 nM with a detection limit (DL) of 2.5 nM (Blank signal ± 3σ). Despite ΔG of OA31 (-8.30 kcal/mol) suggesting better stability compared to the OA63 (-0.91 kcal/mol), both aptamers behaved similarly after optimization of experimental conditions highlighting the need for verification from silico design to real application. Furthermore, the E-aptasensors demonstrated excellent recovery rates (94-101%) for OA spiked in mussel extracts, suggesting future applicability in real samples.

Acknowledgements: This research was funded by EU Interreg Italy-Croatia, VA-CBC Programme 2014–2020, AdSWiM project, ID 10046144

References

[1]Marty J-L, Prieto-Simon B., 2014, Ligand and method for detection of okadaic acid, France, EP 2 770 058 A1,European Patent Office



Theme C - Advances in Physical Chemistry

Mechanism of Action of a Ru-based Photosensitizer for Photoactivated Chemotherapy

Pierraffaele Barretta[1*], Fortuna Ponte[1], Daniel Escudero Masa[2], Gloria Mazzone[1]

[1]Department of Chemistry and Chemical Technologies, University of Calabria, Rende, Italy
[2]Department of Chemistry, KU Leuven, Heverlee, Leuven, Belgium

**pierraffaele.barretta@unical.it*

The medical techniques based on the use of light for activating drugs are occupying a prominent place in the cancer treatment due to their selectivity that contributes to reduce undesirable side effects of conventional chemotherapy. Among these therapeutic treatments, photodynamic therapy (PDT) and photoactivated chemotherapy (PACT) are emerging as complementary approaches for selective destruction of neoplastic tissues through direct cellular damage. Both techniques rely on the employment of a molecule, photosensitizer PS, able to absorb within the so-called therapeutic window. Thus, the exposure to light of otherwise inert molecules promotes the population of excited states of the drug, that in PDT are able to produce the cytotoxic species, such as $^1O_2$ and other ROS, in PACT can be responsible for the active species release. In recent years, transition metal complexes, especially based on Ru(II) metal center, have been explored as anticancer agents for applications in different medical approaches, including PDT and PACT, in order to improve their chemical, biological and photophysical properties. From one side, they are able to generate $^1O_2$ and other ROS but, more importantly, they can selectively release other active molecules by photo-release of one of their ligands. Recently, a Ru(II) complex was synthesized, called Ru-sora, which exhibits a double action for cancer therapy, as, upon light irradiation, it can exert PDT action and release one of its ligands (Fig. 1), a drug commercially known as Sorafenib, used for Heapotocellular carcinoma HCC[1]. This strategy helps to control the dosage of Sorafenib, that is the unique drug used for HCC treatment, but has few sides effects at high concentration.

In this work, we studied the main photophysical properties of Ru-sora with a computational approach. Density Functional Theory and its Tamm–Dancoff approximation (TDA) were employed for this purpose and used to clarify the whole mechanism of action in dark and upon light irradiation.

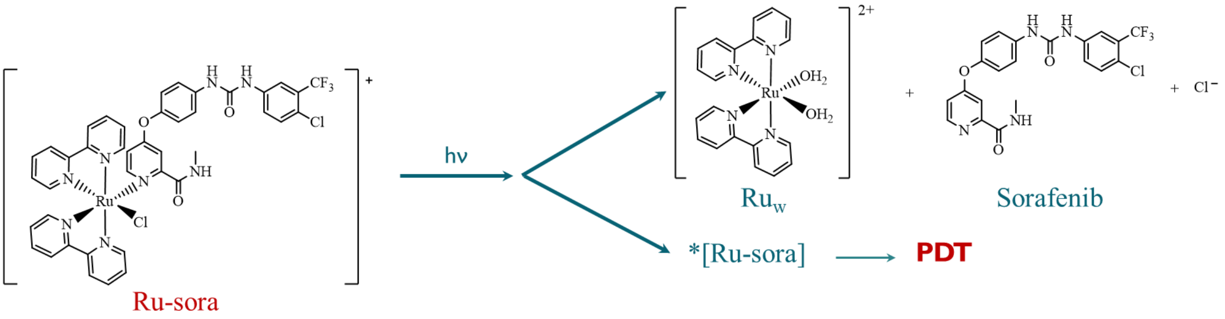


Fig. 1 Mechanism of action of sorafenib.

References

[1] Yidan L., Nong L., Shuangling L., Haobing W., Pingyu Z. *J. Med. Chem.*, 2022, **65**, 13041-13051.

Computational study on the photodissociation mechanism of ruthenium complexes for photoactivated chemotherapy

Daniele Belletto[1*], Fortuna Ponte [1], Gloria Mazzone[1], Emilia Sicilia[1]

[1]*Department of Chemistry and Chemical Technologies, Università della Calabria, Ponte P. Bucci, 87036 Arcavacata di Rende, CS, Italy*

**daniele.belletto@unical.it*

In order to enhance action specificity and overcome drawbacks such as dose escalation, drug resistance, low bioavailability and acute side effects of the drugs currently in use to treat cancer, a good way seems to be photoactivated chemotherapy (PACT). The basis of this type of therapy is the use of light-activatable agents such as polypyridyl Ru(II) complexes thanks to their low propensity to exchange ligands in dark and their high photoreactivity. In fact, these compounds to be effective for PACT, first undergo photosubstitution reactions under light irradiation involving ligand replacement by a solvent molecule. In this study, a detailed computational investigation of the photosubstitution reaction of a novel trisheteroleptic Ru(II) complex recently synthesized by Bonnet and co-workers, [1] $[Ru(dpp)(bpy)(mtmp)]^{2+}$ (**Fig.1**), in which dpp is 4,7-diphenyl-1,10-phenanthroline, bpy is 2,2'-bipyridine and mtmp is 2-methylthiomethylpyridine, has been carried out applying density functional theory (DFT) and its time-dependent extension (TD-DFT). In particular, the photosubstitution mechanism for the photolabile ligand, mtmp, detachment leading to the formation of the active drug that binds DNA inducing cell death, has been explored describing all involved singlet and triplet states. Furthermore, the involvement of solvent molecules in photosubstitution and the role of pyridyl–thioether chelates as caging groups has been elucidated. With this study, it has been demonstrated that the mtmp ligand stabilizes the vacant MOs responsible for the generation of ^{3}MC states, facilitating their population and promoting photosubstitution. During the photosubstitution, the starting complex first evolves through a pentacoordinated monoaquated complex in triplet state and, then, into the corresponding biaquated one in singlet state. These outcomes are useful for the comprehension of the photosubstitution process and the synthesis of new efficient PACT agents.

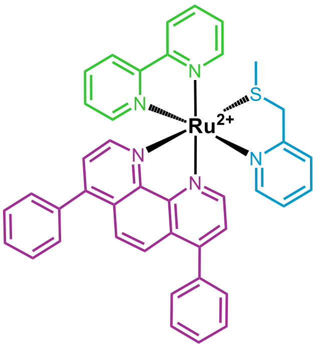


Fig.1 Structure of the Ru(II) complex under investigation.

References

[1] Q. Chen, J.-A. Cuello-Garibo, L. Bretin, L. Zhang, V. Ramu,Y. Aydar, Y. Batsiun, S. Bronkhorst, Y. Husiev, N. Beztsinna, L. Chen, X.-Q. Zhou, C. Schmidt, I. Ott, M. J. Jager, A. M. Brouwer, B. E. Snaar-Jagalska, S. Bonnet, *Chem. Sci*., 2022, **13**, 6899.

Implementing osmosis into a simulation model for passive permeation through lipid bilayers

S. Boi[1*], M.A. Scorciapino[1]
[1]*Department of Chemical and Geological Sciences, University of Cagliari, Monserrato, Italy*

**sara.boi95@unica.it*

The transport of substances across lipid membranes, either passive or active, is of vital importance for any living organism [1]. The permeability of the membrane determines which substances can pass through it and depends on the physicochemical properties of both the membrane components and the permeating substance. Being able to predict permeability is fundamental in therapeutic agent design, because even the most active one becomes ineffective if it is unable to cross the membrane(s) and reach the final target. Our work is focused on passive transport and aims at providing a mathematical model that explicitly considers all the main processes that are involved. Mathematical models presented in the literature [2] are either too simplistic, by focusing on a few physicochemical parameters, or too complex, by including so many parameters to result of low human interpretability. Other models are too time and resource demanding making them unsuitable for screening campaigns. Despite the model being considered, consistent experimental data are needed to check it. However, methods for permeability measurement are only a few, each one with its own limitations. We have investigated the direct passive transport across the lipid bilayer, by using the liposome swelling assay (LSA) [3-5], which although dates back to the 80s, it provides direct evidence of permeation, while being easy to apply. We built a mathematical model by starting from our first simulation algorithm [6], where we have implemented the osmosis. This code is able to reconstruct the experimental curves by considering all the relevant processes, namely, partition, diffusion, and osmotic pressure, with the corresponding parameters. The model allows to investigate in-silico the effect of each parameter separately. Here we present a series of simulated curves to show the information provided by our code and its performance. On the experimental side, both non-permeant and permeant species have been investigated, thus, obtaining water and substrates apparent permeability coefficients. Good repeatability was achieved even by reducing substrate concentration as much as possible. We observed that vesicle swelling offers too low sensitivity, whereas working in the direction of shrinkage gave the best results. Thus, in the presence of a permeant substrate, it is advantageous to work with a higher concentration of the substrate inside the vesicle; in the presence of a non-permeant substrate, the concentration of the external solution must be higher. In the first case, the experimental curve is influenced by both the membrane permeability to the substrate and to water, whereas in the second case, only water permeability is important. Furthermore, the results have shown that the value of water permeability depends on the presence of the substrate itself whether permeable or not, and on any electrolytes present in the internal and external solutions, as well as their absolute concentration. Finally, simulated curves were fitted to the experimental data through a Monte Carlo scheme in order to retrieve water and substrate permeability coefficient.

References

[1] Stillwell W., *An Introduction to Biological Membranes (2nd ed)*, 2016, 19, 423-451, Elsevier, Amsterdam, The Netherlands.
[2] Bernardi A., et al., *Membranes*, 2023, **13**, 851.
[3] Ghosh P., Singh U.N., *Biochimica et Biophysica Acta*, 1992, **1110**, 88-96.
[4] Lande M.B., Donovan J.M., Zeidel M.L., *The Journal of General Physiology*, 1996, **106**, 67-84.
[5] Horner A., et al., *Science Advances*, 2015, **1**.
[6] Scorciapino M.A., et al., *Membranes*, 2022, **12**, 292.

Revealing the structural organisation of 5-hydroxymethhylfurfural (HMF) through X-ray scattering and Molecular Dynamics.

G.A. Bracchini[1,*], E. Mangiacapre[2], O. Russina[2]
F. Lo Celso[3], A. Triolo[1]

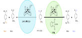
[1] *Laboratorio Liquidi Ionici, Istituto Struttura della Materia, Consiglio Nazionale delle Ricerche (ISM-CNR), Roma 00133, Italy*
[2] *Department of Chemistry, University of Rome Sapienza, Rome 00185, Italy*
[3] *Department of Physics and Chemistry, Università di Palermo, Palermo, Italy*

**giuliaadriana.bracchini@artov.ism.cnr.it*

5-hydroxymethylfurfural (HMF) is an aromatic furan derivative that can be synthesized in a sustainable way, starting from raw biomass. It is highly versatile, serving as a precursor for biofuels, biopolymers, and various solvents [1].

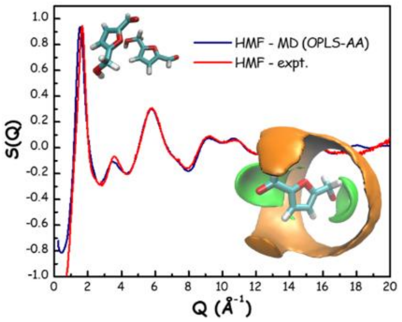
In this work, we present results concerning the microscopic structural arrangement of liquid HMF at 40°C, obtained through the synergy of classical Molecular Dynamics (MD) simulation and Small-Wide-Angle X-ray Scattering (SWAXS) experiments.

The excellent agreement of simulated data with experimental ones provides support to the robustness of our present atomistic description.

Our analysis highlights the important role played by hydrogen bonding (HB) interactions in determining liquid HMF structure. The most relevant hydrogen bond occurs between aldehyde oxygen and hydroxyl hydrogen. We also detect a bidentate interaction between the aldehyde hydrogen and both the ether oxygen and a neighbor aldehyde moiety. It is also notable the occurrence of O··H—π HB interaction, analogously to other aromatic systems [2]. Consistently with the aromatic nature of the furan ring, the existence of a  stacking interaction between neighbor furan rings was observed, with a typical parallel and staggered organization, at small distances of ca. 4.5 Å. In this organization, the ring functional groups are not perfectly aligned due to steric hindrance effects.

Our study highlights the heterogeneity and complexity of the interactions driving the liquid state structural organization in HMF. Robust knowledge of the atomistic details of such interactions is fundamental to properly explore and rationalize solutions and reactivity of HMF in different environments, including deep eutectic solvents, which is the topic of the PRIN2022 project supporting this research.

This research was supported by the PRIN2022 *SEED4GREEN* Project (20223W4RT9).



References

[1] A. Rosatella, S. Simeonov, R. Frade, C. Afonso, *Green Chemistry*, 2011, **13**, 754.
[2] E. Mangiacapre, A. Triolo, F. Ramondo, F. Lo Celso, O. Russina, *Journal of Molecular Liquids*, 2024, **394**, 123778.

Exploring the Effect of a Quencher on the Fluorescence Decay of Tryptophan in Water: a Computational and Experimental Study

G. Ciattaglia[1*], C. G. Chen[1], M. L. De Sciscio[1], L. Desiderio[1], M. Giustini[1], M. D'Abramo[1],

[1] *Department of Chemistry, Sapienza University of Rome, Rome, Italy*

**giulia.ciattaglia@uniroma1.it*

Tryptophan is known to have characteristic fluorescence properties. The bi-exponential behaviour of its fluorescence decay has been widely studied: experimental evidence shows that the emission of tryptophan occurs with two different lifetimes[1]. Several hypotheses have been put forward to explain this behaviour. The most widely accepted is the one that considers the existence of three different conformers (defined as A, B, or C) of tryptophan in water, distinguished by a different C_α-C_β rotation. The rotamers are thought to exist in solution as [A]>>[C]>[B][1,2]. It can also be assumed that B is rapidly interconverted to A due to electronic repulsion between the indole ring and the COO^- group[2]. This could explain the two rather than the three components of the decay. In this work, we investigate the interaction between the tryptophan conformers and the succinimide molecule (which is known to be a soft quencher of tryptophan fluorescence[3]) and the role of the conformers in the fluorescence lifetimes using a combined computational (MD simulations) and experimental (fluorescence spectroscopy) approach. Our preliminary results confirm the existence of the two fluorescence lifetimes for tryptophan in water which we have identified as a slow (3.037 ns) and a fast (0.926 ns) component. The two lifetimes contribute 80% and 20% respectively to the decay. When the quencher is added, a decrease in the contribution of the slow phase is observed, so that the decay is supposed to assume a mono-exponential behaviour in the presence of a large amount of the succinimide. Following this result, we run MD simulations to investigate the conformational dynamics of tryptophan and its interaction with succinimide. An analysis of the trajectories based on the value of the C_α-C_β and C_β-C_γ rotations shows that when the tryptophan interacts with succinimide, only one of the three conformers is sampled. This suggests a preferential interaction of the succinimide with one of the tryptophan conformers.

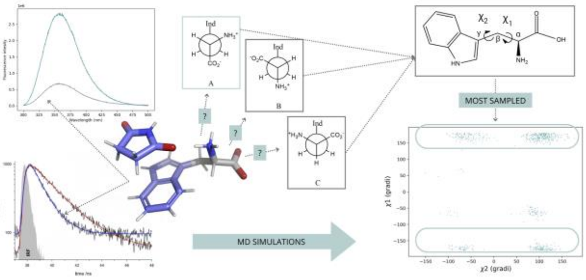


Figure 1. *Schematic representation of the study*

References

[1] G. Szabo, D. M. Rayner. *Journal of the American Chemical Society*, 1980, **102** (2), 554-563.
[2] L.X.-Q. Chen, R. A. Heng, G. R Fleming. *Chemical Physics Letter*, 1986, **126** (3,4), 365–372.
[3] M.R Eftink, C.A. Ghiron. *Biochemistry*, 1984, **23**, 3891–3899.

On the thermodynamics of Barium Oxyfluoride precursor in YBCO growth via MOD process

Michele De Angelis[1,2*], Massimo Tomellini[1]

[1] *Department of Chemical Sciences, Tor Vergata University, Rome, Italy*
[2] *Department of Fusion and Technologies for Nuclear Safety and Security, ENEA, Rome, Italy*

**michele.deangelis.01@alumni.uniroma2.eu*

The typical layered structure of superconducting cuprates, such as $YBa_2Cu_3O_{7-\delta}$ (YBCO), requires proper alignment of conduction planes to ensure optimal transport properties. For this reason, YBCO thin films must be grown with a specific orientation. The best superconducting properties are observed in the YBCO grown along the c-axis, perpendicular to the substrate. Against the background of extensive scientific literature on the growth of YBCO on crystalline substrate by chemical deposition technique [1]-[5], only a few works concern the study of the nucleation process, although it is crucial for the growth of the film [2]-[5]. A thermodynamic and kinetic model for the growth of YBCO has been proposed in references [5]-[6]. This model is based on the calculation of the free energy of oxide formation using thermodynamic data, experimental and theoretical, for the formation reaction of YBCO, to obtain information on the preferential growth of the film along the *a* or *c*-axis. This study is significant to identify the role of Barium Oxyfluoride, as precursor species, in the nucleation and growth of YBCO via the Metal Organic Decomposition (MOD) route. In this contribution, we present a study on the thermodynamics of the Oxyfluoride (OF) by processing experimental data on the YBCO growth at $LaAlO_3$ (LAO) substrate. The analysis allows one to determine the standard enthalpy and the standard entropy changes for Oxyfluoride formation from Barium oxide and Barium fluoride. To identify the thermodynamically more favorable route to the OF formation in the MOD process, the free energy change for the formation of the precursor, through several reactions involving gas water, has been determined. The free energy of formation via fluoride and water indicates higher stability of oxygen rich Oxyfluoride for $P_{HF}^2/P_{H_2O} < 10^{-6}$. In the framework of the nucleation theory the present results are needed to study the effect of precursor composition on film orientation.

Acknowledgements:

The authors are indebted with Dr. V. Pinto for the helpful discussions and the critical reading of the paper. M.D.A. work has been carried out within the framework of the XXXIX Doctoral program in Chemical Sciences, Department of Chemical Science and Technologies, University of Rome Tor Vergata. The PhD grant has been partially funded by ENEA, Italian National Agency for New Technologies, Energy and Sustainable Economic Development.

References

[1] T. Araki and I. Hirabayashi, Supercond. Sci. Technol., 2003, 16, R71.
[2] X. Obradors et al, Supercond. Sci. Technol., 2012, **25**, 123001.
[3] Y. Ichino et al, Trans. Appl. Supercond., 2003, **13**, 2735.
[4] X. Obradors et al, Physica C: Superconductivity and its Applications, 2012, **482**, 58.
[5] V. F. Solovyov et al, Supercond. Sci. Technol., 2005, **18**, 239.
[6] V. Pinto et al, Supercond. Sci. Technol., 2020, **33**, 115006.

Deciphering the Kinetics of Methionine Oxidation by Hydrogen Peroxide in Proteins

Maria Laura De Sciscio[1*] and Marco D'Abramo[1]

[1]*Department of Chemistry, University of Rome, Sapienza, P.le Aldo Moro 5, Rome, Italy*

**marialaura.desciscio@uniroma1.it*

The easily oxidable thioetheric form of the sulfur atom of Methionine (Met) makes the residue particularly susceptible to the action of Reactive Oxygen Species. Among the possible reactions, hydrogen peroxide-induced oxidation is a clean process with high relevance in both physiopathological and pharmaceutical context[1]. It helps in the preservation of cellular redox homeostasis while acting as a scavenger and protecting the protein backbone from highly damaging modifications. On the other side, the presence of Met-Sulfoxide – the main oxidation product – can affect the chemical stability and biological activity of the protein and is linked with ageing and many pathological conditions, including neurological, vascular and pulmonary diseases. Lastly, Met oxidation may seriously compromise the efficacy and safety of the biotherapeutics products[2]. Even though many efforts have been made to understand Met oxidation susceptibility, the molecular basis of the different residue-specific kinetics rates are not yet completely unravelled. Aiming to a full-side perspective, we comprehensively characterized Met oxidation by hydrogen peroxide in a model system and Leptin protein case study. To do that, the free energy profiles of oxidation were obtained through the Perturbed Matrix Method[3], a hybrid QM/MM approach, while classical molecular dynamics (MD) simulations were conducted to estimate the kinetics of the hydrogen peroxide approach towards Met. Such a procedure, validated by experimental data comparison[1], led to the identification of new conformational features of the Met side chain and the role of protein tunnels. Finally, analysis of known descriptors for predicting the oxidation susceptibility of Met residues together with our results allowed us to identify the main environmental factors affecting the overall kinetics of this reaction.

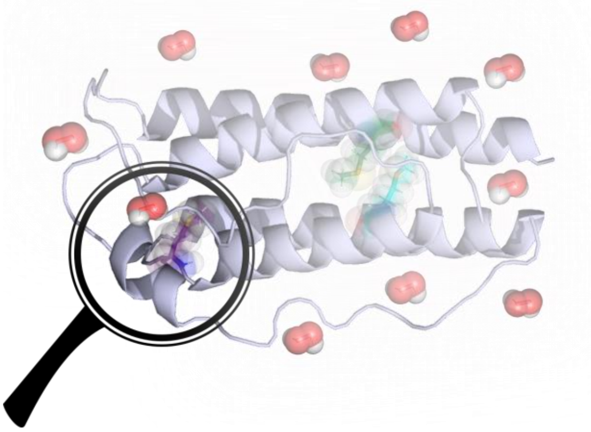


Figure 1. *Met residues within Leptin protein and surrounding hydrogen peroxide molecules.*

References

[1] M.L. De Sciscio, V. D'Annibale, M. D'Abramo. *Int J Mol Sci*, 2022, **23**(23), 14515.
[2] Aledo, J. C., Cantón, F. R., & Veredas, F. J. *Sci Rep*, 2015, ***5***, 16955.
[3] L. Zanetti-Polzi, S. Del Galdo, I. Daidone, M. D'Abramo, V. Barone, M. Aschi, A. Amadei. *PCCP*, 2018, **20**(37), 24369-24378.

Multiscale Modeling of the Photoinduced Enantioselective Radical Cyclization of α-Chloroamides in Flavin-Dependent Ene-Reductases

G. Dell’Orletta[1*], M. Capone[1], G. D. Scholes[2], T. K. Hyster[2], M. Aschi[1], I. Daidone[1]

[1]*Department of Physical and Chemical Sciences, University of L’Aquila, Italy*
[2]*Department of Chemistry, Princeton University, Princeton, United States*

**gianluca.dellorletta@graduate.univaq.it*

Photobiocatalysis has recently emerged as a valuable strategy for conducting chemical reactions that are challenging with conventional organic chemistry tools. This approach involves the use of photenzymes, i.e. enzymes that absorb light to promote substrate transformation. The photexcitation of these catalysts enables access to electronic excited states with different properties compared to the ground state, thus providing new reaction modes. Additionally, the chiral active sites of these enzymes can control the stereoselective outcomes of these processes.

While there are only few natural photoenzymes, irradiating non-natural photoenzymes, which are enzymes dependent on cofactors with latent photochemical properties, can broaden the range of available catalysts. Notably, Todd Hyster and coworkers discovered that the photoexcitation of flavin-dependent ene-reductases (EREDs) can facilitate non-natural transformations involving radical intermediates, such as the 5-exo-trig radical cyclization of alkene-tethered α-chloroacetamides to yield a chiral γ-lactam.1 Specifically, they found that two enzymes from this family, the triple mutant T36A-K317M-Y343F of Gluconobacter oxydans ene-reductase (GluER-G6) and the Old Yellow Enzyme 1 (OYE1), produce opposite enantiomers.[1,2]

We present a computational study of this reaction catalyzed by GluER-G6, employing a multiscale approach based on Molecular Dynamics (MD), Quantum Mechanics (QM), and the Perturbed Matrix Method (PMM)[3]. Firstly, we focused on the initial step, namely the mesolytic cleavage of a C-Cl bond triggered by photoexcitation. We observed that productive mesolytic cleavage occurs only in certain conformations of the substrate, while the others undergo back electron-transfer. Then we addressed the subsequent radical cyclization step using the same tecniques. On the base of our results, we proposed an enatioinduction scenario in which the relative stability of prochiral transition states is not determined by direct interaction with the protein but is rather dependent on a degree of freedom within the substrate, which is controlled by the enzyme through conformational selection.[4]

References

[1] K. F. Biegasiewicz, S. J. Cooper, X. Gao, D. G. Oblinsky, J. H. Kim, S. E. Garfinkle, L. A. Joyce, B. A. Sandoval, G. D. Scholes, T. K. Hyster, Science 2019, **364**, 1166 – 1169.
[1] B. T. Nicholls, D. G. Oblinsky, S. I. Kurtoic, D. Grosheva, Y. Ye, G. D. Scholes, T. K. Hyster, Angew. Chem. Int. Ed. Engl. 2022, **61**, e202113842.
[2] A. Amadei, M. D’Alessandro, M. D’Abramo, M. Aschi, J. Chem. Phys. 2009, **130**, 084109.
[3] M. Capone, G. Dell’Orletta, B. T. Nicholls, G. D. Scholes, T. K. Hyster, M. Aschi, I. Daidone, ACS Catal. 2023, **13**, 15310 - 15321.

A graph theory-based order parameter for the structural and dynamic characterization of supercooled water

Nico Di Fonte[1*], Chiara Faccio[2,3], Laura Zanetti-Polzi[4], Isabella Daidone[1]

[1]Department of Physical and Chemical Sciences, University of L'Aquila, L'Aquila, Italy
[2]Scuola Normale Superiore, Pisa, Italy
[3]Department of Mathematics, University of Padova, Padova, Italy
[4]Center S3, CNR Institute of Nanoscience, Modena, Italy

**nico.difonte@graduate.univaq.it*

Our reaserch is focused on the development of a graph theory-based order parameter for the characterization of liquids. In particular, we applied it to the delicate framework of the Liquid-Liquid Phase Transition (LLPT) in supercooled liquid water, simulated via molecular dynamics (MD). In the LLPT scenario, liquid water exists in two states, the high-density liquid (HDL) and the low-density liquid (LDL).

Despite the structural, dynamic and thermodynamic differences between the HDL and LDL state, distinguishing between the HDL and LDL state, distinguishing them even with computational methods is challenging and, therefore, several order parameters have been introduced to differentiate the two phases. We recently proposed the Node Total Communicability (NTC) as an order parameter, testing its ability to distinguish between HDL/HDL-like and LDL/LDL-like molecules at high pressure where the coexistence line is crossed [1], and at ambient pressure, where the Widom line is crossed [2] .

This descriptor, borrowed from graph theory, yields information about the local connectivity of each water molecule within a simulation box and highlights the influence of the medium-to-long range effects, allowing us to characterize the structural and dynamical behaviour of the system at the microscopic level [1,2] .

We found that HDL-like forms are not homogeneous but rather characterized by the presence of high connectivity patches composed of molecules with an increased local density and mobility. Small highly connected patches are also found in the LDL phase (Fig. 1), and we hypothesize that they could function as initial sites from which the HDL phase starts forming and growing during a phase transition.

Expanding on this hypothesis, we are currently using the NTC to study and characterize the transition of an LDL system to an HDL-like composition with a spinodal-like decomposition mechanism.

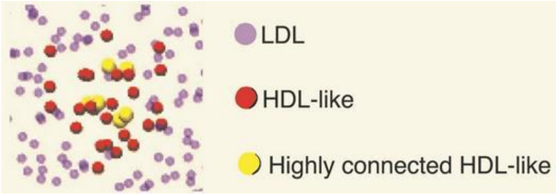


Figure 1: Visualization of highly connected patches and HDL-like patches in an LDL environment.

References

[1] C. Faccio, I. Daidone, L. Zanetti-Polzi, Journal of molecular liquids 2022, 355, 118922.
[2] C. Faccio, N. Di Fonte, I. Daidone, L. Zanetti-Polzi, Journal of molecular liquids 2023, 392, 123425.

Tetrabutylammonium based Deep Eutectic Solvents: effects of counter-anion and HBD in the formation of liquid phases.

Simone Di Muzio[1,2*], Oriele Palumbo[2], Annalisa Paolone[2], Giulia Adriana Bracchini[3], Francesco Trequattrini[4], Fabio Ramondo[1]

[1]*Department of Chemistry, Sapienza University of Rome, P.le Aldo Moro 5, 00185, Rome*
[2]*Istituto dei Sistemi Complessi, Consiglio Nazionale delle Ricerche, P.le Aldo Moro 5, 00185, Rome*
[3]*Istituto di Struttura della Materia, Consiglio Nazionale delle Ricerche, Rome*
[4]*Department of Physics, Sapienza University of Rome, P.le Aldo Moro 5, 00185, Rome*

**simone.dimuzio@uniroma1.it*

In the last years, scientific research has significantly focused on the quest for solvents alternative to traditional ones, with the aim of enhancing solvent properties and reducing environmental impact.
Eutectic solvents (ESs) and deep eutectic solvents (DESs) have attracted the attention since they are easily prepared and their physicochemical properties are readily tunable, heavily dependent on the chemical nature of the components. Combinations of quaternary ammonium, such as tetrabutylammonium (TBA) salts and hydrogen bond donors (HBDs) lead to the formation of eutectic mixtures that can show melting points significantly lower than those of their pure components. The term DES have been introduced by Abbot and coworkers[1] in 2003: they noted an abnormally deep melting point depression at the eutectic composition. The significant factor contributing to the differences in melting points between the mixtures and the starting materials, or the deviation from ideality, is the formation of intermolecular contacts. The depth of the deviation from ideal behavior depends on the nature of the hydrogen bond donor (HBD) and acceptor (HBA), as well as the strength of the hydrogen bond network formed during the mixing of components. The microscopic arrangement of the components and the strength of secondary interactions, particularly hydrogen bonds, have a substantial role on the chemical and physical properties of these materials. In order to propose solvents with a low degree of hydrophilicity, we studied various tetrabutylammonium-based systems with different anions (bromide[2], acetate and triflate) which exhibit variation in dimension, shape and acid-base characteristics. These salts were mixed with various hydrogen bond donors, such as long chain alcohols or acids and imidazoles with different substitutions on the ring. The structure of the starting materials and mixtures were investigated by experimental infrared spectroscopy at the AILES beamline of SOLEIL Synchrotron in Paris, conducting the measurements both in the far- and mid-infrared range (FIR and MIR). The obtained results were interpreted performing quantum chemical (DFT) and classical molecular dynamics simulations. The thermal behavior of the obtained mixtures were investigated with differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). An interesting observation is that the depht of deviations from ideal behavior vary depending on the hydrogen bond donor. For example, in systems composed of octanol and octanoic acid, deviations from ideality are minimal, while they are significantly more pronounced in mixtures containing imidazoles. The changes in the melting points of mixtures thus strongly depend on the varying ability to accept and donate H-bonds with different strengths. Indeed, our spectroscopic and computational investigations demonstrate that significant H-bonds interactions are present in all systems. An additional stabilization effect arises from the dispersion interactions (van der Waals) that occur between the TBA chains and the HBD.

References

[1] A. P. Abbott, et. al. *Chem. Commun*. 2003, **1**, 70.
[2] S. Di Muzio, A. Paolone, O. Russina, F. Ramondo et. al. *J.Mol.Liq*. 2022, **352**, 118427

Analysis of the Effect of Aliovalent Substitutions in Ca/K-1144 Iron Based Superconductors

A. Duchenko[1,2], A. Augieri[3] , L. Barba[5] , G. Campi[4] , G. Celentano[3] , L.Gigli [6] , A. Masi [3] , D. Mirabile Gattia [2] , J. R. Plaisier [6], N. Pompeo [1], A. Rufoloni [3], Z-H Sung [7], F. Varsano [2]

[1] Università degli Studi RomaTre, Dipartimento di Ingegneria Industriale, Elettronica e Meccanica, Via Vito Volterra, 62, 00146 Roma, Italy
[2]ENEA, SSPT-PROMAS-MATPRO, Via Anguillarese, 301, 00123 Roma, Italy
[3]ENEA, NUC-FUSEN-COND, Via Enrico Fermi, 45, 00044 Roma, Italy
[4] CNR- Istituto di Cristallografia, Via Salaria Km 29,300, 00015, Monterotondo (Roma), Italy
[5] CNR- Istituto di Cristallografia, Strada Statale 14 km 163,5, 34149 Basovizza (Trieste), Italy
[6] Elettra-Sincrotrone Trieste S.C.p.A., Strada Statale 14 km 163,5, 34149 Basovizza (Trieste), Italy
[7] Fermi National Accelerator Laboratory, Batavia, IL, USA
**aduchenko@os.uniroma3.it*

The discovery of new-generation superconducting materials, with more favorable superconducting properties than traditional superconductors (e.g. Nb-based metal alloys), has prompted the use of these materials in large-scale applications, such as power distribution, the latest quantum computing and the design of magnets for high fields (> 20 T)

In particular, Iron Based SuperConductors (IBSCs) form a relatively new class of materials, discovered in 2008 [1] and promising for their high critical fields. Structurally, IBSCs consist of a ‘layered’ structure in which Fe ions tetrahedrally coordinated by pnictogen (P, As) or chalcogen (S, Se, Te) ions form planes interspersed with various elements. The different combinations of the elements lead to different structural characteristics, resulting in various ‘families’ of IBSCs. Among these, the 1144 family ($Ae_1A_1Fe_4As_4$, where A and Ae represent alkali and alkaline-earth metals, respectively) [2], attracts significant attention due to its stoichiometric nature, which guarantees solid superconductive properties that do not depend on doping levels as is the case with other IBSC families. The aim of this research activity is to investigate the role of the chemical composition on different material properties, such as the lattice parameters, electronic state and microstructure of the material, and the influence of these parameters on the superconductive properties of the material. To this end, the possibility of partially replacing Ca and K with elements of similar ionic radius in $CaKFe_4As_4$ is demonstrated. Furthermore, it was observed that the partial introduction of ions of different chemical nature into the lattice causes a change in the lattice parameters, which plays an important role in the critical temperature value of the variously substituted compounds [3]. A dome-shaped trend was observed for the T_c of variously substituted samples as a function of the degree of lattice distortion, which depends on the chemical nature and quantity of the substituent. [4], [5].

Furthermore, a better dependence of the critical current density J_c as a function of the applied magnetic field B was observed in the variously substituted samples than in the unsubstituted $CaKFe_4As_4$ sample [6]. However, chemical substitution results in both structural changes in the sample and a change in the chemical nature of the grain boundary; since in polycrystalline samples it is not possible to separate the contribution of the grain boundary on the superconducting effects, it is not possible to attribute this enhancement effect to either factor. This remains an aspect to be investigated.

Acknowledgements: This work has been partially carried out within the framework of the EUROfusion Consortium, funded by the European Union via the Euratom Research and Training Programme (Grant Agreement No 101052200 — EUROfusion). Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the European Commission. Neither the European Union nor the European Commission can be held responsible for them.

References

[1] Kamihara Y., Watanabe T., Hirano M., *Journal of the American Chemical Society*, 2008, **130**, 3296–3297.
[2] Iyo A., Kawashima K., Kinjo T., *Journal of American ChemicalSociety*, 2016, **16**, 3410- 5.
[3] Masi A., Duchenko A, Celentano G., *Superconductor Science and Technology*, 2021, **35**.
[4] Duchenko A., Augieri A., Barba L., *IEEE Transactions on Applied Superconductivity*, 2024, **34**.
[5] Duchenko A., Masi A., Augieri A., *IEEE Transactions on Applied Superconductivity,* 2024, **34**.
[6] Augieri A., Duchenko A., Armenio A., *IEEE Transactions on Applied Superconductivity,* 2024, **32**.

Unveiling the Catalytic Mechanism of Horse-Liver Alcohol Dehydrogenase in reduction reactions through a computational approach

M.Farina[1*], E. Bodo[1], I. Daidone[2], M. Aschi[2], M. Capone[2], A. Marrone[3]

[1] Università "La Sapienza", Piazzale Aldo Moro 5, Roma
[2]Università degli Studi dell'Aquila, Via Vetoio-Coppito, L'Aquila
[3]Università degli Studi "G. D'Annunzio" Chieti-Pescara, Via dei Vestini 31, Chieti

** matteo.farina@uniroma1.it*

Enzymes have the remarkable ability to exert precise chemo and stereoselective control over catalytic reactions. Furthermore, their operation under mild conditions makes them highly appealing for the development of environmentally friendly chemical processes. Our focus here lies on horse liver alcohol dehydrogenase (HLADH), a versatile enzyme known for its broad substrate tolerance. Particularly in the reduction reaction of ketones, HLADH mediates hydride transfer (HT) from NADH to the re-face of the carbonyl group, yielding S alcohols as products[1,2]. The use of biomimetic cofactors emerges as an innovative strategy, offering notable advantages in versatility, efficiency, and tunability. These attributes make them invaluable tools for driving progress across various fields of chemistry. Nevertheless, the catalytic reaction mechanisms remain not fully explained.

We know that, in the reaction center, the Zn^{2+} is tetrahedrally coordinated by: Cys46, Cys174, His67 and the oxygen atom of the substrate.[2] The NADH is located very near the substrate. The most probable mechanism for reduction, is a sequential reaction that involves firstly the hydride transfer from NADH to the carbonylic C of the ketone and then a series of proton transfers from His51 to the same carbon atom, that is mediated by the ribosidic part of NADH.[2,3]

In a previous study, another mechanism was proposed for the reduction of 2-pentanone catalyzed by HLADH, employing 1,4-dihydro-N-benzylnicotinamide (BNAH) as a biomimetic cofactor.[1] This alternative reaction path involves the detachment of His67 from the catalytic Zn(II) metal ion center as the first step, followed by the formation of a complex that entails η2-coordination of the 5,6 double bond of the biomimetic to the zinc, culminating in HT.

Here, we have investigated the two possible catalytic mechanisms of this system using a multiscale approach, that includes also Perturbed Matrix Method-Molecular Dynamics (PMM-MD) calculations[4]. We have determined with a good accuracy the most thermodynamically favorable path for this reduction reaction, when NADH is replaced by BNAH as biomimetic.

References

[1] A. Marrone et al., J. of Organom. Chem. 2021, 943, 121810
[2] C. Bruice et al., J. Am. Chem. Soc. 2001, 123, 11952-11959
[3] M. Karplus et al., J. Phys. Chem. B. 2002, 106, 2721-2740
[4] L. Zanetti-Polzi et al., J. Phys. Chem. Lett. 2017, 83321-3327

A dark charge-transfer state mediates vibronically coherent energy transfer in nadh (nicotinamide adenine dinucleotide) dimer

Vishal Kumar Jaiswal[a*], D. A. Ruiz[b], V. Petropoulos[c], P. Kabaciński[c], F. Montorsi[a], S. Ugolini[a], F. Santoro[d], S. Mukamel[e], G. Cerullo[c], M. Garavelli[a], Artur Nenov[a]

(a) Department of Industrial Chemistry, University of Bologna, Italy
(b) Instituto de Ciencia Molecular, Universidad de Valencia, Spain
(c) Dipartimento di Fisica, Politecnico di Milano, Italy
(d) ICCOM, CNR di Pisa, Pisa, Italy
(e) Department of Chemistry and Department of Physics and Astronomy, University of California, Irvine, United States

**vishalkumar.jaiswal3@unibo.it*

Excitation energy transfer (EET) is relevant for energy harvesting and excitation quenching in biological chromophores. The co-enzyme NADH when solvated in water displays a sub-100fs EET process[1] from adenine to nicotineamide upon excitation of the adenosine moiety. We demonstrate how photoexcited molecular vibrations enable a coherent transport of electronic population. We model the photoinduced dynamics on variety of solvated conformers employing multidimensional wavepacket dynamics on potential energy surfaces parametrized at highly accurate multireference level of theory with a QM/MM protocol. We clearly disentangle the effects of structural (i.e. stacking) and solvent heterogeneity on the EET process. The polar aqueous solvent environment leads to the active participation of a dark charge transfer state, accelerating the vibronically coherent EET process in favorably stacked conformers and solvent cavities.

Our work[2] demonstrates how the interplay of structural and environmental factors leads to diverse pathways for the EET process in flexible heterodimers and provides general insights relevant for EET in stacked multichromophoric aggregates like DNA strands.

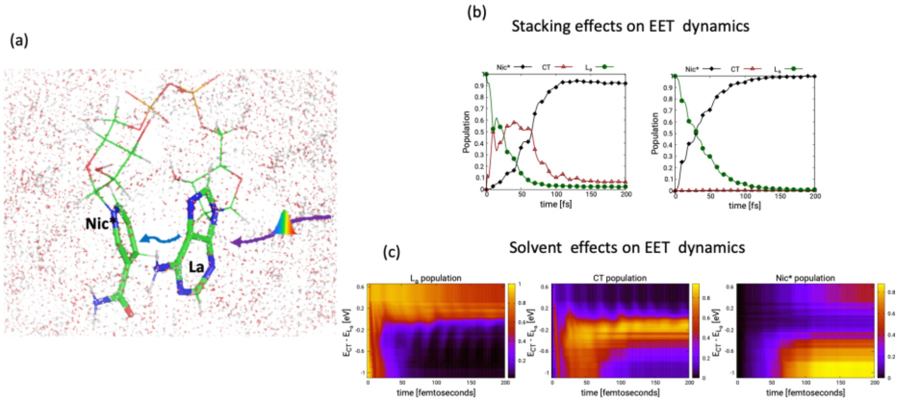


Figure 1. (a) Schematic of EET from La state of adenine to Nic* state of nicotinamide. (b) wavepacket dynamics on two different conformers. (c) wavepacket dynamics on a solvent ensemble of 100 diverse solvent configurations

References

[1] WEBER, G. Intramolecular Transfer of Electronic Energy in Dihydro Diphosphopyridine Nucleotide. *Nature* **1957**, *180* (4599), 1409–1409. https://doi.org/10.1038/1801409a0.
[2] Manuscript accepted for publication in Nature Communications

WFOT: a WaveFunction Overlap Tool Between Single- and Multi-Reference Electronic Structure Methods for Spectroscopy Simulation

Alessandro Loreti[1*], Victor Manuel Freixas[2], Davide Avagliano[1,3], Francesco Segatta[1], Huajin Song[4], Sergei Tretiak[4], Shaul Mukamel[2], Marco Garavelli[1], Niranjan Govind[5,6], Artur Nenov[1]

[1]Dipartimento di Chimica Industriale “Toso Montanari”, University of Bologna, Bologna, Italy
[2]Department of Chemistry and Department of Physics and Astronomy, University of California, Irvine, USA
[3]Institute of Chemistry for Life and Health Sciences Chimie Paristech, Paris, France
[4]Physics and Chemistry of Materials, Theoretical Division, Los Alamos, USA
[5]Physical and Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, USA
[6]Department of Chemistry, University of Washington, Seattle, USA

**alessandro.loreti5@unibo.it*

We report the development of a novel diagnostic tool, named WFOT[1], which is designed to evaluate the overlap between wavefunctions computed at single-reference (e.g., TDDFT) and multi-reference (e.g., CASPT2) levels of theory allowing to quantitatively compare the performance of these two families of methods for solving the electronic structure. The tool works by truncating the wavefunction of both methods to CIS-like expansions spanning the same configurational space and maximizes the overlap between molecular orbitals through a pseudo-unitary transformation. To validate its functionality, we performed on-the-fly non-adiabatic dynamics of Acetylacetone at the TD-DFT level of theory and mapped the photo-active state onto the CASPT2 manifold. The single- to multi-reference mapping was used to compute the transient absorption spectrum with multi-reference quality and completeness.

The WFOT tool has been interfaced with the COBRAMM[2] package, allowing access to software such as NWChem, Gaussian, and OpenMolcas.

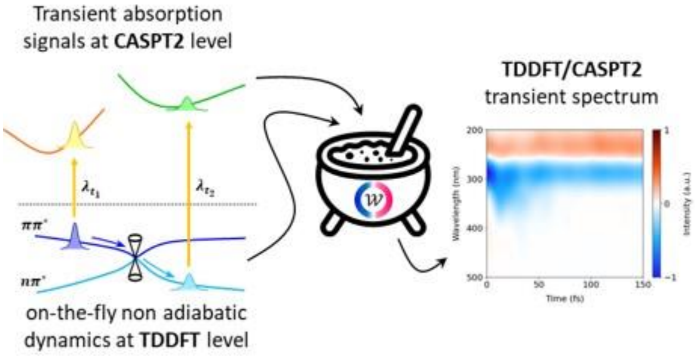


Figure 7. *Schematic application of the WFO tool, used to properly interface TDDFT non-adiabatic dynamics with CASPT2 transient absorption signals, thus taking advantage of the efficiency of TD-DFT and completeness of CASPT2 calculations.*

References

[1] Loreti, A.; … JCTC, accepted.
[2] Weingart, O.; Nenov, A.; Altoè, P.; Rivalta, I.; Segarra-Martí, J.; Dokukina, I.; Garavelli, M. COBRAMM 2.0 — A software interface for tailoring molecular electronic structure calculations and running nanoscale (QM/MM) simulations. Journal of Molecular Modeling 2018, 24 .

Ab initio Prediction of Isotherms for Water Adsorption in the Metal-Organic Framework Mg-MOF-74

Nicole Mancini[1*], Fabian Berger[1], Marcin Rybicki[1], Kaido Sillar[2], and Joachim Sauer[1]

[1]*Department of Chemistry, Humboldt-University of Berlin, Germany.*
[2]*Institute of Chemistry, University of Tartu, Estonia*

**nicole.mancini@hu-berlin.de*

The purification of water is a critical challenge in view of the growing shortages of drinking water. Metal-organic frameworks (MOFs) offer promising solutions, yet understanding their behavior at the molecular level is essential for designing improved materials.

As a representative system, we investigate the adsorption of H_2O in the metal–organic framework Mg-MOF-74. Experimental data on water adsorption on Mg-MOF-74 exhibit significant variations in maximum loading capacity. Computational studies have not been of much help so far, as their predictions also vary greatly. To explain these differences, this study identifies five adsorption sites and the structures adopted by water molecules up to the maximum loading of 5 H_2O/Mg^{2+}, verified by comparison with a powder X-ray diffraction (PXRD) structure.[1]

Utilizing a local-harmonic QM:QM embedding approach (QM – quantum mechanics), this study provides chemically accurate (±4 kJ/mol) coupled cluster quality adsorption energies, enthalpies, and Gibbs free energies of adsorption. Employing an ideal MOF crystal structure and assuming a water-free initial state, a multi-Langmuir model predicts simulated adsorption isotherms that closely match experimental data by Walton[2] and Ahn[3] (±2 kJ/mol). We show that the large variations among experiments can be attributed to sample imperfections or incomplete removal of water before measurements. Overall, by gaining detailed insights into the structure of water within Mg-MOF-74 and by providing accurate thermodynamic data, we demonstrate that our non-standard, chemically accurate simulations can be used to bring consensus to conflicting experimental observations.

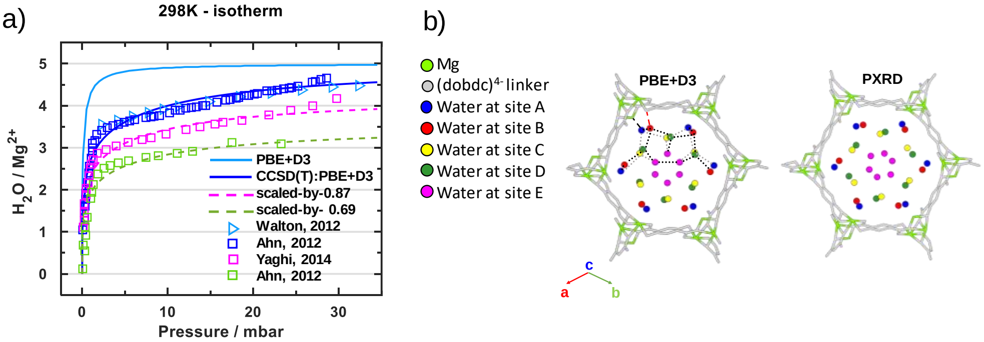


Figure. a) Simulated multi-Langmuir isotherms at PBE+D3 (solid – light-blue) and CCSD(T): non-scaled (solid – blue), scaled by 0.87 (dashed – magenta), scaled by 0.69 (dashed – green). Experimental isotherms: Walton (triangles – light-blue),[3] Ahn (squares – blue and green),[2] Yaghi (squares – magenta).[4] b) Comparison between fully loaded Mg-MOF-74 with water molecules structures: PBE+D3 optimized (left) and PXRD data (right). The pressure is P = 0.1 MPa and the temperature is T = 298 K

References

[1] P. D. C. Dietzel, R. Blom, H. Fjellvåg *Eur. J. Inorg. Chem.*, 2008, 3624-3632.
[2] D.-A. Yang, H.-Y. Cho, J. Kim, S.-T. Yang, W.-S. Ahn *Energy Environ. Sci.* 2012, **5**, 6465-6473.
[3] P. M. Schoenecker, C. G. Carson, H. Jasuja, C. J. J. Flemming, K. S. Walton *Ind. Eng. Chem. Res.* 2012, **51**, 6513-6519.
[4] H. Furukawa, F. Gándara, Y.-B. Zhang, J. Jiang, W. L. Queen, M. R. Hudson, O. M. Yaghi, Water *J. Am. Chem. Soc.* 2014, **136**, 4369-4381.

Sustainable aroma entrapment: exploring the potentiality of the β-CD-lactic acid SUPRADES

Emanuela Mangiacapre[1, *], Sophie Fourmentin [2], Alessandro Triolo[3], and Olga Russina[1]

[1] Chemistry Dept. - University of Rome Sapienza, Rome, Italy.
[2] Université du Littoral Côte d'Opale, Dunkerque, France.
[3] Istituto Struttura della Materia – Consiglio Nazionale delle Ricerche (ISM-CNR), Rome, Italy.

**emanuela.mangiacapre@uniroma1.it*

Deep Eutectic Solvents (DESs), sustainable low-freezing mixtures, offer alternatives for various applications. The convergence of DESs' wide liquid state window with the encapsulation capability of macrocyclic molecules like cyclodextrins (CDs) has led to the development of Supramolecular DESs (SUPRADESs) [1]. Recently, our team reported on the structural characteristics of the DiMeβ:levulinic acid (1:27) SUPRADES, highlighting the existence of an extended hydrogen bonding network and dispersive interactions that prevent CD aggregation and precipitation [2]. In this study, we investigate the potential of a new SUPRADES composed of β-CD and lactic acid (LA) at a molar ratio of 1:30 for capturing *trans*-anethole (AN), with differential scanning calorimetry indicating a glass transition temperature (T_g) near -70 °C [3]. Molecular dynamics simulations and X-ray scattering experiments confirm the absence of CDs aggregation and elucidate the nature of β-CD and LA intermolecular interactions. Headspace gas chromatography reveals a roughly 25-fold increase in AN retention in pure SUPRADES compared to the β-CD-water mixture, while UV-visible spectrophotometry demonstrates that the SUPRADES-water mixture with 10 wt% water has an AN solubility approximately 20,000 times greater than pure water. Finally, a 2D ROESY NMR experiment confirm the formation of an inclusion complex between β-CD and AN. Overall, these preliminary findings strongly advocate for the use of SUPRADESs as effective and sustainable tools for entrapping aromas and volatile organic compounds.

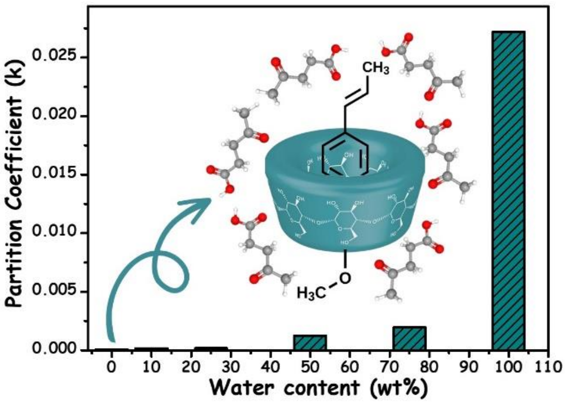


Figure 8: HS-GC results and graphical representation of the anethole-SUPRADES complex.

References

[1] T. El Achkar, T. Moufawad, S. Ruellan, D. Landy, H. Greige-Gerges, S. Fourmentin, Chemical Communications, 2020, **56**, 3385-3388.
[2] A. Triolo, F. Lo Celso, S. Fourmentin, O. Russina, ACS Sus. Chem. Eng., 2023, **24**, 9103-9110.
[3] M. Kfoury, F.-X. Legrand, S. Ruellan, S. Fourmentin, J. Mol. Liq., 2024, **394**, 123696.

How deep is your DES? Unveiling the Driving Forces Behind a Deep Eutectic Solvent Formation

Giorgia Mannucci[1*], Gabriel Teixeira[2], Lorenzo Augusto Rocchi[1], Angela Capocefalo[3], Matteo Busato[1], Andrea Martinelli[1], Paolo Postorino[3], and Paola D’Angelo[1]

[1] Department of Chemistry, University of Rome ”La Sapienza”, P.le A. Moro 5, 00185 Rome, Italy
[2]CICECO, Aveiro Institute of Materials, Complexo de Laboratórios Tecnológicos, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal
[3] Department of Physics, University of Rome ”La Sapienza”, P.le A. Moro 5, 00185 Rome, Italy

**giorgia.mannucci@uniroma1.it*

Deep eutectic solvents (DESs) are formed by two or more compounds that present a melting point (MP) that is not only lower than those of the pure constituents but also than the predicted one assuming thermodynamic ideality.[1] The MP depression in eutectic solvents has always been attributed to the formation of a strong hydrogen bond (HB) network between the components. Additionally, it has been demonstrated that when molecules with high polarity asymmetry are used, the MP depression is more consistent. An example is the DES formed by thymol and L-menthol (1:1 molar ratio). Due to resonance effects, the hydroxyl group of thymol is more positive than usual, making it a strong hydrogen bond donor (HBD) and a weak hydrogen bond acceptor (HBA). Thus, when thymol is mixed with a regular HBA such as L-menthol, it can establish a stronger HB than that of the pure compound, leading to eutectic formation. [2] Although numerous studies in the literature concerning the possible contributions to eutectic formation exist, a strict definition is still missing. Consequently, it is of great interest to expand the existing knowledge and to correlate the deviation from ideality to the electronic and structural properties of the DES components.

In this study, mixtures of L-menthol (MEN) with butylated hydroxytoluene (BHT), 2-tert-butyl-p-cresol (TBC), and p-cresol (PC) were investigated to understand the impact of steric hindrance on the MP depression. Indeed, TBC and PC are analogous to the BHT species, but with one and no tert-butyl groups, respectively, in the ortho position to the hydroxyl group.[3] Subsequently, the impact of different functional groups on the hydrogen bonding capability, and thus on the eutectic formation, was investigated by studying the structural properties of mixtures formed by MEN with 4-methoxyphenol (4-Met), 2-tert-butyl-4-methoxyphenol (BHA), 2-tert-butyl-4-ethylphenol (TBEP), and tert-butylhydroquinone (TBHQ). [4]

Thanks to a combined approach of experimental techniques such as differential scanning calorimetry (DSC) and Raman spectroscopy, along with computational methods like DFTB molecular dynamics simulation and COSMO-RS solvation model, it was possible to understand which of the studied systems can be classified as DES and to discern the main contributing factors to the deviation from ideality.

References

[1]Abbott, Andrew P., et al. *Chemical communications*, 2003, **1**, 70-71.
[2] Abranches, Dinis O., et al. *Chemical communications*, 2019, **55.69**, 10253-10256.
[3] Busato, Matteo, et al. *ACS Sustainable Chemistry & Engineering*, 2023, **11.24**, 8988-8999.
[4] Mannucci, Giorgia, et al. *ACS Sustainable Chemistry & Engineering*, 2024, **12.7**, 2862–2870.

Cost-effective and eco-friendly polyols-DESs for supercapacitors

Daniele Motta[1*], Giuseppe Antonio Elia[2,3], Alessandro Damin[1], Stefano Nejrotti[1], Simone Galliano[1], Claudio Gerbaldi[2,3], Claudia Barolo[1,2], Matteo Bonomo[1,2]

[1] *Department of Chemistry and NIS Interdepartmental Centre, University of Turin, Torino, Italy*
[2] *National Reference Center for Electrochemical Energy Storage (GISEL) - INSTM, Firenze, Italy*
[3] *GAME Lab, Department of Applied Science and Technology (DISAT), Politecnico di Torino, Torino, Italy*
**daniele.motta@unito.it*

Efforts to reduce dependence on fossil fuels have resulted in notable advancements in photovoltaic and wind energy systems. To address the intermittent nature of these renewable sources, efficient electrochemical energy storage systems (EESS) like batteries and supercapacitors are essential for ensuring a consistent and reliable energy supply [1]. The exploration of alternative electrolytes from the traditional unstable ones has given rise to Ionic Liquids (ILs), which however tend to be expensive and corrosive to current collectors [2]. In contrast, Deep Eutectic Solvents (DESs) have emerged as a cost-effective and environmentally friendly solution [3], offering suitable properties such as high thermal stability, low vapor pressure, biodegradability and resistance to air and humidity [4].

Our research focuses on investigating DESs, specifically metal salt-polyol mixtures. By employing thermal analysis (DSC) and vibrational spectroscopic techniques (Raman and FIR), we have been able to categorize our mixtures as DES or "salt-in-solvent" and to establish correlations with the structural features of molecular components and intermolecular interactions [5], particularly hydrogen bonds. These factors are pivotal in determining the ionicity and electrochemical performance of the systems in fully assembled EES devices.

Figure 1. Essential measurements performed on our DESs.

Acknowledgements: this project has received support from Project CH4.0 under the MUR program "Dipartimento di Eccellenza 2023–2027" (CUP D13C22003520001). This study was carried out within the GENESIS project funded by the Ministero dell'Università e della Ricerca within the PRIN 2022 program. S.G. acknowledges the project NODES which has received fundings from the MUR-M4C2 1.5 of PNRR funded by the European Union - NextGenerationEU (Grant agreement no. ECS00000036).

References

[1] Notton, G., Nivet, M. L., Voyant, C., Paoli, C., Darras, C., Motte, F., & Fouilloy, A. *Renewable and Sustainable Energy Reviews*, 2018, **87**, 96.
[2] Ferrari, S., Falco, M., Muñoz-García, A. B., Bonomo, M., Brutti, S., Pavone, M., & Gerbaldi, C. *Advanced Energy Materials*, 2021, **11**, 2100785.
[3] Nejrotti, S., Antenucci, A., Pontremoli, C., Gontrani, L., Barbero, N., Carbone, M., & Bonomo, M. *ACS Omega*, 2022, **7**, 47449.
[4] Di Pietro, M. E., & Mele, A. *Journal of Molecular Liquids*, 2021, **338**, 116597.
[5] Cappelluti, F., Mariani, A., Bonomo, M., Damin, A., Bencivenni, L., Passerini, S., Carbone, M., & Gontrani, L. *Journal of Molecular Liquids*, 2022, **367**, 120443.

Development of Interaction Models for Simulating the Effects of Cosmic Rays on Ion-Molecule Reactions in the Atmosphere.

F. Nicolanti[1,2,*], B. Caccia[3], A. Cartoni[4], R. Colalillo[5], D. Emfietzoglou[6*], R. Faccini[1,2], S. Incerti[7], I. Kyriakou[6], M. Satta[4,7] , H. N. Tran[7], C. Mancini-Terracciano[1,2]

[1]Physics Dep., Sapienza U. of Rome, Italy.
[2]INFN Sec. of Rome, Italy.
[3]ISS (Italian National Institute of Health), Rome, Italy.
[4]Chemistry Dep., Sapienza U. of Rome, Italy.
[5]Chemistry Dep., Sapienza U. of Rome, Italy.
[6]INFN Sec. of Naples and Federico II U. of Naples, Italy.
[7]Med. Phys. Lab., U. of Ioannina Medical School, Greece.
[8]CENBG/IN2P3/CNRS, U. of Bordeaux, France.
[9]ISMN-CNR, Rome, Italy.

**francesca.nicolanti@uniroma1.it*

Background: Cosmic rays are a primary source of molecular ionization in the lower atmosphere, capable of altering chemical reaction rates by up to ten orders of magnitude, based on the ionization state of the involved molecules. For this reason, cosmic rays can have an impact on altering the atmospheric chemical composition. Current atmospheric models do not provide information on the quantity and ionization state of ions produced, nor their spatial distribution, which contributes to the incomplete understanding of cosmic rays' role in atmospheric chemical processes. This work aims to employ an alternative simulation approach, using the Geant4-DNA Monte Carlo simulation toolkit, that incorporates a molecular-level description of the physical interaction between particles and matter, allowing us to obtain the aforementioned quantities.

Material and Methods: We developed and implemented in Geant4-DNA new cross section models for electron impact ionization, electronic excitation, and elastic scattering with $N_2, O_2,$ and $CO_2,$ in an energy range from ionization threshold up to 10 MeV. We validated these models through the simulation of stopping power and range in $N_2, O_2, CO_2,$ and in a simplified Air material. A simulation using the CORSIKA code was conducted to model the cosmic ray shower and derive the spectrum of electrons in the lower atmosphere (10-20km altitude). These secondary electrons were then tracked using the newly developed Geant4-DNA models to obtain the ion density produced.

Preliminary results: The simulation results for stopping power and electron range agree within 5% with experimental data, demonstrating the effectiveness of our models in simulating electron interactions within the atmosphere. Preliminary results regarding the ion density and their spatial distribution in the lower atmosphere will also be discussed. These new developments open up for the first time the possibility to accurately simulate the complicated physicochemical processes involved in the atmosphere.

References

[1] Nicolanti, F. et al.; Phys Med. 114:(2023), p. 102661. [10.1016/j.ejmp.2023.102661]
[2] Satta, M. et al.; Perspectives of gas phase ion chemistry: spectroscopy and modeling. In: Condens. Matter 2022. [10.3390/condmat7030046]

Finding Collective Variables form Molecular Transition Paths

A. Olivieri[1*], L. Holdijk[2] , F. Hooft, M. D'Abramo[1], B. Ensing[3]

[1]*Department of Chemistry, Sapienza University of Rome, Rome, Italy*
[2]*Department of Computer Science, University of Oxford, Oxford, United Kingdom*
[3]*Faculty of Science, Van't Hoff Institute for Molecular Sciences, Amsterdam, The Netherlands*

**alessio.olivieri@uniroma1.it*

Molecular dynamics (MD) simulations have proven to be a powerful tool in several fields of science providing meaningful details regarding chemical and biological processes. However, standard MD is unable to sample transitions between two metastable configurations separated by high energy barriers, such as chemical reactions and protein folding. To overcome this problem, several methods for enhanced sampling have been developed [1, 2]. Most of these methods rely on a bias potential, to push the system to cross the energy barrier between the two states. Furthermore, a set of collective variables (CVs), which are functions of the atomic coordinates, are used to reduce the complexity of the biasing potential by only biasing the studied system along them. However, finding a proper set of CVs is prohibitively difficult for all but the simplest systems. To this end, machine learning algorithms of varying complexity have been applied [3, 4]. Recently, B. Ensing and collaborators propose PIPS (Path Integral stochastic optimal control for Path Sampling): a ML algorithm for sampling molecular transition paths [5]. Unlike previous approaches, PIPS does not require to prespecify a set of CVs along which the system should be biased. Here, we build on this approach by learning on-the-fly the mean transition path using a path-collective variable during PIPS transition paths simulations. We show that the learned path can be used to obtain a low-dimensional free energy profile and committor profile, from which mechanistic and kinetic insight is gained.

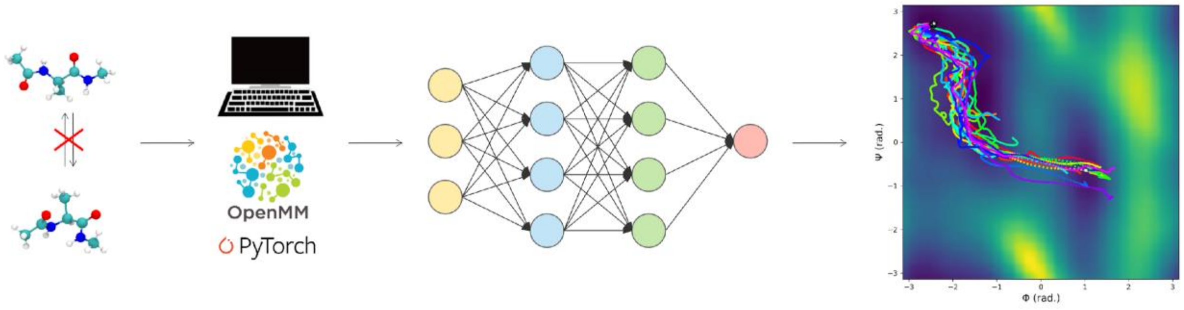


Fig. 1: Schematic representation of the workflow of PIPS.

References

[1] Torrie M. G., John P. V. *Journal of Computational Physics*, 1977, **23**, 187.
[2] Laio M., Parrinello M. *Proceedings of the National Accademy of Sciences*, 2002, **99**, 12562.
[3] Bonatti L., Rizzi V., Parrinello M. *The Journal of Physical Chemistry Letters*, 2020, **11**, 2998.
[4] Hooft F., Pérez de Alba Ortíz A., Ensing B., *Journal of Chemical Theory and Computation, 2021*, **17**, 2294.
[5] Holdijk L., Du Y., Hooft F., Jaini P., Ensing B., Welling M. *arXiv*, 2023, 2207.02149.

Polarizable force field development and MD simulations of novel electrolytes for Li-ion batteries

Adriano Pierini[1*], Vanessa Piacentini[1], Sergio Brutti[1,2], Enrico Bodo[1]

[1]Department of Chemistry, Sapienza University of Rome, Rome, Italy
[2]Consiglio Nazionale delle Ricerche, Istituto dei Sistemi Complessi, Rome, Italy

* *adriano.pierini@uniroma1.it*

The pursuit for safe and reliable energy storage devices is questioning the current limitations of state-of-art lithium-ion batteries (LIBs), and research efforts have drastically increased in the field of new materials for next-generation batteries. Glyoxal acetals have recently emerged as a promising innovation for electrolyte formulations in LIBs. Thanks to their thermal stability, they can be used as co-solvents, together with highly conductive organic carbonates, in order to accomplish higher standards in terms of safety and thermal stability of the battery [1]. Also, their superior film-forming ability has been highlighted as a potential remedy to the severe drawbacks related with the large volume changes occurring in high-capacity anode materials such as Si, Si/C and Fe_2O_3/C [2,3]. However, achieving optimal formulation of glyoxal acetals-containing electrolytes demands a thorough understanding of their interaction with co-solvents and salts at a molecular level.
Fundamental insights into the intermolecular interactions, solvation properties and ionic transport mechanisms inside the electrolyte, which are hardly accessible to experiments, can be provided by molecular dynamics (MD) simulations. When it comes to electrolytes and ionic systems, the inclusion of polarization effects in the force field model was found to generally improve the description of both structural and dynamical properties [4]. On the other hand, fixed-charge models often require a case-specific tuning of the parameters to improve the prediction of certain properties, which can compromise its transferability and overall reliability [5]. Polarizable force field parameters, however, are not readily available in most cases.
We therefore developed an extension of the polarizable AMOEBA force field model, to perform a computational study of new LIBs electrolyte formulations based on glyoxal acetals. The resulting parametrisation of the different electrolyte species was first tested and validated against reference ab-initio calculations and experimental bulk properties. Then, we performed MD simulations to investigate the impact of many different formulations on the electrolyte properties. In particular, we studied ion solvation, ion-pair dynamics and ionic transport mechanisms to elucidate the relation between molecular interactions and electrochemical performances, and to suggest tuning strategies for the practical design of optimal electrolyte formulations.

Acknowledgements: the authors want to acknowledge the financial support of the European Union's Horizon Europe transport program under the project SIGNE (grant agreement No. 101069738).

References

[1] Hess L. H., Wankmüller S., Köps L. et al., *Batteries and Supercaps*, 2019, **2**, 852.
[2] Gehrlein L., Leibing C., Pfeifer K. et al., *Electrochimica Acta*, 2022, **424**, 140642.
[3] Bothe A., Gahrlein L., Fu Q. et al., *Batteries and Supercaps*, 2022, **5**, e202200152.
[4] Bedrov D., Piquemal J.-P., Borodin O. et al., *Chemical Reviews*, 2019, **119**, 7940.
[5] Grossfield A., Ren P. and Ponder J. W., *Journal of American Chemical Society*, 2003, **125**, 15671.

Exploring the depth of type V deep eutectic solvents

E. Pietropaoli[1*], M. Busato[1], G. Mannucci[1], P. D'Angelo[1]

[1]*Department of Chemistry, University of Rome La Sapienza, Rome, Italy*

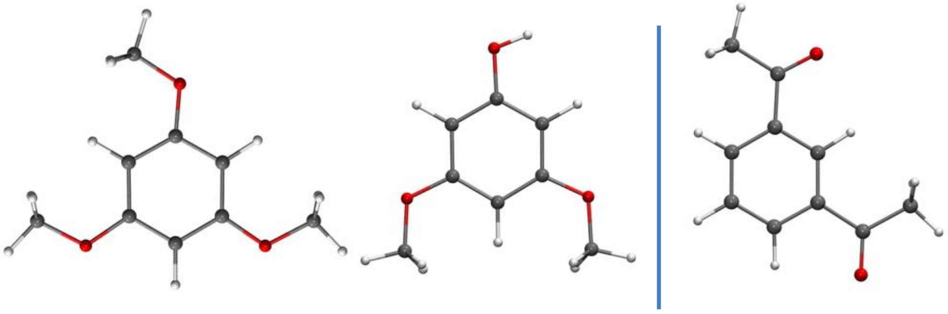
**eva.pietropaoli@uniroma1.it*

Deep eutectic solvents (DESs) have emerged as a promising and eco-friendly alternative to conventional organic solvents, owing to their superior biocompatibility and sustainable characteristics. These solvents are simply prepared through the strategic combination of two compounds, resulting in a remarkable depression of the mixture's melting recent class of type V DESs have achieved point (MP). Among the latest developments in DESs, the recent class of type V DESs has achieved significant attention. It is reasonable to distinguish type V DES's precursors in two species: hydrogen bond acceptors (HBAs) and hydrogen bond donors (HBDs). However, despite their growing popularity, the precise interactions that take part in the formation of DESs remain inadequately understood.

The purpose of this study is to define the "deep" eutectic behaviour exhibited by DESs. This attempt requires conducting an in-depth structural analysis of the selected precursors to elucidate the underlying molecular interactions. While hydrogen bonding is a pivotal factor in DES formation, we seek to unravel additional contributions, particularly focusing on the influence of π-π stacking.

We have carefully selected two different combinations of molecules with varying capacities to form hydrogen bonds. Specifically, our investigation focuses on systems comprising 1,3,5-trimethoxybenzene (TMB) and 1,3-diacetylbenzene (13DAB), as well as similar systems featuring 3,5-dimethoxyphenol (DMP) and 13DAB. Through interdisciplinary approach including theoretical analysis and experimental validation, we aspire to provide deeper insights into the fundamental processes underlying DES formation.

The eutectic behaviour is predicted using conductor-like screening model (COSMO) calculations. Subsequently, thermal characterization is performed using differential scanning calorimetry (DSC), while molecular level insights is gained through molecular dynamics (MD) simulations.



TMB DMP 13DAB

Figure 1: The molecules of TMB, DMP and 13DAB are respectively reported.

References

[1] M. Busato, G. Mannucci, P. D'Angelo, ACS Sustainable Chem. Eng. 2023, **11**, 8988-8999.
[2] G. Mannucci, J. A. P. Couthinho, P. D'Angelo, ACS Sustainable Chem. Eng. 2024, 12, 2862–2870.

Rethinking Physical Aging: Unveiling an Additional Molecular Mechanism in Poly-4-Chlorostyrene and Other Polymeric Glasses

Lorenzo Augusto Rocchi[1*], Valerio Di Lisio[2], Andrea Martinelli[1], and Daniele Cangialosi[2,3]

[1] *Department of Chemistry, Sapienza University of Rome, Piazzale Aldo Moro 5, 00185 - Rome, Italy*
[2] *Donostia International Physics Center (DIPC), Paseo Manuel de Lardizabal 4, 20018 - San Sebastián, Spain*
[3] *Centro de Física de Materiales (CSIC-UPV/EHU), Paseo Manuel de Lardizabal 5, 20018 - San Sebastián, Spain*

**lorenzoaugusto.rocchi@uniroma1.it*

Glassy materials lack an ordered structure and exist in a metastable state with a "frozen-in" disorder. Even if the glass looks “frozen” on the laboratory time scale, below the glass transition temperature T_g molecular mobility exist and, thus, slow structural relaxation phenomena occur in the material to reduce the energy of the system trying to reach an equilibrium condition [1]. This process is known as “physical aging” and it consists on the variation of the properties of the material as a function of the storage time at constant temperature, without the application of any other stimuli. Physical aging is an inevitable and crucial phenomenon in determining and predicting long-term performance of a large class of materials in the glassy state, it affecting, for example, sample dimension, mechanical properties and permeability [2]. Due to technological and fundamental implications, physical aging has been extensively studied in recent decades. From a molecular point of view, the primary α-relaxation with super-Arrhenius temperature dependence has been traditionally considered the only relevant molecular mechanism occurring during physical aging. However, this archetypal model has been recently challenged by accumulating evidences of a secondary relaxation phenomenon in the glassy state that strongly deviate from the timescales associated solely to the α relaxation [3]. This research delivers a method to uncover secondary relaxation mechanisms contributing to the physical aging of materials. Fast scanning calorimetry was employed to explore the aging kinetics of poly(4-chlorostyrene), a key glass-forming material, alongside other polymeric glasses. A wide range of aging temperatures (390 - 412 K) and aging time (0.1 - 10^5 s) were examined. The novelty of the methodology relies on following two different physical parameters, that are the recovered enthalpy and the width of the devitrification peak, both determined from thermograms. While the width of devitrification, linked to the glass structural heterogeneity, exhibits pure α-relaxation kinetics, the enthalpy recovery shows faster kinetics at the lower aging temperatures. This implies that the enthalpy of the glass reaches its equilibrium value before the completion of the spontaneous structural reorganization (at the enthalpic plateau, DH = 0 but DG < 0). Therefore, a second relaxation mechanism assists the glass enthalpic relaxation, but it doesn't affect the structural heterogeneities in the glass. This study highlights the inherent complexity of glassy materials by pushing the limits of our understanding of physical aging. This paves the way for the formulation of more comprehensive models to describe the behaviour of glasses, which may eventually lead to the design and optimization of novel materials with tailored properties.

References

[1] J. M. Hutchinson, “Physical aging of polymers”, Prog. Polym. Sci., vol. 20, pp. 703-760, 1995.
[2] S. J. D. Smith et al. “Control of physical aging in super-glassy polymer mixed matrix membranes”, Acc. Chem. Res., 53, 1381–1388, 2020.
[3] D. Cangialosi et al. “Direct evidence of two equilibration mechanisms in glassy polymers”, Phys. Rev. Letters, 111, 095701, 2013.

Simulations of Model Biological Molecules in Choline Amino Acid Ionic Liquids

Stefano Russo*[1], Enrico Bodo[1]

[1]*Department of Chemistry, University of Rome "Sapienza", Rome, Italy*

**stefano.russo@uniroma1.it*

Ionic liquids and eutectic solvents have attracted many research efforts due to their applications in many fields of technology. A recent implementation of ionic liquids with choline and amino acids (AAILs) is particular interesting thanks to their biocompatibility and their cheaper production, compared to the traditional ionic liquids based on imidazolium [1]. Since this new type of ionic liquids has recently started to be experimentally tested, there are many crucial mechanisms to be investigated. Molecular dynamics simulations represent a powerful tool to study the structure of the ionic liquid and the interactions between their components. If neutral liquids can be easily simulated with classical parametrized force field keeping the charge fixed, ionic liquids required special treatments. The highly ionic nature of ionic liquid requires a more detailed model to be simulated. There is evidence of the effects of charge oscillation on the energy of the system; the result is greater errors in properties derived from energy (ionic binding energy or vaporization enthalpy) or from dynamic of atoms (diffusion and transport properties) which is dependent from polarization [2].

Our work focus on building a new force field for the AAILs based on AMOEBA model which explicitly introduce polarization. The new parameters have been validated on pure bulk and has been used to study the interactions between the ionic liquid components and a couple of small biological molecules. The results show how the properties of those ionic liquids can stabilize proteins and DNA sequences [3] and polarization has an important role in those findings.

References

[1] Le Donne A., Bodo E. *Biophys. Rev*., 2021, **13**, 147-160.
[2] Bedrov D., Piquemal J.P. et al. *Chem. Rev*, 2019, **119**, 7940-7995
[3] Russo S., Bodo E., *Molecules*, 2024, **7**, 29, 1524

Sublimation Study of Four 2-Methyl-n-Nitro Benzoic Acids

J.M. Silva Ferraz[1*], B. Brunetti[2], A. Ciccioli[2], S.P. Verevkin[4], S. Vecchio Ciprioti[1]

[1]*Department of Basic and Applied Sciences for Engineering, Sapienza University of Rome, Rome, Italy*
[2]*Department of Chemistry, Sapienza University of Rome, Rome, Italy*
[3]*Department of Physical Chemistry, University of Rostock, Rostock, Germany*
**josemiguel.silvaferraz@uniroma1.it*

In the context of our interest on the thermophysical characterization of nitrogen containing organic compounds, this communication is concerned with the experimental thermophysical studies that have been recently developed on four solid 2-methyl-n-nitro benzoic acids (where n = 3,4,5,6) (figure 1). It aims at determining the standard molar enthalpies of sublimation and to validate a newly described experimental method by comparison between the different methods but also with literature. [1]

The vapor pressures were determined in suitable temperature ranges by Knudsen Effusion Mass Loss (KEML).[2] From the temperature dependencies of vapor pressure, the molar sublimation thermodynamic parameters were calculated at the corresponding average temperature. The values obtained by KEML experiments were adjusted to 298.15 K. Additionally, the transpiration method has been employed to determine the respective standard molar enthalpies of sublimation.

An open-cell quartz crystal microbalance technique (OC - QCM) has also been employed to determine the sublimation enthalpies under non-equilibrium conditions. This method uses the frequency change to correlate with the mass loss rate via the Saurbrey equation.[3]

A comparison between the aforementioned methods has been done in order to validate the OC - QCM method against the other two well established methods. Plus, the results obtained provide a deeper understanding of the phase transition behavior for these compounds from the condensed phase to the gaseous phase, shedding light on the intermolecular forces inherent to the species. This knowledge contributes to the comprehensive characterization of the thermophysical properties of these nitrogen containing organic compounds.

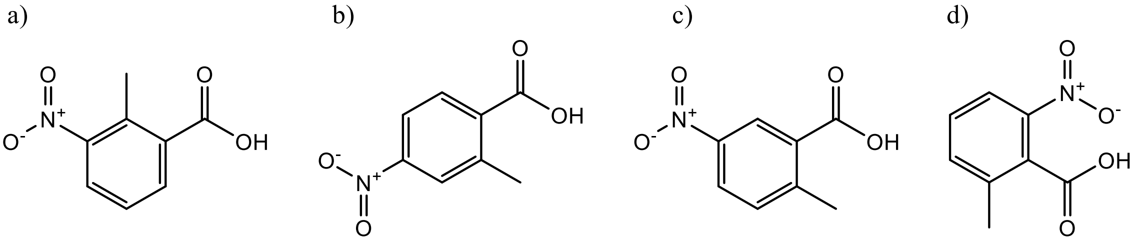


Figure 9. Structural formulae of the 2-methyl-n-nitrobenzoic acids (n = 3,4,5,6 and a,b,c,d respectively).

References

[1] M. J. S. Monte and D. M. Hillesheim, The Journal of Chemical Thermodynamics, 2001, 33, 103.
[2] B. Brunetti, A. Ciccioli, G. Gigli, A. Lapi, N. Misceo, L. Tanzi, S. Vecchio Ciprioti, Phys Chem Chem Phys, 2014, 16, 15653.
[3] S. P. Verevkin, D. H. Zaitsau, V. N. Emelyanenko, A. Heintz, J Phys Chem B, 2011, 115, 12889.

Investigating the Interaction between PFAS and Nanoplastics: An Ab Initio Computational Study

Federica Simonetti[1*], Marco Mancini[2], Valentina Di Gioia[2], Rosaceleste Zumpano[1], Alessandro Frugis[2], Valentina Migliorati[3]

[1]Department of Pharmaceutical Science and Technologies, Sapienza University of Rome, Italy
[2]Department of Organic Micropollutants, 442 Acea Elabori, 00191 Rome, Italy
[3]Department of Chemistry, Sapienza University of Rome, Italy

**federica.simonetti@uniroma1.it*

Microplastics and nanoplastics are widely used in many fields, such as industrial, domestic, and pharmaceutical, thus entering water bodies, with significant implications for human health and ecosystems. Although the effect of microplastics on human health has not yet been well established, nanoplastics are probably more toxic, due to their size which facilitates migration and ingestion with consequent trophic magnification [1]. Of particular concern is their propensity to adsorb other organic pollutants, owing to their large surface area, thus acting as enhanced vectors that may impact the uptake and bioaccumulation of these compounds in living organisms during co-exposure. Several research papers demonstrated the interaction of micro(nano)plastics with a class of highly toxic and persistent aqueous contaminants, perfluoroalkyl compounds (PFAS), but the mechanism of adsorption still needs to be elucidated [2]. The objective of this work is to investigate the mechanism of adsorption of PFAS onto nanoplastics, focusing on nanoplastics made from one of the most used polymers, namely polypropylene, which has been largely employed in face masks during Cov-19 pandemic and it was shown to be able to rapidly adsorb PFAS [3]. To achieve this goal, a computational model of polypropylene nanoplastic (PPNP) was constructed through consecutive molecular dynamics simulations and optimized at the DFT level of theory [4]. Finally, the inner/outer adsorption of one of the most widespread PFAS in water, perfluorooctane sulfonic acid (PFOS) on surface of the PPNP was investigated and the stability of the PFOS-PPNP complex characterized. PFOS and PPNP were found to form stable complexes trough Van Der Waals interactions, with an adsorption energy comparable to the energy identified in other studies [5]. To confirm the computational results, high-performance liquid chromatography tandem mass spectrometry (HPLC-MS/MS) analyses were carried out on nanoplastics synthesized following the solvent-antisolvent precipitation route.

Acknowledgements: The results of this study are a product of the PROMISCES Project funded by European Union’s Horizon2020 research and innovation program under Grant Agreement. The authors thank ACEA Elabori for providing standards and materials.

References

[1] Shoumi Haldara et al., *Science of the Total Environment* 2023, **861**, 160571.
[2] A. Valiyaveettil Salimkumar, *Management of Micro and Nano-plastics in Soil and Biosolids: Fate, Occurrence, Monitoring, and Remedies*, 2024, Chapter ‘Adsorption Behavior and Interaction of Micro-Nanoplastics in Soils and Aquatic Environment’, 283-311, Springer Nature Switzerland.
[3] Mancini Marco et al., S. *Evaluation of Pure PFAS Decrease in Controlled Settings,* ACS Measurement Science Au, 2023, **3**, 444–451.
[4] Diego Cortés-Arriagada, Environmental Pollution, 2021, **270**, 116192.
[5] Omobayo A. Salawu et al., *Journal of Hazard Materials* 2024, **470**, 134185.

Bond Decomposition Analysis: Can acidity be correlated to bond identity?

Nikola Stamenković[1,2*], Janez Cerkovnik[2]

[1]Department of Food Science and Technology, Biotechnical Faculty, University of Ljubljana, 1000 Ljubljana, Slovenia
[2]Department of Organic chemistry, Faculty of Chemistry and Chemical Technology, University of Ljubljana, 1000 Ljubljana, Slovenia

**Presenter email: ns6960@student.uni-lj.si*

Bonds have been a source of debate in the chemical sciences since the development of modern chemistry. They received particular attention when theoretical chemistry started to be a rather evasive field in chemistry and physics, as it was assumed that only a quantum mechanical approach could explain the deeper nature of a chemical bond. This was an additional motive and driving force for experimental chemists to focus on some theoretical aspects and include them in the chemical thought process. Nowadays, no data can be found in the literature on existing methods for in-depth analysis of bonds that include the type of bond, the nature of the bond by the type of electrons and the versatility in different bonding processes as well as their general relationship to the atoms in the given type of topologies. Furthermore, the evolution of bonds can be monitored and quantitatively described using NMR time scales if an appropriate bond decomposition methodology is applied. Therefore, such a methodology needs to be optimised to work in so-called dynamic theoretical chemical environments and not only in static environments (where no bond changes can be observed). The most recent method was published by Head-Gordon and co-workers [1], but from a mathematical and methodological point of view it can be defined as a static binding analysis. However, we present a theoretically relatively improved set of bond decomposition protocols that can be described as a mathematical apparatus that utilises multiple scaling transformations with essentially no computational cost. This approach allows us to theoretically decompose a bond in a static and/or dynamic chemical environment and quantitatively determine its stability and reactivity. [2] The results can be divided into two different treatments: 1) qualitative bond character: determination of the exact hybridisation origin and orbital type, based on the accuracy of the basis set, 2) qualitative bonding character: interaction type (e.g. σ- or π-bond etc.), 3) qualitative bond type (e.g. σ- or π-bond, ionic, covalent or non-covalent character, with emphasis on short non-covalent interactions, which are more important in chemical systems, and finally 4) quantitative bond type – static and dynamic relationship of the bond type to its atomic influence (hybridisation type and orbital involvement). On the other hand, this method, called Bond Decomposition Analysis, was used to determine bonding trends in acidity function. Such a methodologically and systematically complex analysis of bond type and atomic hybridisation on different atom pairs in E−H bonds would reveal the hybridisation pattern that determines acidity trends in both organic and inorganic systems of different sizes – from binary to medium and large systems. Further investigation should reveal the hypothesis that this larger phenomenon in the acidity/basicity trend lines is related to some sort of density “interplay” in the bonding and near-bonding regions.

References

[1] Sterling, A. J., Levine, D. S., Aldossary, A. and Head-Gordon, M. *J. Am. Chem. Soc.* 2024, **146**, 9532−9543. DOI: 10.1021/jacs.3c10633

[2] This methodological path was achieved by NBO 7 code: NBO 7.0. E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, P. Karafiloglou, C. R. Landis, and F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison, WI (2018).

Unveiling collective oscillatory behaviour in the Belousov-Zhabotinsky reaction by X-ray Absorption Spectroscopy

F. Tavani[1]*, F. Frateloreto[1], D. Del Giudice[1], M. Di Berto Mancini[1], G. Capocasa[1], M. Busato[1], O. Lanzalunga[1], S. Di Stefano[1] and P. D'Angelo[1]

[1]*Department of Chemistry, Sapienza Università di Roma, Piazzale A. Moro 5, 00185 Rome, Italy*

* *francesco.tavani@uniroma1.it*

The Belousov-Zhabotinsky (BZ) reaction[1,2] involving the cerium/iron catalyzed oxidation and bromination of malonic acid (MA) by bromate is the most extensively studied oscillating chemical reaction and continues to fascinate chemists to this day. The main mechanistic features of the BZ reaction were elucidated in 1972 by Field, Körös and Noyes (FKN)[3], experimental and theoretical efforts have been devoted to investigate the BZ reaction mechanistic details, e.g. those regarding the reaction destabilizing, negative feedback processes. A revised semiquantitative model of the BZ reaction based on 80 elementary reactions and 20 concentration variables was proposed by György, Turányi and Field[4], and reaction pathways are still being revised and added upon collection of additional experimental evidences.

Nonetheless, it appears clear that when tackling such a complex chemical system with many variable parameters the availability of experimental techniques that may accurately track the oscillating concentration time evolution of the key reaction intermediate species is of paramount importance. Herein, we tackle the previously unaddressed issue of gaining comprehensive real time spectroscopic insights into the speciation of the Br reactants during the BZ oscillatory reaction by resorting to X-ray absorption spectroscopy (XAS), an advanced spectroscopic tool that is an element-specific probe due to core electron excitation.

In this presentation, we will provide new insights into the behaviour of the Br–related species of the cerium ion catalyzed BZ reaction and show that periodic oscillations not only occur in the concentrations of Br^-, $HBrO_2$, HOBr and Br_2, but also in those of the main reactants BrO_3^- and bromomalonate. Specifically, we measure detectable oscillations in the concentrations of BrO_3^- and bromomalonate by monitoring the BZ reaction through Br K-edge XAS. Further, by coupling XAS with UV-Vis spectroscopy, we simultaneously track the oscillatory time evolution of the Ce and main Br reactants. Unsupervised machine learning, Multivariate Curve Resolution (MCR) and two-dimensional reaction-diffusion analyses are used to interpret the oscillatory patterns in both a time- and space-resolved fashion. Our work evidences collective oscillations in the BZ system and extends the use of X-ray spectroscopy to investigate the mechanisms of oscillatory chemical systems whose key species are often silent to conventional methods of detection.

References

[1] B. P. Belousov, Sbornik ReJeratov po Radiaisionnoi Meditsine 1958, 145 (in Russian).
[2] A. M. Zhabotinskii, Biofizika 1964, 9, 306 (in Russian).
[3] R. J. Field et al. J. Am. Chem. Soc. 1972, 94, 8649.
[4] L. György et al. J. Phys. Chem. 1990, 94, 7162.

Selection of Transition Metal Complexes as potential Photosensitizers based on UV-vis absorption wavelength with Machine Learning Classification Algorithms

V. Vigna[1*], T.F.F. Cova[2], A. C. C. Pais[2] and E. Sicilia[1]

[1] *PROMOCS Laboratory, Department of Chemistry and Chemical Technologies, University of Calabria, Italy*
[2] *Coimbra Chemistry Centre, Department of Chemistry, Institute of Molecular Sciences (IMS), Faculty of Sciences and Technology, University of Coimbra, Coimbra, Portugal*

**vincenzo.vigna@unical.it*

In the field of photodynamic therapy (PDT), the selection of transition metal complexes as potential photosensitizers relies heavily on their absorption properties, particularly within the therapeutic window of UV-vis spectrum[1]. This study presents a machine learning-based approach for binary classification of transition metal complexes, focusing on their suitability as photosensitizers based on UV-vis absorption wavelength falling within or outside the therapeutic window. A dataset comprising UV-vis absorption spectra of transition metal complexes, annotated with their photosensitizer activity, was utilized for model training and evaluation. Various machine learning algorithms were employed to develop predictive models capable of classifying the complexes as photosensitizers or non-photosensitizers. The performance of the models was assessed using metrics such as accuracy, precision, recall, and F1-score. Additionally, feature importance analysis was conducted to identify the critical spectral features influencing the classification decision. The results demonstrate the efficacy of the proposed machine learning framework in accurately classifying transition metal complexes based on their UV-Vis absorption properties and their potential utility as photosensitizers. This approach holds promise for expediting the discovery and development of novel photosensitizer candidates for photodynamic therapy applications.

Acknowledgements:

This research has been supported by MUR, Autorità di Gestione PON “Ricerca e Innovazione” 2014–2020 (CCI 2014IT16M2OP005) and Università della Calabria.

References

[1] J. Li, T. Chen, *Coord. Chem. Rev.*, 2020, **418**

Theme D - Advances in Analytical Chemistry

One-phase extraction coupled with aza-Paternò-Büchi reaction allows the in-depth lipid characterization of hempseeds by untargeted lipidomics

Sara Elsa Aita*, Andrea Cerrato, Carmela Maria Montone, Enrico Taglioni, Anna Laura Capriotti

Department of Chemistry, Sapienza University of Rome, Rome, Italy

**saraelsa.aita@uniroma1.it*

Following the revitalization of the cultivation and supply chain of industrial hemp, several hemp-derived products from hempseeds have recently been placed in the market as food and food ingredients [1]. Despite being long treated as a byproduct of fiber production, hempseeds are nowadays considered a rich source of dietary proteins, lipids, fibers, vitamins, and minerals [2]. In particular, the lipid composition of hempseeds has raised interest for their rich content in biologically active polyunsaturated fatty acids with an optimum ratio of omega-3 and omega-6 compounds. At present, however, the overall polar lipidome composition of hempseeds remains largely unknown. In the present work [3], an analytical platform was developed for the extraction, untargeted HRMS-based analysis, and detailed annotation of the lipid species. First, five one- and two-phase solid-liquid extraction protocols were tested and compared on a hempseed pool sample to select the method that allowed the overall highest efficiency as well as easy coupling with lipid derivatization by photochemical [2 + 2] cycloaddition with 6-azauracil. Underivatized lipids were annotated employing a data processing workflow on Compound Discoverer software that was specifically designed for polar lipidomics, whereas inspection of the MS/MS spectra of the derivatized lipids following the aza-Paternò-Büchi reaction allowed pinpointing the regiochemistry of carbon-carbon double bonds. A total of 184 lipids were annotated, i.e., 26 fatty acids and 158 phospholipids. Once the platform was set up, the lipid extracts from nine hempseed samples from different hemp strains were characterized, with information on the regiochemistry of free and conjugated fatty acids. The overall analytical approach helped to fill a gap in the knowledge of the nutritional composition of hempseeds.

References

[1] Aloo S.O., Mwiti G., Ngugi L.W., Oh D.H. *Critical Reviews in Food Science and Nutrition*, 2022, **28**, 1-20.
[2] Callaway J.C. *Euphytica*, 2004, **140**, 65-72.
[3] Cerrato A., Aita S.E., Cannazza G., Cavaliere C., Cavazzini A., Citti C., Montone C.M., Taglioni E., Laganà A. *Talanta*, 2024, **271**, 125686.

PAM-Engineered Toehold Switches as Input-Responsive Activators of CRISPR-Cas12a for Sensing Applications

Neda Bagheri*, Alejandro Chamorro, Andrea Idili, Alessandro Porchetta

Department of Sciences and Chemical Technologies, University of Rome Tor Vergata, Rome, Italy

**neda.bagheri@uniroma2.it*

The RNA-programmed CRISPR effector protein Cas12a has emerged as a powerful tool for gene editing and molecular diagnostics. However, additional bio-engineering strategies are required to achieve control over Cas12a activity.[1] Here, we introduce a novel class of Cas12a regulators termed PAM-engineered Toehold Switch DNA, featuring re-engineered locked protospacer adjacent motif (PAM) within the loop.[2] This design enables precise control of Cas12a cleavage activities in response to specific molecular targets via structure switching and PAM complementation. Our approach involves reconfiguring the Toehold Switch DNA from a hairpin to a duplex conformation through a strand displacement reaction. This strategy effectively regulates the accessibility of the PAM, thereby controlling the binding and cleavage activities of Cas12a. By leveraging proximity-based strand displacement reactions upon target binding, we illustrate the potential to trigger downstream Cas12a activity (Figure 1). Furthermore, by exploiting the trans-cleavage activity of Cas12a as a means of signal transduction, we showcase the versatility of our method for sensing applications. Our system facilitates rapid, one-pot detection of IgG antibodies and small molecules with high sensitivity and specificity, even within complex matrices. Beyond its bioanalytical utility, the switchable PAM-engineered Toehold Switches represent programmable tools adept at controlling Cas12a-based targeting and DNA processing in response to molecular stimuli, holding considerable promise for a diverse range of biotechnological applications. The outcomes of our research highlight the imminent expansion and practical implementation of CRISPR technology in diagnostics, offering a promising horizon for enhanced diagnostic capabilities beyond nucleic acid targets.

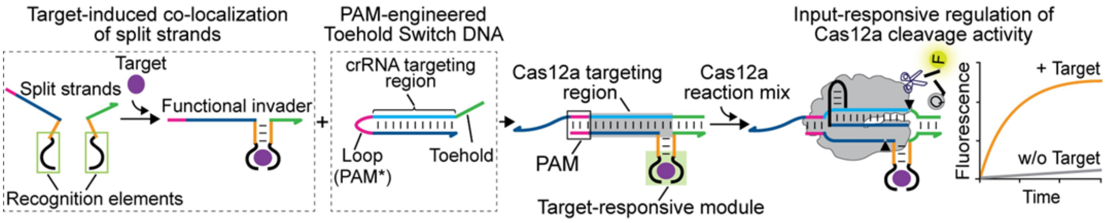


Figure1. PAM-engineered Toehold Switch DNA reconfiguration enables precise control of Cas12a activities in response to specific molecular targets via structure switching and PAM complementation within a proximity-based reaction network.[2]

References

[1] S. Del Giovane, N. Bagheri, A. C. Di Pede, A. Chamorro, D. Migliorelli, L. Burr, S. Paoletti, H. Altug, A. Porchetta. *TrAC, Trends Anal. Chem*. 2024, **172**, 117594.
[2] N. Bagheri, A. Chamorro, A. Idili, A. Porchetta. *Angew. Chem. Int. Ed*. 2024, e202319677.

Design of experiments for optimizing electrochemical biosensor towards miRNA detection on chip

Wanda Cimmino[1*], Simona Esposito[1], Nunzia Iaccarino[1], Stefano Cinti[1,2]

[1]Department of Pharmacy, University of Naples "Federico II", 80131 Naples, Italy
[2] BAT Center – Interuniversity Center for studies on Bioinspired Agro-Envioronmental Thechnology,
University of Naples "Federico II", 80055 Naples, Italy

**Wanda.cimmino@unina.it*

Chemometrics and experimental design approaches play a key role in the optimization of experimental variables for the production of advanced analytical devices. Indeed, they enable us to optimize experimental conditions with fewer experiments and also allow us to evaluate the interaction between the varibles involved. In this work, we employed experimental design, specifically, a D-optimal design, to develop a paper-based electrochemical biosensor for miR-29c detection. This biosensor is based on a signal-off architecture, which has already been developed by our research group[1, 2]. A total of 6 variables were evaluated. Two varibles were taken into account that relate to the production stage of the sensor itself which are the volume of gold nanoparticles and the concentration of capture probe with which to modify the working electrode. Next, variables related to the measurement stage, such as the concentration of NaCl in the working solution and the hybridization time between probe and target, were evaluated. Finally, variables related to the electrochemical technique used were analyzed, including the amplitude and the frequency of the square wave voltammetry (SWV) [3]. This focused approach allowed us to optimize the biosensor with only 30 experiments versus the 456 that would have been required with a one-variable-at-a-time (OVAT) approach and allowed us to achieve accurate and sensitive detection of miRNAs, demonstrating the importance of experimental design in biochemical analysis and advanced diagnostics.

Acknowledgements:

The research leading to these results has received funding from AIRC under MFAG 2022 - ID. 27586 project P.I. Cinti Stefano.

References

[1] Miglione A, Raucci A, Amato J, Marzano S, Pagano B, Raia T, Lucarelli M, Fuso A, Cinti S (2022) Printed Electrochemical Strip for the Detection of miRNA-29a: A Possible Biomarker Related to Alzheimer's Disease. Anal Chem 94:15558–15563. https://doi.org/10.1021/acs.analchem.2c03542

[2] Raucci A, Cimmino W, Grosso SP, Normanno N, Giordano A, Cinti S (2024) Paper-based screen-printed electrode to detect miRNA-652 associated to triple-negative breast cancer. Electrochimica Acta 487:144205. https://doi.org/10.1016/j.electacta.2024.144205

[3] Gulaboski R, Mirceski V (2024) Calculating of square-wave voltammograms—a practical on-line simulation platform. J Solid State Electrochem 28:1121–1130. https://doi.org/10.1007/s10008-023-05520-y

Multiplatform targeted/untargeted approaches for the identification of possible biomarkers of occupational exposure

Michele De Rosa[1*], Fabio Sciubba[2,3], Ottavia Giampaoli[2,3], Daniela Pigini[4], Federico Marini[1,3], Giovanna Tranfo[4], Renata Sisto[4], Mariangela Spagnoli[4]

[1]Department of Chemistry, Sapienza University of Rome, Rome, Italy
[2] Department of Environmental Biology, Sapienza University of Rome, Rome, Italy
[3] NMR-Based Metabolomic Laboratory, Sapienza University of Rome, Rome, Italy
[4] Department of Occupational and Environmental Medicine, Epidemiology and Hygiene, INAIL, Via Fontana Candida 1, 00078 Monte Porzio Catone, Italy
**michele.derosa@uniroma1.it*

During the last decades, exposure to chemicals in the workplace it's shown to be associated with an increased risk of different occupational diseases [1]. Nowadays several strategies can be used to monitor the health status of workers, such as air monitoring or biomonitoring of chemicals and their metabolites, in workers' biofluids [2]. The application of Metabolomics to the field of occupational exposure is innovative and rapidly evolving since it could correlate a metabolic phenotype with several exposure parameters. Among the analytic platforms, nuclear magnetic resonance (NMR) spectroscopy is particularly suitable for metabolomics studies, as it allows the simultaneous quali-quantitative analysis of hundreds of metabolites belonging to different chemical classes in complex real matrices. On the other hand, liquid chromatography coupled to mass spectrometry represents another important platform for target analysis with lower LOD and LOQ than NMR. Therefore, a combined approach where different platforms' outputs were fused together could provide important advantages over traditional exposure assessment techniques. For this purpose, data fusion strategies and multivariate statistical analysis were necessary used to evaluate urinary metabolic profiles and identify key metabolites associated with exposure. The choice of biological matrix to investigate fell on the urine due to the low invasiveness of the sampling and the possibility of repeated sampling in the short term. Over the years several biological monitoring campaigns were carried out, during which urinary samples from both professionally exposed subjects (employed in various industrial sectors) and healthy volunteers were collected. Subsequently all samples have been analyzed by NMR for the evaluation of metabolic profile, and by HPLC-MS/MS, for known exposure biomarkers determination. From profiling analysis approximately 40 metabolites have been identified and quantified and then correlated with target analysis' results. The observed subclinical metabolic alterations provided information about novel possible exposure biomarkers to be monitored to predict the onset of an occupational diseases [3]. Interestingly, some molecules were common between groups, indicating a nonspecific response of the organism, such as a redox state alteration, while others have been correlated to specific xenobiotic exposure. The described approach allows for early evaluation of occupational exposures, and it could be a useful tool that focuses attention on aspects that remain unclear still today, such as the long-term effects at concentrations of toxics below the threshold limit values, or the evaluation of exposure to mixtures of substances or again exposures to both physical and chemical agents. The scope is to promote targeted risk assessments and developing personalized protective measures for the health of specific individuals or vulnerable groups.

Acknowledgements: Research was funded by Grant: BRIC ID 09/2019, ID 31/2019, ID 08/2022, from INAIL.

References

[1] Jakubowski M. *J Environ Monit.*, 2012 Feb;**14**(2):348-52.
[2] Nicholson J.K., Lindon J.C., Holmes E. *Xenobiotica*, 1999;**29**:1181–1189.
[3] Giampaoli O., Sciubba F., Tranfo G., et al. *Toxics* 2024, **12**, 182.

Kombucha: From High-Field NMR to Benchtop NMR to monitor the complex fermentation process

G. Di Matteo[1*], M. Spano[2], S. Zamboni[2], M. Bruschi[3], L. Mannina[1]

[1]Department of Chemistry and Technology of Drugs, Sapienza University of Rome, Rome, Italy
[2]Legendary Drink srl, Verona, Italy
[3]Bioniks srl, Verona, Italy

** giacomo.dimatteo@uniroma1.it*

Kombucha is a sweetened tea fermented with a symbiotic culture of yeasts and bacteria. The beverage present a balanced taste among sweet, due to the residual sugars, and sour, due to organic acids produced by acetic acid bacteria. In order to evaluate the quality and production reproducibility of kombucha produced through a natural fermentation process an NMR metabolomics approach was applied. Kombucha samples were collected every 5 days for 25 days of fermentation and analysed by ^{1}H-NMR untargeted analysis. The levels of sugars (sucrose, glucose, fructose, trehalose, 2-O-β-Larabinopyranosyl-myo-inositol), organic acids (acetic acid, lactic acid, succinic acid, malic acid, citric acid, formic acid, quinic acid, fumaric acid and gluconic acid), amino acids (alanine, isoleucine, leucine, valine, glutamate, pyro-glutamate, aspartate, and GABA) ethanol, glycerol, caffeine, theanine and gallic acid were quantified. A Benchtop NMR instrument was also used monitoring the quantity of sucrose, lactic acid, acetic acid and succinic acid. The PLS-R statistical analysis with the Benchtop NMR quantitative data was performed obtaining a good prediction of the fermentation stage of kombucha and an indication about its quality and production reproducibility. Finally, the Benchtop NMR spectrometer was demonstrated to be an useful on-line process monitoring tool in the kombucha production. Moreover, this fast analysis method could be applied on different kombucha industrial productions around the world to expand the knowledge about the dynamics of the substrates consumption and metabolites production.

Acknowledgements:

Funder: Project funded under the National Recovery and Resilience Plan (NRRP), Mission 4 Component 2 Investment 1.3 - Call for tender No. 341 of 15 March 2022 of Italian Ministry of University and Research funded by the European Union – NextGenerationEU;
Award Number: Project code PE00000003, Concession Decree No. 1550 of 11 October 2022 adopted by the Italian Ministry of University and Research, CUP D93C22000890001, Project title "ON Foods - Research and innovation network on food and nutrition Sustainability, Safety and Security – Working ON Foods".

A new analytical method based on solid phase microextraction-gas chromatography tandem mass spectrometry for the assay of polycyclic aromatic hydrocarbons in human saliva

R. Elliani[1*], A. Naccarato[1], A. Tagarelli[1]

[1]*Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Via Pietro Bucci Cubo 12/C, I-87030 Arcavacata di Rende (CS), Italy*

**rosangela.elliani@unical.it*

In recent years, biomarkers monitoring in biological fluids for human exposure assessment to pollutants is having increasing importance related to their possible adverse effects on the human health. In this context, this work aimed at developing an easy method for the quantitative determination of polycyclic aromatic hydrocarbons (PAHs) in real saliva. PAHs can be present in the environment both naturally and anthropogenically. This class of contaminants can derived by the incomplete combustion of organic matter, industrial activities, automobile exhausts, food processing and tobacco smoke. The United States Environmental Protection Agency (U. S. EPA) classified PAHs as ubiquitous and priority enviromental pollutants due to the combination of their frequency of occurrence, toxicity, and potential for human exposure. The International Agency for Research on Cancer (IARC), based on evidence of carcinogenicity in experimental animals, defined benzo[*a*]pyrene as carcinogenic to humans, dibenzo[*a*,*h*]anthracene and chrysene as probable or possible cancer-causing, respectively [1,2]. Among the different biological matrices, saliva represents a valid alternative to a conventional biological fluids due to its simplicity of collection, is not invasive, expensive and allows to evaluate the exposition to several enviromental pollutants [3]. In this work a simple, efficient and solvent free analytical method for the determination of 13 PAHs in human saliva based on solid-phase microextraction, followed by gas chromatography-triple quadrupole mass spectrometry (SPME-GC-QqQ-MS) analysis in selected reaction monitoring (SRM) acquisition was proposed. A matrix pre-treatment tests were conducted to evaluate possible interactions between target analytes and other components of saliva. The optimization of the factors affecting SPME extraction highlighted the good performance of the commercially available overcoated fiber (PDMS/DVB/PDMS) in the sorption process of the target analytes. Multivariate approach through the use of central composite design was used to optimize salt concentration, extraction temperature and time that may have affected the SPME extraction. SPME fiber coating lifetime was evaluated in order to verify the stability of the coating by exposing the fiber directly in matrix for a large number of analyses. Finally, the developed SPME-GC-MS/MS method was evaluated in terms of matrix effect, linearity, accuracy, precision, limit of detection.

References

[1] United State Environmental Protection Agency, Polycyclic aromatic hydrocar-bons (PAHs), Office of Solid Waste, Washington, DC, 2008.
[2] K. Straif, A. Cohen, J. Samet, *Air pollution and cancer*, 2013, 7, 75, International Agency for Research on Cancer, Lyon, France.
[3] A. Naccarato, R. Elliani, A. Tagarelli, *Journal of Chromatography A*, 2023, **1707**, 464303.

Enhancing Productivity and Flexibility in LC-MS/MS using PerkinElmer QSight 420 with Dual ESI-APCI Source Capability

Alessandro Fabiani[1*], Stefano Derrù[2]

[1]Perkin Elmer Scientifica Italia, Milan, Italy
[2]Arpa Sardegna – Dipartimento Sassari,3Arpa Campania – Dipartimento Benevento

**Alessandro.fabiani@perkinelmer.com*

This abstract provides an overview of the dual source capabilities of the PerkinElmer QSight™ Triple Quadrupole LC/MS/MS system, focusing on its ability to sensitively detect organic contaminants requiring distinct ionization methods. It also discusses the procedural efficiencies, analytical speed, and improved sensitivity achieved by utilizing this dual source configuration for contaminant assessment across various matrices, while maintaining compliance with European regulations.

The switch between ElectroSpray Ionization (ESI) and Atmospheric Pressure Chemical Ionization (APCI) sources involves a systematic process of cooling, manual exchange, and subsequent heating to reach operational temperatures. This meticulous procedure often leads to reduced productivity in analyses requiring both sources simultaneously, leading many analysts to prefer using only the ESI source for its perceived simplicity, albeit at the expense of flexibility and quantitative robustness.

Collaborating with ARPA Sardegna and Campania, we evaluated and optimized concurrent analytical methodologies employing dual source Qsight 420 for routine screening of different environmental and food matrices.

To comprehensively assess ionization efficiency and analyte quantification, a diverter valve was strategically integrated between the LC column and the mass spectrometer. This addition facilitated the redirection of flow from the LC column to both ESI and APCI sources, enabling comparative analysis and simultaneous quantification within a single chromatographic run.

Instrument control, data acquisition, and processing were efficiently managed using the Simplicity™ 3Q software platform, ensuring smooth operation and reliable analytical results.

GC-MS/MS analytical solution for challenging volatile compounds

Andrea Fricano[1*], Federica Bianchi[1], Valeria Buccilli[1], Giulia Simonetti[1]

[1]*Department of Chemistry, University of Rome "La Sapienza", Piazzale Aldo Moro 5, 00185 Rome, Italy*

**andrea.fricano@uniroma1.it*

Gas chromatography coupled with mass spectrometry (GC-MS) and/or tandem mass spectrometry is an effective analytical technique, due to its excellent resolution, accuracy and sensitivity, for the quali-quantitative determination of volatile and semi-volatile organic compounds (VOCs and sVOCs). VOCs and sVOCs can be challenging due to their relatively low boiling points and molecular weights, especially when sample preparation is required. Despite an efficient extraction procedure for these compounds, their presence in trace quantities in samples can make extract enrichment a crucial step in sample preparation. Nevertheless, attempting to enrich the extract (e.g. evaporating solvent), may often lead to partial or total evaporation of the analytes, due to their distinctive volatility, eventually resulting in low recoveries at smaller volumes of extract.

Meanwhile, Electron Ionization (EI) often used in GC-MS systems, can generate mostly small fragments with low *m/z* ratios when applied to low molecular weight compounds, like most sVOCs. These ions can be strongly matrix interfered in a real sample, causing low signal-to-noise ratios, and making it harder to lower limits of detection and quantification (LOD and LOQ) in a single ion monitoring (SIM) quantitative analysis.

In order to overcome these analytical limits, this work aimed to achieve better recoveries of sVOCs optimizing a sample preparation procedure that would carry out an extract enrichment, minimizing evaporation losses. At the same time, using gas chromatography combined with triple quadrupole mass spectrometry (GC-MS/MS), allowed to achieve low LOD and LOQ operating in a multiple reaction monitoring (MRM) mode.

We focused on ten different volatile analytes for which the current laboratory standard procedures didn't produce acceptable results in terms of recoveries and method sensitivity. In particular, we analysed three fluorotelomer alcohols (FTOH), three sulfluramides (FOSA) and four different adipic acid esters (AAEs) for which a gas chromatographic separation run was optimized in MRM acquisition mode using a DB-624 GC column. The method was then validated in terms of linearity, reproducibility, and sensitivity, achieving satisfying results.

Extractions of analytes were carried out using a Büchi pressurized solvent extractor (PSE) and further enrichment was performed partially evaporating the solvent at low pressure with a SyncorPlus Büchi evaporator, achieving better recoveries for all analytes considered.

In the end, as an example of application of the method, preliminary extraction and quantification tests were performed on real samples, coming from packaging material and airborne particulate matter sampled in a working place.

PLA-based nanocomposite microbeads for magnetic solid phase extraction of xenobiotics from urine samples

Lorenzo Antonelli[1], Maria Chiara Frondaroli[2*], Massimo Giuseppe De Cesaris[1],
Nina Felli[1], Chiara Dal Bosco[1], Elena Lucci[1], Alessandra Gentili[1]

[1]Department of Chemistry, Sapienza University of Rome, Rome, Italy
[2]Department of Science and Technology for Humans and the Environment, University Campus Bio-Medico of Rome, Rome, Italy

**m.frondaroli@unicampus.it*

In recent years, research in analytical chemistry moved towards sustainable applications. According to the Green Sample Preparation principles, new materials should be "sustainable, reusable and renewable" (3rd principle), with the further need to reduce waste (4th principle) and to "minimize samples, chemicals and materials" (5th principle) [1]. In this way, magnetic micro-scale materials offer a large specific surface area, a good sorption capacity and a rapid attainment of adsorption equilibrium [2].

In this work, a novel type of nanocomposite microbeads was synthesized, characterized and applied for the extraction of 14 xenobiotics from urine samples of occupationally exposed individuals.

The microbeads were prepared by a microemulsion-solidification method and were the combination of a polymeric support, a carbon-based sorbent and magnetite nanoparticles. The biopolymer was polylactic acid (PLA), recovered from heated tobacco electronic cigarettes (HEETS®) filters, which have become one of the most diffuse solid wastes in the last few years. The microbeads were characterized via Fourier-transform infrared (FTIR) and UV–VIS spectroscopy, thermogravimetric (TGA) and X-ray diffraction (XRD) analyses and scanning electron microscopy (SEM).

The optimized extraction procedure involves the use of 15 mg of microbeads to extract the target analytes from a 1-mL aliquot of urine. The analytes adsorption was assisted by mixing on a vortex-stirrer for 5 min. The analytes were then desorbed three times with 500 μL of methanol. The pooled extract was dried under nitrogen flow and the residue was reconstituted in 100 μL of a 1:1 (v/v) solution of acetonitrile and water; finally, 10 μL was injected in the high-performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS) system.

The method was validated in accordance with the main guidelines of the FDA for the validation of bioanalytical methods. The recoveries were between 57% and 100%. The limits of detection and the lower limits of quantification were in the range of 0.1–1.8 $\mu g\ L^{-1}$ and 0.3–3.0 $\mu g\ L^{-1}$, respectively. Precision was less than 11% and accuracy was below 15%. Matrix-matched calibration curves were studied in the range of 1-15 $\mu g\ L^{-1}$ and showed good linear relationship ($R^2 > 0.99$).

In conclusion, the PLA-based nanocomposite microbeads are easy to prepare and allow a great simplification of the extraction process due to their micrometric size and reactivity to magnetic fields. Furthermore, this work proposes a PLA recycling strategy and a new application of such bioplastic.

Acknowledgements: The authors would like to acknowledge their appreciation to Prof. Andrea Martinelli, Prof. Anna Maria Girelli, and Dr. Elisabetta Lacolla for their availability during the research (TGA, FTIR and UV-VIS analyses).

References

[1] López-Lorente Á.I., Pena-Pereira F., Pedersen-Bjergaard S., Zuin V.G., Ozkan S.A., Psillakis E., TrAC Trends in Analytical Chemistry, 2022, **148**, 116530.
[2] Soriano M.L., Zougagh M., Valcárcel M., Ríos Á., Talanta, 2018, **177**, 104.

Urinary steroids analysis by dilute & shoot LC-MS/MS: the case of Pregnanediol-3-Glucuronide and future perspectives

Laura Leoni[1*], Federica Rosmini[2], Federico Ponzetto[3], Antonello Nonnato[4], Fabio Settanni[4], Paolo Moghetti[2], Giulio Mengozzi[1,4]

[1]Clinical Biochemistry Laboratory, Department of Medical Sciences, University of Turin, Turin, Italy
[2] Endocrinology, Diabetes and Metabolism, Department of Medicine, University of Verona, Verona, Italy
[3] Endocrinology, Diabetology and Metabolism, Department of Medical Sciences, University of Turin, Turin, Italy
[4] Clinical Biochemistry Laboratory, City of Health and Sciences University Hospital, Turin, Italy

**laura.leoni@unito.it*

The dilute & shoot (DS) analysis is a simple procedure where the sample is directly diluted with an appropriate solvent before the injection or “shooting” into the LC-MS/MS system. This approach, which allows the use of limited sample volume, is thus quick, easy and cost-saving. Furthermore, the absence of pre-analytical sample extraction step could help increase lab productivity making the method more attractive to clinical biochemistry laboratories thanks to its adaptability to automation.

In our work a first DS LC-MS/MS method was developed for measuring Pregnanediol-3-Glucuronide (PDG) urinary concentration from 7µL of spot urine samples for the detection of ovulation. The analysis was performed employing a fully-porous C18 analytical column and adding 2mM ammonium fluoride to aqueous mobile phase to reach the high sensitivity level needed, for a total chromatographic run time of a 6 min. The method was validated in accordance with ISO 17025 requirements for quantitative methods and it was applied to two sets of real samples. Firstly, a series of 24 daily samples collected from a female individual across a menstrual cycle were analyzed, then a population of 7 healthy female volunteers were recruited and a set of 4 spot urine samples (1 per week) was collected from each individual and analyzed.

The optimized analytical method allowed to efficiently separate PDG from other structurally similar glucuro-conjugated steroid metabolites, guaranteeing a sufficient sensitivity for detecting target analyte down to 0.01 µg/mL. The performed validation protocol, including the assessment of selectivity, quantitative performance, carry-over, sample stability and robustness gave satisfactory results. The application to real spot urine samples allowed proving method’s ability to measure PDG throughout an entire menstrual cycle, highlighting the ovulation period also when only one sample per week was collected, and opening the way for the implementation of this DS analysis in routine clinical laboratories.

In the future, it would be possible to extend the number of steroidal analytes monitored by DS analysis, starting with additional ovulation markers such as Estrone Glucuronide, which is another ovarian steroid whose monitoring, combined with the determination of PDG concentration, could help in determining more efficiently whether ovulation has occurred. Moreover, research efforts are currently focused on developing a novel DS method for the measurement of up to 50 urinary steroid hormones as well as selected glucuro- and sulpho-conjugated phase II metabolites. Following its analytical validation, such extended steroid panel will be applied to various clinical settings with the aim of characterizing the steroidal asset in physiological conditions as well as in rare and chronic non-communicable endocrine diseases.

Terahertz spectroscopy: a selective approach for diagnostic and preventive conservation in the Cultural Heritage field

Candida Moffa[1*], Camilla Merola[2], Fernando Jr Piamonte Magboo[1], Lucia Giuliano[1], Anna Candida Felici[1], Luigi Palumbo[1], Mauro Migliorati[1], Massimo Petrarca[1]

[1] Department of Basic and Applied Sciences for Engineering (SBAI), Sapienza,
University of Rome, Via Antonio Scarpa, 16, Rome, 00161, Italy
[2] Department of Environmental Biology (DBA), Sapienza, University of Rome, Piazzale Aldo Moro, 5, Rome, 00185, Italy

**candida.moffa@uniroma1.it*

Methodologies exploiting terahertz (THz) radiation are non-invasive and non-destructive. Furthermore, it is worth noting that THz waves can penetrate most non-metallic materials and biological tissues without causing ionization (THz photon energy in the order of 4.2 meV at 1 THz), thus ensuring the safety of biological tissues and materials under investigation.

Additionally, some materials commonly present in Cultural Heritage artefacts (for example, parchment, paper, some varnishes, and binders, etc.) can be considered transparent in this spectral range, allowing for the selective identification of painting materials and mineral compounds on Cultural Heritage objects.

Moreover, the portability and compactness of THz systems make these techniques potentially complementary methodologies for Cultural Heritage applications. However, there is still a lack in the existing datasets for substances of interest in the field of THz diagnostic.

In this work, the optical properties of mineral compounds (i.e., atacamite, antlerite, etc.) are characterised for the first time by exploiting THz-based approaches. Furthermore, examples concerning the ability of THz spectroscopy to discriminate and quantify pure components in binary mixtures are reported.

Another valuable application of THz-based techniques is represented by the identification of gaseous compounds (i.e., VOCs, GHGs) through THz spectroscopy. The selective and fast identification of these compounds is valuable in applications of preventive conservation and environmental monitoring.

For example, the presence of some of the selected compounds in historical and archaeological contexts can envisage a selective tracer to detect fungal development and/or degradation byproducts of organic materials.

Therefore, the results reported prove that THz-based approaches can represent innovative applications in the Cultural Heritage field.

Acknowledgements:

This work was supported by Sapienza Large Projects Research Call 2023 titled "TforCH: R&D on the potentiality of THz radiation for Cultural Heritage"; “TREX a prototype of a portable and remotely controlled platform based on THz technology to “measure” the ONE HEALTH vision: environment, food, plant health, security, human and animal health” funded by the European Union - Next Generation EU CUP B53D23013610006 – Project Code 2022B3MLXB PNRR M4.C2.1.1; "R-SET: Remote sensing for the environment by THz radiation" Large Research Projects of Sapienza, University of Rome and by Sapienza competitive grants: Grandi Attrezzature Scientifiche (2018) titled "SapienzaTerahertz: THz spectroscopic image system for basic and applied sciences".

Advanced Chemometric Approaches to Study Metabolic Crosstalk in Patients with Multiple Health Conditions

Greta Petrella[1*], Erica Pitti [1], Domitilla Vanni [1], Nicola Viceconte [2], Angelo Lembo [1], Gaetano Tanzilli [2], Valeria Raparelli [3], Daniel Oscar Cicero [1]

[1] Department of Chemical Science and Technology, University of Rome "Tor Vergata," 00133 Rome, Italy.
[2] Department of Cardiovascular, Respiratory, Nephrological, Anesthesiologic and Geriatric Sciences, Sapienza University of Rome, Policlinic Umberto I, 00161 Rome, Italy.
[3] Department of Experimental Medicine, Sapienza University of Rome, 00161 Rome, Italy

**petrella@scienze.uniroma2.it*

Metabolomics is an expanding field, pivotal for identifying markers that signify disease presence. Traditionally focused on single diseases, this approach often overlooks patients with comorbidities [1].

Our research adopts a novel methodology to examine metabolic interactions across multiple disease states, aiming to uncover complex interrelations not evident when considering single conditions in isolation.

In a cohort of 306 patients at medium to high risk for coronary artery disease (CAD), we quantified plasma concentrations of 83 metabolites using Nuclear Magnetic Resonance (NMR). Our analysis employed statistical techniques, integrating linear regression with multivariate analysis to map the intricate connections between metabolite levels and prevalent risk factors, including diabetes, hypertension, and dyslipidemia.

The chemometric analysis provided a detailed visualization of metabolic interactions, revealing distinctive and opposing metabolic profiles when comparing individual and combined disease states. We identified compensatory metabolic mechanisms among the conditions studied, primarily in ketone body metabolism and fatty acid β-oxidation [2,3]. These insights suggest underlying metabolic compensations that could inform targeted therapeutic strategies.

This study introduces a cutting-edge approach to metabolomics that captures the dynamic complexity of metabolic interactions in patients with multiple coexisting conditions. By delineating the metabolic compensations between diabetes, hypertension, and dyslipidemia, we offer new perspectives that could enhance the precision of treatments tailored to such complex clinical profiles.

References

[1] Fortin M., Dionne J., Pinho G., *Ann Fam Med.* 2006, **4(2)**, 104-108.
[2] Ke C., Zhu X., Zhang Y., *Metabolomics*. 2018, **14(9)**, 1-11.
[3] Laffel L., *Diabetes Metab Res Rev*. 1999, **15(6)**, 412-426

Influence of pedoclimatic conditions on *Arctium lappa.* L polyphenolic profile: development of hydroalcholic roots extractions and chemical-biological characterization proceses

E. Romano[1], L. Mannina[1], G. Domínguez-Rodríguez[2,3], E. Ibáñez[2], A. Cifuentes[2]

[1]Dipartimento di Chimia e Tecnologie del Farmaco, Sapienza Università di Roma, Pizzale Aldo Moro 5, 00185, Roma, Italy.
[2]Instituto de Investigación en Ciencias de la Alimentación CIAL (CSIC-UAM). C/Nicolás Cabrera 9, Universidad Autónoma de Madrid, 28049 Madrid, España.
[3]Departamento de Química Analítica, Química Física e Ingeniería Química, Universidad de Alcalá, Ctra. Madrid-Barcelona km 33.600, 28871, Alcalá de Henares, Madrid, España.

e.romano@uniroma1.it

Arctium lappa L., also called burdock, is a plant belonging to the Asteraceae (Compositae) family. Although this plant prefers moist soil and temperate areas, it can grow in fertile and clay soils with sun. Burdock grows in disturbed and nutrient-rich habitats from sea level up to 3300 m excepting for Central Asia where this plant grows at higher altitudes (Helena Duistermaat, 1996).

Arctium lappa L. is widely known as a potential source of phenolic compounds with healthy properties (Alcázar Magaña et al. 2021). Particularly, burdock roots are characterized by their high contents in phenolic compounds (Sama et al., 2021). However, its polyphenol profile and biological activity may change depending on pedoclimatic conditions. Thus, to evaluate the influence of pedoclimatic conditions on polyphenol composition and bioactivity of burdock roots, three different ecotypes were analysed in this study: Spontaneous Land Ecotype (SPLE), Spontaneous Mountain Ecotype (SPME), and Organic Land Ecotype (OLE). For that, an optimization of the extraction temperature (50°C, 100°C and 150°C) to recover the highest content of antioxidant and anticholinergic phenolic compounds from the three different ecotypes of Burdock roots was carried out using Pressurized Liquid Extraction (PLE). In addition, a solid-liquid extraction (SLE) was carried out using the same extraction solvent for PLE, at room temperature for 24 h. After that, to determine the influence of the extraction technique on the recovery of bioactive phenolic compounds, PLE extracts were compared with SLE extracts in terms of total polyphenol content determined by Folin-Ciocalteu assay, antioxidant capacity by DPPH and ORAC assays, and the anticholinergic capacity by AChE and BuChE tests. In addition, a characterization of phenolic compounds of PLE and SLE extracts was performed by HPLC-DAD-IT-MS. The results shown that PLE provided the extracts with the highest bioactivity and polyphenol content compared with SLE. In addition, the three ecotypes exhibited slightly different biological activity and chemical composition. High altitude in growing conditions of burdock implied higher content of phenolic compounds.

References

[1] Helena Duistermaat. 1996. Monograph of Arctium L. (Asteraceae).

[2] Magaña A.A, Kamimura N., Soumyanath A., Stevens Jan F., and Maier C.S. (2021). ‘Caffeoylquinic Acids: Chemistry, Biosynthesis, Occurrence, Analytical Challenges, and Bioactivity’. The Plant Journal 107(5):1299–1319. doi: 10.1111/tpj.15390.

[3] Sama H., Dieudonné K.T., Samson G., Adama H., Mamoudou H.D. (2022). ‘Effect of Pedo-Climatic Conditions on Physicochemical Characteristics and Agro-Industrial Potential of Three Native Oilseeds Fruits from Burkina Faso’. BMC Plant Biology 22(1):321. doi: 10.1186/s12870-022-03713-7.

Traceability of high-quality Italian rice cultivars through chemometric approaches

Claudia Scappaticci[1*], Alessandra Biancolillo[1], Angelo Antonio D'Archivio[1], Sara Fiore[1], Camilla Filauro[1] and Martina Foschi[1]

[1]*Department of Physical and Chemical Sciences, University of L'Aquila, L'Aquila, Italy*

**claudia.scappaticci@graduate.univaq.it*

In recent years, there has been a rise in interest in rice (Oryza sativa L.) within both scientific research and the agri-food industry. The growing importance of preserving the authenticity of different rice varieties, especially those highly valued commercially, has led to the development of advanced traceability technologies like Protected Geographical Indication (PGI) and Protected Designation of Origin (PDO) [1]. These certifications ensure where rice comes from and its quality, helping to protect its genetic diversity and support local farming. Italy is a top rice producer in Europe, with many different types of rice. Our study aims to protect valuable Italian rice varieties by developing specific traceability technologies for those with PGI and PDO labels. To do this, we collected various PDO rice types from the Baraggia region, like Carnaroli, S. Andrea, and Arborio, directly from different producers. We also collected Carnaroli rice from different parts of Italy, such as Piana di Sibari (CS), Valle Lomellina (PV), Roseto degli Abruzzi (TE), and the Carnaroli PGI rice from the Delta del Po area. We carefully studied these samples using different techniques like Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FT-IR), Multivariate Image Analysis (MIA), and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). These methods helped us quickly and efficiently check the quality of the rice. Even though ICP-MS is expensive and needs careful sample preparation, it gave us important information about the minerals in the rice and where it comes from. Finally, we analyzed the data using chemometrics to learn more about the rice's traceability, where it was grown, and if it's authentic Carnaroli PGI or PDO rice.

References

[1] Uawisetwathana U., Karoonuthaisiri N. *Curr. Opin. Food Sci*, 2019, **28**, 58-66.

Theme E - Advances in Coordination and Inorganic Chemistry

Unraveling the polyol synthesis mechanism of CoO and $CoFe_2O_4$ with *in-situ* synchrotron light experiments

Miran Baričić[1,2,3*], Roxana Mirshahi[2], Youssef Snoussi[1], Jasper Plaisier[4], Lara Gigli[4], Alessandro Mariani[4], Barbara Sartori[4], Sophie Nowak[1], Paolo Centomo[5], Davide Peddis[6], Souad Ammar[1], Carlo Meneghini[2]

[1]*IMM, ITODYS, Université Paris Cité, Paris, France*
[2]*Università degli Studi Roma TRE, Rome, Italy*
[3]*ISM, CNR, Piana Bella di Montelibretti, Italy*
[4]*Elettra Sincrotrone Trieste SCpA, Area Science park, Basovizza, Italy*
[5]*Università degli Studi di Padova, Padova, Italy*
[6]*DCCI, Università degli Studi di Genova, Genova, Italy*
**miranbaricic@yahoo.com*

Cobalt (II) oxide (CoO) is a material of remarkable importance in research. Apart from being a surprisingly intricate playground for basis research[1], [2], it is intensely studied for several applicative research topics playing and important role in the theme of sustainability, such as catalysis, lithium ion batteries, water splitting, and permanent magnets[3]–[6]. CoO can be synthesized by means of the polyol method[7], which provides CoO aggregates a ~ 100 nm diameter with high porosity, a desirable feature for catalytic applications[6]. Within this framework, we have decided to employ *in-situ* synchrotron light techniques (XRD and SAXS) combined with *ex-situ* experiments to clarify the formation mechanism of CoO. Among our results, the approach allowed us to observe in real time the formation of layered hydroxide intermediates anticipating that of CoO, to gain kinetic details about the reaction, and to reconstruct the aggregation process. Furthermore, we show that employing tetra-ethylene glycol instead of di-ethylene glycol, the synthesis mechanism presents important changes. The same techniques were employed to study the synthesis process of $CoFe_2O_4$, a fundamental material in the field of magnetism. Synchrotron techniques allowed us to observe the formation of pre-nucleation clusters in the synthesis, opening new possibilities to the possible tuning capabilities of the method.

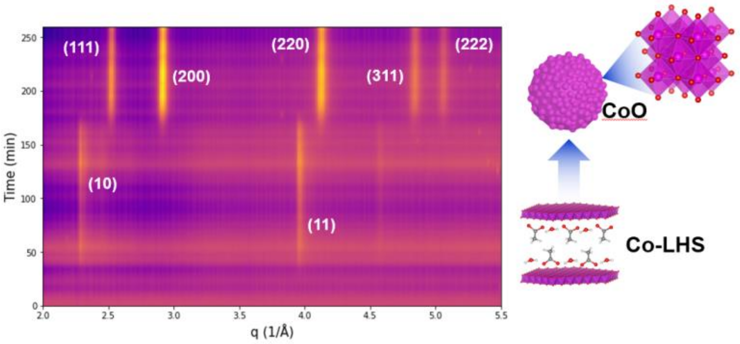


Figure 1: time evolution of *in-situ* XRD experiment, with a phase evolution scheme on the right side

References

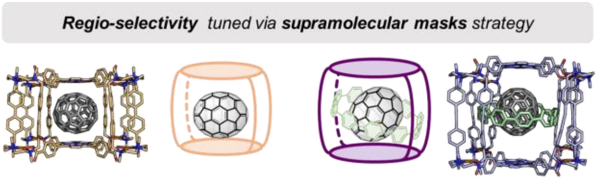
[1] P. M. Sarte *et al.*, *Physical Review B*, vol. 024415, pp. 1–7, 2018
[2] V. Skumryev, D. Givord, J. Nogués *et al.*, *Nature*, vol. 423, no. June, pp. 19–22, 2003,
[3] L. Liao *et al.*, *Nature Nanotechnology*, vol. 9, no. December 2013, pp. 69–73, 2014
[4] K. Park and A. M. Kolpak, *Journal of Catalysis*, vol. 365, pp. 115–124, 2018
[5] N. Flores-Martinez *et al.*, *Part. Part. Syst. Charact.*, vol. 35, no. 11, pp. 1–8, 2018
[6] X. Zheng *et al.*, *J. Mater. Chem. A*, vol. 1, pp. 1394–1400, 2013
[7] F. Fiévet *et al.*, *Chem. Soc. Rev.*, vol. 47, no. 14, pp. 5187–5233, 2018

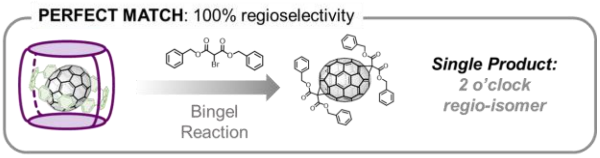
Regioswitchable Bingel bis-functionalization of fullerene C_{70} via supramolecular masks

Valentina Iannace,[1] Clara Sabrià,[1] Youzhi Xu,[2] Max von Delius,[3] Inhar Imaz,[4] Daniel Maspoch,[4]
Ferran Feixas,[1] and Xavi Ribas.[1]

[1]Institut de Química Computacional i Catàlisi(IQCC) and Departament de Química, Universitat de Girona, Campus Montilivi, 17003 Girona, Catalonia, Spain
[2] Institute of Organic Chemistry, University of Ulm, 89081 Ulm, Germany; Present Address: College of Chemistry and Molecular Sciences, Henan University, Kaifeng 475004, China
[3] Institute of Organic Chemistry, University of Ulm, 89081 Ulm, Germany.
[4] Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and The Barcelona Institute of Science and Technology, 08193 Bellaterra, Catalonia, Spain.
* *valentina.iannace@udg.edu*

Isomer-pure functionalized fullerenes are required to boost the development of fullerene chemistry in any field, but their multiple functionalization renders a mixture of regio isomers that are very difficult to purify by chromatography. For the specific case of C_{70}, its non-spherical geometry makes its regioselective functionalization more challenging than that of spherical C_{60}. In this work, the supramolecular mask approach is applied for the first time to C_{70}, which is encapsulated in two different nanocapsules to achieve the Bingel bis-cyclopropanation at α-bonds of opposite poles. Based on the tetragonal prismatic geometry imposed by the smaller supramolecular mask tested [1], the obtained major bis-adduct is completely reversed (major 5 o'clock) compared to bare C_{70} functionalization (major 2 o'clock). Moreover, by further restricting the accessibility of C_{70} using a three-shell Matryoshka mask [2] and dibenzyl-bromo malonate, a single regiospecific 2 o'clock bis-isomer is obtained [3], owing to the perfect complementarity of the mask and the addend steric properties. The outcome of the reactions is fully explained at the molecular level utilizing a thorough molecular dynamics (MD) study of the accessibility of the α-bonds to produce the different bis-adducts.





Acknowledgements:

This work was supported by grants from MINECO-Spain (CTQ2016-77989-P and PID2019-104498GB-I00 to X.R., and a PhD grant to V. I.), Generalitat de Catalunya (2017SGR264). X.R. is also grateful for ICREA-Academia awards. We thank STR-UdG for technical support.

References

[1] C. Fuertes-Espinosa, C. García-Simón, M. Pujals, X. Ribas et al. *CHEM*. 2020, **6**, 1. 6.
[2] E. Ubasart, O. Borodin, M. Von Delius, X. Ribas, et al. *Nat. Chem.* 2021, **13**, 420.
[3] V. Iannace, C. Sabrià, F. Feixas, X. Ribas, et al. *J. Am. Chem.Soc*. 2024,**146**, 5186−5194.

Unraveling the molecular oxygen-based methane to methanol oxidation over the MIL-100(Fe) metal-organic framework

Alessandro Tofoni[1*], Francesco Tavani[1], Marco Vandone[2], Luca Braglia[3], Paolo Ghigna[4], Elisa Borfecchia[5], Valentina Colombo[2] and Paola D'Angelo[1]

[1]Department of Chemistry, Sapienza University of Rome, Rome, 00185, Italy
[2]Department of Chemistry, University of Milan, Milan, 20133, Italy
[3]Istituto Officina dei Materiali, CNR, Trieste, 34149, Italy
[4]Department of Chemistry, University of Pavia, Pavia, I21700, Italy
[5]Department of Chemistry, University of Turin, Turin, 10125, Italy

**alessandro.tofoni@uniroma1.it*

As the current large-scale methanol production technologies rely on expensive and non-environmentally friendly processes operated at elevated temperatures and pressures (T>400 °C, P>30 bar), achieving the direct oxidation of methane to methanol (MTM) under mild conditions is considered the holy grail of modern catalysis [1]. Natural enzymes efficiently perform the MTM reaction [2], and have therefore inspired the development of upscalable artificial catalysts able to reproduce this exceptional reactivity. Metal-organic frameworks (MOFs) are hybrid porous materials composed of metal nodes and organic linkers, regarded as promising candidates to accomplish an efficient MTM process because of their intrinsically high tunability and porosity. MIL-100(Fe) is a MOF containing trimeric Fe(III) units and the benzene-1,3,5-tricarboxylate (BTC) linker, which is known to form open Fe(II) sites upon thermal treatment above 200 °C [3]. These open metal sites are known to catalyse the N_2O-based MTM oxidation through a highly reactive Fe(IV)=O intermediate [4], but an in-depth spectroscopic characterization of their formation process is lacking. Additionally, the low availability of N_2O limits the application of this gas in the MTM process to academic studies, with limited industrial relevance. Exploring a more economically convenient process based on molecular oxygen therefore appears of high interest.

Here, we present a detailed spectroscopic characterization of the direct MTM conversion at ambient pressure and moderate (200 and 100 °C) temperatures over MIL-100(Fe), using O_2 as the oxidant. We first characterize the thermally induced self-reduction of some Fe(III) sites to Fe(II), with operando high energy resolution fluorescence detected X-ray absorption spectroscopy (HERFD-XAS) and resonant inelastic X-ray scattering (RIXS), determining the intermediate species involved in this process as well as the final Fe(II) abundance. Subsequently, we characterize the MOF under catalytic conditions, highlighting the fate of the Fe(II) sites during the MTM reaction and the propensity of the material towards active site regeneration. We also identify the species formed upon catalyst deactivation with the help of valence-to-core X-ray emission spectroscopy (VtC-XES). To monitor the catalyst stability, we employ operando powder X-ray diffraction (PXRD) throughout the entire process. Finally, we complement this experimental characterization with density functional theory (DFT) calculations steered by the experimental evidence, validating both the proposed activation and MTM reaction mechanisms.

References

[1] R. De María et al., Int J. Chem. React. Eng., 2013, **11**, 469.
[2] M. Ross et al., J. Biol. Inorg. Chem., 2017, **22,** 307.
[3] P. Horcajada et al., Chem. Commun. 2007, **27**, 2820
[4] M. C. Simons et al., J. Am. Chem. Soc., 2019, **45**, 18142.

Theme F - Colloids and Materials

Exploring Bile Salt Aggregation: Insights from Deep Eutectic Solvents

Leonardo Ariodante[1*], Luciano Galantini[1]

[1]*Department of Chemistry, "La Sapienza" University of Rome, Rome, Italy*

**leonardo.ariodante@uniroma1.it*

In order to reach a more sustainable future, it is imperative to rethink and replace materials and technologies that have a negative impact on the ecosystem of our planet. In this project, the aim is to do so by using greener solvents, like Deep Eutectic Solvents (DESs), to study the aggregation behavior of bile salts, a class of naturally occurring surfactants. Bile salt micellization and their supramolecular assembly structures have been extensively studied in our group[1–3] in conventional solvents but investigating their properties in innovative solvents such as DESs might shed new light on their behavior and possibly inspire enhanced materials and solutions.

A Small Angle Neutron Scattering (SANS) study was conducted on systems of sodium cholate (NaC) in reline[4], one of the first presented DESs in the literature[5], uncovering its micellization properties and the peculiar influence of water percentage on its aggregation in this medium. It was possible to determine the dimension and shape of the micelles, as well as the formation of higher dimension aggregates at specific DES:water ratios. These latter aggregates have been investigated through Scanning Electron Microscope (SEM) imaging in order to reveal their structure, and the study is ongoing in order to capture in higher quality the supramolecular aggregates observed.

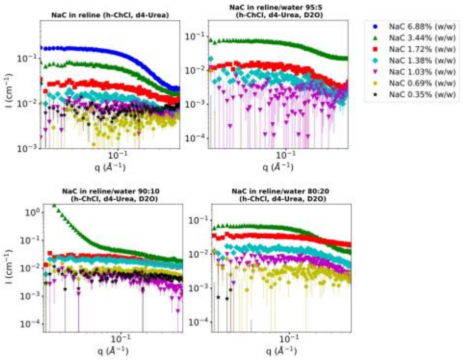


Figure 1 – SANS data of NaC/reline/water systems

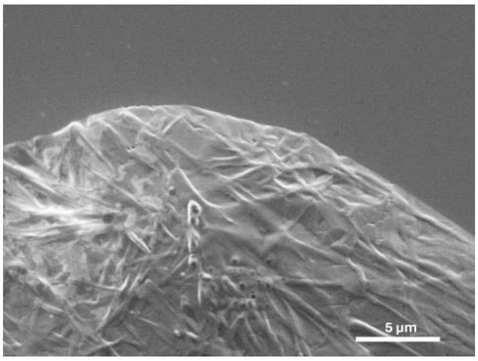


Figure 2 – SEM images of NaC in reline/water

References

[1] M. C. Di Gregorio, L. Travaglini, A. Del Giudice, J. Cautela, N. V. Pavel and L. Galantini, *Langmuir*, 2019, **35**, 6803–6821.

[2] M. C. di Gregorio, J. Cautela and L. Galantini, *Int. J. Mol. Sci.*, 2021, **22**, 1780.

[3] L. Galantini, M. C. di Gregorio, M. Gubitosi, L. Travaglini, J. V. Tato, A. Jover, F. Meijide, V. H. Soto Tellini and N. V. Pavel, *Curr. Opin. Colloid Interface Sci.*, 2015, **20**, 170–182.

[4] 10.5291/ILL-DATA.9-10-1797 - ILL Data Citation, https://doi.ill.fr/10.5291/ILL-DATA.9-10-1797, (accessed 28 March 2024).

[5] A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed and V. Tambyrajah, *Chem. Commun.*, 2003, 70–71.

Aqueous co-precipitation of iron oxide nanoparticle in the presence of amino acids

M. Casale[1*], A. Omelyachik[1,2], S. Slimani[1,2], D. Peddis[1,2], D. Colombara[1], M. Piccinni[1]

[1]*Department of Chemistry, University of Genova, Genova, Italy*
[2]*Institute of Structure of Matter, National Research Council, nM2-Lab, Via Salaria km 29.300,*
Monterotondo Scalo 00015, Roma,

michael.casale@edu.unige.it

Monodomain iron oxide nanoparticles with spinel structure (MNPs) are widely studied for many applications, from catalysis to biomedicine [1]. The methodology to synthesize MNPs is well-established [2] but the co-precipitation mechanism in the presence of ligands is not well-understood yet. The co-precipitation of magnetite nanoparticles occurs after the addition of a base to the solution of precursors, typically Fe(II) and Fe(III) chlorides. In this contribution, we titrate Fe(II)/Fe(III) solutions with sodium hydroxide in the presence of L-glutamic acid as a capping agent to explore the formation mechanism of magnetite nanoparticles in the presence of the amino acid. In these titration/co-precipitation experiments, the base is injected at a constant temperature in the reaction batch containing the precursors and the capping agent. X-Ray Diffraction (XRD) and Transmission Electron Microscopy (TEM) provide the morpho-structural features of the MNPs. The molecular coating on the surface of MNPs is investigated by coupling thermogravimetric analysis to Fourier-transform infra-red spectroscopy (TGA-FTIR). Colloidal stability of the dispersions and hydrodynamic diameter of the MNPs are evaluated by Dynamic Light Scattering (DLS). The magnetic properties (i.e. field and temperature dependent magnetization) and Hyperfine structure of MNPs will be investigated by VSM magnetometry and Mössbauer spectroscopy, respectively.

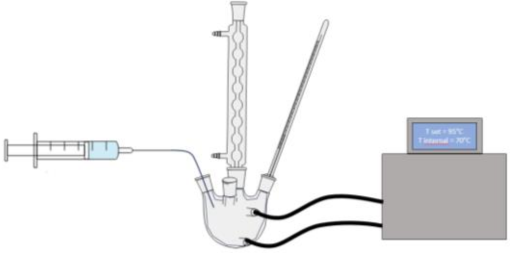


Figure 1. Scheme of the experimental setup

Acknowledgements: REMAP has received funding from the European Commission PathFinder open programme under grant agreement No. 101046909. Funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or European Innovation Council and SME Executive Agency (EISMEA). Neither the European Union nor the granting authority can be held responsible for them.

References

[1] M. Bilal, S. Mehmood, T. Rasheed, and H. M. N. Iqbal, “Bio-catalysis and biomedical perspectives of magnetic nanoparticles as versatile carriers,” Magnetochemistry, vol. 5, no. 3. MDPI, Sep. 01, 2019. doi: 10.3390/magnetochemistry5030042.

[2] M. Usman et al., “Magnetite and Green Rust: Synthesis, Properties, and Environmental Applications of Mixed-Valent Iron Minerals,” Chemical Reviews, vol. 118, no. 7. American Chemical Society, pp. 3251–3304, Apr. 11, 2018. doi: 10.1021/acs.chemrev.7b00224.

Gold nanoparticles: tailoring plasmonic properties for SERS-based sensing applications

Sara Cerra[1*], Chiara Romeo[2], Emil Milan[3], Eros Radicchi[3], Francesca Loschi[3], Tommaso A. Salamone[1], Beatrice Pennacchi[1], Martina Mercurio[1], Ilaria Fratoddi[1], Adolfo Speghini[3]

[1] *Department of Chemistry, "La Sapienza" University, Rome, Italy*
[2] *Department of Industrial Engineering, Trento University, Trento, Italy*
[3] *NRG, Department of Biotechnology, University of Verona, Verona, Italy*

**sara.cerra@uniroma1.it*

Plasmonic gold nanoparticles (AuNPs) are considered a breakthrough in sensing, ranging from biomolecules[1] to toxic or poisonous analytes and pollutants[2–4]. For these applications, it is crucial to tailor the AuNPs properties controlling their structural parameters (*i.e.*, size and shape) and the chemical nature of the stabilizing ligand shell, which is relevant when dealing with colloidal dispersions[2–5]. Different synthetic methods have been studied to take control over these parameters through careful choice of the reaction conditions during synthesis or by post-synthetic modifications. In this work, noncovalently capped plasmonic nanostructures were obtained through bottom-up approaches in the presence of surfactants, *i.e.*, cetyltrimethylammonium bromide (CTAB) and cetyltrimethylammonium chloride (CTAC) as templating capping agents. Exploring different wet chemical synthesis methods, hydrophilic anisotropic gold nano bipyramids (AuNBPs) with different aspect ratios and spherical gold nanospheres (AuNSs) were obtained (**Figure 1**). In view of surface-enhanced Raman scattering (SERS)-based sensing applications, different aliphatic and aromatic thiols were chosen: 3-mercapto-1-propanesulfonate (3MPS), thiosalicylic acid (TSA), 4-mercapto phenylboronic acid (4MPBA), and 4-mercaptobenzoic acid (4MBA), as proof-of-concept of unknown analytes in aqueous environment using the gold–sulfur affinity as the main driving force for molecules recognition. Optimization of synthesis parameters, control over colloidal properties, and investigation of thiol-exchange reaction were done using different spectroscopic and electron microscopy techniques.

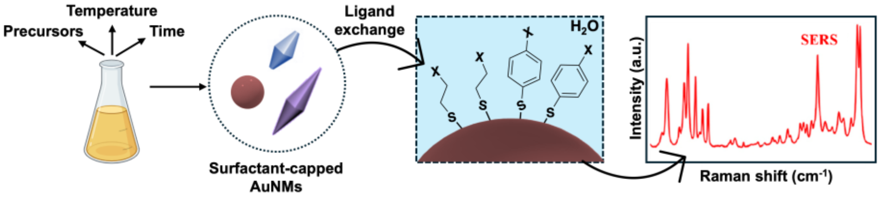


Figure 10. *Spherical and bipyramidal gold nanostructures as SERS-based sensing platform in aqueous environment.*

References

[1] Kusuma S.A.F., Harmonis J.A., Pratiwi R. Hasanah A.N. *Sensors* 2023, **23**, 8172.
[2] Cerra S., Salamone T.A., Sciubba F. Marsotto M., Battocchio C., Nappini S., Scaramuzzo F.A., Li Voti R., Sibilia C., Matassa R., Beltran A.M., Familiari G., Fratoddi I. *Coll. Surf. B* 2021, **203**, 111727.
[3] Fratoddi I., Cerra S., Salamone T.A., Fioravanti R., Sciubba F., Zampetti E., Macagnano A., Generosi A., Paci B., Scaramuzzo F.A., Matassa R., Familiari G., Battocchio C., Marsotto M., Papa P., Bearzotti A. *ACS Appl. Nano Mater.* 2021, **4**, 2930−2940.
[4] Cerra S., Salamone T.A., Bearzotti A., Hajareh Haghighi F., Mercurio M., Marsotto M., Battocchio C., Fioravanti R., Diociaiuti M., Fratoddi I. *Part. Part. Syst. Charact.* 2023, 2200189.
[5] Salamone T.A., Rutigliano L., Pennacchi B., Cerra S., Matassa R., Nottola S., Sciubba F., Battocchio C., Marsotto M., Del Giudice A., Chumakov A., Davydok A., Grigorian S., Canettieri G., Agostinetti E., Fratoddi I. *J. Colloid Interface Sci.* 2023, **649**, 264−278.

The supramolecular dance of Porphyrins and Bile Salts towards chiral sensing devices

Valeria D’Annibale[1,2*], Luca Piccirillo[1,2], Alessandra Del Giudice[1] , Mauro Giustini[1], Karin Schillén[3], Reiko Oda[4], Dario Bassani[5], Guillaume Raffy[5], Donato Monti[1], Luciano Galantini[1]

[1] Department of Chemistry, Sapienza University of Rome, Rome, Italy
[2] Department of Basic and Applied Sciences for Engineering, Sapienza University of Rome, Rome, Italy
[3] Division of Physical Chemistry, Chemistry Department, Lund University, Lund, Sweden
[4] Institut Européen de Chimie et Biologie, Bordeaux University, Bordeaux, France
[5] Institut des Sciences Moleculaires, Bordeaux University, France

**valeria.dannibale@uniroma1.it*

The feature of chirality marks the elements of life from the sub-molecular to the macroscopic scale. Understanding what induces the symmetry breaking from an achiral system has notable value from both theoretical and applicative point of view [1]. In this context, porphyrins are versatile building blocks for the constitution of chiral supramolecular systems [2], due to the strong aggregating tendency driven by hydrophobic effects and electrostatic interactions and for the ability of reading and transferring the chirality at different levels of organization [3]. Achiral porphyrins, in presence of a chiral effector, are able to sensitively break the symmetry towards a chiral aggregation.

Within this scenario, we studied the self-assembly behaviour of achiral porphyrins (i.e. a carboxy-tetraphenyl porphyrin in the free base and Zn(II) form), in presence of cholate (C) and deoxycholate (DC) bile salts [4], unconventional surfactants, with the role of templating chiral agents.

Carefully exploring the porphyrin/bile salt molar ratio and the proper stoichiometry of water/ethanol solvent mixture, the optimal conditions to induce and enhance the chirality transfer were defined, allowing for the formation in solution of chiral aggregates of fibrillar structures (Fig. 1, *a*), featuring CD signal of remarkable intensities (Fig. 1, *b*). The obtained species were deeply characterized by spectroscopic techniques (UV-Vis, CD and Fluorescence) and by transmission electron microscopy (TEM).

Noteworthy, on the way to exploit new smart materials, the property of chirality was preserved also in the solid state, upon deposition on a quartz slide (Fig. 1, *c*), paving the route for the construction of stereoselective sensing devices.

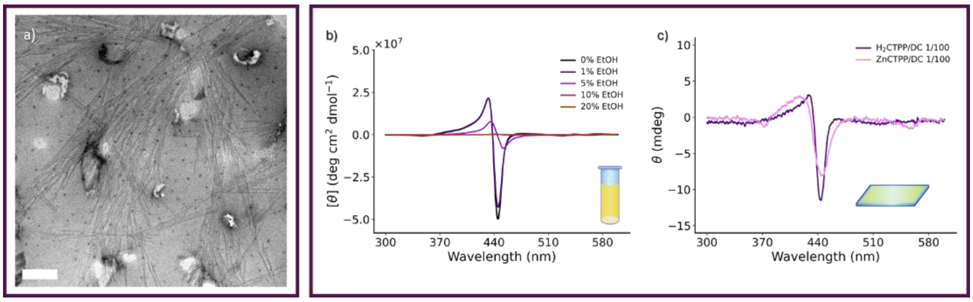


Figure 1: TEM image of fibrillar porphyrin-bile salt aggregates *(a)*, size bar of 500 nm; CD signal for the aggregates in solution *(b)* and after deposition upon a quartz slide *(c)*.

References

[1] Kondepudi, *Int. J. Quantum Chem.*, 2004, **98**, 222-227.
[2] Stefanelli et al., *ACS Appl. Mater. Interfaces*, 2019, **11**, 12077-12087.
[3] Simoncini et al., *RSC Adv.*, 2014, **4**, 55362-55366.
[4] di Gregorio et al., *Langmuir*, 2019, **35**, 6803-6821.

Determination of the optimal pH for doxorubicin encapsulation in polymeric micelles.

Lucrezia Desiderio[1], Natalie Solfried Gjerde, Elisamaria Tasca, Luciano Galantini, Irantzu Llarena, Paolo Di Gianvincenzo, Sunisa Thongsom, Sergio E. Moya, Mauro Giustini.

[1] *Department of Chemistry, Sapienza University of Rome, Rome, Italy*

The Doxorubicin hydrochloride (DX) is one of the most widely used drugs in anticancer therapies. Thanks to the positive charge in the ammonium group, the drug shows a high solubility in aqueous solutions. However, considering drug-delivery systems such as polymeric micelles (PMs), which can form hydrophobic domains, this feature negatively affects the drug encapsulation.

It is well known that at basic pH, the ammonium group of DX deprotonates, as well as phenolic groups on the anthracycline moiety. Hence, both the rate and the efficiency of encapsulation will be increased by selecting an optimal pH value, whereby the molecule is in its neutral form.

By considering the DX encapsulation in PMs based on commercial poloxamers and a diblock copolymer methoxy-poly(ethylene glycol)$_{17}$- b-poly(ε-caprolactone)$_9$, an optimal pH value of 8.1 was determined by fluorescence spectroscopy, following the time evolution of both the intensity ratio of the first and the second emission bands of DX and its fluorescence lifetime, both sensitive to the environment polarity changes.

In-vitro tests on selected cancer cell lines were followed by Confocal Scanning Laser Microscopy (CSLM) and the sulforhodamine B (SRB) assay. The drug release is slow and controlled and the PMs system shows lower cytotoxicity than free DX.

This new approach offers a greener, faster and more efficient way to encapsulation of DX in PMs.

Enhancement of Enantioselective Light-matter Interaction by Chiral Plasmonics

Jeong Hyun Han [1*], Ryeong Myeong Kim [1], Ki Tae Nam [1]

[1] *Seoul National University, Department of Materials Science and Engineering, Seoul National University, Seoul 08826, Republic of Korea*

**e-mail:hanjh@snu.ac.kr*

Detection of the chirality of molecules plays a crucial role in various biochemical applications. The method mainly used for this has been spectroscopy, and there has been a severe limitation that the signal strength is weak due to the large scale difference between light and molecules. Plasmonic metamaterials have thus attracted significant attention for their ability to enhance local interactions between chiral light and matter on a sub-wavelength scale, improving spectroscopic detection limits. Although understanding the plasmonic enhancement on the detection of chiral molecules often focus on the increased intrinsic excitation rate of molecules and following signal enhancement, there still remains a theoretical gap. This gap stems from the difference between the wavelength of molecular electronic absorption, usually in the ultraviolet (UV) region, and the optical response of plasmonic materials in the visible and near-infrared ranges. Recent research has shifted focus to interpreting plasmonic sensing through perturbation theory, considering how the backaction of molecular energy absorption affects the electromagnetic energy stored in plasmonic structures. This perspective allows for understanding the shift in plasmonic resonance modes as a collective effect of dielectric perturbation due to changes in refractive index and chiral perturbation from near-field optical helicity density and the medium's chirality parameter. Consequently, this interpretation expands detection capabilities regarding sample type, concentration, and chirality. We introduce the theoretical background's physical significance and present two innovative enantioselective chiral plasmonic sensing strategies derived from chiral perturbation theory. First, by creating and integrating chiral plasmonic nanoparticles into 2D photonic crystals to generate spinning dipoles responsive to circularly polarized light, we achieve strong and uniform optical helicity density in three dimensions. This demonstrates exceptional sensing feasibility across various methods such as transmission, reflection, and sample immobilization. Second, utilizing machine learning for the simultaneous optimization of dielectric and chiral perturbations enhances the effect of medium backaction on electric fields, optical helicity density, and following spectroscopic responses, thus achieving tailored sensing capabilities. Our perspective can also be implanted to the molecular signals as UV circular dichroism or SERS under the same logic. We aim to introduce a robust methodology for detecting molecular chirality using plasmonic nanostructures based on colloidal synthesis and a scientifically grounded optimization approach.

References

[1] Kim, R. M., Han, J. H., Lee, S. M., Kim, H., Lim, Y-C., Lee, H-E., Ahn, H-Y., Lee, Y. H., Ha, I. H., Nam, K. T. *The Journal of Chemical Physics*, 2024, **160**, 061001.

[2] Kim, R. M., Huh, J. H., Yoo, S., Kim, T. G., Kim, C., Kim, H., Han, J. H., Cho, N. H., Lim, Y-C., Im, S. W., Im, EJ., Jeong, J. R., Lee, M. H., Yoon, T-Y., Lee, H-Y., Park, Q-H., Lee, S., Nam, K. T., *Nature*, 2022, **612**, 470-476.

[3] Han, J. H., Lim, Y-C., Kim, R. M., Lv, J., Cho, N. H., Kim, H., Namgung, S. D., Im, S. W., Nam, K. T., *ACS Nano*, 2023, **17**, 3, 2306.

Investigating Temperature-Dependent Carrier Transport and Persistent Photoconductivity in WSe_2/MoS_2 Nanocomposite Thin Films

Akshay Kumar[1*], Manjot Kaur[2]

[1]*Department of Physics, Sardar Patel University -Mandi, Himachal Pradesh-175001, India.*
[2]*University Centre for Research and Development, Chandigarh University -*
Mohali, Punjab-140413, India.

**akshaykumar.tiet@gmail.com*

The emergence of 2D Transition Metal Dichalcogenides (TMDs) presents new opportunities for device applications like photodetectors, photovoltaic cells, heterojunction devices, and field-effect transistors. Tungsten diselenide (WSe_2) has unique properties making it attractive for sensors, transistors, and flexible electronics, but intrinsic defects and Fermi level positioning within the bandgap hinder effective carrier mobility. Nanocomposites with other TMDs such as molybdenum disulfide (MoS_2), offering high carrier density and tunable band gap, provide a promising solution. This study investigates the temperature-dependent electrical transport and persistent photoconductivity in WSe_2/MoS_2 nanocomposite thin films. Using a thermal evaporation technique, we fabricated n-type semiconductor films with a thickness of approximately 150 nm and a carrier concentration of 10^{23} cm^{-3}. Film uniformity and thickness were confirmed through FESEM analysis, while XPS analysis validated the presence of WSe_2 and MoS_2, discernible by the +4 oxidation state of W and Mo and the -2 oxidation state of S and Se. Raman modes (E^1_{2g}) further acted as reliable indicators of interlayer coupling in the deposited films. Our investigation revealed a distinctive photoluminescence emission peak at 1.59 eV, corresponding to the exciton bound to defects, introducing mid-bandgap states. Notably, the films exhibited a substantial abundance of trap/defect states and high levels of disorder, shedding new light on carrier transport mechanisms in these materials.

Exploring carrier transport mechanisms over a temperature range of 150 to 350 K, we highlighted the pivotal roles played by trap states originating from chalcogenide vacancies in WSe_2/MoS_2. These trap states significantly contributed to the formation of localized states. In the temperature range of 150–250 K, the electrical conductivity of the composite adhered to Mott's variable range-hopping model due to the presence of these localized states. At higher temperatures, electrical transport was primarily facilitated by nearest-neighbor hopping and a thermally activated conduction mechanism. Additionally, our study delved into the influence of defect/trap states and random local potential fluctuations on persistent photoconductivity. The entrapment of carriers within trap states led to delayed carrier recombination. Notably, the incorporation of oxygen into sulfur vacancies, resulting in acceptor states, engendered a greater photocurrent when the nanocomposite thin films were exposed to air compared to vacuum. These findings provide profound insights into the conduction mechanism of multifunctional transition-metal dichalcogenide-based nanocomposites, paving the way for advancements in diverse applications.

References

[1] Kaur, M., Singh, K., Kumar, A. *Journal of Applied Physics*, 2021, **130**, 125308.
[2] Kaur, M., Singh, K., Sharma, R. K., Kumar, A. *Journal of Alloys and Compounds*, 2022, **909**, 164833.

CTAB and a thermoresponsive bile acid derivative form catanionic tubules: sorting out an unexpected composition ratio.

Valerio La Gambina[1*], Alessandra Del Giudice[1], Maria Chiara di Gregorio[1], Luciano Galantini[1]

[1]*Department of chemistry, Sapienza University of Rome, Rome, Italy*

valerio.lagambina@uniroma1.it

Self-assembly catanionic nanotubes are an odd architecture with relevant applicative interests. Their formation is very rare and there is currently no clear understanding of their chemistry. Here we report the intriguing assembly of mixtures formed by CTAB (flexible surfactant) and a thermoresponsive bile salt derivative[1] (rigid surfactant, Tb or TBAC). The pure bile salt derivative aggregates into tubules at a temperature above 37°C.When catanionic mixtures are prepared, a peculiar phenomenon was observed: nanotubes form at a specific critical ratio, requiring a minimum portion of CTAB, namely bile salt derivative : CTAB = 9:1. Slightly different variations in CTAB amount, both up or below the critical ratio, create unfavorable conditions for the tubules homogeneity and stability. UV, Circular dichroism, SAXS and microscopy data suggest a molecular packing where the bile acid derivative creates the scaffold of the tubule's bilayer whereas CTAB co-adjuvates in screening the charged heads. Moreover, this system enables for a temperature induced tubule-tubule interconversion: indeed, by increasing the temperature on the catanionic tubules, the catanionic tubules break up and the pure Tb tubules form. The data highlight an innovative case within the narrow umbrella of catanionic nanotubes and encourage further exploration of the possibility offered by the catanionic combination of rigid molecules and flexible surfactants.

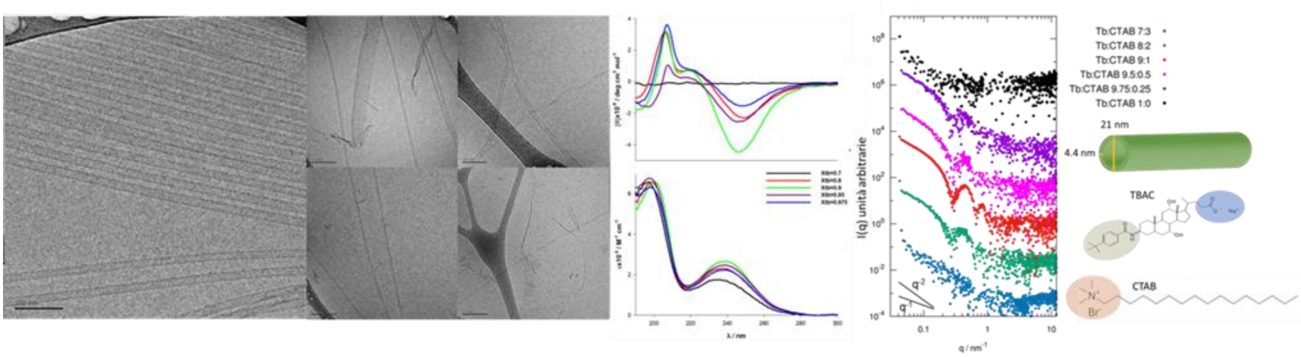


Figure 1: UV, Circular dichroism, SAXS and Cryo-TEM data.

References

[1] Luciano G., Claudia L., Aida J. *Soft Matter*, 2009, **5**, 3018-3025.

Multifunctional inorganic nanomaterials: synthesis, characterization and surface functionalization for advanced applications

Martina Mercurio[1*], Sara Cerra[1], Tommaso A. Salamone[1], Beatrice Pennacchi[1], Ilaria Fratoddi[1]

[1]*Department of Chemistry, Sapienza University, P.le Aldo Moro 5, 00185, Rome, Italy*

**e-mail: martina.mercurio@uniroma1.it*

Inorganic nanoparticles, especially titania (TiO_2NPs) and silver nanoparticles (AgNPs) are widely used for a variety of applications, ranging from sensing to agricultural or antibacterial applications (**Figure 1**)[1-3]. For such uses, surface functionalization is the keyword that allows to control the shape, size, and colloidal stability, all parameters to obtain versatile nanomaterials that can be tailored to the desired application. The present work focuses on the synthesis, functionalization, spectroscopic, and structural characterization of functionalized AgNPs, design and development of nanohybrids, through the covalent combination of AgNPs decorating TiO_2NPs surface, in order to obtain a single multifunctional hybrid nanoplatform (TiO_2-AgNPs). For this conjugation process, the first step is related to the sol-gel surface functionalization of commercial TiO_2NPs (size range of 30-40 nm), using the covalent linker 3-(mercaptopropyl)trimethoxysilane (MPTMS). Here, four reaction parameters (time, concentration, solvent, and ammonia catalyst) were studied to obtain well-dispersed nanoparticles of suitable size that would be useful for the next step, *i.e.*, the silver decoration. Notably, MPTMS is a bifunctional alkoxysilane linker that provides terminal -SH groups suitable for attaching Ag surface, quantified by a rhodamine-based dye. Subsequently, with an *in-situ* method, a chemical reduction of Ag^+ precursor was achieved using sodium borohydride as a reducing agent, in the presence of the functionalized TiO_2NPs and hydrophilic thiol 3MPS (sodium 3-mercapto-1-propanesulfonate). In addition, hydrophilic TiO_2NPs-AgNPs were prepared with a different amount of silver nitrate ($AgNO_3$) precursor to tune the content of AgNPs decorating the surface of TiO_2NPs. Several spectroscopic and morphostructural characterizations were employed to elucidate structure-properties correlations.

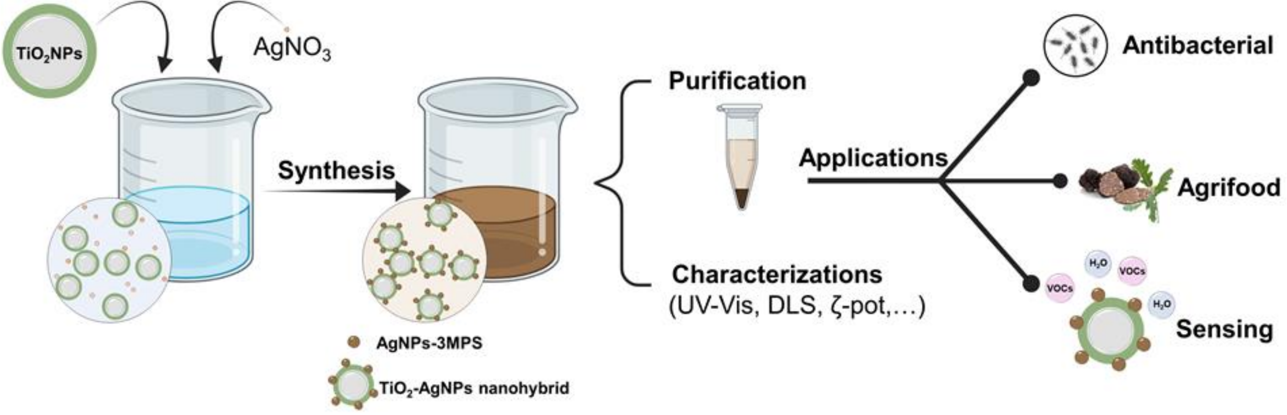


Figure 1. Synthesis of multifunctional TiO_2-AgNPs nanohybrid for several applications.

References

[1] Hajareh Haghighi F., Mercurio M., Cerra S., Salamone T. A., Binaymotlagh R., Palocci C., Romano Spica V., Fratoddi I. *J. Mater. Chem. B*, 2023, **11**, 2334

[2] Schiesaro I., Burratti L., Meneghini C., Fratoddi I., Prosposito P., Lim J., Scheu C., Venditti I., Iucci G., Battocchio C. *J. Phys. Chem. C*, 2020, **124**, 25975−25983

[3] Porcaro F., Carlini L., Ugolini A., Visaggio D., Visca P., Fratoddi I., Venditti I., Meneghini C., Simonelli L., Marini C., Olszewski W., Ramanan N., Luisetto I., Battocchio C., *Materials*, 2016, **9**, 1028

Linoleic acid-based covalent adaptable networks (CANs) with recyclability and self-healing properties

Valerio Napoleone[1*], Francesca Leonelli[2], Luisa Maria Migneco[3], Andrea Martinelli[4], Fabrizio Vetica[5]

[1]*Department of Chemistry, University La Sapienza, Rome, Italy*

**Valerio.napoleone@uniroma1.it*

The current plastic annual production is 395 million tons and it will exceed 1000 million tons by 2039 if the growth of polymer production continues at its current rate of 5% each year. Indeed, only 9% of the plastics that are currently produced are recycled while most of these materials end up in landfills or leak into oceans, thus creating severe environmental challenges. Covalent adaptable networks (CANs) materials can play a significant role in reducing the burden posed by plastics materials on the environment because they are reusable and recyclable. [1]CANs are polymers whose chains, unlike thermosetting polymers, are linked by reversible covalent bonds. This means that, under certain stimuli, such as an increase in temperature, mechanical stress or UV radiation, the structure of the material can be rearranged by breaking and reforming the bonds that make up the network. The result of this is that, although CANs are cross-linked materials, with all the advantages that this entails, they are capable of being reprocessed and remodeled under conditions as mild as those of thermoplastics and in some cases are even capable of repairing themselves. Previous results obtained in our laboratory [2] have shown the formation of CANs from monounsaturated fatty acids with self-healing properties. In the light of this result, in this work, we wished to synthesise a CANs produced from linoleic acid derived from grape processing waste and which presents a higher cross-linking due to the double unsaturation present in the molecule. The polymer synthesis was therefore carried out from linoleic acid in a series of three synthetic steps. The cross-linking agent used was 4-amino diphenyl disulphide (4-ADS), which forms new bonds by opening the epoxy function. The obtained material, when hated, give rise to the typical mechanism of action of CANs.In fact, the polymer chains throught homolytic cleavage of the disulphide bond, recombine each other making the material reprocessable. The polymer synthesis was carried out by varying the ratios of dimer to 4-ADS and the different chemical, physical and thermal properties of the various samples were studied.

References

[1] Christopher J. Kloxin, Timothy F. Scott, Brian J. Adzima *Covalent Adaptable Networks (CANs): A Unique Paradigm in Crosslinked Polymers, Macromolecules*. **43**(6): 2643–2653.

[2] L.Pettazzoni, F. Leonelli, A.Martinelli, L.M. Migneco, S. Alfano, D. Di Luca, L. Celio, V. Di Lisio *Transamidation-based vitrimers from renewable sources, Journal of applied polymer science* (2022)

Network assembly of Gold Nanoparticles

B. Pennacchi[1*], G. Melchiorre[1], F. Frateloreto[1], D. Del Giudice[2], S. Cerra[1], T. Salamone[1], M. Mercurio[1], S. Grigorian[3], G. Ziaco[1], C. Sappino[1], S. Di Stefano[1], I. Fratoddi[1]

[1] *Department of Chemistry, "La Sapienza" University, Rome, Italy*
[2]*Department of Chemical Engineering and Chemistry, "Eindhoven University of Technology", Eindhoven, Netherlands*
[3] *Institute of Physics, University of Siegen, Siegen, Germany*

**beatrice.pennacchi@uniroma1.it*

Transient self-assembly of metal nanoparticles influences electronic and optical properties of nanomaterials and can be achieved by chemical (known as fuel), optical, electronic, or other stimuli. In this work, a dissipative dynamic covalent system based on the transimination reaction [1] is exploited using hydrophobic gold nanoparticles (AuNPs), as acid-base stimuli-responsive nanomaterials. Using an activated carboxylic acid (ACA) as fuel, a covalent interconnection of nanoparticles occurs, leading to the formation of a dissipative (out of equilibrium) state. The initial isolated and in equilibrium state AuNPs give rise to a transient AuNPs covalent network (**Figure 1**): once the decarboxylation of ACA takes place and an *in-situ* generation of a base occurs, the assembled system can go back to the starting point. Hydrophobic AuNPs were synthetized and functionalized with different thiols in mixture, *i.e.* 1-dodecanethiol (DDT) and 4-aminophenyl disulfide (Ani) and the reactivity was compared with 9,9-didodecyl-2,7-dibromofluorene (FL) dithiol derivative [2-3]. The obtained AuNPs have a 5 nm hydrodynamic diameter with excellent colloidal stability in both cases. Stable AuNPs networks were obtained in the case of AuNPs-DDT-FL and transient covalent networks are achieved starting from AuNPs-DDT-Ani, adding an aliphatic imine linker in the presence of an activated carboxylic acid acting as a fuel. Extensive characterization studies were carried out *via* conventional techniques, *i.e.*, UV-Visible, FT-IR, ^{1}H- ^{13}C-NMR, DLS, also supported by electron microscopies and X-ray scattering techniques.

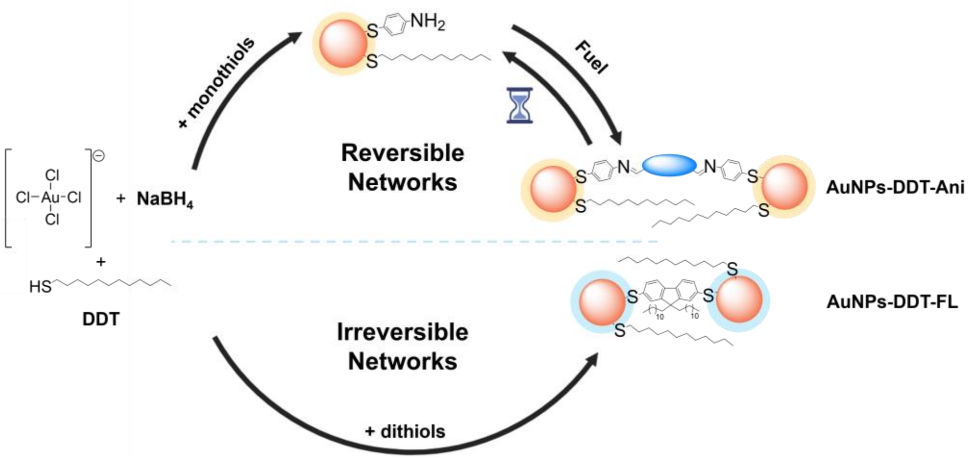


Fig. 1. Schematic depiction of the transient self-assembly of AuNPs (top), and of the irreversible self-assembly with dithiol linkers (bottom).

References

[1] Del Giudice D., Valentini M., Melchiorre G., Spatola E., Di Stefano S., *Chem. Eur. J.*, 2022, **28**, e202200685.

[2] Grigorian, S., Fontana, L., Cerra, S., Pietsch U., Scaramuzzo, F.A., Fratoddi, I. *Synthetic Metals*, 2022, **283**, 116973.

[3] Cerra S. Carlini L., Salamone T. A., Hajareh Haghighi F., Mercurio M., Pennacchi B., Sappino C., Battocchio C., Nottola S., Matassa R., Fratoddi I. *ChemistrySelect*, 2023, **8(13)**, e202300874.

Green synthesis of Pummerer's ketones by heterogeneous photo-biocatalysis

D. Piccinino[1*], N. Ceccotti Vlas[1], E. Capecchi[1], and R. Saladino[1]

[1]*Department of ecological and biological sciences, University of Tuscia, Viterbo, Italy*

**d.piccinino@unitus.it*

Pummerer's ketones are well known pharmacophores belonging in the morphine family. They are usually synthesized by tedious and multi-steps procedures which requires toxic metals as catalysts. Here we describe a sustainable alternative for the one-pot preparation of Pummerer's ketones by applying blue-LED irradiation in the presence of meso-tetraphenylporphyrin (meso-TPP) as photosensitizer and Horseradish Peroxidase (HRP), to catalyze the oxidative coupling of substituted phenols. In this process, HRP is activated by generated in situ organic hydro-peroxide of 2-Me THF avoiding the direct use of hydrogen peroxide which is recognized to inhibit the enzyme by over-oxidation of the iron atom in the prosthetic group. In particular, the reaction pathway involves singlet oxygen activation by blue-LED photon irradiation in the presence of meso-TPP, and its successive insertion into the tertiary α-ethereal carbon atom of 2-MeTHF to yield the corresponding organic hydro-peroxide. The photo-insertion process was highly selective and undesired radical species were not detected. In order to further improve the overall system, HRP was immobilized on the surface of electroactive lignin nanoparticles by using natural linkers, improving the stability of the enzyme and allowing the reuse of the catalyst. The heterogeneous system showed high catalytic activity and selectivity under buffer limiting conditions comparable to homogeneous counterpart. The application of lignin nanoparticles extended the effectiveness of the process to successive runs.

Acknowledgements:

We thank the large equipment building (CGA) located on the Riello's campus (University of Viterbo) for granting the analytical instrumentation that allowed the experimental activity of this work.

Formation of supramolecular structures of chiral porphyrin-bile salt conjugates

Luca Piccirillo [1,2], Valeria D'Annibale [1,2], Maria Chiara di Gregorio [2], Andrea Molella [2], Andrea D'Annibale [2] , Luciano Galantini [2] and Donato Monti [2]*

[1]Dept. of Basic and Applied Sciences for Engineering, Sapienza University of Rome
[2]Department of Chemistry, Sapienza University of Rome

Presenting author e-mail: luca.piccirillo@uniroma1.it

Porphyrin derivatives play a fundamental role in supramolecular chemistry thanks to their unique physical-chemical and structural characteristics, which make them versatile building blocks for construction of systems with broad interesting scientific and technological applications. Supramolecular chirality, one of the most fascinating aspects of supramolecular chemistry, allows the transfer of asymmetry information, within multimolecular systems through noncovalent interactions. It has profound implications in the field of nanotechnology, materials technology, catalysis, medicine, recently storage and data processing and in the construction of sensor devices with stereoselective properties.[1] The proposed project is aimed at the synthesis and characterization of chiral porphyrin derivatives, obtained through covalent conjugation with bile salts. In addition to inducing chirality, conjugation allows to impart amphiphilic characteristics to the aromatic macrocycle, important for their aggregation. Bile salts, natural surfactants with an important biological role, in fact show a rigid and chiral amphiphilic molecular structure, typical of steroids, which gives them specific auto-associative characteristics. These properties can be effectively exploited for the construction of highly organized supramolecular systems in aqueous solvents, characterized by a high degree of asymmetry, for applications in sensing and the biomedical field.[2] Circular dichroism studies have shown the presence of highly organized supramolecular structures, in water/organic solvent mixtures in different ratio, characterized by intense chirality, detectable by very intense CD signals. Morphological studies (SEM, AFM) have shown the high regularity of the morphology of the structures obtained, well-formed tubules, with a hierarchical fine structure (Fig. 1), were imaged, whose size (from nano to micro scale) depends on the selected conditions. Slight variations in solvents composition can strongly affect the kinetic of the aggregates formation.

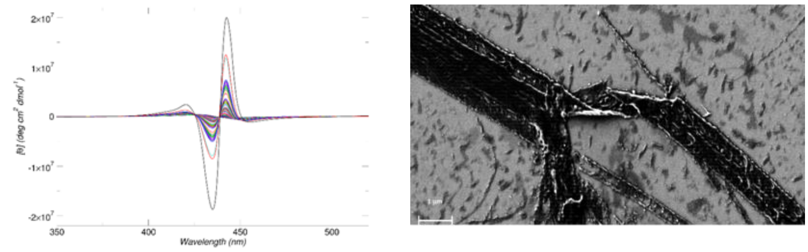


Figure 1. Intense CD signal, indicating the formation of chiral supramolecular aggregates (left). Micrometric tubular elongated structures observed with SEM (right).

References

[1] R. Paolesse, D. Monti, L. La Monica, M. Venanzi, A. Froiio, S. Nardis, C. Di Natale, E. Martinelli, A. D'Amico, Chem. Eur. J. 2002, 8, 2476 – 2483
[2] M. C. di Gregorio, L. Travaglini, A. Del Giudice, J. Cautela, N. V. Pavel, L. Galantini, Langmuir, 2019, 35, 6803-6821

Nanostructured Cerium Oxide-based catalysts for direct synthesis of dimethyl carbonate from methanol and CO_2

Rusta N[1*], Mameli V [1], F. Secci[1], S. Porcu[2], P. Seeharaj[3], D. Gazzoli[4], P. C. Ricci[2], Rombi E[1], Cannas C[1]

[1]*Department of Chemical and Geological Sciences, University of Cagliari, Cagliari, Italy*
[2]*Department of Physics, University of Cagliari, Cagliari, Italy*
[3]*Department of Chemistry, King Mongkut's Institute of Technology Ladkraban, Bangkok, Thailand*
[4]*Department of Chemistry, University "La Sapienza", Rome, Italy*

**n.rusta@studenti.unica.it*

Dimethyl carbonate (DMC) is a valuable eco-friendly compound, and its increasing demand is due to its various applications (polycarbonates, fuel and the lithium-ion battery industries). There are several synthetic pathways that are used for the production of DMC, but most of them involve toxic and dangerous substances, as reagents, catalysts, and by-products. For example, most of the industrial production of DMC still uses phosgene, a highly toxic chemical that can cause several health issues. In recent decades, research has been focused on developing more sustainable synthetic approaches that can replace the phosgene method. Currently the attention has been paid on the direct synthesis from methanol and CO_2, converting the latter from waste into fuel. However, this strategy still remains at laboratory level because of poor conversions and low yields of DMC, due to thermodynamic stability and kinetic inertness of CO_2. In order to overcome these drawbacks, new and efficient catalysts have been developed. Among all, Ce-based catalysts are particularly promising for their chemical stability, redox properties, and high catalytic activity.

In this work, low porosity CeO_2 and Fe-doped CeO_2 were prepared through hydrothermal (nanorods) and sol-gel self-combustion (SC) synthesis, mesoporous CeO_2 was obtained with a surfactant-assisted precipitation method, and impregnation methods were used to obtain mesostructured nanocomposites (10%wt CeO_2@SBA-15). The as-obtained catalysts were characterized using PXRD, TEM, FTIR, Raman and N_2-physisorption. In some cases, XPS measurements were performed.

The direct formation of DMC from methanol and CO_2 was carried out in a batch reactor by studying different parameters such as temperature, pressure, amount of catalyst, and volume of methanol. GC-FID was used to evaluate the DMC formation. The various synthetic strategies led to the obtainment of ceria-based systems with different microstructures and textures. CeO_2 and particularly Fe-doped CeO_2 nanorods are the most promising ones from the catalytic point of view, mainly due to the peculiar morphology. The superior performance of the Fe-doped nanorods could be ascribed to the co-presence of the hematite phase and the creation of the ceria/hematite interface. The worse catalytic performance is observed for the SC sample doped with iron where a complete insertion of iron into the ceria structure was achieved. Mesoporous CeO_2 shows intermediate performances. The homogeneous dispersion of ceria on SBA-15 through proper impregnation strategies (CeO_2@SBA-15) resulted to be a promising approach to design efficient catalysts. The effect of dehydrating agents is under study.

Intercalated polymeric hybrid structures designed for the removal of dyes from wastewater

Riccardo Sergi[1*], Roberta G. Toro[2], Tilde De Caro[2], María D. Alba[3], Abeer M. Adel[4], Daniela Caschera[2]

[1]*Department of Chemistry, University of Rome “La Sapienza”, Roma, Italy*
[2]*Institute for the Study of Nanostructured Materials, ISMN-CNR, Roma, Italy*
[3]*Instituto Ciencia de Materiales de Sevilla, CSIC-Universidad de Sevilla, Sevilla, Spain*
[4]*National Research Center, Cellulose and Paper Department, Giza, Egypt*

**riccardo.sergi@uniroma1.it*

Water pollution from industrial waste poses significant concerns due to its detrimental impacts on natural ecosystems and human health. Industrial waste, through various forms, contributes substantially to the contamination of water resources. The simultaneous presence of organic and inorganic pollutants in the wastewater has claimed the need for multiple pollutant removal. One technique used for this purpose is the adsorption process using adsorbent materials like clays or polymeric-based composites. In particular, special attention is focused on hybrid materials that, combining an inorganic matrix (host) with functional compounds (guest), have shown enhanced sorption properties and selectivity for heavy metals and hazardous dyes adsorption from wastewater. In this contest, cellulose-based adsorbents are considered promising as low-cost, easily available, biodegradable and nontoxic materials for the removal of contaminants [1].

In this work, we developed a hybrid host-guest system for the absorption of dyes from water. As inorganic matrix (host) was used a family of synthetic swelling fluorophlogopite ($Na_Y[Si_6Al_2]Mg_6O_{20}F_4 \cdot XH_2O$) (Micas), in particular Na-2-Mica and Na-4-Mica, containing respectively two and four sodium atoms [2]. The guest material consisted of cellulose nanocrystals (CNCs) extracted from date palm sheath fibers. A commercial polysaccharide, carboxymethylcellulose (CMC), was also tested as a guest compound to compare the adsorption of the composite materials obtained with CNCs. ATR-FTIR and Raman spectroscopy, X-ray diffraction analysis (XRD) and Thermogravimetric analysis (TGA) were conducted to study the formation of intercalated hybrid structures. The adsorption experiments were conducted on a solution of Methylene blue (MB) (3,7-bis(dimethylamino)-phenothiazin-5-ium chloride), a thiazine cationic dye extensively used to dye textiles, such as cotton, cellulose, wood, and silk. The results showed that the intercalation of polysaccharides (both CNC and commercial CMC) in Na-4-Mica structure permitted to obtain the highest absorption of MB, reaching a value of 86%. On the contrary, the hybrid cellulose-Mica composites obtained with Na-2-Mica showed a decrease in absorption, even compared to the pristine mica. This behaviour could be attributed to the different host structure and starting porosity of the Mica, which can influence the final absorption properties of the hybrid materials.

Sample	**Na-2-Mica**	**CNC-M2**	**CMC-M2**	**Na-4-Mica**	**CNC-M4**	**CMC-M4**
Absorption	70%	60%	58%	42%	86%	84%

Table 1. Absorption of MB with pristine Micas and hybrid materials in 24h.

References

[1] R. G. Toro, M. Diab, T. de Caro, M. Al-Shemy, A. Adel and D. *Materials* 13, **1326-1345**, 2020

[2] M. Carolina Pazos, Lisette Ruiz Bravo, Sebastián E. Ramos, Francisco J. Osuna, Esperanza Pavón, María D. Alba, *Applied Clay Science, Volume 196*, 2020

Gellan-chitosan polyelectrolyte complexation: from experiments to numerical simulations

Leonardo Severini[1*], Letizia Tavagnacco[1], Simona Sennato[1], Ester Chiessi[2], Claudia Mazzuca[2],
Emanuela Zaccarelli[1]

[1] Institute for Complex Sysytems, National Research Council (CNR-ISC) and Physics Department Sapienza University of Rome, Piazzale A. Moro 5, 00185, Rome, Italy
[2] Department of Chemical Science and Technologies, University of Rome "Tor Vergata", Via Della Ricerca Scientifica 1, 00133 Rome, Italy

*leonardo.severini@roma1.infn.it

Unveil the mechanisms that rule the self-assembly of macromolecular structures, at the nanoscale, is still considered the greatest challenge in soft matter. The fundamental aspects knowledge of the behavior of many colloidal systems is also relevant for improving the design and control of their technological applications. Indeed, due to their unique properties, colloids are widely involved in several different fields, spanning from bio-medicine to cultural heritage.[1,2] In this panorama, polyelectrolyte complexes (PECs) are still able to attract huge attention both for their complex phenomenology, arising from the balance between long-range electrostatic interactions, and short-distance steric ones, and for their important applications.[2] However, precisely this complexity makes them among the less known systems. To fill this knowledge gap, we performed an extensive study by means of experimental and numerical techniques in order to shed new light on the fundamental interactions and microscopic organization of the PECs, resulting from self-assembly of two well known oppositely charged polysaccharides, gellan and chitosan. Gellan is a water-soluble negatively charged exopolysaccharide, with a p*Ka* value of about 3.5.[3] Chitosan, a positively charged polysaccharide, is a product of deacetylation of chitin, with p*Ka* value spanning from 6.2 to 7 depending on degree of deacetylation.[4] Both polysaccharides are widely used in the field of biomedicine and food industry due to its biocompatibility, biodegradability and, for chitosan only, strong anti-bacterial properties.[5] The rapid and easy preparation strategy of gellan-chitosan PECs and the good dimensional control and time stability allow their use for many different applications.[5] In the present investigation the combination of light scattering, AFM microscopy, ATR-FTIR and CD spectroscopy with atomistic molecular dynamics simulations, exploiting our recently developed and validated gellan force field,[3] allowed to get significant clues to shed light on the microscopic aggregation mechanism of these two polysaccharides (Fig. 1).[6]

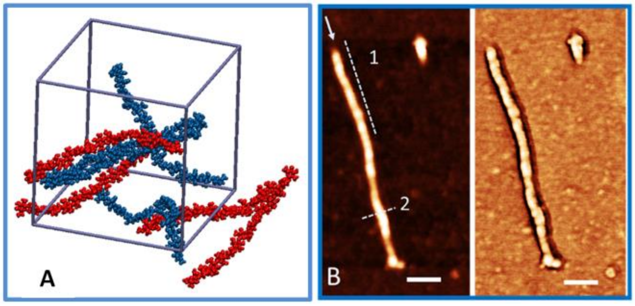


Figure 11. Representative snapshots A) and AFM images B) of gellan-chitosan PECs.

References

[1] Di Napoli B., Franco S., Severini L., Tumiati M., Buratti E., Titubante M., Nigro V., Gnan N., Micheli L., Ruzicka B., Mazzuca C., Angelini R., Missori M., Zaccarelli E. *ACS Applied Polymer Materials*, 2020, **2**, 2791-2801.
[2] Meka V.S., Sing M.K.G., Pichika M.R., Nali S.R., Kolapalli V.R.M., Kesharwani P. *Drug Discovery Today*, 2017, **22**, 1697-1706.
[3] Tavagnacco L., Chiessi E., Severini L., Franco S., Buratti E., Capocefalo A., Brasili F., Mosca Conte A., Missori M., Angelini R., Sennato S., Mazzuca C., Zaccarelli E. *Science Advances*, 2023, **9**, eadg4392.
[4] Kou S., Peters L.M., Mucalo M.R. *International Journal of Biological Macromolecules*, 2021, **169**, 85-94.
[5] Picone C.S.F., Cunha R.L. *Carbohydrate Polymers*, 2013, **94**, 695-703.
[6] Severini L., Tavagnacco L., Celi E., Sennato S., Chiessi E., Mazzuca C., Zaccarelli E. *Submitted*, 2024.

Theme G - Energy, Environment and Sustainability

Combined processes in the remediation of trichloroethylene-contaminated groundwater: Reductive Biological Dechlorination coupled with adsorption on biochar and supported by alternative materials from orgsnic wastes

M. Abruzzese[1*], L.Lorini[1], B. Matturro[2], M. Petrangeli Papini[1]

[1]*Department of Chemistry, University of Rome La Sapienza.*
[2]*Institute of Water Research (IRSA-CNR)*

**micaela.abruzzese@uniroma1.it*

In the context of the remediation of groundwater contaminated with chlorinated solvents, the issue of circularity appears essential for the design of truly sustainable environmental remediation interventions. In this regard, an approach to remediation of chlorinated solvent (SC)-contaminated groundwater using combined technologies is proposed. Specifically, we exploit the dechlorinating capacity of microorganisms of the genus Dehalococcoides, which typically select in situations of SC contamination, capable of degrading high-chlorinated compounds by successive steps of hydrogenolysis, producing 1,2 cis-dichloroethylene (c-DCE), vinyl chloride (VC) and finally the nontoxic ethylene. This approach is subject to limitations mainly due to the slow degradation kinetics of the contaminant, which typically conflicts with low residence times in the aquifer, and the lack of an electron donor. To solve the first critical issue, the possibility of combining Reductive Biological Dechlorination (BRD) with adsorption on a Biochar from pine wood (PWB), a solid by-product of pyrolysis of wood waste for energy valorization, was investigated [1]. For the electron donor, a biomass, taken from a water treatment plant, enriched in polyhydroxyalkanoates (PHAs), consequently to a stress condition, and using a solution rich in volatile fatty acids from the fermentation of the Organic Fraction of Municipal Solid Waste (FORSU) was used [2]. The experimental set-up included a vertical cylindrical mini-pilot-scale reactor, 144 cm high with a diameter of 10 cm, filled with sand and 4% w/w biochar, along the entire length, and also 4% w/w PHA, in the initial section; the reactor was continuously fed with tap water at a concentration of 0.1 mM in TCE, chosen as representative of SCs. The experiment was conducted continuously by varying the feed rate to investigate the process for widely varying residence times. The results show that the combination of adsorption with BRD supported by slow fermentation of PHA-rich biomass resulted in complete abatement of TCE up to 728 pore volumes passed. To date, more than 4,000 liters of contaminated water have been treated, the system is still active, and the process has not yet required material replacement. The very comforting results suggest the possibility of scaling up the process for both on-site applications (PRB/RZ) but also for on-site systems with possible recirculation of treated water.

References

[1] Rossi, M.M., Silvani, L., Amanat, N., Petrangeli Papini, M., 2021. Biochar from Pine Wood, Rice Husks and Iron-Eupatorium Shrubs for Remediation Applications: Surface Characterization and Experimental Tests for Trichloroethylene Removal. Materials (Basel). 14, 1776.

Recuperation systems for fluorinated gas at the CERN LHC Experiments

M. C. Arena[1,2], R. Guida[2], B. Mandelli[2], A. Profumo[1], D. Dondi[1], G. Rigoletti[2], M. Verzeroli[2,3]

[1]Dipartimento di Chimica - Università di Pavia, Via Torquato Taramelli, 12 27100 Pavia (PV)
[2]CERN, Esplanade des Particules 1, Meyrin, Switzerland
[3]Universitè Claude Bernard Lyon 1, Lyon, France

maria.cristina.arena@cern.ch

In the context of particle physics, different families of gaseous detectors are operated with gas mixtures containing fluorinated gases for different purposes at the Large Hadron Collider (LHC) at the European Organization for Nuclear Research (CERN). The main gases used in these detectors are tetrafluoromethane (CF_4), tetrafluoroethane ($C_2H_2F_4$), sulphur hexafluoride (SF_6), perfluorobutane (C_4F_{10}). Given their high Global Warming Potential (GWP) and the increasingly stringent European regulations regarding the use and trade of these gases, different approaches have been adopted for reducing the Green House Gas (GHG) emissions. One of the strategies, currently operating at the LHC Experiments, is the use of gas recuperation systems [1].

At the CERN LHC experiments four operational GHG recovery systems are operational: two for the CF_4, one for the R134a ($C_2H_2F_4$), and one for the C_4F_{10}. They are industrial-scale systems, each of which relies on different principles of gas separation and purification. Indeed, in most cases, fluorinated gases are used within gas mixtures where other components have lower Global Warming Potential (GWP). Considering the unique gas mixtures used in particle detectors, these recovery systems have been specifically developed as no industrial apparatus currently exists to address these particular requirements.

The separation of fluorinated gases is carried out mainly through membranes, absorbers, or distillation. In the case of CF_4, it is separated from a CF_4/Argon/CO_2 mixture (in the proportions of 10/40/50) [2]. The R134a is recuperated from a gas mixture of $C_2H_2F_4$/iC_4H_{10}/SF_6 (in the proportions of 95.2/4.5/0.3) where freon forms an azeotropic mixture with the isobutane. The C_4F_{10} is separated from CO_2, O_2 and N_2. The recovery system efficiencies are approximately 70% for the CF_4, 80% for the R134a, and 90% for the C_4F_{10}.

The goal is to reuse the purified gases within gas mixtures sent to detectors in variable fresh/recovered fractions, depending on the purity of the obtained gas (usually between 90% and 98%).

The various stages of the recovery processes are monitored through gas chromatographic analyses, GC/MS (Gas Chromatography/Mass Spectrometry), and infrared (IR) analyses.

The use of these recovery systems in recent years has led to significant savings both in economic and emissions terms at CERN. In 2023, 950 kg of recovered CF_4 were utilized out of a total of 2800 kg, and 1200 kg of R134a were used out of a total 20000 kg. It's worth noting that the R134a system is still under test, and it was operational only for some weeks starting from September 2023 onward.

The development and construction of two new recovery systems for SF_6 and C_4F_{10} are still ongoing, and they are expected to be operational by the end of 2024.

References

[1] R. Guida and B. Mandelli, Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment, 2020, vol. 958.

[2] M. Capeans, R. Guida, S. Haider and F. Hahn, 2011 IEEE Nuclear Science Symposium Conference Record, Valencia, Spain, 2011

Surfactant Enhanced Mobilization of Polycyclic Aromatic Hydrocarbons from Marine Sediment by Washing and Flushing Processes

Berardino Barbati[1*], Gabriele Moscatelli[2], Laura Lorini[1], Marco Petrangeli Papini[1]

[1]*Chemistry Department, Sapienza University of Rome, Rome (RM), Italy*
[2]*Chimcec S.p.A. Pomezia (RM), Italy*

**berardino.barbati@uniroma1.it*

Polycyclic aromatic hydrocarbons (PAHs) are one of the most impactful pollutant classes of soil, sediments, and groundwaters quality due to their strong toxicity and the high persistence of their secondary sources[1]. Thus, development of new methods to mobilize and make them more available are necessary for remediation purposes. In recent years, great scientific efforts have been concentrated on the possibility of employing surfactant solutions in flushing or washing processes of the contaminated matrix to increase the mobility and solubility of hydrophobic organic compounds (such as PAHs) and their mass transfer in aqueous phase[2]. In this context, a lab-scale study was carried out to evaluate the ability of eight biodegradable non-ionic surfactants, such as synthetic alkylpolyglycides (APGs), biological sophorolipids (SLs) and biological rhamnolipids (RLs) to solubilize and mobilize PAHs from a historically heavy contaminated marine sediment. The investigated sediment comes from the Italian National Priority Site of Bagnoli-Coroglio (Naples), which suffers from historical hydrocarbon contamination attributed to local steel industries that began operations in the early 20th century and were decommissioned in the early 1990s[3]. Consequently, this represents an aged contamination scenario where the remaining pollutants are highly recalcitrant, constituting the most persistent fractions, and exhibit markedly reduced mobility under standard environmental condition.

To evaluate the effectiveness of surfactants in solubilizing PAHs, a systematic study was conducted. First, the sediment was characterized to measure the initial PAH contamination level. Then, a preliminary batch washing test was performed at a surfactant concentration of 5 times the critical micelle concentration (CMC) to evaluate the ability of the surfactants to solubilize PAHs in the aqueous phase. Finally, a continuous configuration column experiment was carried out by selecting the best surfactants in terms of mobilization efficiency and their optimal concentration. Column experiments allowed to investigate PAHs mobilization under conditions representative of a real flushing process.

The present work provides a systematic guideline for the preliminary selection of surfactants for flushing/washing operation, the optimal operative conditions, and the technical approach for PAHs extraction from the sediment, especially in the context of a real aged contamination scenario. Experimental results showed that all investigated surfactants contributed to enhance the mass transfer of pollutants in the aqueous phase, with respect to the water. Column test showed a great efficiency of these surfactants in PAHs mobilization in continuous flushing of the contaminated matrix. Surfactants' performances resulted 40 times greater than water mobilization ability. Moreover, it will be shown almost the totality of the mobilization in the flushing process with the selected surfactants occurred in just 2 pore volumes of the feeding flushing solution. These data clearly underline and emphasize the incredible potential of surfactants in the treatment of matrices impacted by hydrophobic organic contaminants even in situations of historical contamination and particularly aged sources.

References

[1] Idowu O, Semple KT, Ramadass K, O'Connor W, Hansbro P, Thavamani P. Beyond the obvious: Environmental health implications of polar polycyclic aromatic hydrocarbons. *Environ Int*. 2019;123:543-557. doi:10.1016/j.envint.2018.12.051

[2] Bianco F, Race M, Papirio S, Esposito G. A critical review of the remediation of PAH-polluted marine sediments: current knowledge and future perspectives. *Resour Environ Sustain*. 2023;11(October 2022):100101. doi:10.1016/j.resenv.2022.100101

[3] Ruocco N, Bertocci I, Munari M, et al. Morphological and molecular responses of the sea urchin Paracentrotus lividus to highly contaminated marine sediments: The case study of Bagnoli-Coroglio brownfield (Mediterranean Sea). *Mar Environ Res*. 2020;154:104865. doi:10.1016/j.marenvres.2019.104865

Self-Assembling Peptide-Based Magnetogels for the Removal of Heavy Metals from Water

Roya Binaymotlagh [1*], Farid Hajareh Haghighi [2], Laura Chronopoulou [2], Sara Cerra [2], Andrea Giacomo Marrani [2], Francesco Amato [2], Cleofe Palocci [2], Ilaria Fratoddi [2]

[1] *Department of Chemistry, Sapienza University of Rome, Piazzale Aldo Moro 5, 00185 Rome, Italy*
[2] *Department of Chemistry, Sapienza University of Rome, Piazzale Aldo Moro 5, 00185 Rome, Italy*

**roya.binaymotlagh@uniroma1.it*

In this study, we present the synthesis of a novel peptide-based magnetogel obtained through the encapsulation of γ-Fe2O3 -polyacrylic acid (PAA) nanoparticles (γ-Fe2O3NPs) into a hydrogel matrix, used for enhancing the ability of the hydrogel to remove Cr(III), Co(II), and Ni(II) pollutants from water. Fmoc-Phe (Fluorenylmethoxycarbonyl-Phenylalanine) and diphenylalanine (Phe2) were used as starting reagents for the hydrogelator (Fmoc-Phe3) synthesis via an enzymatic method. The PAA-coated magnetic nanoparticles were synthesized in a separate step, using the co-precipitation method, and encapsulated into the peptide-based hydrogel. The resulting organic/inorganic hybrid system (γ-Fe2O3NPs-peptide) was characterized with different techniques, including FT-IR, Raman, UV-Vis, DLS, ζ-potential, XPS, FESEM-EDS, swelling ability tests, and rheology. Regarding the application in heavy metals removal from aqueous solutions, the behavior of the obtained magnetogel was compared to its precursors and the effect of the magnetic field was assessed. Four different systems were studied for the separation of heavy metal ions from aqueous solutions, including (1) γ-Fe2O3NPs stabilized with PAA, (γ-Fe2O3NPs); (2) Fmoc-Phe3 hydrogel (HG); (3) γ-Fe2O3NPs embedded in peptide magnetogel (γ-Fe2O3NPs@HG); and (4) γ-Fe2O3NPs@HG in the presence of an external magnetic field. To quantify the removal efficiency of these four model systems, the UV-Vis technique was employed as a fast, cheap, and versatile method. The results demonstrate that both Fmoc-Phe3 hydrogel and γ-Fe2O3NPs peptide magnetogel can efficiently remove all the tested pollutants from water. Interestingly, due to the presence of magnetic γ-Fe2O3NPs inside the hydrogel, the removal efficiency can be enhanced by applying an external magnetic field. The proposed magnetogel represents a smart multifunctional nanosystem with improved absorption efficiency and synergic effect upon applying an external magnetic field. These results are promising for potential environmental applications of γ-Fe2O3NPs-peptide magnetogels to the removal of pollutants from aqueous media.

Acknowledgments: The authors acknowledge the financial support of Sapienza Funding Grants Ateneo 2022 (RM1221867C322C1 and RM12218167B480E0).

References

[1] Binaymotlagh, R.; Chronopoulou, L.; Hajareh Haghighi, F.; Fratoddi, I.; Palocci, C. *Materials*, 2022, **15**, 5871.

[2] Hajareh Haghighi, F.; Mercurio, M.; Cerra, S.; Salamone, T.A.; Bianymotlagh, R.; Palocci, C.; Romano Spica, V.; Fratoddi, I. *J. Mater. Chem. B*, 2023, **11**, 2334–2366.

Material Characterization of Battery components through orthogonal techniques

Dario Bozzo[1*]

[1] *Alfatest Strumentazione Scientifica, Via Giulio Pittarelli, 97 00166 Roma (RM)*

**dario.bozzo@alfatest.it*

Since the battery market is rapidly growing within the last few years, the R&D is still trying to identify the best analytical techniques to fully characterize the single components and verify the final product fullfill all the requirements.

During this speech, we will briefly sum up which techniques Alfatest can propose for a full characterization of battery components, from raw materials up to the recycle.

In particular, we will show specific cases in which Scanning Electron Microscopy (SEM) and Laser Diffraction are applied to identify particle size and shape of cathode materials and the presence of contaminants, as well how to use Picnometry or Powder Rheometry to determine respectively the density and flowability of the powders.

Concerning the anode structure, we will show how porosimetry can help optimize the PSD of the separator and how SEM can help measure fiber size and membrane porosity, as well as explaining how different Thermal Analysis techniques can help evaluate the thermal properties of components in every phase of the process.

Composite Anion Exchange Membranes Based on Graphene Oxide for Water Electrolyzer Applications

Nicholas Carboni [1], Lucia Mazzapioda[1], Angela Caprì[2], Irene Gatto[2], Alessandra Carbone[2], Vincenzo Baglio[2], Maria Assunta Navarra[1,3]

[1]Dipartimento di Chimica, Università di Roma La Sapienza, P.le Aldo Moro 5, 00185 Rome, Italy
[2]Istituto di Tecnologie Avanzate per l'Energia "Nicola Giordano" (ITAE-CNR), Salita S. Lucia sopra Contesse 5, 98126 Messina, Italy
[3]Centro di Ricerca Hydro-Eco, Università di Roma La Sapienza, Via Antonio Scarpa 16, 00161 Rome, Italy

nicholas.carboni@uniroma1.it

Alkaline technology, alongside proton exchange membrane (PEM) electrolysis, constitutes one of the two primary low-temperature operation methods, spanning from room temperature up to 80°C. However, conventional alkaline technology faces limitations in renewable electricity storage due to poor performance and compatibility issues with intermittent operations, attributed to factors like large inter-electrode distances and the absence of a membrane separator. While alkaline water electrolyzers (AWEs) are surpassed by proton exchange membrane water electrolyzers (PEMWEs) in efficiency, PEMWEs suffer from durability issues and higher costs due to the use of PEMs like Nafion and Platinum Group Metal (PGM)-based catalysts. An emerging alternative, the polymer-based Anion Exchange Membrane Water Electrolyzer (AEMWE) holds promise by employing non-precious metal catalysts (NPMC) and less expensive membranes, aiming to combine the resilience of AWEs with the performance of PEMWEs in less corrosive environments. However, the poor hydroxide ion (OH^-) conductivity compared to protons (H^+) as well as thermal and chemical stability pose significant challenges in the development of anion exchange membranes (AEMs) [1].

To address these challenges, this study incorporated varying amounts (3%, 5%, and 7% w/w relative to polymer) of a filler into the Fumion® FAA-3 ionomer (10% w/w in NMP) using the solvent casting technique to fabricate AEMs. Graphene oxide (GO), synthesized via a modified Hummers method, was utilized as the additive to enhance hydroxide conductivity and membrane stability [2]. Electrochemical investigations were carried out in a 5 cm^2 single electrolysis cell, alongside morphological and structural characterizations employing various techniques [3,4].

Acknowledgements

This work has been developed within the framework of the project AMPERE funded by the Italian Ministry of University and Research MUR (FISR2019_01294; agreement CIG: 90877719DD – CUP: B84G19000220008)

References

[1] M. Carmo et al. Int. J. Hydrogen Energy 38, (2013), 4901
[2] C. Dongyang et al. ACS Appl Mater Interfaces 4(11), (2012), 5775
[3] I. Arunkumar et al. Int. J. Hydrogen Energy 52, (2024), 139-153
[4] J. Chen et al. Carbon 64, (2013), 225-229

On the Composition and Isomerism Effect in the Thermal and Structural Properties of Choline Chloride/Hydroxyphenol Deep Eutectic Solvents

Paolo Casu[1*], Matteo Palluzzi[1], Matteo Busato[1], Riccardo Spezia[2], Paola D'Angelo[1]

[1]Department of Chemistry, Sapienza University, Piazzale Aldo Moro 5, Rome, Italy
[2] Sorbonne Universite, CNRS, Laboratoire de Chimie Théorique, 4 place Jussieu, 75005 Paris, France

**paolo.casu@uniroma1.it*

Deep Eutectic Solvents (DESs) are a novel class of solvents formed by a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD), with a melting point considerably lower than what would be expected for the eutectic composition. DESs possess minimal vapor pressure, are non-flammable, exhibit high conductivity, strong solvation capabilities, and low toxicity, rendering them safer and more environmentally friendly solvents compared to typical organic solvents. In addition to these benefits, DESs can be customized for specific applications by altering one of the components or introducing new substituents. Many DESs documented in literature feature choline chloride as the HBA and a wide range of chemical species acting as HBDs, resulting in diverse characteristics and physical properties.

This study aims to illustrate how structural alterations in the HBD component can significantly impact the thermal properties of DESs, which are intricately linked to the interactions occurring at the atomic level in solution. Specifically, the investigation focuses on three systems formed by choline chloride with isomers of the hydroxyphenol: Catechol (ortho-isomer), Resorcinol (meta-isomer), and Hydroquinone (para-isomer). Differential scanning calorimetry (DSC) measurements were conducted on mixtures of these components at various molar ratios to analyze their thermal behavior. Infrared spectra were recorded to examine the formation of hydrogen-bond networks, particularly in the O-H stretching region. Molecular dynamics simulations were employed to provide detailed insights into the microscopic interactions among the components. This multidisciplinary approach enabled the elucidation of the structure-property relationship in these systems, laying the groundwork for the synthesis and development of novel DESs tailored for diverse applications.

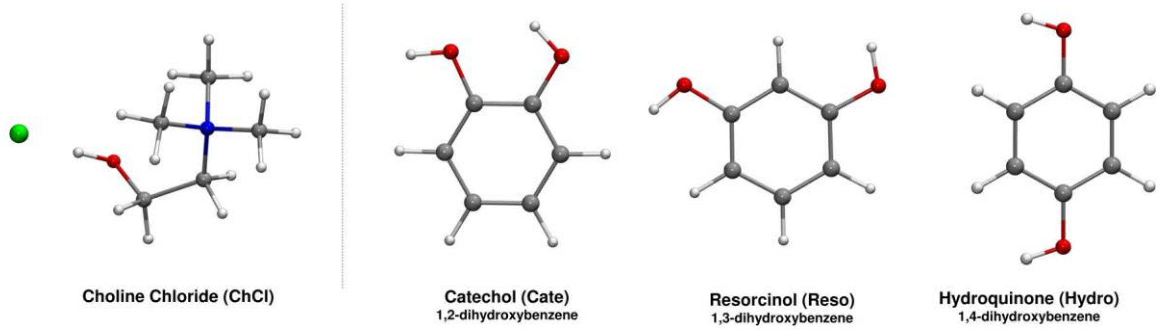


Fig. 1: Molecular structure of the pristine components employed in this work

References

[1] E. L. Smith, A. P. Abbott and K. S. Ryder, Chem. Rev. 2014, 114, 11060.

Calcium-zinc alloys as anodes for rechargeable non-aqueous calcium-ion batteries at room temperature

Andrea Ceppetelli[1,2], Mikaël Beaudhuin[2], Bernard Fraisse[2], Laure Monconduit[2,3,4], Sergio Brutti[1,3], Lorenzo Stievano[2,3,4]

[1] *Dipartimento di Chimica, Univ. di Roma La Sapienza, P.le Aldo Moro 5, 00185 Roma, Italia*
[2] *ICGM, Univ. Montpellier, CNRS, ENSCM, 34095 Montpellier, France*
[3] *ALISTORE-ERI, CNRS, Amiens, France*
[4] *RS2E, CNRS, Amiens, France*
* *andrea.ceppetelli @uniroma1.it*

Thanks to its low redox potential, its abundance on Earth's crust and its environmental compatibility, calcium metal batteries are emerging as alternatives to lithium-ion batteries [1]. However, the irreversible passivation of calcium metal anodes strongly hinders their development [2] and therefore to so-called calcium-ion batteries (CIBs) paradigm can represent a viable alternative. In fact, the adoption of alternative negative electrodes, not relying on the unsatisfactory reversibility of calcium metal plating-stripping processes, might allow new high energy density energy storage systems [3].

In this study we investigate the synthesis and characterisation of Ca-Zn alloys as negative electrodes. In this work, the possible application of calcium-zinc alloys as alloying anodes for CIBs is studied for the first time. Among various synthesis approaches, including electrochemical and thermal alloying as well as ball milling, arc-melting emerged as a straightforward technique for producing such alloys. This method consists on a direct application of electric arc which almost instantaneously melts calcium and zinc in the wanted stoichiometric ratio to obtain a homogeneous molten mass, which solidifies upon cooling forming dense ingot. The synthesized alloys were characterized by XRD (Figure 1a) and SEM/EDX, and their electrochemical activity was studied by cyclic voltammetry and galvanostatic charge/discharge experiments in symmetric (Figure 1b) and half-cell configurations with $Ca(TFSI)_2$-based electrolyte. Our findings reveal promising prospects for the future application of such alloys as negative electrodes in CIBs. Further details and implications of these results will be discussed during the presentation.

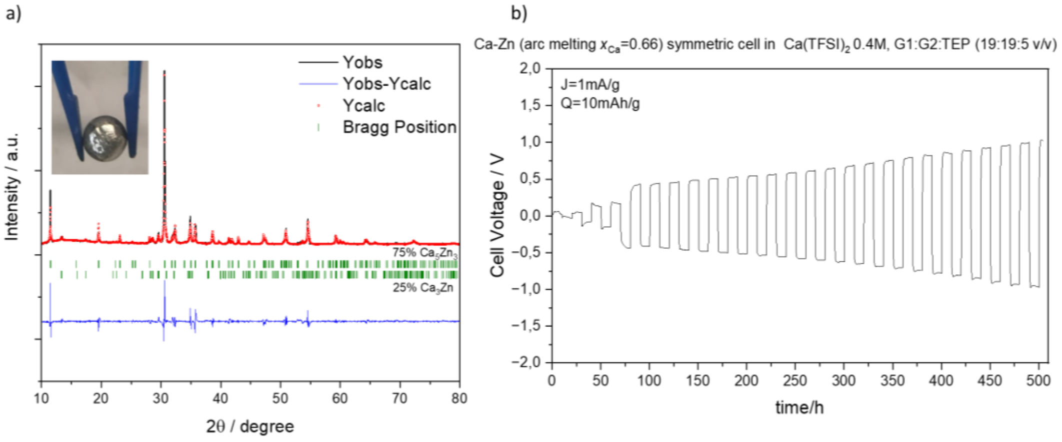


Figure 12 a) Rietveld refinement of Ca-Zn alloy (X_{Ca}=0.66) with inserted the image of the synthesized alloy b) galvanostatic cycling of the same alloy in symmetric cell.

References

[1] L. Stievano, I. de Meatza, J. Bitenc, C. Cavallo, S. Brutti and M. A. Navarra, J. Power Sources, 2021, 482, 228875. DOI:10.1016/j.jpowsour.2020.228875
[2] Zhao Y, Wang A, Ren L, Liu X, Luo J. Revealing the solid electrolyte interface on calcium metal anodes. Journal of Energy Chemistry, 2022, DOI: 10.1016/j.jechem.2022.02.022.
[3] Kwon BJ, Yin L, Bartel CJ, et al. Intercalation of Ca into a Highly Defective Manganese Oxide at Room Temperature. Chemistry of Materials. 2022;34(2):836-846. DOI:10.1021/acs.chemmater.1c03803

Impact of Support Material on *Candida rugosa* Lipase Immobilization Performance

Viviana Chiappini[1]*, Camilla Conti[1], Debora Casbarra[1], Maria Luisa Astolfi[1], Anna Maria Girelli[1]

[1] *Department of Chemistry, Sapienza University of Rome, P.le A. Moro 5, 00185 Rome, Italy*

**viviana.chiappini@uniroma1.it*

The use of lignocellulosic waste materials is becoming increasingly popular in the scientific landscape due to an ever-increasing drive towards a circular economy [1]. In fact, lignocellulosic wastes represent a large portion of the waste produced by the forestry and agriculture industries and can lead to a large environmental impact if not disposed correctly. Using these wastes as supports for enzymatic immobilization allows not only to recycle them but also to transform them into products with great added value [2]. Indeed, immobilized enzymes have considerable potential for their use in industrial processes thanks to their greater stability in harsh environments and the possibility of reusing the solid biocatalyst in more production cycles and keeping it active for a longer time during storage [3]. However, the integration of enzymes into industrial processes via immobilization is a complex effort, influenced by numerous factors including enzyme characteristics and environmental variables. Central to this process is the selection of the optimal immobilization method and suitable support materials, necessitating properties such as high surface area, mechanical strength, and compatibility with the enzyme. For this reason, this study investigates the immobilization of lipase from *Candida Rugosa* (CRL) on lignocellulosic wastes derived from rice husk (RH), brewer's spent grain (BSG), hemp tea waste (HTW), green tea waste (GTW), vine bark (VB), and spent coffee grounds (SCG), focusing on the characterization of these materials and their impact on the lipase-support interaction. The wastes underwent thorough characterization through ATR-FTIR, BET, and SEM analysis, as well as assessments of lignin content and surface hydrophobicity. Analysis of factors impacting immobilization efficacy underscored the significance of hydrophobic interactions. Examination of enzymatic desorption, triggered by varying ionic strength and detergent treatments, highlighted a blend of hydrophobic and electrostatic interactions across most supports, with HTW and GTW showcasing a dominance of hydrophobic interactions. Notably, HTW and SCG emerged as better carriers, displaying superior immobilization performance with the highest activity recovery (%), immobilization yield (%), immobilization efficiency (%), and immobilized activity (U/g).

Acknowledgments:

The authors gratefully recognize the support received from "La Sapienza" University of Rome, Italy.

References

[1] Girelli A.M., Chiappini V. *J. Biotechnol.*, 2023, **365**, 29–47.
[2] Girelli A.M., Astolfi M.L. Scuto F.R., *Chemosphere*, 2020, **244**, 125368.
[3] Mokhtar N.F., Raja Noor Zaliha R.N.Z.R., Muhd Noor N.D., Mohd Shariff F., Ali M.S.M. *Catalysts*, 2020, **10**, 744.

Influence of different synthetic routes in the structure and properties of lithium rich materials with high content of nickel for lithium batteries

Andrea Cioffi, [1] Arcangelo Celeste,[1] Laura Silvestri,[2] Sergio Brutti[1]

[1]*La Sapienza University of Rome, Department of Chemistry, Rome, Italy*
[2]*ENEA - Centro di Ricerche Casaccia - TERIN-PSU-ABI Rome, Italy*

a.cioffi@uniroma1.it

Lithium-ion batteries (LIBs) are the most important rechargeable battery technology for portable electronic devices. Among the array of active materials for positive electrodes, Li-rich layered oxides (LRLO) emerge as a promising class due to their ability to deliver high specific capacity (>250 mAh g-1), high voltage (>4.5V), and minimal or no cobalt content [1].

The most common stoichiometry of Co-free LRLO is $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ [2] to maximise the lithium content, balance the oxidation states of Mn and Ni and minimize the oxygen defectivities. Here we demonstrate the synthesis, characterization and functional properties in aprotic secondary batteries of a Ni-rich LRLO where the nickel content is above the current state-of-the-art benchmark.

Ni-rich LRLO compounds were synthesized via Solid-State (SS), Sol-Gel (SG), and Solvothermal (ST) routes. The synthesized materials underwent comprehensive characterization to assess the influence of synthetic methods on morphology (via scanning electron microscopy and nitrogen absorption), phase purity (using X-ray diffraction, Raman, and infrared spectroscopy), and structure (via synchrotron-based X-ray diffraction at ESRF). Electrochemical performance was evaluated through galvanostatic and voltammetry techniques. Rietveld refinements were conducted to delineate and compare structural variations arising from different synthetic routes, while electrochemical cell performance was evaluated by assembling aprotic secondary batteries with a commercial LiPF6 ethylene-carbonate/dimethyl carbonate electrolyte. Remarkably disorder and morphology have a huge impact on the reversibility of the galvanostatic cycling at room temperature.

References

[1] Impact of Ni Content on the Electrochemical Performance of the Co-Free, Li and Mn-Rich Layered Cathode Materials G. Qi , J. Hu, M. Balogh, L. Wang, D. Darbar and W. Li, *Electrochem* **2023**, *4*(1), 21-30.

[2] Impact of Overlithiation and Al doping on the battery performance of Li-rich layered oxide materials A. Celeste, F. Girardi, L. Gigli, V. Pellegrini, L. Silvestri, S. Brutti, *Electrochimica Acta,* **2022**,*4*28, 140737.

Combined electrochemical and hydrometallurgical approach for direct synthesis of Li-Mn-rich cathode material from end-of-life Li-ion batteries

Ludovica D'Annibale[1*], Pier Giorgio Schiavi[1], Francesca Pagnanelli[1], Pietro Altimari[1]

[1]*Department of Chemistry University La Sapienza of Rome, Piazzale Aldo Moro n.5, 00185, Rome, Italy*
**ludovica.dannibale@uniroma1.it*

In the last years, there has been an exponential increase in the use of lithium-ion batteries (LIBs) due to the rise in electric mobility, electronic devices, and energy storage systems [1]. On the other hand, many of the materials composing LIBs, such as graphite, Li, Co, Ni and Mn, are considered critical for EU [1-2]. To reduce the consumption of primary sources containing these materials and ensure a secure supply chain for the EU, recycling end-of-life (EoL) LIBs allowing to reintroduce LIB key components into the manufacturing chain becomes essential.

In this work, the study of an electrochemical process for Li recovery, and the development of a hydrometallurgical process to produce graphene oxide and Li- and Mn-rich (LMR) cathodes starting from LIBs black mass, are reported. The selective extraction of Li is attained by the electrochemical delithiation of the black mass using itself as anode in an electrochemical cell. Therefore, by its oxidation, the release of Li^+ cations will occur. The idea is to replicate a normal charging process of a LIBs but with an aqueous electrolyte and a counter electrode that allow the water reduction producing OH^-. This way, a LiOH solution will be obtained which can be used to recover lithium hydroxide. For comparison, the delithiation process was also tested on commercial cathode material ($LiMn_2O_4$, $LiCoO_2$, and $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$). For $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ a Li recovery of 99% was obtained while for the black mass from EoL LIBs, the 82% of Li was recovered. The role of black mass components (metal impurities, graphite, and conductive carbon) was evaluated on Li recovery yield. We found that conductive carbon is simultaneously oxidized decreasing the current required for Li extraction and thus lowering the Li recovery. After Li removal, the black masses were treated with the Hummers' method both for the quantitative extraction of metals from the electrodic powder and the production of graphene oxide (GO). The resulting solution contains the metals from the cathode materials (Co, Ni, Mn) with a significant amount of Mn comes from the $KMnO_4$ used as a reagent for the Hummers' method. This solution was used for the co-precipitation of $Ni_{0.375}Mn_{1.375}Co_{0.25}(OH)_2$ precursor for the LMR cathode production by sintering it in air after the addition of a Li source.

The future perspective aims to obtain LiOH salt through the electrochemical recovery of lithium and utilize it for cathode synthesis. This way allows to synthetize a cathode material in which the critical raw materials (Li, Mn, Co, and Ni) come all from spent Li-ion batteries.

Acknowledgements:

This work was funded by the European Union under Grant Agreement No 101069685. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the CINEA. Neither the European Union nor the granting authority can be held responsible for them.

References

[1] Brian M., Qinghua T., Xueyi G., Kinnor C. and Dawei Y., *Journal of Power Sources*, 2021, vol. 491.
[2] Xiaowei D., Wenkun Z., Zhongkui R., Min X., Juan C., and Xiaohan R., Energies, 2022, vol. 15, no. 5.

Methanol – based fuel gels

Alessia De Cataldo[1*], Luigi Gentile[2,3]

[1] Aerospace Science and Engineering (Inter-University Ph.D.) Polytechnic of Bari and University of Bari Aldo Moro, Via Orabona 4, 70126 Bari, Italy
[2] Department of Chemistry, University of Bari Aldo Moro, Via Orabona 4, 70126 Bari, Italy
[3] Center of Colloid and Surface Science (CSGI), Bari Unit, Via Orabona 4, 70126 Bari, Italy

**a.decataldo3@phd.poliba.it*

The growth of the space economy in the last sixty years motivated recent research to identify and characterize eco – friendly fuels for aerospace propulsion, since most of the existing propellant systems are very toxic, hazardous in nature, difficult to store and very expensive to synthesize. [1,2] One of the fuels identified is a gel fuel, that combines both solid and liquid fuels. Gelled fuels have attracted increasing attention because they are resistant to leakage and easy to store and transport as solid fuels and can help realize controllable thrust and multiple starts of engine similar to liquid fuels. [3] Gels are soft semi – solid materials that consist of a gelling agent solubilized in a solvent. Polymers can act as thickener and gellant, leading to the formation of a polymeric 3D - network in which the solvent can penetrate and be stored and entrapped.

In this study, we propose the simple and cheap formulation of methanol – based fuel gels using the polysaccharide methylcellulose (MC) as gelling agent. [4] We introduced calcium chloride ($CaCl_2$) as a thermal additive to improve the sample properties and enhance combustion performance. We solubilized the salt [4,5] in methanol and added the polymer. We then fine-tuned the ratio between the polymer and the salt to optimize the fuel gel formulation. Rheological measurements and thermogravimetric analysis (TGA) were performed to investigate the viscoelastic and thermal properties of the developed gels.

The obtained results demonstrate the phenomenon of gelation process of MC in methanol. TGA reveals that MC exhibits good thermal stability in methanol, with a decomposition temperature close to that of pure MC. Besides, TGA analysis show weight losses at specific temperatures corresponding to the presence of $CaCl_2$ – methanolates. $CaCl_2$ partially prevent methanol evaporation at low temperatures. Temperature sweep measurements show that the gel state is retained until a temperature between 90 and 97 °C, depending on the MC:$CaCl_2$ ratio, due to the non – volatile fraction of methanol bound to $CaCl_2$. Afterward, a solid – like behaviour is observed. The combustion performance indexes calculated from TGA data indicate improved combustion and ignition performance with the addition of $CaCl_2$.

References

[1] M. S. Naseem, B. V. S. Jyoti, S. W. Baek, H. J. Lee and S. J. Cho, *Prop., Explos., Pyrotech.*, 2017, **42**, 676–682.
[2] M. N. Shoaib, B. V. S. Jyoti, S. W. Baek and J. Huh, *Propellants Explo Pyrotec*, 2018, **43**, 453–460.
[3] K. Xue, J. Cao, L. Pan, X. Zhang and J.-J. Zou, *Front. Chem. Sci. Eng.*, 2022, **16**, 819–837.
[4] A. De Cataldo and L. Gentile, *Carbohydrate Polymers*, 2024, **323**, 121413.
[5] K. B. Domovs and E. H. Freund, *Journal of Dairy Science*, 1960, **43**, 1216–1223.

Hybrid geopolymer materials and Neapolitan Yellow Tuff for Cs(I) ions removal from aqueous solution

F. De Paola[1*], G. De Tommaso[1], M. Iuliano[1], O. Tarallo[1], G. Pinto[1], F. Montagnaro[1], M. Balsamo[1], G. Roviello[2], C. Ferone[2], E. Chianese[3], G. Germano[4], G. De Tullio[4], V. Angeletti[5], R. Sabbia[5]

[1] *Department of Chemical Science, University of Naples "Federico II", via Cinthia, 80126, Naples, Italy*
[2] *Department of Engineering, University of Naples "Parthenope", Centro Direzionale, Isola C4, 80133 Naples, Italy.*
[3] *Department of Science and Technologies, University of Naples "Parthenope", Centro Direzionale, Isola C4, 80133 Naples, Italy.*
[4] *Centro Regionale Radioattività, ARPAC, Via Lanzalone 54/56, 84100, Salerno, Italy.*
[5] *Area Analitica del Dipartimento Provinciale di Salerno, ARPAC, Via Lanzalone 54/56, 84100, Salerno, Italy.*

**fulvio.depaola@unina.it*

Cesium is found in the environment in the form of the radioactive isotope (^{137}Cs) caused by radioactive fallout. ^{137}Cs is also widely used as a sterilising agent and in radiotherapy, by using artificial or natural solid phases, the removal of pollutants is possible.

Geopolymers are aluminosilicates characterized by a structure tectosilicate like and are prepared from an alumino-silicate material, treated with an alkaline solution of sodium silicate. By adding a silicone component of 10% (w/w) [1] to the geopolymer, a material with good mechanical properties as well as high fire resistance is obtained. The Neapolitan Yellow Tuff (NYT), which is found as a sedimentary rock in Campania, in the Phlegraean region, has a zeolitic matrix on whose surface there are both acid-base behavior sites (silanol and aluminolic groups) and ion exchange sites.

Aim of this study is to analyse the effectiveness of removing of cesium from aqueous solutions by adsorption A preliminary study of the surface acid-base properties of the NYT and the hybrid geopolymer was conducted by potentiometric titration at 25 °C in 0.01 M $NaClO_4$, with the measurement of the free hydrogen ion concentration (pH). The results of this study indicated that the solids exhibited surface acid-base properties, which were attributed to the silanol and aluminol groups. Due to the presence of these sites, the solids show important adsorbent properties that can be exploited for the decontamination of environmental samples [2]. Kinetic studies were conducted in 0.01 M $NaClO_4$ as an ionic medium and at pH 5.5, the results indicate that equilibrium between the solid and aqueous phases is reached at 25 °C within 3 hours. Furthermore, the adsorption process follows pseudo-second-order kinetics, compatible with two-steps intraparticle diffusion. From the trends of the adsorption isotherms for Cs(I), it can be deduced that the experimental data are compatible with Langmuir's model for both solids, from data collected at different temperatures it is possible to obtain thermodynamic [3] (ΔG^0, ΔH^0, and ΔS^0) and kinetic parameters as the activation energy.

Acknowledgements:

This study was carried out within the RETURN Extended Partnership and received funding from the European Union Next GenerationEU (National Recovery and Resilience Plan – NRRP, Mission 4, Component 2, Investment 1.3 – D.D. 1243 02/08/2022, PE0000003)

References

[1] G. Roviello, L. Ricciotti, A. J. Molino, C. Menna, C. Ferone, R. Cioffi, O. Tarallo, *Molecules*, 2019, **24**, 3510.
[2] G. Pagano, M. Guida, F. Tommasi, R. Oral, *Ecotoxicology and Environmental Safety*, 2015, **115**, 40.
[3] L. Lu, J. Li, D. H. L. Ng, P. Yang, P. Song, M. Zuo, *Journal of Industrial and Engineering Chemistry*, 2017, **46,** 315.

Shifting towards sustainable coagulants for the removal of microplastics

Marco Facchino[1*], Loris Pietrelli[2], Patrizia Menegoni[3], Mauro Capocelli[1], Marcella Trombetta[1], Francesco Basoli[1] and Marcello De Falco[1]

[1] Department of Science and Technology for Sustainable Development and One Health, Università Campus Bio-Medico di Roma, via Álvaro del Portillo, 21, 00128, Rome, Italy
[2] Legambiente, Scientific Committee, Via Salaria 403, 00199 Rome, Italy
[3] ENEA–SSPT, CR Casaccia Via Anguillarese, 301, Rome, Italy

**marco.facchino@unicampus.it*

The present study focuses its attention into the development of a sustainable method for the removal of microplastics (MPs) from secondary wastewater effluents. Coagulation/flocculation treatment has been proposed as a feasible solution for microplastics removal from wastewater, since plants adopting this technology have been found able to reach removal rates up to 99.2% when coupled with a tertiary treatment and to 81.6% if considering the single unit [1]. Nonetheless, one of the major drawbacks of this kind of process lies in the use of chemicals such as polyaluminium chloride and ferric chloride, which application implies further treatment to meet the discharge requirements [2]. Through the last forty years, high molecular weight flocculants have been developed and used to improve flocculation and settling performance simultaneously lowering coagulant dosage, possibly leading to a decrease of both the economic and environmental burdens. Among these, the end of twentieth century saw the spread of natural flocculants, bio-sourced polymers characterized by high biodegradability and lower toxicity in comparison with the more affirmed synthetic ones [3]. Thus, the effectiveness of biopolymers in enhancing coagulation/flocculation performance with regard to microplastics removal from water was tested. Coagulation/flocculation tests were carried out using a 500 mL beaker and a magnetic stirrer. MPs made of polystyrene (PS), high-density polyethylene (HDPE) and polyethylene terephthalate (PET), with different shapes and a size lower than 500 μm were used. The removal of each polymer was studied separately. The MPs were spiked and dispersed into water, at an initial concentration for each test was 300 mg L^{-1}. Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) was used as primary coagulants, while chitosan (CH, $C_{56}H_{103}N_9O_{39}$) and sodium alginate (SA, $NaC_6H_7O_6$) were tested as coagulant aids. Each test was divided in three phases, namely coagulation, flocculation, and sedimentation. pH was maintained between 6.5 and 7.5. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were used for pH adjustment. Three blank tests for each polymer were conducted to estimate the sedimentation of particles without coagulant addition. To assess the removal efficiency achieved by the process, MPs concentration was measure gravimetrically. Results from coagulation experiments have shown that both CH and SA are useful for enhancing the removal performance of ferric chloride with respect to MPs of different polymeric nature. The use of CH allows a reduction of coagulant dosage for removing PS and HDPE particles, while it turned out to be detrimental for the removal of PET fragments. Instead, SA at a concentration of 0.2 mg L^{-1} proved to be useful both to achieve higher removal rate at a medium dosage of coagulant- i.e., 12 mg L^{-1}- and to improve the efficiency of the process at lower dosages.

References

[1] H. Hidayaturrahman and T.-G. Lee, Mar Pollut Bull, vol. 146, pp. 696–702, 2019, doi: https://doi.org/10.1016/j.marpolbul.2019.06.071.
[2] J. Duan and J. Gregory, Adv Colloid Interface Sci, vol. 100–102, pp. 475–502, 2003, doi: https://doi.org/10.1016/S0001-8686(02)00067-2.
[3] M. Lapointe and B. Barbeau, Sep Purif Technol, vol. 231, p. 115893, 2020, doi: https://doi.org/10.1016/j.seppur.2019.115893.

Microbial electrosynthesis from CO_2 with a mixotrophic stage to reduce methanogenesis and the start-up phase

Jacopo Ferretti*[1], Ludovic Jourdin[2], Marianna Villano[1], Marco Zeppilli[1]

[1]*Departmen of Chemistry, University of Sapienza, Rome, Italy*
[2]*Department of Biotechnology, Delft University of Technology, Delft, Netherlands*

**jacopo.ferretti@uniroma1.it*

The development of bioelectrochemical processes for CO_2 reduction into acetate is limited by the presence of competitive reactions, such as methanogenesis. Methanogenesis is usually long-term inhibited using chemical inhibitors, affecting industrial development of the technology. In this study, the possibility of exploiting the ability of acetogens to use organic substrates such as fructose and glucose was evaluated to improve the start-up phase of the process and promote rapid adhesion to the electrode, while promoting the washout of methanogens which they are unable to use carbohydrates in their metabolism. The study was conducted in 4 continuous reactors. Each reactor consisted of a biocathode and an anode compartment of the same volume (0.09 L). A thermally pretreated sludge and a raw one were used as inoculum in the cathodic chamber of the bioelectrochemical reactors. The cathodic chamber of each bioelectrochemical reactor was continuously fed by a mineral medium with a hydraulic retention time (HRT) of 4 days, while, through a sorption column, a mixture of CO_2 and N_2 (50% v/v respectively) was provided as inorganic carbon source. All reactor's catholyte was maintained at pH 5.8 while temperature was controlled at 32°C. During the first operating period, two reactors were conducted under mixotrophic regime, feeding fructose and glucose to the cathodic chamber and providing a current of -63 mA, while the other two reactors were operated under heterotrophic conditions providing only fructose and glucose to the cathodic chamber. The stage 2 operating period, all bioelectrochemical reactors were polarized under galvanostatic condition controlling the current at -63 mA. Mixotrophic regime during stage 1 promoted the production of acetate, butyrate and hexanoate compared to the heterotrophic phase; while stage 2 stably produced acetate at a rate of 1 g L^{-1} d^{-1} with an efficiency of 25.0±6.8%. During stage 1, acetate concentration reached 5.1±0.7 g L^{-1} in the first 5 days, while in strictly autotrophic conditions 30 days were required to reach the same acetate concentration. Interestingly, the same acetate concentration was reached in 110 days (Cabau-Peinado et al.), using autotrophic condition and methanogens chemical inhibitors using the same experimental setup showing the advantage of a mixotrophic startup on biocathode activity. Methane production was activated starting from day 40, reaching a production efficiency of 1.0%, suggesting that it is possible to inhibit it by avoiding the use of chemical inhibitors.

Reference

Cabau-Peinado, O., Winkelhorst, M., Stroek, R., de Kat Angelino, R., Masania, K., Marc Daran, J., & Jourdin, L. (n.d.). *Microbial Electrosynthesis from CO 2 reaches Productivity of Syngas and Chain Elongation Fermentations 2*. https://doi.org/10.1101/2024.02.08.579422

Effect of air quality on oxidative stress and elemental levels in hair and urine of Italian and Chilean students

Roberta Giorgione[1], Manuel Andres Leiva Guzman[2], Daniela Pigini[3], Lorenzo Massimi[1],
Maria Luisa Astolfi[4],

[1]Department of Environmental Biology, Sapienza University of Rome, Rome, Italy;
[2]Department of Chemistry, University of Chile, Santiago, Chile;
[3]Department of Occupational and Environmental Medicine, Epidemiology and Hygiene, INAIL, Monte Porzio Catone, Rome, Italy;
[4]Department of Chemistry, Sapienza University of Rome, Rome, Italy

* *roberta.giorgione@uniroma1.it*

In this study, urinary oxidative stress biomarkers and the concentrations of 41 elements were determined in the hair and urine of students from two universities: one located in Rome and one in Santiago, Chile. In addition to biological samples, PM10 samples were collected and analyzed elemental content and oxidative potential (OP; measured using cell-free DCFH, AA, and DTT assays). All elements were analyzed by ICP-MS and HG-AFS (1,2); while oxidative stress biomarkers were determined by HPLC/MS-MS. The final concentration of the analytes was expressed in μg/g of creatinine to normalize values with respect to urine dilution variability (3). When processing the data, the influence of some variables related to the participating students was evaluated, such as age, sex, body mass index, smoking and diet. The average PM10 concentration was 26 μg m-3 in Rome and 71 μg m-3 in Santiago, Chile, indicating significantly different inhalation exposure levels in the two areas. In particular, levels of Cu, Mo, Sn, and Sb, tracers of non-combustive vehicular traffic (mechanical abrasion of brakes; 4,5), showed significantly higher concentrations in Chilean PM10 samples compared to Italian ones. The OP values measured by the DCFH and AA assays were also clearly higher at the Chilean site, confirming a significant contribution of non-combustive vehicle traffic to the oxidative potential of dust. The different elemental concentrations in PM10 translated into different metal and metalloid accumulation levels in the two studied biological matrices. The elements that presented the most significant differences between Italian and Chilean students in both biological matrices were Cs, Hg, Mg, Mo, Rb, Sr, Tl, Zn. On the contrary Al, and Sn varied significantly in urine and hair, not in reference to the geographical area but depending on the participant's gender.

References

[1] Astolfi, M. L., Protano, C., Marconi, E., Massimi, L., Piamonti, D., Brunori, M., ... & Canepari, S. (2020). *International Journal of Environmental Research and Public Health*, **17**(6), 1911.

[2] Astolfi, M. L., Protano, C., Marconi, E., Massimi, L., Brunori, M., Piamonti, D., ... & Canepari, S. (2020). *Analytical methods*, **12**(14), 1906-1918.

[3] Buonaurio, F., Borra, F., Pigini, D., Paci, E., Spagnoli, M., Astolfi, M. L., ... & Tranfo, G. (2022). *Toxics*, **10**(5), 267.

[4] Thorpe, A., & Harrison, R. M. (2008). *Science of the total environment*, **400**(1-3), 270-282.

[5] Massimi, L., Ristorini, M., Simonetti, G., Frezzini, M. A., Astolfi, M. L., & Canepari, S. (2020). *Environmental Pollution*, **266**, 115271.

Supercritical carbon dioxide-based approach for recovery and purification of polyhydroxyalkanoates from crops-mixed microbial cultures

Farid Hajareh Haghighi[1*], Roya Binaymotlagh[1], Laura Chronopoulou[1,2], and Cleofe Palocci[1,2]

[1] Department of Chemistry, Sapienza University of Rome, Rome, Italy
[2] Research Center for Applied Sciences to the Safeguard of Environment and Cultural Heritage (CIABC), Sapienza University of Rome, Rome, Italy

** farid.hajarehhaghighi@uniroma1.it*

Petroleum-based plastics are non-biodegradable polymers associated with many environmental concerns, including persistence in marine, greenhouse gas emissions, terrestrial ecosystems, land pollution, etc. On the other hand, bioplastics have been developed as a rapidly growing class of biodegradable polymeric materials that are commonly considered as promising alternatives to conventional petroleum-based plastics. Polyhydroxyalkanoates (PHA) are a group of natural biodegradable polymers that are synthesized using fermentation technologies on different microorganisms. Current PHA production methods require organic solvents for the removal of residual fermentation media necessary for high quality products [1]. In this study, the CO_2-supercritical extraction technique (sCO_2) was employed, as a green technology, to selectively recover and purify polyhydroxyalkanoates (PHA's) from crops-mixed microbial cultures using different multi-step protocols including: the presence of co-solvents (methanol, H_2O, and phosphate buffer solution), pre- and post-treatment of the biomass (with enzymes and H_2O_2), different times (2-4 h), temperatures (40-60°C), and pressures (20-35 MPa) of the sCO_2-tretmenat. Among the tested protocols, the post-treatment of biomass with H_2O_2 and enzyme (sCO_2-H_2O_2-trypsin) resulted the highest PHA recovery and purity. The results show the importance of sCO_2-based techniques, as valid alternative to techniques that exploit chlorinated solvents, identifying green chemistry as a turning point for the industrial production of the biopolymer starting from a complex biomass feedstock.

References

[1] Censi V., Saiano F., Bongiorno D., Indelicato S., Napoli A., Piazzese D. Front. Chem., 2022, **10**, 971792.

Evaluation of two electrodeposition methods for the synthesis of Zn-based CO_2 electroreduction catalysts

Silvia iacobelli[1*], Francesca D'alta[1], Olga Russina[1], Pier Giorgio Schiavi[1], Francesca Pagnanelli[1], Pietro Altimari[1]
[1]*Department of Chemistry, Sapienza University of Rome, Rome, Italy*
**s.iacobelli@uniroma1.it*

A promising process to reduce carbon dioxide emissions and simultaneously accumulate energy deriving from renewable sources, is the electroreduction of carbon dioxide (ERC). This is an electrocatalytic process that uses electric energy to convert CO_2 into fuels and/or chemicals (e.g. carbon monoxide, formic acid, methanol) [1], with the products synthesized depending mainly on the different metals used as catalysts. It has been demonstrated that Cu is capable of catalysing the formation of C-C bonds, allowing to synthesize simple hydrocarbons. However, Cu based catalysts typically yield a wide distribution of products, which can make complex and costly the downstream separation. High selectivity (up to 90%) towards CO has been, in contrast, attained by the application of noble metal catalysts (Au, Ag, Pd) [2]. The high costs of such metals have recently shifted the researchers' interest to more widely available metals [3]. Among these, zinc-based catalysts emerged as a promising alternative being selective towards CO.

In this study, two different electrodeposition methods were used to synthesize zinc-based electrocatalysts for the ERC process. The first method is the bubbling electrodeposition. In the application of the method, sufficiently large cathodic potentials are selected to reduce the zinc at the employed substrate, generating, at the same time, hydrogen bubbles through water reduction. The bubbles work as templates, leading to the growth of a foam with hierarchical porous structure with high specific surface, whose thickness can be controlled by modifying the electric charge transferred during the electrodeposition. This structure is particularly suited for the application in electrolyzer configurations with the CO_2 supply mediated by the dissolution into the liquid phase (liquid-fed cells) [4]. In the present study, zinc foams were deposited onto two different substrates (copper foil and carbon paper) under galvanostatic conditions. The influence of different electrodeposition current densities (1, 2 A/cm^2) and transferred charges (60, 120 C) on the morphology, structure and amount of deposited zinc was investigated. SEM images revealed that the average pore size decreased increasing the electrodeposition current density from 1 to 2 A/cm^2 at 60 C transferred charge, which could be imputed to the increased number and lower size of bubbles generated at larger current density. Increasing the transferred charge from 60 to 120 C led, however, to the partial disappearance of the pores, which was accompanied by a decrease in the faradaic efficiency towards CO at all the potentials selected. The activity of fabricated electrodes was evaluated trough catalytic tests carried out in a H-type cell under potentiostatic conditions at different electrode potentials (-1.5, -1.7, -1.9 vs. Ag/AgCl) yielding a maximum faradaic efficiency towards CO of around 60%.

In the future perspective of using zinc-based electrodes in a vapor fed electrolyzer with membrane electrode assembly (MEA) configuration [5], the second electrodeposition method involved applying low constant potentials to deposit thinner films onto the underlying substrate. Both carbon paper and copper foil were used as support and different potentials (-1.5, -2.0 vs. Ag/AgCl) and bath compositions were evaluated. Again, SEM analysis was performed to evaluate the effect of the electrodeposition parameters on the morphology of the electrodes and ERC tests were performed by varying the working electrode potential. For this set of electrodes, it was found that the highest faradaic efficiency towards CO (around 65%) was obtained from electrodes with higher amount of zinc electrodeposited.

Acknowledgements: The research received funding from MUR under the PNRR project "Energy Sustainable Transition - NEST" project (MIUR project code PE000021, Concession Degree No. 1561 of October 11, 2022) – CUP C93C22005230007.

References

[1] Feng. L., Kaiwen Z., Lei Z., Yingjie. Z., Yong L., Xueliang S. *Small*, 2021, **17**, 2100323.
[2] Toru H., Kendra P. K., Etosha R C., David. N. A., Thomas. F. J. *PCCP*, 2014, **16**, 13814-13819.
[3] Dong D. Z., Jin L. L., Shi Z. Q. *Advanced Materials*, 2016, **28**, 3423–3452.
[4] Zekun Z., Shiji L., Yongfang R., Liu Y., Wei Y., Hao X. *Chemical Engineering Journal*, 2024,**479**, 147376
[5] Zheng Z., Xin H., Zhou C., Junjiang Z., Balázs E., Csaba J., Dehui D. *Angew. Chem. Int. Ed.* 2023, **62**, e202302789

Frontiers in 2D Materials for water splitting derived Green Energy: A Focus on Current Challenges and Opportunities

Kassa Belay Ibrahim,[1] Tofik Ahmed Shifa,[1] Elisa Moretti,[1] Alberto Vomiero[1,2]

[1] *Department of Molecular Sciences and Nanosystems, Ca' Foscari University of Venice, Via Torino 155, 30170 Venezia Mestre, Italy*
[2] *Division of Materials Science, Department of Engineering Sciences and Mathematics, Luleå University of Technology, SE-97187 Luleå, Sweden*

**kassabelay.ibrahim@unive.it*

Water oxidation using efficient catalyst, which is the anodic half-reaction of water splitting, plays a critical role in generating clean and abundant H2 fuel. 2D materials have emerged as promising candidates for water oxidation due to their unique properties such as their high surface-to-volume ratio, tunable electronic band structures, and large active surface areas.[1, 2] Yet, the key challenges of the field are (1) the activity, stability, and scalability of 2D nanostructures materials. Surface reconstruction and heterointerface engineering techniques have been employed to enhance properties such as electrical conductivity, stability, facile charge transfer, as well as to activate intrinsically active edge sites. These properties significantly influence the water oxidation performance of 2D nanostructures materials. (2) Another challenge is related to surface engineering, as the surface properties of 2D nanostructures materials greatly impact their performance in water oxidation. Optimizing the surface chemistry and morphology of 2D nanostructures materials is crucial for achieving high catalytic activity and stability. (3) Electrochemical performance is also a critical factor in the efficiency of water oxidation using 2D nanostructures materials. (4) Integration of catalysts is another challenge in the field. Strategies such as anchoring catalysts onto the surface of 2D nanostructures materials[3, 4] or surface confinement[5] have been investigated to achieve efficient water oxidation performance. Furthermore, the synthesis and characterization of 2D nanostructures materials for water oxidation require careful consideration. We will summarize the latest developments in the field, including results from our lab, highlighting the critical role of 2D composites to boost functionality toward efficient water oxidation.

References

[1] K. B. Ibrahim, M.-C. Tsai, S. A. Chala, M. K. Berihun, A. W. Kahsay, T. A. Berhe, W.-N. Su and B.-J. Hwang, *Journal of the Chinese Chemical Society*, 2019, **66**, 829-865.

[2] K. B. Ibrahim, W.-N. Su, M.-C. Tsai, S. A. Chala, A. W. Kahsay, M.-H. Yeh, H.-M. Chen, A. D. Duma, H. Dai and B.-J. Hwang, *Nano Energy*, 2018, **47**, 309-315.

[3] K. B. Ibrahim, W. N. Su, M. C. Tsai, A. W. Kahsay, S. A. Chala, M. K. Birhanu, J. F. Lee and B. J. Hwang, *Materials Today Chemistry*, 2022, **24**, 100824.

[4] K. B. Ibrahim, T. A. Shifa, P. Moras, E. Moretti and A. Vomiero, *Small*, 2023, **19**, 2204765.

[5] K. B. Ibrahim, T. A. Shifa, M. Bordin, E. Moretti, H.-L. Wu and A. Vomiero, *Small Methods*, 2023, **7**, 2300348.

Steering bioelectrochemical methane production with biochar

Clara Marandola[1*], Federico Scopetti[1], Luca Saraconi[1], Gaia Salvatori[1], Marco Zeppilli[1], Antonella Signorini[2], Antonella Marone[2], Luca Di Palma[3], Marianna Villano[1]

[1]*Department of Chemistry, Sapienza University of Rome, Rome, Italy*
[2]*Casaccia Research Center, Italian National Agency for New Technologies Energy and Sustainable Economic Development (ENEA, Rome, Italy*
[3]*Department of Chemical Engineering Materials Environment, Sapienza University of Rome, Rome, Italy*
**clara.marandola@uniroma1.it*

Bioelectrochemical systems (BES) employ solid-state electrodes to directly or indirectly stimulate and control microbial metabolisms and have garnered significant attention for their potential in sustainable energy production and environmental remediation [1]. Among BES, methane-producing microbial electrolysis cells (MECs) represent a promising technology for the biological upgrading of biogas, which is a gas mixture mainly composed of CH_4 (50 - 70 %, v/v) and CO_2 (30 - 50%, v/v). Indeed, in a CH_4-producing MEC, methanogens drive the cathodic CO_2 reduction into CH_4, with the required energy input partially provided by the biologically-driven oxidation of organic (waste) substrates at the MEC bio-anode [2]. The interaction between microorganisms and the polarized electrodes, as well as among different microorganism species, play a crucial role in the MEC performance. The syntrophic relations can be boosted by the utilization of conductive materials, commonly employed to facilitate direct interspecies electron transfer (DIET) processes [3]. Conductive materials, including carbon-based materials like graphite or biochar (i.e., a carbonaceous material deriving from the pyrolysis or gasification of biomass) and conductive nanoparticles (*i.e. magnetite*) offer platforms for electron transfer and biofilm formation, thereby improving microbial electrode interactions [4]. In this study, preliminary batch experiments were conducted to test the effect of a commercially available biochar (obtained from gasification of virgin wood) on methane production by a mixed anaerobic sludge containing methanogens. The obtained results showed a substantial increase (over 200%) in terms of CH_4 production compared to control tests performed in absence of biochar. Then, biochar was used together with graphite granules (16% w/w and 84% w/w, respectively) as cathodic material in a two-chamber MEC, whereby the anode was filled with granular graphite and inoculated with activated sludge. The MEC was operated with the anode polarized @+0.20 vs SHE (Standard Hydrogen Electrode) to allow the electroactive biofilm formation and was continuously fed with a real feedstock. This consisted of the liquid fraction of the effluent deriving from an anaerobic fermentor treating the organic fraction of municipal solid waste, made of ~57% of organic acids with respect to the overall COD (Chemical Oxygen Demand). During the first run (*abiotic cathode*), the maximum current detected was 60.5 mA and the coulombic efficiency (which represents the fraction of the removed substrate diverted into current) reached a value of 100%. H_2 (approximately 196 mEq) was the main product at the MEC cathode. The second run with biotic cathode inoculated with anaerobic unselected sludge is in progress and the CO_2 conversion into CH_4 in presence of biochar by exploiting the electrochemically produced H_2 will be evaluated as a tool to improve the biological biogas upgrading.

References

[1] Singh N. K., Mathuriya A. S., Mehrotra S., Pandit S., Singh A., Jadhad D. Environmental technology, 2023, 1–24.
[2] Zeppilli M., Cristiani L., Dell'Armi E., Majone M., Renewable Energy, 2020, 158, 23-31
[3] Kouzuma A., Kato S., Watanabe K. Frontiers in microbiology, 2015, 6, 477
[4] Valentin M. T., Luo G., Zhan, S., Białowiec A. Biotechnology for biofuels and bioproducts, 2023 16, 146.

Valorisation of Reground Pasta by-product through a multi-stage process for polyhydroxyalkanoates production

Angela Marchetti[1*], Sergio Ciacia[1], Miguel Palhas[2,3], Joana Fradinho[2,3], Maria A.M. Reis[2,3], Marianna Villano[1]

[1] *Department of Chemistry, Sapienza University, Rome, Italy*
[2] *UCIBIO—Applied Molecular Biosciences Unit, Department of Chemistry, NOVA School of Science and Technology, NOVA University Lisbon, 2829-516 Caparica, Portugal.*
[3] *Associate Laboratory i4HB—Institute for Health and Bioeconomy, NOVA School of Science and Technology, NOVA University of Lisbon, 2829-516 Caparica, Portugal*
**angela.marchetti@uniroma1.it*

Currently, the management of by-products and wastes from the food industry has turned into a challenge from an environmental point of view. Among several feasible options, their conversion into biopolymers offers a sustainable solution in their management. In this context, this study focused on the valorisation of Reground Pasta (RP), a farinaceous by-product, through a multi-stage process for polyhydroxyalkanoates (PHAs) production by mixed microbial cultures (MMC). PHAs are fully biodegradable polymers synthesized by over 300 species of microorganisms as intracellular carbon and energy reserve, which can be produced from renewable feedstocks (e.g., organic waste/by-products) and, due to their physico-chemical properties, represent a promising alternative to conventional plastics for several applications, e.g. biomedicine, packaging and environmental remediation [1]. Here, batch tests were firstly performed to assess the fermentation potential of nine food industry by-products and RP by-product emerged as a promising substrate to be converted into organic acids, reaching a fermentation yield equal to 55 ± 2 % (on Chemical Oxygen Demand, COD, basis) [2]. Then, the first stage of the MMC-PHA production process was performed through the RP acidogenic fermentation in a lab-scale sequencing batch reactor (SBR). The resulting fermented solution, rich in organic acids with an acidification degree of 52 ± 2 % ($COD_{ACIDS}/totCOD_{in}$), was directed towards the accumulation stage of the PHA production process by using aerobic MMC (in a lab-scale SBR), and towards both selection and accumulation stages for purple phototrophic culture (PPB) (in a lab-scale continuous reactor). Three Organic Loading Rates (OLRs) were investigated, equal to 2.12, 4.25, and 8.50 $gCOD_{ACIDS}/Ld$ for MMC and 0.53, 0.60, and 0.71 $gCOD_{ACIDS}/Ld$ for the PPB consortium. Moreover, the composition of the RP fermented solution, equal to 6% of lactate and a mixture of acids with odd and even (69% and 26%, respectively) number of carbon atoms (on COD basis), made this effluent suitable to produce the poly(hydroxybutyrate/hydroxyvalerate) P(HB/HV) copolymer. The obtained results showed a PHA content (%, w/w) of around 5% in the selection PPB reactor, with a monomeric composition of 50/50 (HB/HV %, w/w) reaching a maximum polymer content of 10% in the accumulation stage [3]. While, by using the RP fermented solution as substrate during the accumulation stage, performed with the selected biomass of MMC at the different OLRs, a maximum PHA content of 32 ± 1 % (for the biomass selected from OLR equal to 4.25 $gCOD_{VFAs}/Ld$) with a composition of 60/40 (HB/HV %, w/w), was obtained. Such findings emphasize the feasibility of valorising food by-products through a biotechnological approach which offers a sustainable pathway for transforming waste materials into biopolymers. Overall, this study points out the critical importance of substrate selection and fermentation condition optimization to maximize the organic acid yield and subsequent PHA synthesis, contributing significantly to the development of sustainable waste/by-products management and biopolymer synthesis, with potential implications in the environmental and industrial fields.

Acknowledgements: This work has been financially supported by the USABLE Packaging Project (Call: H2020- BBI- JTI-2018; G.A. No 836884).

References

[1] M.G.E. Albuquerque, V. Martino, E. Pollet, L. Avérous, M.A.M. Reis. *Biotechnol*, 2011, **151**, 66–76.
[2] A. Marchetti, G. Salvatori, M.L. Astolfi, M. Fabiani, J. Fradinho, M.A.M. Reis, A. Gianico, D. Bolzonella, M. Villano. *Biochem* Eng J, 2023, **199**, 109029
[3] A. Marchetti, M. Palhas, M. Villano, J. Fradinho. *Catalysts*, 2024, **14**(4), 239.

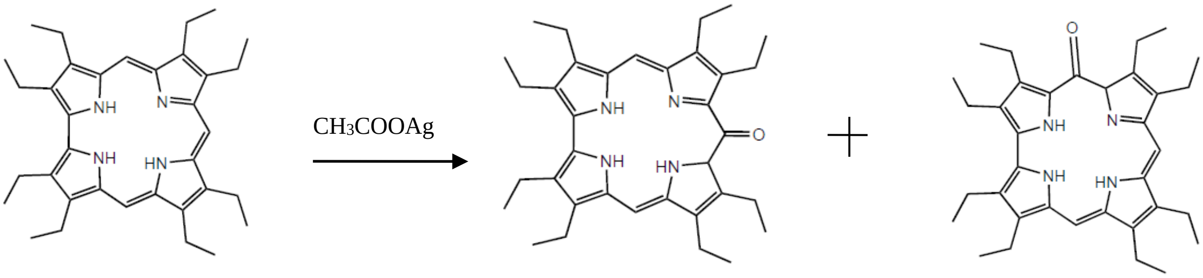
Synthesis and characterization of 5- and 10-oxocorroles from β-octaalkylcorroles

Martina Marsotto[1*], Lorena di Zazzo[1], Roberto Paolesse[1]

[1]*Department of Chemical Sciences and Technology, University of Rome 'Tor Vergata', Roma, Italy*

**martina.marsotto@uniroma2.it*

Corrole can be considered the prototypical example of contracted porphyrins, with one of the meso carbon bridges missing. This class of compounds has received a great attention, because of their promising exploitation in different fields, ranging from medicine to material chemistry. The increase of interest in corrole chemistry at the beginning of this century was possible due to the discovery of simple synthetic procedures for the preparation of 5,10,15-triarylcorroles,[1,2,3] while β-octa-alkylcorroles, the first examples reported for this porphyrinoid,[4] almost disappeared from the scene. In this context, my research aims to explore simple synthetic approaches to β-octaethylcorrole in order to proceed with the synthesis of 5- and 10-oxocorroles[5], as promising compounds in catalysis for the conversion of CO_2 into the desired fine-chemicals.



β-octa-ethylcorrole 5-oxocorrole 10-oxocorrole

Figure 1. Synthetic pathway to 5- and 10-oxocorroles.

References

[1] Z. Gross, N. Galili, I. Saltsman, *Angew. Chem.*, 1999, **38**, 1427.
[2] R. Paolesse, L. Jaquinod, K. M. Smith, *Chem. Commun.*, 1999, 1307.
[3] B. Koszarna, D. T. Gryko, *J. Org. Chem.*, 2006, **71**, 3707.
[4] A. W. Johnson, I. T. Kay, *J. Chem. Soc.*, 1965, 1620.
[5] L. Di Zazzo, S. Nardis, R. Paolesse, *Chem. Commun.*, 2024, **60**, 102.

Exploring the recycling potential of mixed plastic waste through combined thermochemical and biological processes

Flavia Marzulli[1*], Sogand Musivand[2], Benedetta De Caprariis[2], Paolo De Filippis[2], Giulia Simonetti[1], Carmela Riccardi[3] Cristina Prieto Lopez[4], José María Lagarón[4], Marianna Villano[1]

[1] *Department of Chemistry, Sapienza University of Rome, Rome, Italy*
[2] *Department of Chemical Engineering Materials Environment, Sapienza University of Rome, Rome, Italy*
[3] *INAIL-DIT Via Roberto Ferruzzi 38,00143 Rome, Italy*
[4] *IATA (CSIC) Calle Catedrático Agustín Escardino Benlloch 7,46980 Paterna, Spain*

**flavia.marzulli@uniroma1.it*

The fraction of post-consumer plastic waste that cannot be further mechanically recycled is commonly defined as Plasmix. This heterogeneous mixture of waste, often containing many non-plastic materials (e.g., glass, aluminium and paper) [1], represents one of the main obstacles when it comes to plastic waste management [2]. Therefore, given the few available options for the recovery and valorisation of plastic waste, the development of novel recycling techniques is attracting considerable attention, as well as the adoption of biodegradable plastics as viable options to reduce the impact of this plastic waste. Within this framework, this study investigates two distinct pathways for the valorization of Plasmix and its main constituents (mainly polyurethanes, polyethylene therephtalate, and cellulose), leveraging the synergistic effects of coupled biological, thermochemical, and physical processes. The first scenario deals with the valorization of the aqueous matrix resulting from hydrothermal liquefaction (HTL) of Plasmix, through its conversion into organic acids, which can be used for several applications including the microbial production of bioplastics (e.g., polyhydroxyalkanoates, PHAs) with mixed microbial cultures. Here, the plastic waste was subjected to a 2- or 4-hour HTL treatment at 250-330 °C and the resulting aqueous matrix was employed as feedstock for the biological acidogenic fermentation process in batch tests. In this preliminary study, a promising conversion potential (on a Chemical Oxygen Demand, COD, basis) into organic acids of 96 ± 21% (COD/COD) and 53 ± 11% (COD/COD) emerged for Plasmix and PET after 2 hours of HTL treatment, respectively. The lowest conversion yields were obtained for polyurethanes (19 ± 9 %, COD/COD) and cellulose (13 ± 2 %, COD/COD). Nevertheless, negligible inhibitory effects on microbial activity occurred in all cases. The second scenario evaluated throughout the study deals with the possibility of manufacturing a novel material based on commercially available PHAs, in which Plasmix acted as a filler up to 10% (w/w). This allowed for the recovery and valorization of plastic waste while also lowering the market cost of PHA. Through blending and thermocompression, films were thus obtained that exhibited mechanical and barrier properties similar to those of neat PHA. In fact, PHA/Plasmix films showed, on average, an elongation to break (ε_b), tensile strength (σ_b), and water vapor permeability (WVP) of 1.1 ± 0.2 %, 26.4 ± 2.7 MPa, and $1.91 \pm 0.16 \cdot 10^{-15}$ Kg m Pa^{-1} s^{-1} m^{-2}, respectively; in comparison with $\varepsilon_b = 1.5 \pm 0.1$ %, $\sigma_b = 29.1 \pm 3.8$ MPa and WVP = $1.28 \pm 0.15 \cdot 10^{-15}$ Kg m Pa^{-1} s^{-1} m^{-2} of neat PHA.

Overall, the obtained data suggest the possibility to manage and simultaneously valorize plastic wastes, giving them a new life in line with the concept of circular economy.

References

[1] Stefano G., Beatrice D.F., Marco Aldo O., Marco P., *Int. J. Environ. Res. Public Health*, 2022, **19(16)**, 10088.

[2] Camila T.D.M.S., Monica E., Emma O., Mikael G., Sigbritt K., *Conservation and Recycling*, 2022, **176**, 105905.

Beyond the Bin: Investigating the Recovery of Rare Earth Elements from Multimetal Mixtures

Matteo Melegari[1*], Martina Neri[1], Alex Falco[1], Matteo Tegoni[1], Luciano Marchiò[1]

[1]*Department of Chemistry, Life Sciences and Environmental Sustainability, University of Parma, Italy*

**matteo.melegari@unipr.it*

Rare Earth Elements (REEs) are vital for numerous advanced technologies, yet their supply chains are at risk due to geopolitical disputes and fluctuating prices. Therefore, it's critical to boost the recycling rates of REEs to reduce the supply risk associated with them [1]. Our research focuses on creating an alternative method for extracting and recovering REEs from NdFeB magnets, one of the most abundant sources of waste containing lanthanides. We discovered a promising technique that separates Nd and Dy into distinct phases using selective precipitation with 8-hydroxyquinolines, which are commercially available ligands [2].

Our study developed two separation methods. The first removes iron, which makes up 65% of the magnet's weight, from the REEs. The second method achieves the intra-separation of the two lanthanides. We used a quinoline that is not sterically hindered allowing for the fine-tune of the complex topologies formed by Nd and Dy upon changing the reaction conditions [3]. Nd forms a poorly soluble trimeric complex, while Dy forms a soluble terakis complex, allowing for their separation via precipitation. This green, cost-effective, and straightforward strategy has the potential to boost the recycling rate of REEs.

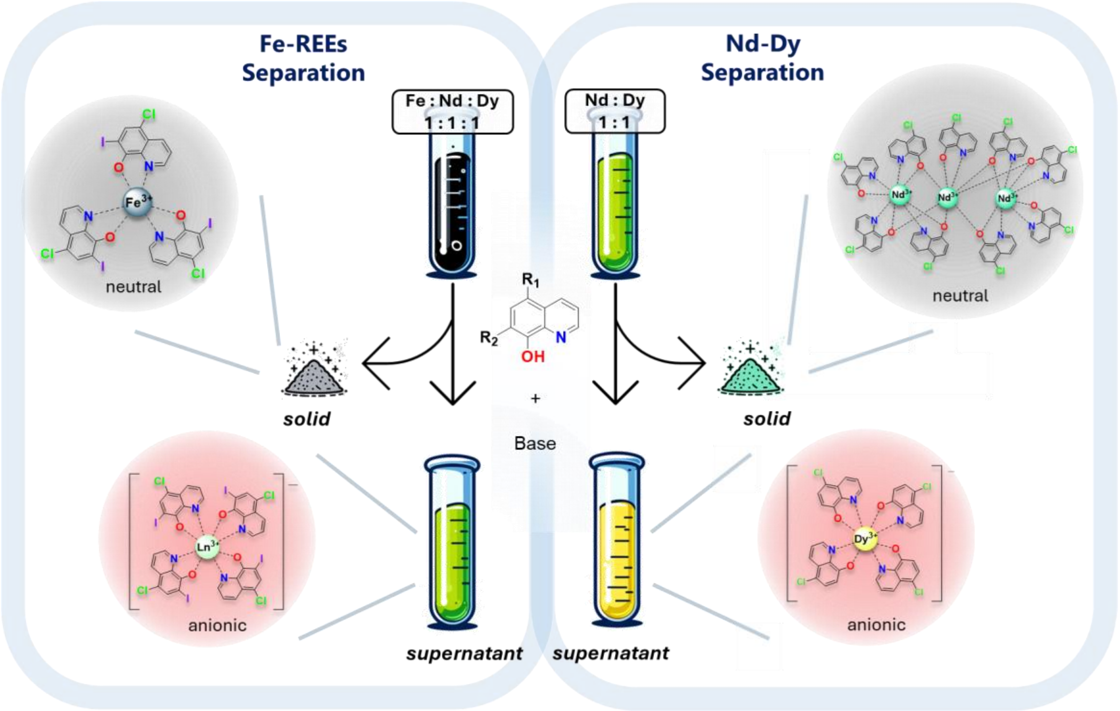


Figure. Schematic representation of the separation processes developed in this work. On the left, the separation of Fe from REEs; on the right, the separation of Nd from Dy.

References

[1] Y. Yang et al., *Journal of Sustainable Metallurgy*, 2017, **3**, 122-149.
[2] R. Van Deun et al., *Inorganic Chemistry*, 2004, **43**, 8461-8469.
[3] F. Artizzu et al., *Advanced Functional Materials*, 2007, **17**, 2365-2376

A novel approach for industrial lipases immobilization on graphene oxide nanosheets for Biodiesel production

Alessandro Milani[1], Laura Chronopoulou[1,2], Francesco Amato[1], Andrea Marrani[1] and
Cleofe Palocci [1,2]

[1]Department of Chemistry, University of Rome "La Sapienza" P.le A.Moro 5 00185 Rome Italy
[2]Research Center CIABC,University of Rome "La Sapienza" P.le A.Moro 5 00185 Rome Italy

* *al.milani@uniroma1.it*

In recent years, nano-immobilized lipases have received extensive attention to the design of robust industrial biocatalysts for biodiesel production [1]. Immobilization technique has been introduced to overcome the drawbacks related to the use of free lipases such as lipase stability and high production costs [2]. In addition to traditional nanomaterials such as nano-silicon, magnetic nanoparticles and nano metal particles, graphene oxide (GO) has emerged as a promising support for enzyme immobilization due to its distinctive characteristics such as the large surface area, ease of functionalization, fascinating electronic properties, and excellent thermal and mechanical stability [3].

In the present work we studied and optimized the use of graphene oxide (GO) nanosheets functionalized as a support for the covalent immobilization of industrial lipases. For this purpose, *Candida rugosa* lipase (CRL) was covalently immobilized with an EDC/sulfo-NHS coupling system on amine-functionalized graphene oxide (GO-NH_2). Lipases chemically conjugated on GO based nano-supports have been characterized by thermogravimetric analysis and Fourier transform infrared spectroscopy (FTIR) showing high stability to high temperatures, organic solvents and pH and stability during extensive reuse. Furthermore, a relationship between the catalytic behaviour of the immobilized enzymes and the content of secondary structures (α-helical content) has been hypothesized. The immobilized lipases (CRL@GO-NH_2) exhibited an improvement in esterase activity with an immobilization efficiency of 89 %, under optimal conditions. Finally, we investigated the use of the immobilized biocatalyst by evaluating reaction yields and stability on the transesterification reaction for fatty acids methyl esters (FAME) production starting from model substrates and waste lipids in the presence of methanol for biodiesel production.

References

[1] Tan, Z., Bilal, M., Li, X., Ju, F., Teng, Y., Iqbal, H.M.N.: Nanomaterial-immobilized lipases for sustainable recovery of biodiesel – A review. Fuel. 316, 123429 (2022).
[2] Zhong, L., Feng, Y., Wang, G., Wang, Z., Bilal, M., Lv, H., Jia, S., Cui, J.: Production and use of immobilized lipases in/on nanomaterials: A review from the waste to biodiesel production. International Journal of Biological Macromolecules. 152, 207–222 (2020).
[3] Adeel, M., Bilal, M., Rasheed, T., Sharma, A., Iqbal, H.M.N.: Graphene and graphene oxide: Functionalization and nano-bio-catalytic system for enzyme immobilization and biotechnological perspective. International Journal of Biological Macromolecules. 120, 1430–1440 (2018).

Arsenic and sulfadiazine adsorption by Fe-hydrochar produced from olive pomace

Serena Monaco[1]*, Giulia Simonetti[1], Fabrizio Di Caprio[1], Francesca Pagnanelli[1], Maria Luisa Astolfi[1], Antonio Brasiello[2], Pietro Altimari[1]

[1]*Department of Chemistry, Sapienza University of Rome*
[2] *Department of Chemical Materials Environment Engineering, Sapienza University of Rome*

**serena.monaco@uniroma1.it*

Arsenic, a toxic metalloid naturally occurring in groundwater, poses health risks when ingested above recommended limits (10 ppb). The implementation of arsenic removal technologies is of primary concern due to widespread exceeding concentrations. Adsorption of arsenic using granulated ferric oxide or hydroxide (GFO or GFH) is a widely used technology, but their high costs (5-9 €/kg) represent a limitation, especially in rural areas. In order to overcome this limitation, adsorbents produced from low-cost biomasses and functionalized with iron oxides/hydroxides are being explored as a more affordable alternative. In this framework, hydrothermal carbonization (HTC) offers a promising technological alternative [1]. HTC involves converting biomass into a solid carbonaceous material known as hydrochar (HC). A notable advantage of HC over GFH and GFO adsorbents is its capacity to adsorb arsenic along with organic pollutants.

This work investigates the adsorption of arsenic (As) and sulfadiazine (SDZ), that was selected as representative emerging organic pollutant [2]. The Fe-hydrochar used was produced at a pilot scale through a process involving hydrothermal carbonization (HTC) at acidic pH, followed by the precipitation of Fe oxides/hydroxides at alkaline pH [3].

Batch experiments were conducted to derive the equilibrium isotherm for As and SDZ. The maximum adsorption capacity q_{max} and the affinity coefficient b were estimated by fitting the Langmuir model to the equilibrium data. The q_{max} and b were determined to be respectively 1.9 mg/g and 0.8 L/mg for As, and 2.3 mg/g and 0.09 L/mg for SDZ. The adsorption kinetics for As and SDZ were analysed in separate tests and fitted to the first-order model, resulting in adsorption times of 40 min for As and 900 min for SDZ. Afterward, the simultaneous adsorption of As and SDZ onto the HC was explored. To this purpose, adsorption tests were conducted at different initial concentrations of As and SDZ. This analysis revealed that the adsorption of SDZ at concentrations exceeding 600 mg/L declined as the As concentration increased to 2.5 mg/L, while it remained constant at lower As concentrations.

Finally, continuous adsorption experiments were carried out by using a packed bed column to assess the removal of SDZ. In the performed test, about 20 L of a 2 mg/L SDZ solution was treated and the temporal evolution of the outlet concentration was analysed to evaluate the adsorption performance.

Acknowledgements:
This work was supported by the European Union in the framework of the LIFE programme (BioAs project - LIFE19 ENV/IT/000512).

References

[1] Khan N., Sooraj M., and P. Dinesha. *Journal of cleaner production* 2021, 288, 125629.
[2] Li-Tang Q., Xin-Rui P., Hong-Hu, Yan-Peng L., Ling-Yun M., Dun-Qiu W., and Jun-Feng D. *Science of the total environment*, 2020, 708, 134552.
[3] Fabrizio D.C., Andrea P., Robertino Z., Maria Luisa A., Pietro A., and Francesca P. *Journal of Environmental Management*, 2022, 302, 114058.

Development of New Materials for High Performance Seawater Batteries

J. Montero[1], G. Di Donato[1,2], A. Tsurumaki[1], S. Passerini[3], M. A. Navarra[1]

[1]Sapienza University of Rome, Piazzale Aldo Moro 5, 00185 Roma, Italy
2KIT-HIU, Helmholtzstraße 11, 89081 Ulm, Germany
[3]KIT Campus Transfer GmbH, Haid-und-Neu-Str.7, 76131 Karlsruhe, Germany
**jorge.montero@uniroma1.it*

Approximately 71% of the Earth's surface is covered by oceans. Seawater is a source of numerous chemical elements and currently, there are several metals that are commercially extracted from it, such as Na, Ca, K, Mg, and Li [1]. Secondary seawater batteries have received considerable interest for marine applications (e.g., life jackets, signal lights, and deep-sea applications), thanks to their affordable and effective active materials by utilizing sodium chloride and oxygen, two of the most abundant chemicals in the marine environment [2]. Their working principle consists in the use of seawater as source of Na-ion reduced at the anode, a selective Na-ion conductive separator employed to isolate the anode compartment from the seawater and, finally, Cl^- anions or water and oxygen dissolved in seawater as the active materials for the positive electrode during charge and discharge, respectively [3–5]. Despite all the electrochemical capabilities of secondary seawater batteries, such as high theoretical voltage (3.48 V) and energy density (3051 WhL^{-1}) [6], there is still low energy efficiency due to the large charge and discharge voltage gap upon cycling, caused by the overpotential of the oxygen evolution and oxygen reduction reactions at the cathode [7]. Furthermore, anolyte decomposition and sodium dendrite growth can cause serious safety issues [8]. To overcome these issues, we investigated different pathways such as anode and anolyte optimization as well as the development of bifunctional electrocatalysts for the cathode to improve battery performance and safety.

Acknowledgements:

This work was developed in the framework of the project SBAM (Stoccaggio di energia con Batterie ad Acqua di Mare), CUP B87H21012170003, funded by MiTE-CSEA within the PTR (Piano Triennale di Realizzazione) 2019-2021 of the national RSE (Ricerca di Sistema Elettrico).

References

[1] Name A., Name B., Name C. *Journal Title*, 2000, **35**, 3523.
[2] Name A. (or Editor), *Title of the book*, 2000, Chapter, page(s), Publisher, City, Country.
[1] L. Barelli, D. Pelosi, G. Bidini, G. Di Donato, M. A. Navarra, S. Passerini, *Renewable and Sustainable Energy Reviews* 2023, **187**.
[2] S. Arnold, L. Wang, V. Presser, *Small* 2022, **18**.
[3] J. Kim, J. Park, J. Lee, W. G. Lim, C. Jo, J. Lee, *Adv Funct Mater* 2021, **31**.
[4] Y. Kim, G. T. Kim, S. Jeong, X. Dou, C. Geng, Y. Kim, S. Passerini, *Energy Storage Mater* 2019, **16**, 56–64.
[5] Y. Kim, A. Varzi, A. Mariani, G. T. Kim, Y. Kim, S. Passerini, *Adv Energy Mater* 2021, **11**.
[6] Y. Kim, W.-G. Lee, *Seawater Batteries Principles, Materials and Technology*, 2022, 37-90, Green Energy and Technology.
[7] Y. Kim, M. Künzel, D. Steinle, X. Dong, G. T. Kim, A. Varzi, S. Passerini, *Energy Environ Sci* 2022, **15**, 2610–2618.
[8] Y. Kim, J. Jung, H. Yu, G. T. Kim, D. Jeong, D. Bresser, S. J. Kang, Y. Kim, S. Passerini, *Adv Funct Mater* 2020, **30**.

Novel continuous-flow process for biopolymers production

Lionel Nguemna Tayou[1*], Claudia Vona[1], Luca Di Leva[1], Simona Crognale[2], Simona Rossetti[2], Marianna Villano[1]
[1]*Department of chemistry, University of Roma la Sapienza, Rome, Italy*
[2] *Water Research Institute, National Research Council (CNR-IRSA), Monterotondo, Italy*
**lionel.nguemna@uniroma1.it*

Over the past decades, the extensive usage of synthetic plastics has led to environmental damage and increased dependency on fossil fuels. To deal with these issues there's growing interest in sustainable materials like polyhydroxyalkanoates (PHA) as potential substitutes. Presently, the widespread diffusion of PHA is mainly limited by their production cost, which is substantially higher than that of conventional plastics (up to 5 €/kg vs 1€/kg, respectively) [1]. In order to overcome these limitations (which are mainly due to industrial processes based on the use of pure microbial strains requiring sterile working conditions and ad-hoc formulated substrates), processes based on the use of mixed microbial cultures (MMC) are being deeply investigated since MMC do not require sterile conditions and can use a variety of low-cost substrates as process feedstock (e.g., agro-industrial wastewaters or residues, urban wastes, etc.).

In the present research, a novel continuous-process for MMC-PHA production has been studied. Conventional processes currently employed (at both laboratory and pilot scale) for MMC-PHA adopt a sequencing batch reactor (SBR) for the selection of PHA-storing microorganisms from an activated sludge through the establishment of the feast/famine (F/F) conditions, which rely on the alternance of excess (feast) and lack (famine) of external carbon source[1]. The use of an SBR requires, in turn, the use of oversized pumps and liquid/solid separation units to manage huge volumes of liquid streams in a short period of time, which further increase the PHA production capital costs. The process developed in this work consists of two distinct reactors connected with a recirculation stream, functioning as the feast tubular reactor (1L working volume) and the famine CSTR reactor (5 L), respectively. In this process the F/F regime is spatially applied and, being the feast reactor continuously fed, there is no need of oversized devices. A key process parameter is the recirculation factor (R_C), which is the ratio between the recirculation flow rate (Q_R) and the feeding flow rate (Q_E). Four R_C values have been tested (between 1 and 8) with the feast reactor fed with a synthetic mixture of acetic and propionic acids at an applied organic load rate (OLR) of 2.12 gCOD/Ld [2]. Overall, R_C4 has been identified as the optimal working condition for the microbial selection and R_C8 as the optimal condition for the batch PHA accumulation step, which allowed obtaining up to 58 % (wt/wt) of intracellular polymer content. Based on these results, the process has been implemented with a further CSTR reactor to continuously perform the PHA accumulation. Also, the establishment of an efficient and environmentally sustainable protocol to continuously extract the polymer from the microbial cells is being developed. In summary, this continuous multi-flow process approach in three separate reactors for PHA production enabled a polymer productivity of around 0.4 – 0.8gPHA/Ld.

Acknowledgements:
The authors want to tank AGRILOOP (2022-2026). This project was funded by European Union's HEU research and innovation programme, the UK Research and Innovation fund under the UK government's HEU funding guarantee (GA n. 101081776) and The National Key Research and Development Funds of China. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union. Neither the European Union nor the granting authority can be held responsible for them.

References

[1] F. Cabrera, Á. Torres, J.L. Campos, D. Jeison, Polymers (Basel), Effect of operational conditions on the behaviour and associated costs of mixed microbial cultures for PHA production, 11, 2019.

[2] L. Tayou Nguemna, F. Marzulli, F. Scopetti, L. Lorini, R. Lauri, B. Pietrangeli, S. Crognale, S. Rossetti, M. Majone, M. Villano, Chemical Engineering Journal, Recirculation factor as a key parameter in continuous-flow biomass selection for polyhydroxyalkanoates production, 455,2023.

Developing eco-friendly methods to produce ionic liquids for a novel use in high-voltage lithium-ion batteries

M. Palluzzi[1*], A. Tsurumaki[1], A. Matic[2], P. D'Angelo[1], M. A. Navarra[1]

[1]*Department of Chemistry, Sapienza University of Rome, Rome, 00185, Italy*
[2]*Department of Physics, Chalmers University of Technology, Göteborg, 412 96, Sweden*

* *matteo.palluzzi@uniroma1.it*

To enhance the energy density of lithium-ion batteries (LIBs), a transition from commonly utilized cathode materials, like $LiCoO_2$, to new ones able to work at higher potentials, such as $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO), is necessary. However, the conventional electrolytes, typically containing carbonate-based solvents, are unstable at high potentials, causing side-reactions on the cathode surface. To tackle this issue, ionic liquids (ILs) have emerged as a potential additive to mitigate electrolyte instabilities. However, industrial application of ILs is hindered by their high cost and environmental unfriendliness associated with their synthesis [1]. In this study, ILs containing oxalatoborate anions, known to form a protective layer on the cathode surface [2] were synthesized primarily using water as a solvent to minimize the environmental impact of the synthesis. Four ILs were synthesized: N-ethoxyethyl-N-methylpiperidinium bis(oxalato)borate/difluoro(oxalato)borate ($PIP_{1,2O2}BOB$/$PIP_{1,2O2}DFOB$) and N-propyl-N-methylpiperidinium bis(oxalato)borate/difluoro(oxalato)borate ($PIP_{1,3}BOB$/$PIP_{1,3}DFOB$). These ILs underwent characterization through spectroscopic techniques and thermal analyses. Subsequently, the ILs were employed as additives to a commercially available electrolyte. The resulting mixtures were tested in Li||LNMO coin-cells by repeated charging/discharging (Fig. 1a). The inclusion of ILs led to a high reversibility of the charge/discharge processes in the cells over the course of 200 cycles. Conversely, systems without ILs, prepared as a reference, experienced failure after approximately 100 cycles. Acknowledging the advantageous effects of ILs, an alternative addiction method was explored: a minimal amount IL was incorporated into the slurry during the preparation of the LNMO electrode. These IL-enriched electrodes were evaluated similarly, revealing comparable enhancements in cell stability (Fig. 1b) but using a much reduced amount of them.

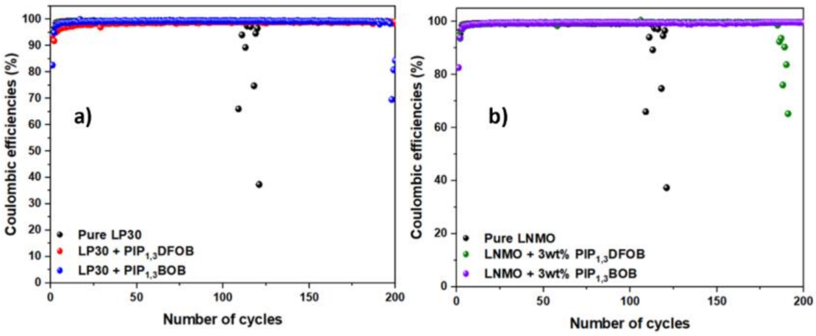


Figure 1 Coulombic efficiencies obtained using ILs as additives a) to the electrolyte or b) to the electrode.

References

[1] E. Simonetti, M. De Francesco, M. Bellusci, G. Kim, F. Wu, S. Passerini, G. B. Appetecchi, *ChemSusChem*, 2019, **12**, 4946– 4952

[2] A. Tsurumaki, M. Branchi, A. Rigano, R. Poiana, S. Panero, M.A. Navarra, *Electrochimica Acta*, 2019, **315,** 17-23

Natural fiber covalent coating with bioinspired gallic acid-iron phenylphosphonate complex for biocomposite flame retardancy application

Alessia Pantaleoni[1*], Maria Paola Bracciale[1], Irene Bavasso[1], Assunta Marrocchi[2], Fabrizio Sarasini[1]

[1]*Department of Chemical Engineering Materials Environment, Sapienza University of Rome, Via Eudossiana 18, 00184 Rome (Italy)*
[2]*Department of Chemistry, Biology and Biotechnology, University of Perugia, Via Elce di Sotto 8, 06123 Perugia (Italy)*

**alessia.pantaleoni@uniroma1.it*

Introduction

In recent years, natural fibers (NFs) have gained attention as an alternative to synthetic fibers in fiber-reinforced polymer (FRP) manufacturing. NFs provide benefits such as recyclability, renewability, low cost, and CO_2-neutrality compared to conventional synthetic options such as carbon, glass, and aramid fibers. However, owing to poor fire resistance and low thermal stability, the commercial use of natural fiber-reinforced composites (NFRCs) is hindered in some engineering applications. Therefore, the use of flame retardants (FRs) is required to ensure safe use and broaden their application field. This work introduces a new bioinspired approach to coat NFs with a gallic acid-iron phenylphosphonate complex (GA-FeP). This hybrid FR has the potential to leverage both the gas-phase radical scavenging effect by the organic component and the condensed-phase catalytic carbonization performed by the inorganic component (1).

Approach

Flax (FF) and basalt (BF) fibers, owing to their distinct chemical and physical characteristics, were used as a model. The coating process of NFs involves three main steps: (I) pre-treatment of the fibers with O_3 resulting in free functional groups on the surface, which are exploited for the subsequent (II) covalent immobilization of biosourced gallic acid (GA) units (2). (III) next, mimicking the bacterial enterobactin process of iron acquisition, the phenolic -OH groups of the GA unit are exploited for the iron phenylphosphonate complexation (3) (Figures 1a).

Results and conclusion

SEM analysis of the treated fibers reveals a globular-shaped surface coating. EDS spectra identify the presence of P and Fe, confirming iron phosphonate complexation ((Figures 1c and 1e).

MP-AES analysis detected an iron content on the FF and BF of 0.1 wt%, confirming Fe^{III} - gallic acid unit complexation on the surface of both samples.

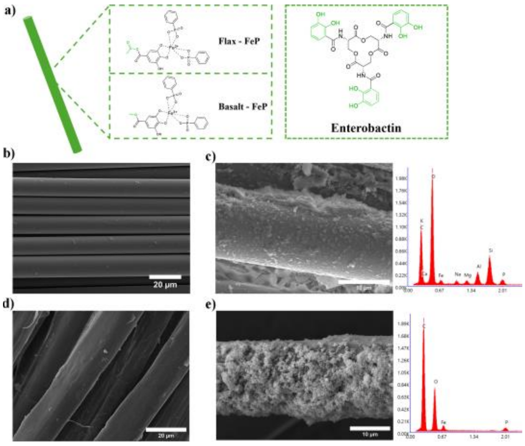


Figure 1. **a)** Schematic rapresentation of fibers surface modification; **b)** SEM micrographs of untreated basalt fiber (BF); **c)** EDS analysis of treated BF; **d)** SEM micrographs of untreated flax fiber (FF); **e)** EDS analysis of FF.

References

[1] Shi, X. H., Liu, Q. Y., Li, X. L., Yang, S. Y., & Wang, D. Y. (2022). Simultaneously improving the fire safety and mechanical properties of epoxy resin with iron phosphonated grafted polyethylenimine. Polymer Degradation and Stability, 206, 110173.
[2] Jiang, Y., Pei, J., Zheng, Y., Miao, Y. J., Duan, B. Z., & Huang, L. F. (2022). Gallic acid: a potential anti-cancer agent. Chinese journal of integrative medicine, 28(7), 661-671.
[3] Raymond, K. N., Dertz, E. A., & Kim, S. S. (2003). Enterobactin: an archetype for microbial iron transport. Proceedings of the national academy of sciences, 100(7), 3584-3588.

Colorless And Transparent Dye Sensitized Solar Cells For Building Integration Photovoltaic Based On NIR Dyes And Transparent Electrolytes

Donato Pasculli[1*], Ana Yancy Segura Zarate[1], Simone Galliano[2], Matteo Bonomo[1], Nadia Barbero[1], Marco Giordano[1], Guido Viscardi[1], Raffaele Borrelli[2], Waad Naim[3], Fionnuala Grifoni[3], Fabio Matteocci[4], Vijay Challuri[5], Pauline Chotard[5], Sylvain Ceurstemont[5], Franck Barath[5], Aldo Di Carlo[4], Frederic Sauvage[3], Claudia Barolo[1].

[1]Dipartimento di Chimica, NIS Interdepartmental and INSTM Reference Centre, Università degli Studi di Torino, Via Pietro Giuria 7, 10125, Torino, Italia.
[2]Dipartimento di Scienze Agrarie Forestali e Alimentari, Università degli Studi di Torino, Largo Paolo Braccini 2 - 10095 Grugliasco, Torino, Italia.
[3]CNRS, UPJV, Université Picardie Jules Verne, LRCS, Laboratoire de réactivité et Chimie du Solide, UMR 7314, Amiens, France.
[4] CHOSE- Centre for Hybrid and Organic Solar Energy, Department of Electronics Engineering, University of Rome "Tor Vergata", Via del Politecnico 1- 00133 Roma, Italia.
[5] G-LYTE SAS – Picardie, Amiens, France

**donato.pasculli@unito.it*

The development of integrated PV in windows/facades on buildings take us deeper in different aspects like aesthetics, stability and performance, because even if the color is one of the principal characteristics of the DSSC, with this technology is possible to offer a sustainable option for transparent and colorless windows, due to their versatility in the selection of dyes [1,2]. Our group synthesized some polymethine dyes (cyanines and squaraines) focusing on the photosensitizer in a wavelength-selective NIR-DSSC [3], and the synthesis of these dyes were done in a one-step reaction under microwave heating, saving time and money in the process, and even increasing yields and purity. A simple crystallization of the crude products yielded a very low cost and industrially scalable product. Until now, some different chromophores (NIR dyes) have been investigated for DSSC devices with promising results in terms of transparency and performance. Another key aspect for the aesthetic of these devices is represented by the redox couple, in fact it must be colorless and has to match the energetic levels of the NIR dye. Two families of redox couples are under investigation: the organic base electrolytes and the organometallic base ones. Due to the joint efforts of different research groups within the IMPRESSIVE project, fully transparent and colorless DSSC were built reaching 80 % transmittance in complete devices [2]. This project results are the starting point of the new CANVAS project, whose aim is to create a library of NIR dyes and a series of colorless electrolytes in order to increase both the device's efficiency and stability without losing transparency.

Acknowledgements:

This project has received funding from the European Union's Horizon 2020 research and innovation program under Grand Agreement n° 826013.

This study is a result of the research project "nuovi Concetti, mAteriali e tecnologie per l'iNtegrazione del fotoVoltAico negli edifici in uno scenario di generazione diffuSa" [CANVAS], funded by the Italian Ministry of the Environment and the Energy Security, through the Research Fund for the Italian Electrical System (type-A call, published on G.U.R.I. n. 192 on 18-08-2022).

References

[1] Grifoni F., Bonomo M., Naim W., Barbero N., Alnasser T., Dzeba I., Giordano M., Tsaturyan A., Urbani M., Torres T., Barolo C., Sauvage F., *Adv. Energy Mat.* **2021**, 11 (43), 2101598.

[2] Naim W., Novelli V., Nikolinakos I., Barbero N., Dzeba I., Grifoni F., Ren Y., Alnasser T., Velardo A., Borrelli R., Haacke S., Zakeeruddin S. M., Graetzel M., Barolo C., Sauvage F., *JACS Au* **2021**, 1, 4, 409-426.

[3] Saccone D., Galliano S., Barbero N., Quagliotto P., Viscardi G., Barolo C., *Europ. J. Org. Chem.* **2016**; 2244–2259.

Mesostructured silica-based materials as sorbents and catalysts for pollutant removal and CCU technologies

Francesca Perra[1,2,3*], Valentina Mameli[1,2,3], Fausto Secci[1,2,3], Nicoletta Rusta[1,2,3], Mauro Mureddu[4], Daniela Meloni[1,2], Elisabetta Rombi[1,2], Carla Cannas[1,2]

[1]*Department of Chemical and Geological Sciences, University of Cagliari, Cagliari, Italy*
[2]*National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence, Italy*
[3]*Italian Chemical Society (SCI), Rome, Italy*
[4]*Sotacarbo S.p.A., Carbonia, Italy*
* *francesca.perra4@unica.it*

In recent years, the concerns surrounding heavy metal pollution and the increasing CO_2 levels contributing to global warming have intensified. This study focuses on the synthesis and functionalization with aminosilanes of mesostructured silicas (MCM-41, MCM-48) for the development of amine-silica sorbents with potential applications in Cd^{2+} removal from aqueous solutions and in Carbon Capture and Utilization (CCU) technologies. Thanks to their highly ordered mesoporous structure, the donation of lone pairs by nitrogen to Cd^{2+} and the amines' high affinity for CO_2, amine-silica sorbents are suitable for such applications. Moreover, mesostructured silica-based composites have been developed by impregnating MCM-41 with oxidic phases of copper, zinc, and zirconium (CZZ), for a perspective application in the catalytic hydrogenation of CO_2 to methanol. Mesostructured silica was synthesized via the sol-gel technique employing a templating agent, a siliceous alkoxide precursor (TEOS) and two distinct solvent systems: water alone (yielding MCM-41) and a combination of water and ethanol (yielding MCM-48). Amine-silica sorbents were obtained from post-synthesis grafting with aminopropyltriethoxysilane and tested for Cd^{2+} removal and CO_2 capture. To lower both environmental and economic impact of the grafting procedure, an eco-friendly solvent (*i.e.* butanol instead of toluene) was used. The CZZ@MCM-41 composites were prepared through auto-combustion. On the other hand, for the development of sorbents for cadmium removal and CZZ-based catalysts, mesostructured silica from an industrial waste (hexafluorosilicic acid, FSA) was also tested. All sorbents were characterized by XRD, TEM-EDX, TEM, N_2-physisorption, thermogravimetric-analysis and ATR-FTIR.

MCM-48 was obtained by adding ethanol as co-solvent, keeping all the other experimental conditions equal to the MCM-41's synthesis, confirming its key role among others synthesis parameters in tuning the mesophase. The replacement of the alkoxide precursor with FSA allowed the production of MCM-41 with similar textural properties, reducing environmental and economic impacts. The same amino groups' concentration was obtained for MCM-41 functionalized with either toluene or butanol. Amino-silica sorbents were tested for Cd^{2+} sorption showing a removal percentage of 98-99% and an adsorbed amount of cadmium (q_e) around 40-45 $mg_{Cd(II)}/g_{sorb}$ for MCM-41 obtained both from TEOS and FSA. This preliminary study suggest that amine-silica sorbents have the potential to remove significant amounts of cadmium ions from aqueous solutions.

The use of butanol instead of toluene in the grafting procedure led to a decline in CO_2 adsorption performances (968 $\mu molCO_{2ads}/g_{sorb}$ *vs.* 480 $\mu molCO_{2ads}/g_{sorb}$), indicating the need to improve functionalization process. Nevertheless, a comparison revealed that toluene-functionalized MCM-41 is more efficient than SBA-15, emphasizing the crucial role of the support's surface area.

Optimization of Li-O_2 aprotic batteries' formulation: from singlet oxygen suppression to lithium metal protection

Angelica Petrongari[1*], Vanessa Piacentini[1], Adriano Pierini[1], Enrico Bodo[1], Mauro Giustini[1], Sergio Brutti[1]

[1]*Department of Chemistry, Sapienza University of Rome, Italy*

**angelica.petrongari@uniroma1.it*

Aprotic lithium-oxygen batteries (aLOBs) are regarded as promising high-capacity rechargeable batteries [1]. However, a major challenge in their widespread adoption lies in the high overpotentials required during charging to oxidize the discharge product Li_2O_2, which is non-conductive. Consequently, the Li-O_2 cell easily reaches operating voltages above 4.0 V vs. Li^+/Li^0, where several detrimental side reactions are activated, leading to cell damage and premature failure [2,3]. One significant factor contributing to these undesired reactions is the formation of highly reactive molecular oxygen in its excited singlet state [4].

To address the issue of high charge overpotentials, various redox mediators (RMs), which are soluble catalysts facilitating the oxidation of Li_2O_2, have been proposed [5]. Among these, lithium halides like LiI and LiBr stand out due to their favorable thermodynamics, simplicity, and cost-effectiveness [6,7]. However, their impact on side reactions, including the generation of singlet oxygen and lithium metal degradation, requires further investigation.

Initially, we studied the relationship between the thermodynamic and kinetic properties of LiX redox mediators, and their tendency to promote the formation of singlet oxygen. A strong correlation between LiX solvation, their kinetics in Li_2O_2 oxidation and the amount of singlet oxygen evolved was found, thanks to Electron Paramagnetic Resonance and Fluorescence measurements during the ongoing of Li_2O_2 oxidation in solvents with different dielectric constants [8,9].

To provide comprehensive insight into LiX reactivity in the Li-O_2 cell and, at the same time, to address the hurdles raised by the crossover of halide redox mediators toward the anodic compartment of the cell, we propose innovative cell formulations that include an iodine/bromine complexing polymer, Polyvinyl Pyrrolidone (PVP), that is also considered a good additive to promote the formation of a stable passivation layer on lithium metal [10].

Acknowledgements:

S.B. and A.Petrongari acknowledge the financial support of Sapienza University of Rome with grants Nr. AR123188B049ECFF and AR1221816B9459F2.

References

[1] Y. Wang, Y.C. Lu, Energy Storage Materials, 2020, 28, 235-246.

[2] A. Varzi, K. Thanner, R. Scipioni, D. Di Lecce, J. Hassoun, S. Dörfler, H. Altheus, S. Kaskel, C. Prehal, S.A. Freunberger, J. Power Sources, 2020, 480, 228803.

[3] A. Pierini, S. Brutti, E. Bodo, npj Computational Materials, 2021, 7:126.

[4] E. Mourad, Y. K. Petit, R. Spezia, A. Samojlov, F. F. Summa, C. Prehal, C. Leypold, N. Mahne, C. Slugovc, O. Fontaine, S. Brutti and S. A. Freunberger, Energy Environ. Sci., 2019, 12, 2559-2568.

[5] C. Zhang, N. Dandu, S. Rastegar, S. N. Misal, Z. Hemmat, A. T. Ngo, L. A. Curtiss, A. Salehi-Khojin, Advanced Energy Materials, 2020, 10(27), 2000201.

[6] W. J. Kwak, D. Hirshberg, D. Sharon, H. J. Shin, M. Afri, J. B. Park, A. Garsuch, F. F. Chesneau, A. A. Frimer, D. Aurbach and Y. K. Sun, J. Mater. Chem. A, 2015, 3, 8855-8864.

[7] W. J. Kwak, D. Hirshberg, D. Sharon, M. Afri, A. A. Frimer, H. G. Jung, D. Aurbach and Y. K. Sun, Energy Environ. Sci., 2016, 9, 2334-2345.

[8] A. Pierini, A. Petrongari, V. Piacentini, S. Brutti, E. Bodo, Journal of Physical Chemistry A, 2023, 127(44), pp. 9229–9235.

[9] A. Petrongari, V. Piacentini, A. Pierini, P. Fattibene, C. De Angelis, E. Bodo, S. Brutti, ACS Applied Materials and Interfaces, 2023, 15(51), pp. 59348–59357.

[10] S. E. Park, K. Shin, J. H. Yang, B. K. Park, S. Y. Kim, H. S. Kim, M. S. Park, K. J. Kim, *Chemical Engineering Journal*, 2022, 445, 136801.

Enhancing the Anaerobic Degradation of Aromatic Hydrocarbons under Sulfate-Reducing Conditions with Electrically Conductive Particles

Marco Resitano[1], Matteo Tucci[1], Verónica Peña-Álvarez[2], Martina Trinchillo[1], Carolina Cruz Viggi[1], Ana Isabel Peláez[2], Federico Aulenta[1,3]

[1] Water Research Institute (IRSA), National Research Council (CNR), Montelibretti (RM), Italy
[2] University Institute of Biotechnology of Asturias (IUBA), University of Oviedo, Oviedo, Spain
[3] National Biodiversity Future Center (NBFC), Palermo, Italy

marco.resitano@irsa.cnr.it

Direct interspecies electron transfer (DIET), which involves microbes exchanging metabolic electrons outside their cells, is increasingly acknowledged as a crucial mechanism supporting the syntrophic/cooperative degradation of organic substances in anaerobic environments. DIET is emerging as a faster and more efficient mechanism of electron transfer when compared to traditional ones. So far, DIET has primarily been explored within the context of anaerobic digestion, aiming to accelerate the conversion of organic waste substrates into methane. Various approaches have been suggested to stimulate DIET, with many of them revolving around the supplementation of electrically conductive nano- or micro-particles to the microbial community. These particles act as electron conduits among syntrophic partners. While there is increasing evidence indicating that the anaerobic biodegradation of diverse organic pollutants in soil and groundwater also relies on syntrophic and/or cooperative metabolisms, the role of DIET in bioremediation processes remains largely unexplored [1] In this study, we examined how various electrically conductive particles affect the anaerobic degradation of toluene under sulfate-reducing conditions. Our recent research has shown that the anaerobic degradation of this hazardous contaminant typically involves syntrophic interactions among various bacterial groups. [2]. A microbial culture capable of anaerobically degrading toluene under sulfate-reducing conditions was enriched from a petroleum hydrocarbon-contaminated groundwater. Analyses indicated a transient accumulation of acetate during the conversion of toluene, suggesting the likely involvement of syntrophic cooperation among various trophic partners, including acetate-producing fermentative bacteria and sulfate reducers. Subsequently, the enriched culture was utilized to inoculate microcosms, each supplemented with varying amounts (from 0% to 5% wt/wt) of electrically conductive materials—such as graphite and biochar microparticles, as well as magnetite nanoparticles—alongside toluene and sulfate. These microcosms were monitored for toluene, sulfate, hydrogen, and organic acids to elucidate the influence of conductive materials on the kinetics and pathways of contaminant degradation. Biomolecular (i.e., FISH) and microscopy (i.e., CLSM) analyses were also conducted in support of the chemical analyses. The findings underscore the environmental importance of Direct Interspecies Electron Transfer (DIET) in the anaerobic biodegradation of organic pollutants and offer valuable input for the development of more efficient bioremediation strategies in the future.

References

[1] Aulenta, F., Tucci, M., Cruz Viggi, C., Dolfing, J., Head, I.M., Rotaru, A., 2020. An underappreciated DIET for anaerobic petroleum hydrocarbon-degrading microbial communities. Microb. Biotechnol. 1751-7915.13654. https://doi.org/10.1111/1751-7915.13654

[2] Tucci, M., Cruz, C., Crognale, S., Matturro, B., Rossetti, S., Laura, A., Cavaliere, C., Cerrato, A., Maria, C., Harnisch, F., Aulenta, F., 2022a. Insights into the syntrophic microbial electrochemical oxidation of toluene: a combined chemical, electrochemical, taxonomical, functional gene-based, and metaproteomic approach. Sci. Total Environ. 850, 157919. https://doi.org/10.1016/j.scitotenv.2022.157919

Microbial valorization of eucalyptus bark enzymatic hydrolysate for polyhydroxyalkanoates production

T. Rodrigues[1,2*], C. A. V. Torres[1,2], S. Marques[3], F.Gírio[3], M. Reis[1,2], F. Freitas[1,2]

[1] Associate Laboratory i4HB – Institute for Health and Bioeconomy, NOVA School of Science and Technology, NOVA University Lisbon, 2829-516 Caparica, Portugal
[2] UCIBIO – Applied Molecular Biosciences Unit, Department of Chemistry, NOVA School of Science and Technology, NOVA University Lisbon, 2829-516 Caparica, Portugal
[3] Laboratório Nacional de Energia e Geologia I.P., Unidade de Bioenergia e Biorrefinarias, Lisboa, Portugal

**ta.rodrigues@campus.fct.unl.pt*

Polyhydroxyalkanoates (PHAs) are biodegradable, sustainable, and thermally stable biopolymers, making eco-friendly alternatives to fossil-fuel-derived polyesters like polyethylene terephthalate and polyamides [1]. Their diverse applications include medicine, textiles, and packaging [2]. However, their widespread use is hindered by high production costs associated with bacterial cultivation. To address this, low-cost feedstocks like agricultural wastes, organic materials and industrial byproducts are being explored to improve the economic feasibility of PHAs, while aligning with the circular economy concept. In Portugal, ¼ of the forest area is covered by *Eucalyptus globulus* wood, making its residues abundant and cheap, standing out as a potential carbon source for PHA production [3]. Eucalyptus bark hydrolysate, obtained through enzymatic saccharification using Cellic® CTec3, was used as a sole feedstock for PHA production [4]. Despite their varying performance, several bacteria were able to grow and accumulate PHA with distinct compositions. *Pseudomonas citronellolis* NRRL B-2504 reached high cell growth (24.4 ± 0.15 g/L), producing a medium-chain-length PHA, but a low biopolymer accumulation was observed under the tested conditions. *Burkholderia thailandensis* E264, on the other hand, exhibited lower growth (8.9 ± 0.34 g/L) but reached a higher polyhydroxybutyrate (PHB) content in the cells (12.3wt.%). A newly isolated *Pseudomonas* sp. strain achieved high PHB accumulation under nitrogen availability (31wt.%). These findings suggest the viability of using eucalyptus bark enzymatic hydrolysate as a sustainable feedstock for PHA production, enabling the development of environmentally responsible plastic products from underutilized residues.

Acknowledgements:

This work was financed by national funds from FCT/MCTES - Fundação para a Ciência e a Tecnologia, I.P., Ministério da Ciência, Tecnologia e Ensino Superior, in the scope of the projects UIDP/04378/2020 and UIDB/04378/2020 of the Research Unit on Applied Molecular Biosciences – UCIBIO, project LA/P/0140/202019 of the Associate Laboratory Institute for Health and Bioe-conomy - i4HB, and the integrated project be@t – Textile Bioeconomy. that has received funding from the Environmental Fund through Component 12 – Promotion of Sustainable Bioe-conomy (Investment TC-C12-i01 – Sustainable Bioeconomy No. 02/C12-i01/202). of European funds allocated to Portugal by the Recovery and Resilience Plan (RRP), within the scope of the European Union (EU) Recovery and Resilience Mechanism. framed in the Next Generation EU. for the period 2021 – 2026. Thomas Rodrigues acknowledges FCT I.P. for PhD Grant 2023.03035.BD.

References

[1] Kopf, S., Åkesson, D., Skrifvars, M. Pol Rev, 2023, **63**(1), pp. 200–245.
[2] Mukherjee, C., Varghese, D., Krishna, J.S., Boominathan, T., Rakeshkumar, R., Dineshkumar, S., Brahmananda, R.C.V.S., Sivaramakrishna, A. Eur Pol J, 2023, **192**, p. 112068.
[3] Neiva, D.M., Araújo, S., Gominho, J., Carneiro, A.C., Pereira, H. Ind Crops Prod, 2018, **123**, pp. 262-270.
[4] Rodrigues, Thomas; Torres, Cristiana; Marques, Susana; Gírio, Francisco; Freitas, Filomena; Reis, Maria. (2024). Polyhydroxyalkanoate Production from Eucalyptus Bark's Enzymatic Hydrolysate. Materials. 17. 1773.

Thermal decomposition of formamidinium tin triiodide ($CN_2H_5SnI_3$) and sublimation of tin(IV) iodide investigated by effusion techniques

Lorenza Romagnoli[1,2*]

[1]*Department of Chemistry, Sapienza University of Rome, Rome, Italy*
[2]*CIQUP-IMS, Department of Chemistry and Biochemistry, University of Porto, Porto, Portugal*

**lorenza.romagnoli@uniroma1.it*

The need to find effective and environmentally friendly technologies for energy production has driven in recent years an increasing effort towards the improvement of tin halide perovskites solar cells. In fact, while the Pb-based ones have witnessed a very rapid increase in power conversion efficiencies (PCE), since their breakthrough in 2009, the presence of toxic lead raises some concerns. On the other hand, Sn-based perovskites, despite possessing similarly favorable optoelectronic properties, have shown up to now additional difficulties in achieving high efficiency photovoltaic cells, with PCE values still far behind those of lead analogues [1]. Similarly to the latter, also tin halide hybrid perovskites suffer from scarce tolerance to physical and chemical environmental agents, with the additional ease of oxidation of Sn^{2+} to Sn^{4+} constituting a further cause of instability. Thus, for the assessment of the real perspectives for their commercial implementation, the evaluation of their stability in conditions comparable to those reached during operations is necessary.

The present study describes thermal degradation of the formamidinium tin triiodide perovskite, investigated by means of Knudsen effusion mass spectrometry, in the temperature range 366-462 K. Through this technique, the composition of the vapor phase produced upon heating was qualitatively and quantitatively analyzed, the partial pressures of gaseous decomposition products were determined, and the main degradative processes, analogous to those occurring in formamidinium lead triiodide [2], were identified:

$CN_2H_5SnI_{3(s)} \rightleftharpoons SnI_{2(s)} + CN_2H_{4(g)} + HI_{(g)}$
$CN_2H_5SnI_{3(s)} \rightleftharpoons SnI_{2(s)} + NH_{3(g)} + 1/3\ H_3C_3N_{3(g)} + HI_{(g)}$
$CN_2H_5SnI_{3(s)} \rightleftharpoons SnI_{2(s)} + NH_{3(g)} + HCN_{(g)} + HI_{(g)}$

Nevertheless, a significant difference with the corresponding lead perovskite was observed, i.e. besides species arising from the decomposition of the organic component, the vapor phase was found to contain also considerable amounts of SnI_2 and SnI_4. The presence of gaseous tin iodides was attributed, respectively, to formation of $SnI_{2(s)}$ as a result of thermal degradation, and subsequent sublimation, and to Sn(IV) impurities in the perovskite, since $SnI_{4(g)}$ was more abundant in the first stages of the experiments and its partial pressure was orders of magnitude lower than that of pure SnI_4.

In this regard, we also carried out an investigation of $SnI_{4(s)}$ sublimation, using Knudsen effusion mass spectrometry and mass loss, to confirm partial pressure measurements, retrieved from the literature, performed with different techniques (static methods instead of effusion-based ones), and to support the results from experiments on the perovskite. Thus, vapor pressures in the temperature range 313-340 K and thermodynamic properties of sublimation of SnI_4 were obtained [3].

References

[1] Lye Y.E., Chan K.Y., Ng Z.N. *Nanomaterials*, 2023, **13**, 585.
[2] Luongo A., Brunetti B., Vecchio Ciprioti S., Ciccioli A., Latini A. *J. Phys. Chem. C, 2021*, **125**, 21851.
[3] Romagnoli L., Almeida A.R.R.P., Ferraz J.M.S., Latini A., Freitas V.L.S., Ribeiro da Silva M.D.M.C., Vecchio Ciprioti S., Ciccioli A. *J. Chem. Thermodyn.*, submitted.

Using of Chemometrics to study the health of Lithium batteries

Eugenio Sandrucci[1*], Sergio Brutti[1],Aleksandar Matic[2], Federico Marini[1]

[1] *Department of Chemistry, “Sapienza” Univesità di Roma, Rome, Italy*
[2]*Department of Physics, Chalmers University of Technology, Göteborg, Sweden*

**eugenio.sandrucci@uniroma1.it*

Here we focus on the study of state of health monitoring of secondary batteries with advanced “green” formulations. European recycle map on battery energy storage plans to replace positive electrodes consisting of cobalt (Co) and fluorinated (F) graphite-based negative electrodes constituents with environmentally sustainable alternatives. Recently, "green formulations" was validated; in particular, recent trends suggest the use of high-capacity negative electrodes (e.g. Si or Li), Co-free positive electrodes, aqueous soluble binders and fluorine-free electrolytes [1]. Our aims are to describe the health and the degradation of the cells with electrochemical techniques and to describe the chemical and morphological changes occurring during the battery cycling, through spectroscopies (Raman and IR) operating in parallel with impedance analysis. These experimental data will be integrated together in a multiblock dataset, which will constitute the basis for chemometric processing. The purpose of this chemometric modelling is to correlate SOH evolution to the chemical and physical state of the battery [1]. Here we illustrate the analysis of SOH of two different pouch cell formulation constituted by LTO (Lithium-Titanate) as anode, LFP (Lithium-Iron-Phosphate) as cathode and the LP30 electrolyte (EC:DMC 1:1 and $LiPF_6$ 1M); the second formulation is constituted by a thin lithium foil of commercial Li metal (purity of 99.7%) as anode, LFP as cathode and an ethers based formulation as electrolyte. After formation cycles (CC-CV), the cells have been submitted to aging tests. The different operating conditions are chosen with an Experimental Design (ED) and supported by a PCA (Principal Component Analysis). The PCA analysis was used to choose the operating parameters for the subsequent aging experiments. Is illustrated also the analysis of SOH of a coin cell formulation consisted by a LRLO (Lithium Rich Layer Oxide) as anode, commercial Li metal layer as cathode and LP30 additive with a ionic liquid (IL) as electrolyte. of which the OCV (Open Circuit Voltage) was correlated with the health of the devices themselves. Turning to the chemometric modelling, as a starting point we verified the ability of PLS regression applied to the voltage profiles during charge cycles to estimate the SOH of a benchmark dataset by Lin et al. [1].

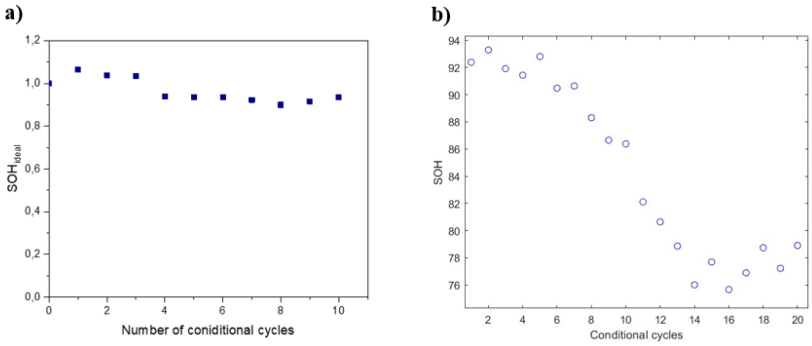


Figure 1: a) SOH trend of Li-ion battery during the aging test; b) SOH trend of Li metal battery during the aging test.

References

[1] M. Lin, D. Wu, *Journal of Power Sources*, 2022, **518**, 23077

Bioelectrochemical removal of trichloroethylene from contaminated groundwater: process optimization in the presence of competitive reactions.

Geremia Sassetto[1*], Marco Zeppilli[1], Laura Lorini[1], Marco Petrangeli Papini[1]

[1] *Department of Chemistry, University of Rome La Sapienza, Rome, Italy*
**geremia.sassetto@uniroma1.it*

Improper industrial handling of chlorinated aliphatic hydrocarbons (CAHs) such as Perchloroethylene (PCE) and Trichloroethylene (TCE) has led to widespread contamination of soil and groundwater. Fortunately, certain microorganisms can naturally degrade these compounds, mainly under anaerobic conditions, through a process called reductive dechlorination (RD). RD proceeds gradually from PCE to Vinyl Chloride (VC) and then to harmless ethylene. However, the effectiveness of each step varies depending on environmental conditions and microbial populations, with incomplete reactions potentially leading to toxic by-product accumulation. In situ bioremediation of matrices contaminated with chlorinated compounds requires the introduction of fermentable organic substances into the contaminated area. Bioelectrochemical systems (BES) offer an alternative technology that provides reducing or oxidizing power through an electrochemical apparatus, eliminating the need for injecting fermentable compounds. This study focuses on analysing a continuous bioelectrochemical process for Trichloroethylene (TCE) removal. The sequential system consists of a reducing reactor supporting the biological reductive dechlorination reaction of TCE, followed by an oxidative reactor facilitating the biological oxidation of low-chlorinated intermediates, thanks to the electrolytic production of oxygen. During the research, the effects of employing galvanostatic and potentiostatic approaches were explored to minimize energy consumption while maximizing contaminant removal. The system was initially studied using a synthetic solution contaminated solely with TCE, to which sulphate and nitrate anions were subsequently added to analyse the effects of competitive reactions for reducing power, such as sulphate reduction and nitrate reduction. The first three were conducted with the solution devoid of anions: the first was carried out potentiostatically, polarizing the cathode at -450 mV vs SHE, while the other two were conducted galvanostatically, applying currents to the reactor of -5 and -1 mA. The remaining four runs were conducted by adding the anions to the feed solution: the first three runs were conducted galvanostatically, applying decreasing currents of -30 mA, -5 mA, and -1 mA; finally, a return to potentiostatic control was made, repolarizing the cathode to -450 mV vs SHE. Throughout all runs of the reducing reactor, the oxidative reactor was operated by polarizing the anode at +1.6 V vs SHE. At the end of the study, the system demonstrated 100% efficiency in removing TCE in all explored runs, except for the galvanostatic run at -1 mA in the presence of anions, during which the process couldn't sustain the reductive dechlorination reaction. Chemical data and electrochemical values analysis revealed that the presence of sulphates and nitrates inhibited reductive dechlorination and worsened process performance. Additionally, a comparison between galvanostatic and potentiostatic approaches showed that galvanostatic control of the reducing reactor could maximize the coulombic efficiency of the reductive dechlorination reaction while minimizing energy consumption.

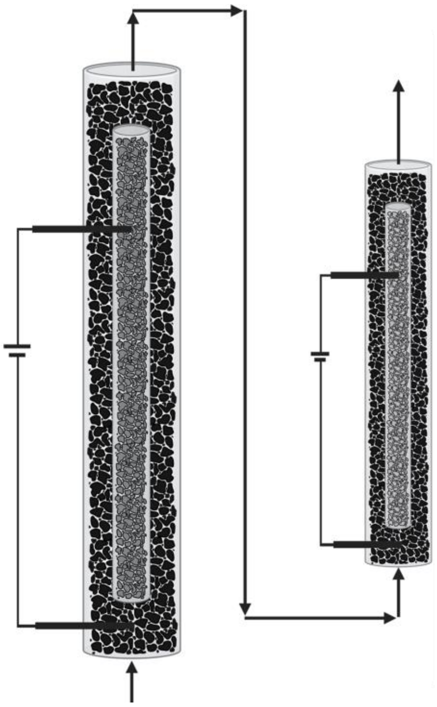


Figure: Sequential Reductive-Oxidative Process Scheme

Activation of Vegetable Oils by Reaction with Maleic Anhydride as a Renewable Source in Chemical Processes

Anna Scettri[1*], Francesco Lanero[1], Elisabetta Schievano[2], Stefano Mammi[2], Giacomo Saielli[2],
Paolo Sgarbossa[1], and Roberta Bertani[1]

[1]Department of Industrial Engineering, University of Padova, Padova, Italy
[2]Department of Chemical Science, University of Padova, Padova, Italy
**anna.scettri@phd.unipd.it*

The increasing ecological concerns have highlighted the importance of switching to renewable resources in terms of materials and energy. Vegetable oils are bio−based and sustainable starting materials for chemical industrial processes because of their availability, biodegradability, inherent safety, sustainability, and affordability. In this study, the functionalization of three vegetable oils (grape, hemp, and linseed) with maleic anhydride was carried out either by conventional heating (5h) or microwave irradiation (1h) to obtain products that, after further reactions, can enhance the water dispersion of oils for industrial applications. A detailed NMR study allowed the identification of the species formed in the reaction with maleic anhydride of trans-3-octene, methyl oleate and ethyl linoleate, taken as standard molecules. The signals in the ^{1}H-NMR spectra of the alkenyl succinic anhydride (ASA) moieties bound to the organic chains were clearly identified, thus allowing us to recognize them in the quite complex spectra of the oil derivatives from both the reactions, as seen in Figure 1. Moreover, also the viscosity was evaluated: it was noted that it increases with time after reaction, about 7 times higher after 6 months, and this effect is particularly evident in the MW reactions.

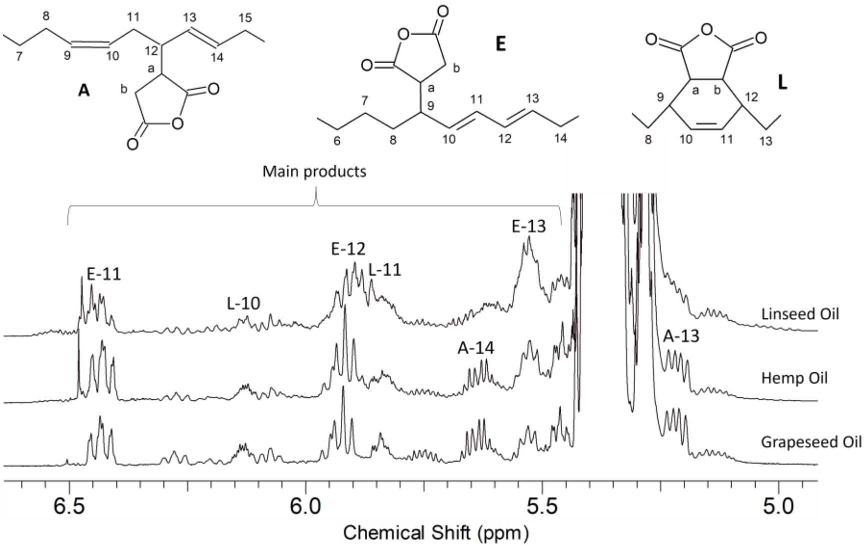


Figure 1. ^{1}H NMR spectral expansion of the most significative region (5.0-6.6 ppm) of oil products with MA and the assignments of the main compounds (A, E, L).

References

[1] Biermann U., Bornscheuer U., Meier M.A.R., Metzger J.O., Schafer H.J. *Angewandte Chemie Int. Ed.*, 2011, **50**, 3854–3871.
[2] Guner F.S., Yagci Y., Erciyes A.T. *Progress Polymer Science*, 2006, **31**, 633–670.
[3] Lanero F., Bresolin B.M., Scettri A., Nogarole M., Schievano E., Mammi S., Saielli G., Famengo A., Semenzato A., Tafuro G., Sgarbossa P., Bertani R. *Molecules* (2022), 27 (23).

Biosorption enhancement by the use of surfactants for PFAS removal from waters

Marta Senofonte[1*], Giulia Simonetti[1], Stefano Parisi[1], Carmela Riccardi[2], Marco Petrangeli Papini[1]

[1]*Department of Chemistry, University of Rome “La Sapienza”, Rome, Italy*
[2]*Department of technological innovations and safety of plants, products and anthropic settlements, National Institute for Insurance against Accidents at Work (INAIL), Rome, Italy*

**marta.senofonte@uniroma1.it*

PFAS are a variety of ecologically persistent compounds of anthropogenic origin loosely included in many industrial products, in which the carbon chain can be fully (perfluoroalkyl substances) or partially (polyfluoroalkyl substances) fluorinated. Because of their ubiquitous presence in many environmental compartments, the scientific community had to deal with the possible adverse effects of PFAS on ecosystem and human health [1]. Among the wide range of technologies developed for the removal of PFAS in aqueous media, adsorption is the most cost-effective and environmentally friendly method [2]. In this study, it was tested the well-known activated carbon material usually employed in PFAS remediation processes and compared to an eco-friendly adsorbent (pinewood biochar), along with a functionalization procedure of the same material developed with surfactants, to enhance its adsorption capacity [3]. This work focused on the treatment of aqueous solutions contaminated by a long-chain PFAS (Perfluorooctanoic acid, PFOA), using a continuous flow-reactor configuration. Unlike activated carbon, pinewood biochar selected in this study is an adsorbent deriving from a source of organic waste, increasingly applied for the removal of contaminants. First adsorption tests showed promising results but limited. A functionalization procedure using ionic surfactants (CTAB) was then developed and tested (Fig. 1). Laboratory set-up consisted of packed columns with the adsorbent of choice (pinewood biochar; pinewood biochar sieved ≤ 200 µm; functionalized pinewood biochar; activated carbon) and inert material (glass beads), through which contaminated water by PFAS is continuously passed in a closed system. Sorption tests were carried out in 24h (concentration at equilibrium). Adsorption isotherms (Freundlich and Langmuir) were also attempted to assess the removal capacity of the adsorbents. All samples of liquid phase collected (every 24h) were analysed by high-performance liquid chromatography (HPLC) coupled with mass spectrometry (MS-MS). Results evidenced a higher removal capacity of the activated carbon for long-chain PFOA, as expected from literature, comparable to the pinewood biochar. However, from the tests performed so far, sieved and functionalized pinewood biochar showed both similar and greater adsorption capacities. Such premises suggest how this biosorbent combined with functionalization could be potentially suitable for a wider range of long-chain PFAS compounds. Moreover, further investigation is necessary to also verify its potential use for short-chain PFAS.

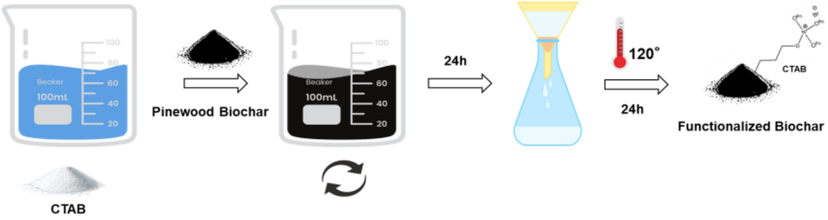


Figure 1. Functionalization procedure.

References

[1] L. Ahrens et al. Journal of Environmental Monitoring, 2011, 13, 20-31.
[2] D. Zhang et al. Environmental Technology, 2021, 42:12, 1798-1809.
[3] Y. Hamid et al. Journal of Hazardous Materials, 2022, 437.

Enhancing the kinetics of hydrogenophilic methanogenesis through magnetite nanoparticle and electroactive microorganism supplementation

Matteo Tucci[1*], Jasper I Antonio Sabangan[1], Bruna Matturro[1], Carolina Cruz Viggi[1], Federico Aulenta[1,2]

[1] Water Research Institute (IRSA), National Research Council (CNR), Montelibretti (RM), Italy
[2] National Biodiversity Future Center (NBFC), Palermo, Italy
**matteo.tucci@irsa.cnr.it*

Biomethanation (i.e., bioconversion of carbon dioxide into methane through hydrogenation) holds significant importance for biogas upgrading and carbon capture and utilization (CCU) technologies. Nevertheless, biomethanation is primarily challenged by the relatively slow intrinsic kinetics of H_2 utilization by methanogenic *Archaea* and the limited H_2 mass transfer caused by its low solubility in water [1]. To overcome these issues, biomethanation via direct interspecies electron transfer (DIET) emerges as a promising approach. DIET facilitates faster electron exchange between microorganisms compared to electron carriers such as H_2, largely due to reduced diffusion limitations [2,3]. Notably, the utilization of conductive nanoparticles, like magnetite, biochar or activated carbon, has attracted increasing attention for enhancing DIET processes. Indeed, these nanoparticles are able to act as conduits for direct electron transfer between electron-donating and electron-accepting microorganisms [4].

In this study, we investigated the impact of magnetite nanoparticles (MNPs), electroactive microorganisms, and a combination thereof, on the kinetics of H_2-fuelled CO_2 conversion into CH_4 bioconversion by a mixed hydrogenotrophic culture. Microcosm experiments were conducted in triplicate using anaerobic serum bottles. Gas phase analyses of the microcosms were performed to characterize methane production and hydrogen utilization kinetics, while microbial population characterization was conducted using next-generation sequencing methods (NGS). Our findings highlight the significance of DIET between methanogenic archaea and electroactive microorganisms in hydrogenophilic biomethanation, offering insights for innovative biotechnological applications.

References

[1] P. Leitão, M. Tucci, C.C. Cruz Viggi, H. Nouws, A.S. Danko, F. Aulenta, Natural Magnetite Minerals Enhance 1,2-Dichloroethane Reductive Dechlorination, Minerals. 12 (2022) 816. https://doi.org/10.3390/min12070816.

[2] H. Dong, J. Cheng, H. Li, L. Yue, R. Xia, J. Zhou, Electron transfer from Geobacter sulfurreducens to mixed methanogens improved methane production with feedstock gases of H2 and CO2, Bioresour. Technol. 347 (2022) 126680. https://doi.org/10.1016/j.biortech.2022.126680.

[3] A.E. Rotaru, P.M. Shrestha, F. Liu, B. Markovaite, S. Chen, K.P. Nevin, D.R. Lovley, Direct interspecies electron transfer between Geobacter metallireducens and Methanosarcina barkeri, Appl. Environ. Microbiol. 80 (2014) 4599–4605. https://doi.org/10.1128/AEM.00895-14.

[4] C. Cruz Viggi, S. Rossetti, S. Fazi, P. Paiano, M. Majone, F. Aulenta, Magnetite particles triggering a faster and more robust syntrophic pathway of methanogenic propionate degradation, Environ. Sci. Technol. 48 (2014) 7536–7543. https://doi.org/10.1021/es5016789.

A Methylene Blue@AuNPs-Modified Electrochemical Platform for the Early Warning of Anionic Surfactants and PFAS in Water Matrices

Rosaceleste Zumpano[1*], Federica Simonetti[1], Riccardo Buccini[1], Marco Mancini[2], Valentina Gioia[2], Alessandro Ciccola[3], Simona Sennato[4], Franco Mazzei[1], Gabriele Favero[5]

[1]Department of Chemistry and Technology of Drugs, Sapienza University of Rome, Rome, Italy
[2]Acea ElaboRi SpA, 00189 Rome, Italy
[3]Department of Chemistry, Sapienza University of Rome, Rome, Italy
[4]Department of Physics, Sapienza University of Rome, Rome, Italy
[5]Department of Environmental Biology, Sapienza University of Rome, Rome, Italy

**rosaceleste.zumpano@uniroma1.it*

Surfactants are a class of organic molecules characterized by a hydrophobic tail and a hydrophilic head. Among these, fluorinated surfactants, known as per- and polyfluoroalkyl substances (PFAS), constitute a distinct subgroup with hydrophobic tails that are either partially or fully fluorinated. The continuous release of anionic and fluorinated surfactants into aquatic environments poses significant risks to both human health and the environment[1]. Due to the trace concentrations of these contaminants in water matrices, their analysis requires appropriate pre-treatment procedures and advanced chromatographic techniques [2], which result in extended analysis times and increased costs. In this study, as a proof of concept, the Methylene Blue (MB) redox probe, previously demonstrated to selectively adsorb anionic and fluorinated surfactants [3], was electropolymerized onto a screen-printed electrode (SPE) modified with multi-walled carbon nanotubes (MWCNTs). The electroanalytical characterization of this platform was carried out using cyclic voltammetry (CV) and square-wave voltammetry (SQW), with sodium dodecyl sulfate (SDS) serving as the calibration standard. The electrochemical response was optimized with respect to pH and the MB polymerization degree. Additionally, to enhance the platform's sensitivity, the electrode surface was modified with gold nanoparticles (AuNPs), which improved the optoelectronic properties of MB. Preliminary studies employing UV-Vis spectroscopy and Surface-Enhanced Raman Spectroscopy (SERS) were conducted to evaluate the interactions between AuNPs and MB, as well as the mechanisms of surfactant interaction with the system. The developed electrochemical sensor exhibited excellent linearity across two calibration ranges (0.05-1 ng/mL and 5-50 ng/mL) and demonstrated good sensitivity, with limits of detection (LoDs) of 0.04 ng/mL and 0.02 ng/mL respectively. With its high selectivity and reproducibility, this platform shows great promise for early-warning monitoring of anionic surfactants and PFAS in drinking water at trace concentrations.

References

[1] M. Tsianou, D. Bedrov, P. Alexandridis, ACS Publications, 2023, 443–462.
[2] S. Taniyasu, L.W.Y. Yeung, H. Lin, E. Yamazaki, H. Eun, P.K.S. Lam, N. Yamashita, Chemosphere 2022, 288, 132440.
[3] M. Sörengård, E. Östblom, S. Köhler, L. Ahrens, J Environ Chem Eng, 2020, 8, 103744.

Theme H - Chemistry and Biology

Plant-Based Food：From Nutritional Value to Health Benefits

Donatella Ambroselli*[1], Fabrizio Masciulli[1], Enrico Romano[1], Cinzia Ingallina[1], Mattia Spano[1], Luisa Mannina[1]

[1]*Food Chemistry Lab, Department of Chemistry and Technology of Drugs, Sapienza University of Rome, P. le Aldo Moro 5, 00185 Rome, Italy*

**donatella.ambroselli@uniroma1.it*

Officinal plants are a source of secondary metabolites with biologically relevant properties [1].
Due to the variability in the production of these secondary metabolites caused by multiple factors (genetics, light, temperature, humidity, altitude, soil nature and cultivation), it is necessary to assess the difference between ecotypes of the same species.
The current study was aimed at characterizing the chemical and biological profile of three different ecotypes (spontaneous, mountain vs. organically ecotypes) of Burdock, Dandelion and Lemon balm to detect possible differences between the ecotypes of the same cultivar
All samples were subjected to the Bligh-Dyer extraction protocol [2] to obtain extracts for the metabolomic analysis by applying NMR spectroscopy.
In addition, the hydroalcoholic extracts of the officinal plants were tested on HypoE22 cells by means of MTT to assess the antioxidant activity and on mice brain specimens to evaluate neuroprotective effect through assay and RT-PCR of some genes.
Different classes of compounds, such as sugars, organic acids, free amino acids, polyphenols, fatty acids and other compounds from NMR analysis were identified and quantified. By comparing the variability of each metabolite, some were found to be tissue-specific markers: arginine was found in the roots of Dandelion and Burdock, whereas myo-inositol, galactose, DGDG, pheophytin and chlorophyll were identified in the Lemon balm and Dandelion aerial parts. In addition, each plant was characterised by the presence of specific polyphenols (3,5 di-caffeoylquinic acid, caftaric acid, cycloric acid, chlorogenic acid and rosmarinic acid). The concentration of metabolites varied significantly depending on the culture, tissue type and ecotype.
The results obtained from biological assay indicated the ability of the extracts to reduce neuroinflammation based on the content of phytochemicals.
The selected plants showed considerable potential for bioactivity, as the identified molecules are well known for their antioxidant and antimicrobial actions, along with their activity in modulating the body's metabolic biochemical processes, and a pronounced anti-inflammatory effect
All this information provided can be used to support the research in the nutraceutical and phytopharmaceutical industry.

References

[1] Aye, M.M.; Aung, H.T.; Sein, M.M.; Armijos, C. A *Molecules* 2019, **24,** 293.
[2] Spano, M., Maccelli, A., Di Matteo, G., Ingallina, C., Biava, M., Crestoni, M. E., Bardaud, J. X., Giusti, A. M., Mariano, A., Scotto D'Abusco, A., Sobolev, A. P., Lasalvia, A., Fornarini, S., & Mannina L.,*Molecules*, 2021, **26**, 5412.

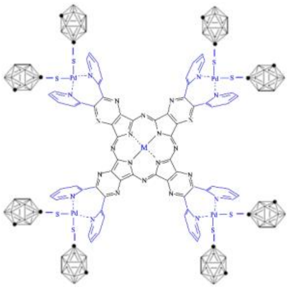
Porphyrazines carrying externally *o*-carboranedithiolate groups as potential bimodal PDT/BNCT anticancer agents

Andrea Angelucci[1*], Claudio Ercolani[1], Maria Pia Donzello[1]

[1]Department of Chemistry, Sapienza University of Rome, P.le Aldo Moro 5, 00185 Rome, Italy
**andrea.angelucci@uniroma1.it*

In our previous extensive studies the synthesis, physicochemical properties and photoactivity as anticancer drugs in photodynamic therapy (PDT) [1] were reported of pentanuclear octa(2-pyridil)tetrapyrazinoporphyrazines complexes, carrying externally eight units of *m*-carborane-1-thiolate (CBT) formulated as $[\{Pd(CBT)_2\}_4Py_8TPyzPzM]\cdot xH_2O$, where $Py_8TPyzPz$ = tetrakis-2,3-[5,6-di(2-pyridyl)pyrazino]porphyrazine and M = $Mg^{II}(H_2O)$, Zn^{II}, Pd^{II} (Figure 1A) [2,3]. The photosensitizer activity for the generation of singlet oxygen, $^1O_2$, the cytotoxic agent in PDT was explored in DMF solution. These species have high quantum yield values ($\Phi_\Delta = 0.6{-}0.7$) which are higher than those obtained for the parent $[(PdCl_2)_4Py_8TPyzPzM]$, and $[Py_8TPyzPzM]$ complexes [4]. Moreover, the presence of high boron content can open perspectives for their use in Boron Neutron Capture Therapy (BNCT), an experimental radiotherapy studied against aggressive and penetrating cancerous pathologies [5,6].

In an extension of our work on new TPyzPzs it was thought interesting to open additional perspectives of application in a bimodal anticancer therapy PDT/BNCT. For this purpose new homo/eteropentanuclear tetrapyrazinoporphyrazines having externally four units of 1,2-dithiolate-*o*-carborane, formulated as $[\{Pd(CBdT)\}_4Py_8TPyzPzM]\cdot xH_2O$ (CBdT = 1,2-dithiolate-*o*-carborane; M = $Mg^{II}(H_2O)$, Zn^{II}, Pd^{II}) (Figure 1B), have been synthesized and characterized. The photosensitizer activity for the generation of singlet oxygen, $^1O_2$, was explored for the Zn^{II} and Mg^{II} complexes in DMF. The high Φ_Δ value obtained for the Zn^{II} macrocycle (0.58) falls within the range 0.4-0.7 obtained for numerous phthalocyanines and Zn^{II} porphyrazines. These results qualify the Zn^{II} complex $[\{Pd(CBdT)\}_4Py_8TPyzPzZn]$ as an excellent photosensitizer for the generation of singlet oxygen and in addition its high boron content suggests the possibility to be used as bimodal anticancer agent (PDT/BNCT).



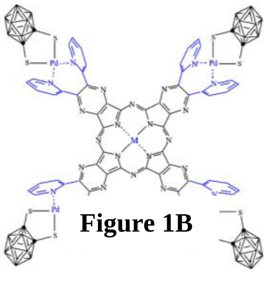


Figure 1B

References

[1] M. Ethirajan, Y. Chen, P. Joshi, R. K. Pandey *Chem. Soc. Rev.*, 2011, **40**, 340.
[2] E. Viola, M.P. Donzello, S. Testani, G. Luccisano, et al. *Inorg. Chem.*, 2019, **58**, 1120.
[3] M.P. Donzello, C. Ercolani, C. Rizzoli, M. Spano, L. Mannina *Inorg. Chim. Acta*, 2024, **564**, 121906.
[4] M.P. Donzello, E. Viola, C. Ercolani, Z. Fu, D. Futur, K.M. Kadish *Inorg. Chem.*, 2012, **51**, 12548
[5] K. Hu, Z. Yang, L. Zhang, L. Xie, L. Wang, H. Xu, et al. *Coord. Chem. Rev.*, 2020, **405**, 213139.
[6] T. D. Malouff, D. S. Seneviratne, D. K. Ebner, et al. *Front. Oncol.*, 2021, **11**, 601820.

Oxazolidinone-based Carbonic Anhydrase inhibitors: a promising strategy to discover antibiotics against gram-positive bacteria?

S. Giovannuzzi[1*], A. Ammara[1], D.P. Flaherty[2], M.N. Seleem[3], A. Nocentini[1], C.T. Supuran[1]

[1]Department of NEUROFARBA, Section of Pharmaceutical and Nutraceutical Sciences, University of Florence, Polo Scientifico, Via U. Schiff 6, 50019, Sesto Fiorentino, Firenze, Italy;
[2]Department of Medicinal Chemistry and Molecular Pharmacology, College of Pharmacy, Purdue University, West Lafayette, IN 47907, USA;
[3]Department of Biomedical Sciences & Pathobiology, Virginia-Maryland College of Veterinary Medicine, Virginia Polytechnic Institute & State University, Blacksburg, VA 24061, USA.

**simone.giovannuzzi@unifi.it*

Over the past decade, bacterial carbonic anhydrases (CAs, EC 4.2.1.1) have emerged as promising targets for the development of novel antibiotic agents. Among the eight identified CA families (α, β, γ, δ, η, ζ, θ, and ι), only the α-, β-, γ-, and ι-classes have been identified in bacteria.1-4 Specifically, α- and ι-CAs are periplasmic and exclusive to Gram-negative bacteria, while β- and γ-CAs are cytosolic and present in both Gram-positive and Gram-negative microorganisms.1,2 Microbial CAs play crucial roles in various physiological processes, including pH regulation, virulence, growth, and acclimatization, making them valuable targets for designing anti-infective strategies.1,4

By applying a multi-target directed ligand (MTDL) approach, we developed oxazolidinone-based CA inhibitors to combine the inhibition of bacterial CAs with the antibiotic effects of oxazolidinones, such as Linezolid and Tedizolid, which disrupt bacterial protein synthesis in Gram-positive bacteria. A novel synthetic pathway was set up to incorporate (hetero)aryl sulfonamides into the oxazolidinone scaffold using various linkers and spacers. All multitargeting compounds were assayed as inhibitors against CAs expressed in Gram-positive bacteria by a Stopped-Flow kinetic assay. A subset of derivatives showed potent anti-enterococcal effects against various multidrug-resistant E. faecium and E. faecalis strains with several compounds significantly surpassing the efficacy of the lead Linezolid and CA inhibitor drugs (MIC values in the range 0.25 to >64 µg/mL).

References

[1] Supuran C.T., Capasso C. *Expert Opinion on Therapeutic Patents*, 2020, **30**, 963-982.
[2] Supuran C.T., Capasso C. *Metabolites*, 2017, **7**, 56.
[3] Abutaleb N.S., Elkashif A. *Antimicrobial Agents and Chemotherapy*, 2021, **65**, e01715-e01720.
[4] Abutaleb N.S., Elhassanny A.E.M. *PeerJ*, 2021, **9**, e11059.

Design, synthesis, and biological activity of benzo[*b*]thiophene-based inhibitors of human monoamine oxidase

Paolo Guglielmi[1*], Emanuela Berrino[1,2], Francesca Diomede[3], Simone Carradori[3], Guya Diletta Marconi[3], Daniela Secci[1]

[1]*Department of Drug Chemistry and Technologies, Sapienza University of Rome, 00185 Rome, Italy;*
[2]*IC2MP UMR CNRS 7285, Université de Poitiers, 4 rue Michel Brunet 86073Poitier scedex 9, France*
3Department of Pharmacy, "G. d'Annunzio" University of Chieti-Pescara, 66100 Chieti, Italy

**paolo.guglielmi@uniroma1.it*

Parkinson's disease (PD), the second most common neurodegenerative disorder after Alzheimer's disease (AD), is characterized by the progressive degeneration of dopaminergic neurons in the *substantia nigra pars compacta*, albeit also other non-dopaminergic pathways have been involved in its pathomechanism [1]. Current treatments focus on symptom relief either with dopamine (DOP) supplementation and/or by blocking DOP breakdown. In this regard, human Monoamine Oxidase Inhibitors (hMAOI) such as selegiline, rasagiline and safinamide are used as monotherapy in early PD or in association with levodopa in advanced PD [2]. These drugs are effective in limiting DOP metabolism, also offering neuroprotection by reducing the amount of hydrogen peroxide (H_2O_2), the by-product of hMAOs enzymatic activity [3]. In the 2019 we reported the benzo[*b*]thiophen-3-ol core as a convenient tool for the design of novel neuroprotective agents. Indeed, the compounds endowed with this scaffold exhibited selective hMAO-B inhibition and promising biological activity on rat cortex synaptosome (*ex vivo* models) in LPS-induced inflammation conditions [4]. Pursuing our efforts in the development of new effective compounds for the treatment of neurodegenerative diseases, we evaluated chemical modification of the benzo[*b*]thiophen-3-ol core by removing the hydroxyl group located at the position 3 of this scaffold (Figure 1).

The designed benzo[*b*]thiophene-based compounds have been synthesised with a novel multistep synthetic approach and exhibited potent inhibitory activity against hMAOs. The most promising derivatives have been further evaluated on the neuroblastoma SH-SY5Y cell line, an established neuronal cell model employed to perform PD research, demonstrating antioxidant activity and neuroprotective profile.

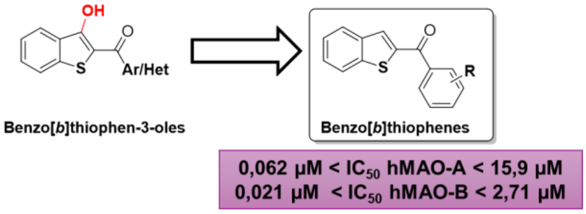


Figure 1. Design of the novel hMAOs inhibitors.

Acknowledgements: Finanziato dall'Unione europea – Next Generation EU

References

[1] Dézsi L., Vécsei L. *CNS & Neurological Disorders - Drug Targets*, 2017, **16**, 425-439.
[2] Jost W.H. *Journal of Neural Transmission*, 2022, **129**, 723–736
[3] Chew Z.X. et al. *CNS & Neurological Disorders - Drug Targets*, 2023, **22**, 329-352.
[4] Guglielmi P., et al. *Journal of Enzyme Inhibition and Medicinal Chemistry*, 2019, **34**, 1511–1525.

Exploring the mechanism of C55-P translocation in bacterial cell walls: a native mass spectrometry approach

Michela Guida[1,2*], Abraham O. Oluwole[2,3], Neha Kalmankar[2,3], Jack L. Bennett[2,3], Giovanna Poce[1], Jani R. Bolla[2,4], Carol V. Robinson[2,3]

[1] Department of Chemistry and Technologies of Drug, Sapienza University of Rome, 00185 Rome, Italy.
[2] The Kavli Institute for Nanoscience Discovery, Oxford, South Parks Road, Oxford, OX1 3QU, UK.
[3] Department of Chemistry, University of Oxford, South Parks Road, Oxford, OX1 3QZ, UK.
[4] Department of Biology, University of Oxford, South Parks Road, Oxford, OX1 3RB, UK.

**michela.guida@uniroma1.it*

Antibiotic resistance is widely recognised as a significant global health concern, underscoring the need for new antibiotics to combat the growing threat of resistant bacteria. Here, we present a work in which native Mass Spectrometry was employed to investigate the interaction and behaviour of a protein involved in a critical bacterial pathway.

The peptidoglycan polymer is a fundamental structural element for the formation of the cell wall of bacteria, so its biosynthetic pathway represents a successful antibacterial drug target [1]. The biosynthesis of peptidoglycan begins in the cytosol, where undecaprenyl monophosphate (UndP or C55-P) plays an important role in the formation of lipid II, which is transported across the inner membrane to the periplasm. Here, the glycopeptide moiety of lipid II is cross-linked into the peptidoglycan polymer, while the lipid carrier is released as undecaprenyl diphosphate (C55-PP), which must be dephosphorylated to form C55-P and then flipped across the inner membrane to re-enter the pathway. The mechanism of this last step is the least understood of the peptidoglycan pathway. DedA and DUF386 domain-containing family membrane proteins were shown to be involved in this translocation of C55-P [2], but the mechanisms remain unknown. A member of the DedA transportes in *Bacillus subtilis* is the protein UptA, which is believed to be responsible for the flipping of C55-P across the membrane.
We used native mass spectrometry (MS) to study how UptA interacts with C55-P, membrane phospholipids and cell wall targeting antibiotics.
The results revealed that UptA, expressed and purified in *E. coli*, forms monomer-dimer equilibria and binds to ligands in a pH-dependent manner. We also find that UptA has a higher affinity for C55-P than for shorter-chain analogues and membrane phospholipids, indicating that C55-P is its preferred endogenous substrate. In addition, we demonstrate that lipopeptide antibiotics, such as amphomycin and aspartocin D, can directly intercept UptA function by outcompeting the substrate for the protein binding site, suggesting that they could interfere with C55-P translocation. Overall, the study suggests that UptA-mediated translocation of C55-P is potentially regulated by anionic phospholipids and provides insights for future development of new antibiotics that target the recycling of carrier lipids in bacteria.

References

[1] Schneider T., Sahl H.G., *International Journal of Medical Microbiology*, 2010, **300**, 161-169.

[2] Roney I. J., Rudner D. Z., *Nature*, 2023, **613**, 729-734.

Biotechnological flow chemistry approach for lignin valorization

Lembo Giuseppe[1,*], Zoia Luca[1], Orlandi Marco[1,2], Lange Heiko[1,2]

[1] *Department of Earth and Environmental Sciences – DISAT, University of Milano-Bicocca, Piazza dell'Ateneo Nuovo, 1 - 20126, Milan,*
[2] *NBFC – National Biodiversity Future Center, 90133 Palermo, Italy*
** giuseppe.lembo@unimib.it*

Lignin is the only abundant aromatic biopolymer present on Earth, holding considerable potential for replacing oil-based aromatic monomeric platform chemicals for the chemical industry. The molecular structure of lignin is, however, complex and dependent on botanical taxonomy as well as biorefinery methods used for its isolation. Once isolated, lignin depolymerization emerges as one prospective inaugural and pivotal stage in its valorization pathway. In natural environments, lignin is effectively degraded through the action of numerous enzymes secreted by fungi and bacteria. The use of enzymatic catalysts, such as laccase, has long been considered an eco-friendly and highly sustainable [1]. Laccase (EC.1.10.3.2), generating phenoxy radical species, can initiate several processes such as: polymerization, depolymerization, oxidation at the C-α position in the β-*O*-4' bonding of terminal phenolic units [2] and demethylation. With respect to the generation of starting materials for the chemical industry, depolymerisation is most interesting. In chemistry, continuous flow technology has firmly established itself as a highly effective production method. Benefits arise from a greater control over reacticities, allowing also for innovative reactions that might pose challenges or prove impractical when employing conventional batch methodologies [3]. Aim of our research was addressing lignin depolymerization through a biotechnological approach, combining enzyme catalysis with flow chemistry, to develop an efficient and environmentally friendly biocatalytic process for the biorefinery sector. To this end, a continuous flow process set-up has been realised on the basis of a delocalised laccase-mediator system (Figure 1). Two different column reactors were filled, respectively, with lignin and with an immobilised laccase, *i.e.*, LbL-LAC@Al_2O_3.

Lignin depolymerisation and monomeric reaction products were analysed by mass spectrometry and by quantitative ^{31}P NMR spectroscopy, as well as gel permeation chromatography (GPC). The oxidation of lignin by the laccase-mediator system in continuous flow has produced several monomeric compounds, such as vanillin, 4-hydroxy benzaldehyde, and 4-hydroxy acetophenone, and, more importantly, also oligomeric fractions that did not undergo repolymerisation thanks to the dynamics inherent to the flow set-up exploiting changes in solubility and thus 'migration' effects in the system. The presentation will detail the conceptual approach and highlight scope and limitations.

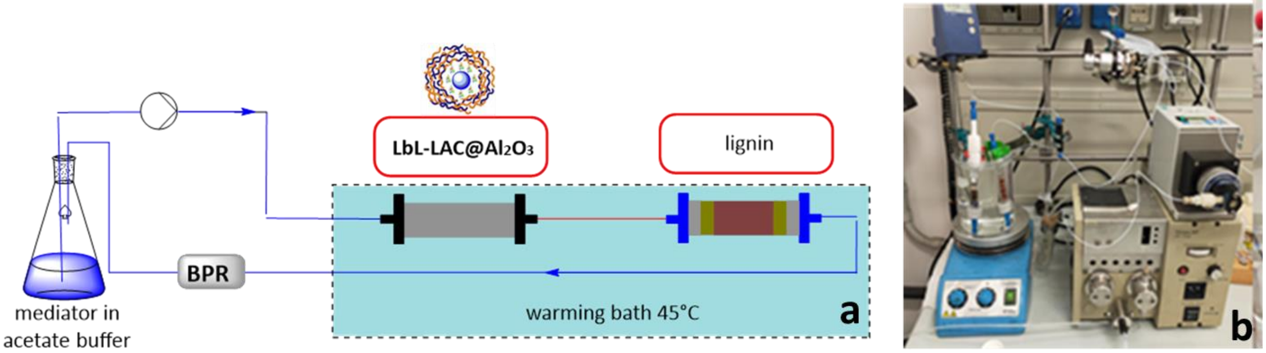


Figure 1: a) Scheme of contunuous flow process for LbL_LAC@AL2O3 conversion of lognin; **b)** Self made flow reactor.

References

[1] Singhania R.R., Patel A.K., Raj T., Chen C.-W., Ponnusamy V.K., Tahir N., Kim S.-H., Dong C.D. *Fuel* 2022 **311**, 122608.

[2] Vignali E., Gigli M., Cailotto S., Pollegioni L., Rosini E., Crestini C. *ChemSusChem* 2022 **15**, e202201147.

[3] Brown E.E. *J. Flow Chem.* 2022 **13**, 91–102

Chemical and biological profile of "Sulmona Red Garlic" ecotype's aerial bulbils

F. Masciulli[1*], D. Ambroselli[1], E. Romano[1], S. C. Di Simone[2], A. Acquaviva[2], M. L. Libero[2],
Nilofar[2], M. Spano[1], G. Di Matteo[1], C. Ingallina[1], A. Salvo[1] and L. Mannina[1]

[1]*Department of Chemistry and Technology of Drugs, Sapienza University of Rome, Piazzale Aldo Moro 5, 00185 Rome, Italy*
[2]*Department of Pharmacy, G. d'Annunzio University of Chieti-Pescara, 66013 Chieti, Italy*

**fabrizio.masciulli@uniroma1.it*

Garlic (*Allium sativum L.*), generally used as food taste-active enhancers, is also of great interest for therapeutic treatments and health benefits antioxidant [1]. Despite this evidence, in literature only few pilots are reported about the potential phytotherapeutic use of the "Sulmona red garlic" (ecotype traditionally cultivated in the Abruzzo region, Middle Italy) [2].

Here, the phytochemical profile of aerial red garlic bulbs and the evaluation of biological properties are reported. Both untargeted (NMR) and targeted (HPLC-DAD-MS) methodologies were used to provide complementary information on metabolite composition of the hydroalcoholic extract [3,4]. In particular, NMR analyses allowed sugars, organic acids, amino acids and the organosulphur compounds alliin and allicin to be determined whereas the HPLC analyses revealed the presence of phenolics compounds (catechin, chlorogenic acid, and gallic acid).

The biological activity of garlic hydroalcoholic extract was assessed towards HCT116 colon cancer cells. A chemopreventive effect was observed. This effect could be related to the inhibition of TRPM8 expression, a receptor possibly involved in inflammatory pathway and carcinogenesis [6]. Moreover, the same extract reduced the gene expression of TNF-α (tumor necrosis factor), HIF1-α (hypoxia-inducible factor) and VEGFA (vascular endothelial growth factor) indicating its ability to contrast cancer development through angiogenic pathway. These finding were supported by *in silico* experiment supported biological effects, according to its prediction, organosulphur compounds, especially alliin, may directly interact with TRPM8. The chemico-biological profile of Sulmona red garlic here reported suggests the potential use of this product in phytotherapeutic remedies for management colon inflammatory diseases.

References

[1] L. Recinella, E. Gorica, A. Chiavaroli, C. Fraschetti, A. Filippi, S. Cesa, et al. Foods, 2022, 11, 3559.
[2] A. Lasalvia, F. Cairone, S. Cesa, A. Maccelli, ME. Crestoni, L. Menghini, et al. Antioxidants, 2022, 11, 2088.
[3] C. Ingallina, AP. Sobolev, S. Circi, M. Spano, C. Fraschetti, A. Filippi, et al. Molecules, 2020, 25, 1908.
[4] M. Spano, G. Di Matteo, C. Ingallina, B. Botta, D. Quaglio, F. Ghirga, et al. Molecules, 2021, 26, 2912.
[5] A. Kopeć, J. Skoczylas, E. Jędrszczyk, R. Francik, B. Bystrowska, J. Zawistowski. Agriculture (Switzerland), 2020, 10, 40.
[6] F. Borrelli, E. Pagano, B. Romano, S. Panzera, F. Maiello, D. Coppola, et al. Carcinogenesis, 2014, 35, 2787.

Novel hybrid magneto-plasmonic nanoclusters for ultrasensitive detection through SERS effect

Francesco Mattii[1*], Greta Feregotto[1,2], Caterina Dallari[1,2], Caterina Credi[1,2]

[1] European Laboratory for Non-linear Spectroscopy (LENS), Department of Physic and Astronomy,
University of Florence, Florence, Italy
[2] National Institute of Optics, National Research Council (CNR-INO), Florence, Italy

mattii@lens.unifi.it

In last decades, research in nanotechnologies has been focused on the development of nano-sized platforms for a wide range of biomedical applications mainly including biosensing, and theragnostic. Among all different kinds of nanomaterials, magnetic nanoparticles (mNPs) are of great interest since they exhibit interesting properties that have been exploited for biomedical applications specifically magnetic resonance imaging, drug delivery, bioseparation, and hyperthermia. [1] However, mNPS suffer from drawbacks, including the poor colloidal stability when used with biological fluids that could limit mNPS applicability with biological samples. [2] At the same time, gold nanoparticles (AuNPs) are widely studied as highly performing biocompatible nanoplatforms, that are characterized by easiness of preparation and surfaces functionalization and increased stability. Moreover, their unique optical properties, due to localized surface plasmon resonance (LSPR) effect, make them ideal as imaging probes and photothermal agents in cancer therapy. AuNPs LSPR properties are exploited also for Surface Enhanced Raman Spectroscopy (SERS), a sensitive optical detection technique used in biochemical assays, disease diagnosis, and environmental monitoring. [3] Furthermore, AuNPs surface provide an interface for easy covalent conjugation, by thiol gold-chemistry. That feature could be exploited to decorate NPs surfaces with bioorthogonal Raman reporters (RRs) to obtain SERS-probes characterized by large Raman cross-sections and narrow peaks in the biologically Raman silent region (1800-2500 cm^{-1}) to further increase SERS sensitivity by decreasing the spurious signal from the background. [4] In this scenario the present work is focused on the development and optimization of both magneto-plasmonic nanoclusters and plasmonic nanoparticles, engineered to selectively bind different analytes in a fluid, magnetically isolate from the sample medium, and detect them at low concentrations. Thus, representing a powerful tool for the development of sandwich-based bioassays with multiplexing capabilities. To this end, magneto-plasmonic nanoclusters, (mAuNPs) were obtained by synthesizing mNPS and further decorating with Au seeds. Subsequently, the mAuNPs were functionalized with hydrophilic bifunctional polymer derivative (HS-PEG-COOH), to stabilize mAuNPs dispersion, and provide binding site for further functionalization with macromolecules for selective analyte targeting. Meanwhile, AuNPs with hyperbranched morphology (AuNSts), were synthesized and functionalized with both HS-PEG-COOH and novel biorthogonal RR. The as labelled AuNSts were engineered with a capture antibody. As a proof-of-concept mAuNPs and AuNSts were engineered to accomplish a biotin-avidin sandwich bioassay, enabling selective neutravidin capture, isolation, and detection. Sandwich formation was demonstrated at concentration down to 0.5 µg/mL. As a step forward, a novel 3D printed microfluidic device, engineered for efficiently mix NPs with analytes, magnetically separate the biotarget, was developed thus opening interesting perspective towards SERS-microfluidic integration.

References

[1] Nguyen M.D., Tran H.-V., Xu S., Lee T.R. Appl. Sci. 2021, **11(23)**, 11301.
[2] Gupta A.K., Gupta M. Biomaterials 2005, **26(18)**, 3995-4021.
[3] Li J., Huang Y., Ding Y. et al. Nature 2010, **464**, 392–395.
[4] Dallari C., Innocenti R., Lenci E., Trabocchi A. Pavone F.S., and Credi C. Int. J. Mol. Sci. 2022, **23**, 5573.

Integrating Omics And Kinetics For Bio-Kinetic Correlations In Chlorinated Solvents Dechlorinating Enriched Consortia: Implications For Field-Scale Biodegradation Modeling

Bruna Matturro[1*], Emiliana Pandolfo[1], Simona Rossetti[1], Andrea Pelino[2], Marco Zeppilli[2], Marco Petrangeli Papini[2]

[1] *Water Research Institute of the National Research Council, IRSA-CNR, Rome, Italy*
[2] *Chemistry Department, Sapienza University, Rome, Italy*
**bruna.matturro@irsa.cnr.it*

Chlorinated solvents contamination poses significant environmental challenges. However, biodegradation processes mediated by specialized organohalide-respiring bacteria offer potential solutions. Establishing stable dechlorinating microbial cultures is paramount for advancing bioremediation research, particularly in understanding large-scale biological processes. Although dechlorinating consortia exist, knowledge of their metabolic properties and functionalities within mixed microbial communities remains incomplete. Furthermore, understanding the relationship between reaction kinetics and biological parameters is crucial.

While various kinetic models describe the reductive dechlorination (RD) process, data on kinetics and biomass often rely on broad indicators, overlooking specific dechlorinating populations. Consequently, there exists a gap in understanding the dynamics and activity of specialized dechlorinating biomass, including *D. mccartyi* (Dhc) and reductive dehalogenase genes involved in the RD, and their correlation with kinetic performance. These parameters influence the RD rate, emphasizing the need to accurately define the biodiversity and functional properties of dechlorinating communities, quantify biomarkers involved in the biological RD process, and evaluate kinetic parameters for establishing bio-kinetic correlations.

This study presents a multi-integrated approach that combines various biological parameters and kinetics to establish precise bio-kinetic correlations. Our focus has primarily been on a Dhc-enriched consortium, enabling the extrapolation of critical kinetic parameters essential for modeling RD processes. Active dechlorinating consortia, maintained in our lab for over a decade, were utilized. The cultures were fed with TCE and a range of electron donors for the RD process, including H_2, lactate, or bio-based materials like polyhydroxybutyrate (PHB) and biochar. TCE degradation kinetics were monitored, and known dechlorinating biomarkers were evaluated during the biodegradation process using epifluorescent microscopy (FISH) and -omics approaches, including Digital Droplet PCR (ddPCR) and long-read sequencing (Oxford Nanopore Technologies).

Based on biological and kinetics data, we established correlations between the abundances of RD biomarker genes and the maximum reductive dechlorination rates (RD max, mmol Cl^-/L/day). Per-cell respiration rates (Kmax, mmol Cl^-/Dhc/day) were defined, enabling the extrapolation of these bio-kinetic parameters, which holds significant implications for biokinetic modeling of the process. The findings of this study is promising for applications in both engineered systems and field-scale scenarios.

Acknowledgements: The project BISURE (2022AXYMKY) has been funded within the framework of the PIANO NAZIONALE DI RIPRESA E RESILIENZA (PNRR) Missione 4 “Istruzione e Ricerca” - Componente C2, Investimento 1.1, “Fondo per il Programma Nazionale di Ricerca e Progetti di Rilevante Interesse Nazionale (PRIN).

Are carbonic anhydrase modulators suited for designing multitargeting ligands to treat multifactorial pathologies?

Alessio Nocentini[1*]

[1] *NEUROFARBA Department, University of Florence, Sesto Fiorentino 50019, Firenze, Italy.*

**alessio.nocentini@unifi.it*

Drug combination therapies are clinically adopted as successful strategies to treat multi-factorial pathologies such as tumors and neurodegenerative disorders, according to their simultaneous action on more biological targets [1]. Lately, the design of multi-targeting directed ligands (MTDLs) has been significantly rising over combined drug therapies. In fact, MTDLs, or molecular hybrids, show an improved pharmacokinetics, the absence of drug-drug interactions, and a greater synergistic effect [1,2]. Over the last lustrum, we have been showing that carbonic anhydrase (CA) modulators are well suited to multi-targeting drug design strategies for the treatment of diseases such as ocular pathologies, tumors, inflammation, infections, neurodegeneration and memory disorders [4-9]. Our early-stage *in vivo* studies demonstrate that MTDLs including CA modulators produce a markedly enhanced pharmacological effect compared to the single target drugs and their combined administration.

References

[1] Zhou J, Jiang X, He S, et al. *J. Med. Chem.* **2019**, 62, 8881-8914.
[2] Costantino L, Barlocco D. *Future Med. Chem*. **2013**, 5, 5-7.
[3] Gilad Y, Gellerman G. *Cancers (Basel).* **2021**, 13, 669.
[4] Nocentini A, Ceruso M, Bua S, et al. *J. Med. Chem.* **2018**, 61, 5380-5394.
[5] Nocentini A, Trallori E, Singh S, et al. *J. Med. Chem.* **2018**, 61, 10860-10874.
[6] Bua S, Lucarini L, Micheli L, et al. *J. Med. Chem*. **2020**, 63, 2325-2342.
[7] Berrino E, Milazzo L, Micheli L, et al. *J. Med. Chem.* **2019**, 62, 7233-7249.
[8] Bonardi A, Micheli L, Di Cesare Mannelli L, et al. *J. Med. Chem.* **2022**, 65, 13143-13157.
[9] Giovannuzzi S, Chavarria D, Provensi G, et al. *J. Med. Chem.* **2024**, 67, 4170-4193.

Computational insight on drug-like natural and tailored monoterpenoids

Silvia Pezzola[1*], P. Galloni[1], V. Conte[1], F. Sabuzi[1], G. Bocchinfuso[1], M. Venanzi[1]

[1] *Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, via della Ricerca Scientifica, Roma, Italy*

* *silvia.pezzola@uniroma2.it*

Natural terpenoids and their derivatives are raising new interest as antifungal agents, inspired by traditional medicine and plant protection strategies. Among all, thymol and carvacrol are widely investigated for their activity as antibacterial/antimycotic agents [1]. Recently, tailored modifications, such as acetylation or bromination, led to thymyl acetate and 4-bromothymol, respectively. The latter compound has been synthesized and purified through eco-friendly approaches [2]. Interestingly, 4-bromothymol antimycotic activity resulted up to 6 times higher than that of thymol on 8 yeast strains, even in the case of acclaimed resistant species [3]. To elucidate the 4-bromothymol mechanism of action, a thorough computational study has been performed, exploiting Quantum Mechanics (QM) and Molecular Dynamics (DM). QM afforded the characterization of the reactivity, the moieties acting as hydrogen bonds donor/acceptor in water, and the partition coefficients. MD, through the Minimum Bias Approach (MBA), showed out the “real” displacement of active compounds into the simulated double layer of eukaryotic-like membrane, meanly 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (POPC). MBA returned two possible interactions of compounds with lipid, POSE_1 and POSE_2. Further, results confirmed the density alteration of the leaflet, and the shrinkage of the membrane thickness, as experimentally observed [3]. At the lipid level, only POSE_1 affected in a meaningful manner the PO_4^-—N^+ dipole and the order parameter of the double layer. Overall, the computational findings were in excellent agreement with the experimental results [3], and they clarified, for the first time, the mechanisms of action of thymol, carvacrol, and 4-bromothymol, likely explaining their different antimicrobial efficiency (Figure 1)

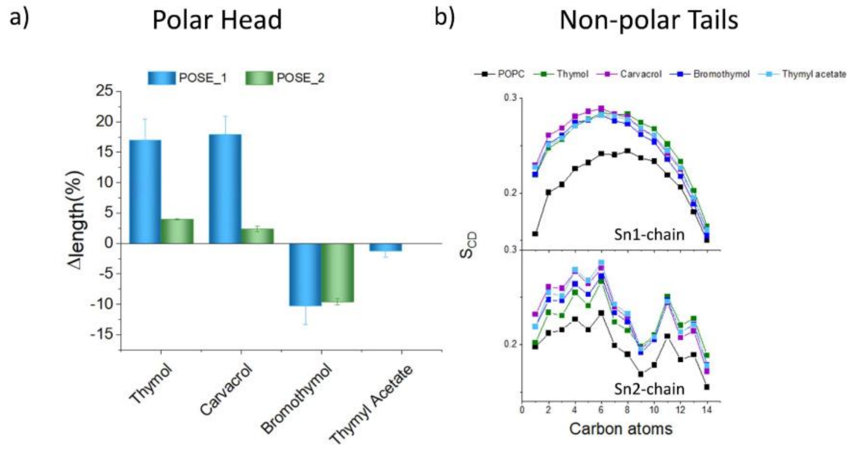


Figure 1. Average tune changing in lipid/s morphology. Panel a: percentage of variation of the distance PO_4^-—N^+ dipole in presence of each compound, setting the POPC one as reference, 0. Order parameter (S_{CD}) of lipid bilayer in the presence and in the absence of compounds. a) sn1-chain of lipid and b) sn2-chain of lipid.

References

[1] Floris, B.; Galloni, P.; Conte, V.; Sabuzi, F. *Biomolecules* 2021, **11**, 1325.
[2] Sabuzi, F. Churakova, E., Galloni, P., Wever, R., Hollmann, F., Floris, B., Conte, V. Eur. J. *Inorg. Chem.* 2015, 3519–3525
[3] Y. Lyu, N. Xiang, J. Mondal, X. Zhu, G. Narsimhan, J. *Phys. Chem.* B 2018, **122**, 2341-2354

Design of hypermodified NIR-responsive RNA conjugates for a spatio-temporal delivery of therapeutic oligonucleotides

Luca Pisano[1*], Gabriele Cianfoni[1], Stefano Lupi[2], Alberto Boffi[3], Bruno Botta[1], Masad Damha[4], Deborah Quaglio[1]

[1]*Department of Chemistry and Technology of the Drug, Sapienza Università di Roma, Roma, Italy*
[2]*Department of Physics, Sapienza Università di Roma, Roma, Italy*
[3]*Department of Biochemistry, Sapienza Università di Roma, Roma, Italy*
[4]*Department of Chemistry, McGill University, Montreal, Canada*
*[*luca.pisano@uniroma1.it](mailto:luca.pisano@uniroma1.it)*

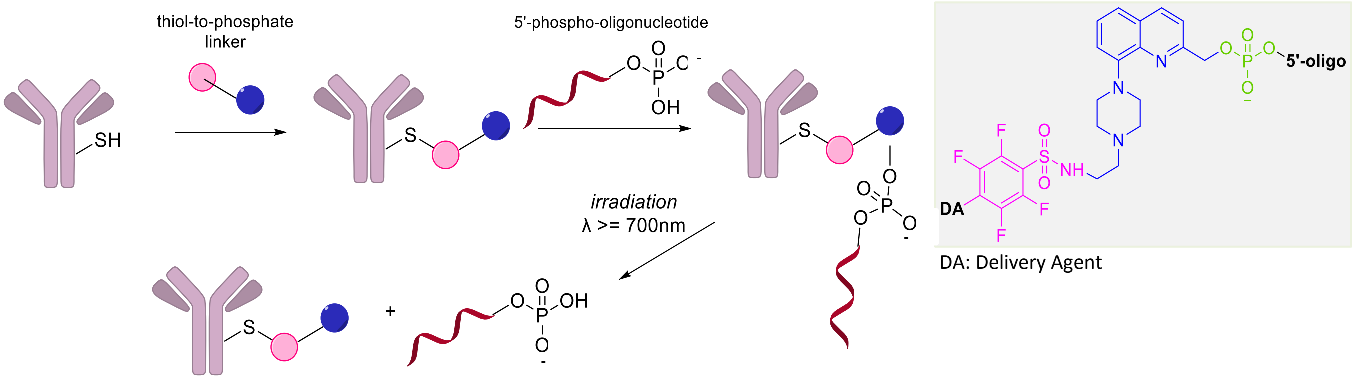
Therapeutic oligonucleotides (TOs) hold tremendous advancements for precise cancer treatment by modulating cellular pathways, yet their delivery to cancer cells poses a significant challenge (1). Chemical modifications play a pivotal role in surmounting biological barriers and improving TO delivery, thereby enhancing their pharmacokinetic/pharmacodynamic properties (2).

In this study, we propose a pioneering method leveraging hypermodified NIR-responsive RNA conjugates for spatio-temporal TO delivery, designing and optimising an efficient synthetic strategy for a quinoline-based photo-caging compound. Our approach integrates a two-photon excitable system, specifically a quinoline moiety, to encapsulate therapeutic RNAs (siRNAs and ASOs), enabling controlled release upon activation. Additionally, through covalent linkage of the quinoline scaffold to a cysteine-selective molecular component, such as an antibody, we impart tissue selectivity to our delivery system.

By incorporating a photolabile protecting group obtained in our laboratory, we aim to achieve precise spatiotemporal control over drug release. Recent advancements in caging groups have optimized absorption maxima for long-wavelength light, minimizing phototoxicity and enhancing tissue penetration, facilitating multi-photon excitation for controlled drug release (3).

Moreover, we designed a library of five modified TOs (siRNA and ASOs) targeting the Smo receptor, pivotal in aberrant Hedgehog pathway expression implicated in various malignancies, including Pediatric Medulloblastoma (4). This library will be integrated into our selective photo-labile system, enhancing its therapeutic potential.

Our innovative approach synergizes chemical modification strategies and optochemical biology to move targeted cancer therapy forward, offering promising ways for clinical translation and ultimately improving patient outcomes.



References

[1] Wu et al., *Delivery of therapeutic oligonucleotides in nanoscale*, 2022, Bioactive Materials, **7**, 202-323.
[2] Mangla et al., *Therapeutic Oligonucleotides: An Outlook on Chemical Strategies to Improve Endosomal Trafficking*, 2023, Cells, **12**, 2253.
[3] Bardhan et al., *Development of Photolabile Protecting Groups and their Application to the Optochemical Control of Cell Signaling*, 2020, Current Opinion in Structural Biology , **57**, 164-175.
[4] Sherri Y. Huang et al., *Targeting the Hedgehog Pathway in Pediatric Medulloblastoma*, 2015, Cancers, **7**, 2110-23.

The pyran-2-one core: a novel scaffold for potent and selective inhibition of tumor-related carbonic anhydrase isoforms IX and XII

Virginia Pontecorvi[1,3*], Mattia Mori[2], Antonella Bordin[3], Andrea Angeli[4,6], Susi Zara[5], Simone Carradori[5], Paolo Guglielmi[1], Elena De Falco[3], Daniela Secci[1], Claudiu T. Supuran[6].

[1]Department of Drug Chemistry and Technologies, Sapienza University of Rome, P.le A. Moro 5, 00185 Rome, Italy.
[2]Department of Biotechnology, Chemistry and Pharmacy, University of Siena, Via Aldo Moro 2, 53100 Siena, Italy
[3]Department of Medico-Surgical Sciences and Biotechnologies, Sapienza University of Rome, Corso della Repubblica 79, 04100, Latina, Italy.
[4]Department of Food and Drug, University of Parma, Parco Area delle Scienze, 27/A, 43124 Parma, Italy
[5]Department of Pharmacy, "G. d'Annunzio" University of Chieti-Pescara, Via dei Vestini 31, 66100 Chieti, Italy
[6]Neurofarba Dept., Section of Pharmaceutical and Nutriceutical Sciences, Università degli Studi di Firenze, Via U. Schiff 6, 50019 Sesto Fiorentino (Florence), Italy.

**email: virginia.pontecorvi@uniroma1.it*

Tumorigenesis is a dynamic process characterised by uncontrolled cell growth and proliferation leading to a massive amount of oxygen required. The adaptive response to oxygen deprivation, or hypoxia, is the stabilisation of the hypoxia-inducible factor (*HIF*) resulting in the transcription of HIF target genes such as *CAIX* and *XII* (Carbonic Anhydrase isoforms IX and XII) [1]. Particularly, the overexpression of the tumour-related isoforms IX and XII in hypoxic tumours has highlighted their role as promising targets for the treatment of cancer [2]. For this reason, based on the molecular simplification of the coumarin scaffold [3] that has been widely exploited for selective CA IX and XII inhibitor development, a series of pyran-2-one derivatives have been designed, synthesised, and evaluated as promising molecules for the selective inhibition of the tumour-related isoforms IX and XII. The novel compounds have been endowed with an amide or ester linker, bearing different (un)substituted aromatic or (hetero)(cyclo)aliphatic residues [4]. Moreover, an additional variation by binding a triazole ring substituted with the previously mentioned residues to the linkers has been evaluated. The design of the different libraries was aimed at expanding the chemical space exploitable for inhibitory activity. Furthermore, the different physic-chemical properties of the substituents allow the evaluation of the different interactions occurring between the compounds and the active site of the enzyme. The novel pyran-2-one derivatives are endowed with potent and selective inhibitory activity against the tumour-related hCA isoforms IX and XII, whereas being inactive against the two cytosolic off-target isoforms hCA I and II. The compounds exhibiting the best results in the hCA inhibition assay were further investigated in both cellular models and docking and molecular dynamics simulations (MD) studies to evaluate the actual inhibition mechanism.

References

[1] Ivanov S. et al., *American Journal of Pathology,* 2001, **158**, 905–919.
[2] Thiry A. et al. *Trends in Pharmacological Sciences*, 2006, **27**, 566–573.
[3] Cornelio B. et al., *European Journal of Medicinal Chemistry*, 2019, **175**, 40–48.
[4] Pontecorvi V. et al., I*nternational Journal of Molecular Sciences. 2022,* ***23****, 7950.*

From CO_2 to proteins and fatty acids: a novel approach for valorizing acetate-rich gas fermentation stream using microalgae through a two-step process

Giacomo Proietti Tocca[1,2], Francesco Regis[1], Caterina Celi[1], Silvia Fraterrigo Garofalo[1], Barbara Menin[3]*, Valeria Agostino[2], Fabrizio Di Caprio[4], Tonia Tommasi[1], Debora Fino[1,2].

[1]*Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, Turin, Italy.*
[2]*Centre for Sustainable Future Technologies, Fondazione Istituto Italiano di Tecnologia, Turin, Italy*
[3]*Istituto di Biologia e Biotecnologia Agraria, Consiglio Nazionale delle Ricerche, Milan, 20133, Italy*
[4]*Dipartimento di Chimica, Università Sapienza di Roma, Rome, Italy.*

giacomo.proietti@polito.it

Microalgae represent an innovative and sustainable food source for humans and animals [1]. The use of acetate as carbon substrate is a promising solution to enhance microalgal biomass productivity and reduce cost and environmental impacts in comparison to phototrophic cultivation [2]. Indeed, acetate can serve as an excellent intermediate to link many industrial facilities, as it can be synthesized from different processes like syngas fermentation starting from CO_2 and waste [2,3].

A novel approach based on a two-step process is here proposed: a real acetate-rich gas fermentation stream is directly valorized as acetate-rich medium for microalgal heterotrophic growth. The main aim of this study is to simultaneously increase the economic sustainability of gas fermentation and microalgal biomass production by transforming a low-value product (acetate) into high-value protein-rich biomass.

Through gas fermentation with *Thermoanaerobacter kivui*, an output stream with an acetate concentration of 13.3 g L^{-1} was obtained. This stream was then tested at various concentrations until 13.3 g L^{-1} (real and undiluted stream) for the heterotrophic growth of *Chlorella sorokoniana*. It demonstrated the ability to grow heterotrophically using the residual acetate present in the gas fermentation stream as a carbon and energy source. This resulted in high biomass productivities (1.61 g L^{-1} day^{-1}) along with specific growth rates and yields consistent with values observed under heterotrophic conditions with acetate.

After highlighting high protein accumulation in microalgal biomass (50% of dry matter), the well-balanced profile of essential amino acids and its comparison with human and fish nutritional requirements confirmed the nutraceutical potential of the heterotrophic biomass obtained through this innovative process. This is further enhanced by the high quantity of polyunsaturated fatty acids and the substantial percentage of alpha-linolenic acid ω3 (15% of total lipids).

Gas fermentation stream has a great potential to be valorized in microalgal biomass. Compared to other streams, it originates from a sterile process that ensures an initial active microbial load of zero. In addition, the essential amino acids profile of the *T. kivui* residual biomass obtained by the centrifugation of the gas fermentation stream was analyzed to verify its potential valorization in aquafeed.

References

[1] E. Wolfgang Becker, *Handbook of Microalgal Culture: Applied Phycology and Biotechnology*, 2013

[2] Giacomo Proietti Tocca, Valeria Agostino, Barbara Menin, Tonia Tommasi, Debora Fino, Fabrizio Di Caprio, *Reviews in Environmental Science and Biotechnology*, 2024

[3] Jiyun Bae, Yoseb Song, Hyeonsik Lee, Jongoh Shin, Sangrak Jin, Seulgi Kanga, Byung-Kwan Cho, *Chemical Engineering Journal*, 2022

Hydrophilic gold nanoparticles as multimodal agents for plasmonic nanomedicine

T. A. Salamone[1,2*], B. Pennacchi[2], M. Mercurio[2], S. Cerra[1], S. Marotta[1], S. Mrmic[1], M. Alimandi[1],
Vincenzo Visco[1], M. Taurino[1], P. Trivedi[3], I. Fratoddi[2], E. Anastasiadou[1]

[1] *Department of Clinical and Molecular Medicine, Sapienza University of Rome, Rome, Italy*
[2] *Department of Chemistry, Sapienza University of Rome, Rome, Italy*
[3]*Department of Experimental Medicine, Sapienza University of Rome, Rome, Italy*
**Tommaso.salamone@uniroma1.it*

Gold nanoparticles (AuNPs) show physicochemical and plasmonic properties that make them suitable for various fields, including medicine and optoelectronics [1]. In the treatment of tumours, hydrophilic gold nanoparticles can be used in multipurpose applications, from drug delivery to diagnosis and imaging. Small-sized AuNPs can penetrate inside tumour tissue, and if loaded on the surface with the appropriate bioactive agent, they can be released in the desired place and enhance the drug's bioactivity [1].

Surface functionalisation of AuNPs is of paramount importance, in this work, two hydrophilic thiols with a net charge were chosen as ligands: sodium 3-mercapto-1-propane sulfonate (3MPS) and 2-(diethylamino)ethane thiol (DEA) hydrochloride. These were chosen not only for their ability to interact with bioactive agents such as drugs, antibodies or oligonucleotides, but also to fine tune physicochemical properties of the system, *i.e.* size, stability, dispersibility, and surface charge.

Before the applicative studies, the nanoparticles system was thoroughly characterised, both *via* spectroscopic means (UV-Vis, DLS, FT-IR, NMR XPS) and morpho-structural techniques (FESEM, TEM, AFM, SAXS).

Gold nanoparticles (AuNPs) were loaded with trastuzumab, a monoclonal antibody that targets the human epidermal growth factor receptor-2 (HER-2). To investigate potential synergistic effects, we utilized the HER-2-positive ovarian cancer cell line SK-OV-3 [2], transfected with a plasmid encoding the microRNA miR-200c [3]. Following treatment with the trastuzumab-loaded AuNPs, we conducted cell viability assays (MTT) and western blot analysis to evaluate changes in cell proliferation and the expression of genes within the HER-2 pathway.

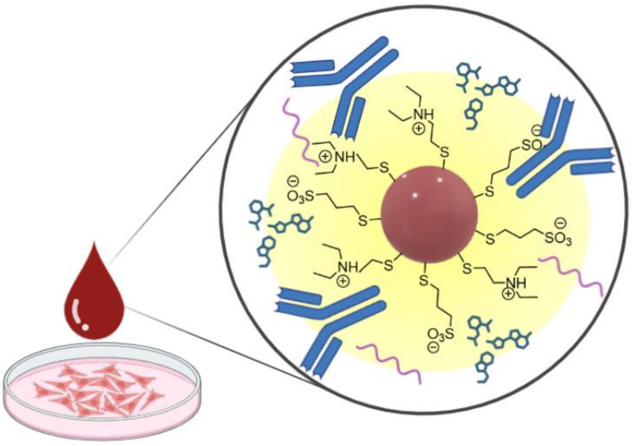


Figure 1. Schematic depiction of the AuNPs system loaded with drugs, oligonucleotides, or antibodies.

References

[1] Salamone T. A. *et al.*, *J. Colloid Interface Sci.*, 2023, **649**, 264-278.
[2] Anastasiadou E. *et al.*, *Cells*, 2021, **10**, 1–21.
[3] Thouvenin L. *et al.*, *Gynecol. Oncol. Rep.*, 2021, **37**, 100787

Hit optimization of new potent inhibitors of Coxsackievirus A9

Chiara Tammaro[1*], Zlatka Plavec[2], Laura Myllymäk[3], Critopher Mitchell[2], Sara Consalvi[1], Mariangela Biava[1], Alessia Ciogli[1], Simone Manetto[1], Pietro Sciò[1], Antonio Coluccia[1], Mira Laajala[3], Varpu Marjomäki[3], Sarah J. Butcher[3] and Giovanna Poce[3]

[1]Department of Drug Chemistry and Technologies, Sapienza University of Rome, Roma, Italy
[2]Faculty of Biological and Environmental Sciences, Molecular and Integrative Bioscience Research Program, & Helsinki Institute of Life Sciences-Institute of Biotechnology, University of Helsinki, Helsinki, Finland
[3]Department of Biological and Environmental Sciences, Nanoscience Center, University of Jyväskylä, Jyväskylä, Finland

*chiara.tammaro@uniroma1.it

Enteroviruses (EVs), comprising EV-A-B-C-D and three rhinovirus species, infect millions of humans every year. Among the EV-B serotypes, Coxsackievirus A9 and B3 (CVA9-B3) can cause severe diseases in human hosts, especially in neonatal and immune-compromised populations. However, the management of these infections primarily involves supportive care, as no selective antivirals are currently available. For many years, research has been focused on the development of capsid binders, resulting in the identification of potential drugs such as pleconaril (Picovir) and vapendavir (BTA789; Avigen). Unfortunately, none of these candidates have entered the market, due to the emergence of resistant viral strains and significant adverse effects [1]. Hence, there is an urgent need to develop more effective treatments and identify novel antivirals against these EV serotypes. In this context, a promising class of *N*-phenyl benzamides were here identified, through the cell-based phenotypic screening of an in-house chemical library against CVA9. The two screening hits, **CL212** and **CL213**, inhibit CVA9 in the micromolar range. Moreover, time of addition and capsid stability experiments have shown a strong indication that they prevent viral uncoating through capsid interactions with the VP1 viral protein. Preliminary structure activity relationship (SAR) studies have revealed that both the phenyl benzamide and the methylpiperazinyl moieties seem to be essential for the antiviral activity [2]. To expand SAR around this chemical scaffold, 29 analogues have been designed and prepared by modifying three blocks of the backbone of the initial hits, as following i) *N*-phenylbenzamides; ii) *N*-phenylbenzilamines; iii) sulfamoylbenzamides and benzene sulfonamide analogues. The infectivity assays highlighted that *N*-phenylbenylamines were the most promising compounds. Thereby, they were selected to identify some critical drug-like properties, such as kinetic solubility and lipophilicity (LogD). Finally, to better evaluate the mechanism of action and the binding mode of the most active derivatives, both cryo-electron microscopy (cryo-EM) and docking analysis were carried out. The obtained results confirmed that the target is the viral capsid protein VP1, and that antiviral activity occurs through capsid stabilization, thereby preventing its expansion and subsequent release of the genome [3].

References

[1] Tammaro, C., Michela, G., Appetecchia, F., Biava M., Consalvi S., Poce G., *Pharmaceuticals,* 2023, **16**, 203.
[2] Laajala, M., Kalander, K., Consalvi, S., Amamuddy O. S., Bishop O. T., Biava M., Poce G., Marjomaki V., *Pharmaceutics*, 2023, **15**, 1028.
[3] Tammaro, C., Plavec, Z., Myllymäkic L., Mitchell C., Consalvi S., Biava M., Ciogli A., Domanska A., Leppilampi V., Buckner C.,Manetto S., Sciò P., Coluccia A., Laajala M., Marjomäki V., Butcher S., Poce G., *J Med Chem, under revision.*

Novel pyrazole- based compounds active against *Mycobacterium tuberculosis*

Francesco Vallini[1*], Chiara Tammaro[1], Michela Guida[1], Benedetta Salvucci[1], Sara Consalvi[1]
Mariangela Biava,[1] Tania Olivier,[2] Sandeep R. Ghorpade,[2] Kelly Chibale[2] and Giovanna Poce[1]

[1]*Department of Chemistry and Technology of Drugs, Sapienza University of Rome, Rome, Italy*
[2]*Drug Discovery and Development Centre (H3D), Department of Chemistry, University of Cape Town, South Africa*

**francesco.vallini@uniroma1.it*

Tuberculosis (TB) is still one of the leading causes of death worldwide from a single infectious agent. Despite advancements in TB diagnosis and treatment, there is a pressing need for novel anti-TB drugs with distinct bactericidal mechanisms, particularly due to the rising prevalence of immunodepressive conditions like HIV and the emergence of multi and extensively drug-resistant (MDR and XDR) strains. A series of pyrrole- based compounds for TB treatment was previously synthesized by our research group. Among them, **BM635** was identified as the most promising derivative active against TB. This derivative is characterized by notably low minimum inhibitory concentration (MIC), unfortunately it exhibited low water solubility and high lipophilicity. Moreover, through the generation of spontaneous resistant mutants and genome sequencing, the target protein of this compound series was determined to be *Mycobacterium* membrane protein Large 3 (MmpL3) [1]. To optimize **BM635** drug-like properties, isosteric pyrazolic analogues were synthesized, among which only the 1,3,5-trisubstituted pyrazoles demonstrated MIC values in the low micromolar range [2]. The primary objective of this study was to enhance the understanding of structure-activity relationships (SAR) pertaining to pyrazole derivatives, with the intention of synthesizing compounds, characterized by increased *in vivo* activity and improved drug metabolism pharmacokinetic (DMPK) characteristics. To pursue this aim, specific structural modifications within the pyrazole scaffold have been realized: i) several substituents were introduced at the N1 position, encompassing small alkyl groups to aliphatic and aromatic heterocycles; ii) various cyclic amines, with a preference for morpholine, decorated position C3; iii) the isopropyl group at the *para* position of the phenyl in C5 was replaced with different functional groups, predominantly electron-withdrawing ones. All the synthesized compounds were prepared by using a multi-step synthetic procedure. The synthesized derivatives were biologically evaluated to determinate MIC, water solubility, cytotoxicity on hepatic cells, and clearance on murine hepatocytes. The new pyrazoles retained potent activity against *Mycobacterium tuberculosis* (Mtb) with improved solubility and low cytotoxicity.

References

[1] Poce, G.; Cocozza, M.; Alfonso, S.; Consalvi, S.; Venditti, G.; Fernandez-Menendez, R.; Bates, R. H.; Barros Aguirre, D.; Ballell, L.; De Logu, A.; Vistoli, G.; Biava, M. Eur. J. Med. Chem. 2018, 145, 539–550.
[2] Poce, G.; Consalvi, S.; Venditti, G.; Alfonso, S.; Desideri, N.; Fernandez-Menendez, R.; Bates, R. H.; Ballell, L.; Barros Aguirre, D.; Rullas, J.; De Logu, A.; Gardner, M.; Ioerger, T. R.; Rubin, E. J.; Biava, M. ACS Med. Chem. Lett. 2019, 10 (10), 1423–1429.

Theme I - Functional Materials

Design of Emissive Liquid Crystals based on Copper (I) complexes with Benzoyl thiourea, having a Cyano or Fluoro group peripherally connected

Muhammed Alkali [1*], Monica Iliş [1], and Viorel Cîrcu[1]

[1] *Department of Inorganic and Organic Chemistry, Biochemistry and Catalysis, University of Bucharest,*
Boulevard Regina Elisabeta Nr. 4-12, 030018 Bucharest, Romania

**Muhammed.alkali@s.unibuc.ro*

Introduction: Liquid crystals are generally referred to as substances that integrate the structure and properties of solid and liquid states. Although the study of copper(I) complexes concerning their mesomorphic behaviour are quite limited, some metallomesogens prepared with different structural components and ligands are known, including liquid crystalline compounds made of fluorinated Benzoyl thiourea (BTU) ligands. In this study, we successfully synthesized a new set of luminescent liquid crystals of the smectic type, based on copper(I) complexes whose structures have a terminal cyano or fluoro group attached to the BTU ligand. The incorporation of the cyano group generally resulted in a shift of the clearing temperature to higher values, whereas the fluoro effects were more prominent in the stabilization of the liquid crystalline phase at longer temperature ranges. The study also indicated a higher effect of the chloride ion on the liquid crystal temperature range of the copper (I) complex for the single alkoxy-substituted analogues of the studied compounds. In contrast, the effects of the halides in the matrix were almost identical for the double-substituted analogues. The compounds were stable throughout their mesophase temperature ranges and displayed emission in the solid state as well as weak emission in solution.

Materials and methods: All the complexes reported in this work were prepared based on the reaction scheme shown in Figure **1(a)**. Each BTU ligand was reacted with $CuBr_2$, $CuCl_2$, and CuI in a 2:1 ratio to obtain the corresponding metallomesogens. The structures of the prepared compounds were confirmed by NMR, MS and IR studies, and their liquid crystalline properties were investigated via a combination study using polarizing optical microscopy (POM), X-ray powder diffraction, and differential scanning calorimetry (DSC). The stability of the compounds was studied by thermogravimetric analysis (TGA).

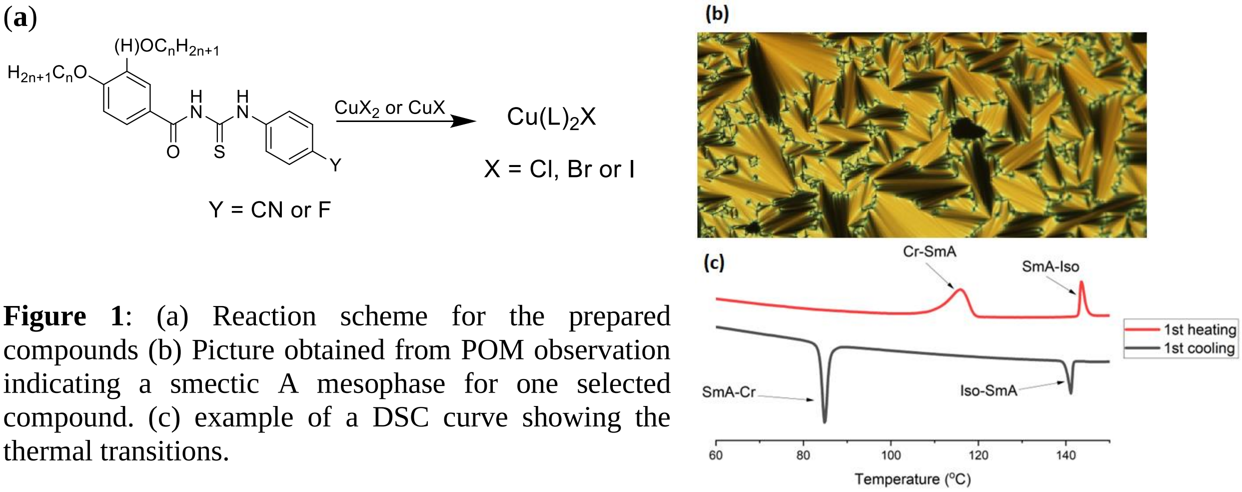


Figure 1: (a) Reaction scheme for the prepared compounds (b) Picture obtained from POM observation indicating a smectic A mesophase for one selected compound. (c) example of a DSC curve showing the thermal transitions.

Study of PLA Fibers obtained by Melt Electrowriting using rotation collector

Rosa Barranco-García[1,2*], Alexandra Muñoz-Bonilla[1], Maria L. Cerrada[1], Coro Echeverria[1], Marta Fernández-García[1]

1 Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC), C/ Juan de la Cierva 3, 28006 Madrid, Spain
2 Departamento de Química Orgánica. Facultad de Ciencias Químicas. Universidad Complutense de Madrid. Avda. Complutense s/n, 28040 Madrid, Spain

**robarran@ucm.es*

Polymeric fibers at the micro- or nanometric scale possess unique characteristics such as high porosity and a high surface-to-volume ratio, which make them key for applications requiring excellent mechanical resistance. These fibers are also highly versatile and can be used in diverse fields such as filtration, catalysis, textiles, and biomedicine [1]. Currently, electrospinning is the most commonly used technique for obtaining fibers whose diameters range from microns to just a few nanometers. This technique also enables the creation of scaffolds that mimic cellular matrix structures [2], allowing the fabrication of various tissues and organs. However, a fundamental problem with this technique is the use of organic solvents, which are highly detrimental to health and the environment. An alternative technique that eliminates the use of solvents and is gathering increasing industrial interest is melt electrowriting (MEW) [3]. This technique involves depositing micrometer or sub-micrometer thick fibers from a melted polymer, applying an electric voltage, and controlling the process through programming. Key parameters in this process include the processing temperature, voltage, nozzle-to-collector distance, and the speed at which the fiber is deposited. Proper selection of parameters allows for continuous fiber extrusion, enabling the creation of precise patterns [3]. Particularly in biomedical applications such as scaffolds for tissue engineering, polylactic acid (PLA) has emerged as one of the most promising polymers because its renewable-resource-based origin, biocompatibility, biodegradability, and ease of processing by numerous techniques, including electrospinning and melt electrowriting.

This work focuses on analyzing the influence of the different parameters that govern the MEW technique on the production of PLA fibers. This will help to enhance its applications and achieve complex geometries for its potential use in biomedicine.

Acknowledgments: This work was funded by the Ministerio de Ciencia e Innovación (project PID2022-136516OB-I00) and PTI Salud Global. R. Barranco-García thanks the Ministerio de Ciencia e Innovación for her Juan de la Cierva contract.

References

[1] Kade, J.C.; Dalton, P.D. Polymers for Melt Electrowriting. Adv. Healthc. Mater. 2021, 10.
[2] Zhang, Y.; Ouyang, H.; Chwee, T.L.; Ramakrishna, S.; Huang, Z.M. Electrospinning of Gelatin Fibers and Gelatin/PCL Composite Fibrous Scaffolds. J. Biomed. Mater. Res. - Part B Appl. Biomater. 2005, 72, 156–165.
[3] Dalton, P.D. Melt Electrowriting with Additive Manufacturing Principles. Curr. Opin. Biomed. Eng. 2017, 2, 49–57.

Synthesis of Metal-Free Semiconducting Polymers via Organocatalysis: Sustainable Materials for Renewable Energies

Luca Caponecchia[1,2*], Patrick Y. Toullec[2], …Cyril Brochon[1]

[1]LCPO, Université de Bordeaux, Bordeaux, France
[2]ISM, Université de Bordeaux, Bordeaux, France

**luca.caponecchia@u-bordeaux.fr*

Semi-conducting π-conjugated polymers are key organic materials for the development of green and low-cost optoelectronic devices [1] and for renewable energy production. Nowadays, such polymers are obtained through metal-based catalyzed cross-coupling routes and usually rely on complex protocols by resorting to costly and hardly removable catalysts. In addition, residual metal traces can affect performances, hence numerous and often tedious purification steps are required [2]. It is thus highly desirable to develop versatile, alternative synthetic approaches to semi-conducting polymers.

The aim of this work is to develop new synthetic methodologies for π-conjugated polymers in a "green" way using "metal-free" organocatalysis. Original polymers with aryl-vinylidene repeating units are targeted with the possibility to tune their optoelectronic properties, by playing on the planarity of the chain, the nature of the substituents, the stereo- and enantio-selection to use them as active materials in OPV cells. We focused on the synthesis of regio-/stereo-regular PPV-like polymers (Figure 1) obtained via hydroarylation reaction [3]. One of the key aspect of this project is to obtain these materials using a metal-free reaction; in fact, because of the presence of metals (that are at the most widely used polymerization reactions), their properties can be affected by the presence of metal residues that can act as recombination centers for both positive and negative charges. So, the use of a metal-free polymerization technique and the possibility of use bio-based monomers open to the possibility of getting 'greener' and purer materials for OPV devices.

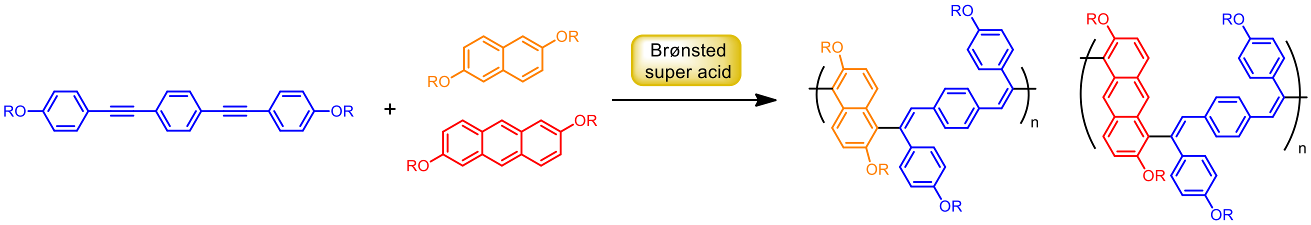


Figure 1: Summary of synthesis and structure of PPV-like polymers obtained via Brønsted acid organocatalysis.

References

[1] Facchetti A.; π-Conjugated Polymers for Organic Electronics and Photovoltaic Cell Applications; Chem. Mater. 2011, 23, 733–758 733
[2] Ö. Usluer, M. Abbas, G. Wantz, L. Vignau, L. Hirsch, E. Grana, C. Brochon, E. Cloutet, and G. Hadziioannou; Metal Residues in Semiconducting Polymers: Impact on the Performance of Organic Electronic Devices; *ACS Macro Lett.* 2014, 3, 1134−1138.
[3] Gicquiaud, J., Dhara, K., Karnat, A., Berlande, M., Hermange, P., Sotiropoulos, J. M., Toullec, P. Y.; Brønsted Acid-Catalyzed Enantioselective Cycloisomerization of Arylalkynes; *Chem. Eur. J.* 2020, 26, 16266–16271.

Conductometric polycorrole sensor array for sensing applications

Lorena Di Zazzo[1], Gabriele Magna[1], Ilaria di Filippo[1], Larisa Lvova[1], Manuela Stefanelli[1], Sara Nardis[1], Corrado Di Natale[2] and Roberto Paolesse[1]

[1]*Department of Chemical Science and Technology, University of Rome Tor Vergata, 00133, Italy*
[2]*Department of Electronic Engineering, University of Rome Tor Vergata, 00133, Italy*
Email: Lorena.Di.Zazzo@uniroma2.it

Corroles and related macrocycles are widely employed in the field of chemical sensors where they are used as sensing materials for optical, electrochemical, and conductometric transducers [1]. Concerning the conductive sensors, since corrole aggregates are scarcely conductive, a novel approach to building conductive sensors with low-conductive materials could be the polymerization form of molecules. Here, we explore the possibility of simply depositing conductive polymeric films of metal-5,10,15-(4-aminophenyl) corrolato] on interdigitated electrodes. The key step is the electropolymerization of corrole by cyclic voltammetry (CV) (figure 1A). The CV shows the continuous increase of the anodic current amplitudes with repeated potential scans. The mechanism of polymerization starts with the oxidation of the peripheral phenylamino groups of the monomer with the consecutive coupling to a second monomer molecule, forming a diphenylamine species, which is then further oxidated and coupled, leading to the final phenazine bridge [2]. Conductive films are obtained, and the film thickness can be controlled by tuning both the number of potential scans and the potential ranges, to investigate their chemical and sensing properties. However, the nature of the resulting polymer is affected by the electropolymerization conditions, playing a key role in the selection of the semiconductive nature of the films. Finally, fabricated sensors show high selectivity toward nitrogen oxide with detection limits around tens of ppb. Furthermore, using Principal Component Analysis, the slight differences in selectivity between sensors are sufficient for clustering NO, CO, CO_2, and H_2 samples at relatively low concentrations (figure 1B), confirming the possibility of using these materials for the development of sensor arrays.

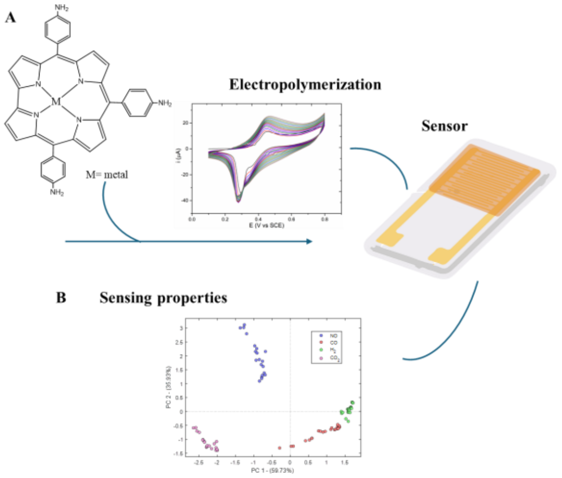


Figure 1. (A) Sensor fabrication via cyclic voltammetry, (B) Scores projection onto the first two Principal Components.

References

[1] R. Paolesse, S. Nardis, D. Monti, M. Stefanelli, and C. Di Natale. *Chemical reviews*, 2017, *117*(4), 2517-2583.

[2] M. G. Walter, and C. C. Wamser. *The Journal of Physical Chemistry C*, 2010, 114.17: 7563-7574.

Targeted Drug Delivery by Electrically Conductive Gelatin-Based Hydrogels

Flores, Brandhon F.[1*], Gutiérrez, Eduart [1], Moya, Sergio E.[1]

[1]*SoftMatter Nanotechnology Lab, CICbiomaGune, San Sebastián, Guipuzkoa,Spain*

**bflores@cicbiomagune.es*

The search for new stimuli-responsive materials has grown in recent years due to their multiple potential applications in biomedicine, regenerative medicine, drug delivery and cell culture. An example of such materials are hydrogels, which exhibit tuneable properties in response to changes to the environment such as hydrophilicity, swelling, stretchability, biodegradability, elasticity, etc.[1] Furthermore, the incorporation of conductive polymers, such as polypyrrole (PPy) into the hydrogel matrix brings electrical conductivity,[2] expanding the range of potential applications of the hydrogels in biosensors, biostimulators, cell scaffolds. Electro responsiveness can as well as used for the controlled release of drugs or divalent ions.[3] Here, we discuss the synthesis and characterization of conductive hydrogels made from gelatin and various polymers (Alginate, Polyacrylic acid and Cellulose), incorporating PPy into the matrix using a one-step method. Our one-step synthesis yielded conductive hydrogels, as confirmed by various characterization techniques. Scanning electron microscopy (SEM) revealed a highly porous structure, suggesting the encapsulation of PPy within the pores of the hydrogel matrix. Electrochemical techniques such as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) reveal the electrical properties of these electroconductive-hydrogels.

Acknowledgements: This work was supported by the Horizon Europe research project *CROSSBRAIN* Distributed and federated cross-modality actuation through advanced nanomaterials and neuromorphic learning, with reference number: 101070908.

References

[1] Chai, Q.; Jiao, Y.; Yu, X. Hydrogels for Biomedical Applications: Their Characteristics and the Mechanisms behind Them. *Gels*. MDPI AG March 1, 2017.
[2] Shen Wang, Jinfeng Lei, Xueling Yi, Lun Yuan, Liming Ge, Defu Li, and Changdao Mu. *ACS Applied Polymer Materials* **2020** *2* (7), 3016-3023.
[3] Jiafu Shen, Yu Dai, Fan Xia, Xiaojin Zhang. *Progress in Polymer Science*. 2022, 101622.

Nano-lithography with high-χ block copolymers: inter-relation between self-organization and dewetting kinetics

G. Forcina[1*], M. Zelsmann[1], G. Fleury[2]

[1]Univ.Grenoble Alpes, CNR, LTM, 38000 Grenoble, France
[2]Université de Bordeaux, CNRS, LCPO, 33607 Pessac, France
**gianluca.forcina@cea.fr*

The directed self-assembly (DSA) of block copolymers (BCPs) is a powerful method that can be implemented in the manufacture of high-resolution (sub-10 nm) features in microelectronics, but there still are many critical issues to be addressed, such as dewetting. Indeed, ultrathin films with high-χ (χ being the Flory-Huggins interaction parameter between the BCP blocks) deposited on/between neutral layers (to favor an orientation of the nano-features perpendicularly to the substrate as depicted in Fig. 1 a), suitable for lithography) are thermodynamically unstable and will tend to dewet if no external constraint is imposed on them, such as a physical constraint coming from a rigid top layer (top-coat, TC) [1].

There is no clear picture of how such dewetting correlates to the microphase separation. Therefore, this work aims at better understanding the coupling of the two phenomena by designing an experimental set-up that allows to observe them simultaneously in a controlled manner. Samples are prepared with a neutral polymer brush layer, the BCP layer and a polymer TC. The TC has the ability to crosslink upon exposure when in the presence of a photo-acid generator (PAG) and therefore it can be patterned as any other photoresist by lithography. By doing so, it is possible to form patterns with BCP beneath a crosslinked TC and BCP exposed to air (Fig. 1 b)). Upon thermal annealing, the BCP will begin to self-assemble and to dewet and both phenomena should be present simultaneously in the two different regions of the sample but with different magnitudes (Fig. 1 c)).

Another important aspect of the dewetting is that it can be used to either direct the assembly of the BCP [2] or to create various designs, such as ordered droplets [3]. The same experimental set-up designed to study the coupling of dewetting and microphase separation allows then also to explore what shapes the BCP takes when it dewets in constrained spaces with different geometries.

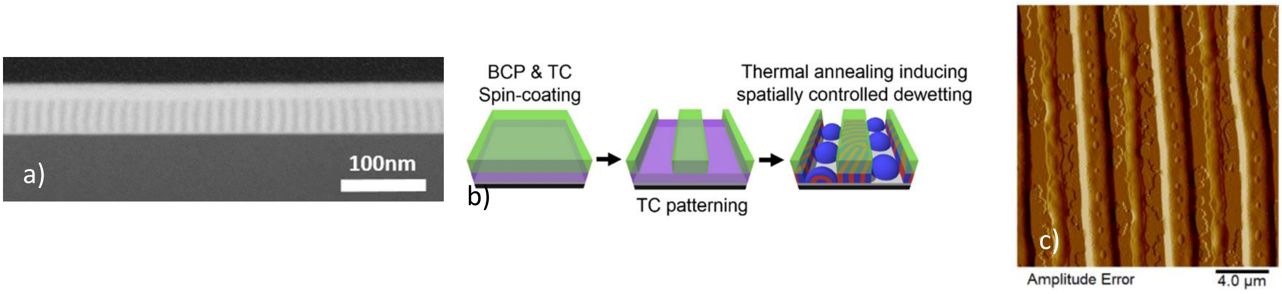


Fig.1. a) STEM cross-section of vertically-aligned 9-nm resolution polymer lamellae on flat surfaces; b) Representation of possible design; c) AFM topography of a sample with line-space lithography pattern.

References

[1] X. Chevalier et al., Nanotechnology, 34, 175602 (2023).
[2] H. Zhang et al. Macromolecules, 53, 21, 9631-9640 (2020)
[3] F. F. Lupi et al., ACS Nano, 12, 7, 7076–7085 (2018)

Polymer mixtures of polylactic acid with biobased, chemically recyclable, and self-healing thermosetting materials

Gamberini Luigi[1*], Liguori Anna[1], Focarete Maria Letizia[1]

[1]*Department of Chemistry "G. Ciamician", University of Bologna, Bologna, Italy*

**luigi.gamberini2@unibo.it*

Today, vehicle lightening is a major challenge for the automotive industry because it improves vehicle performance and reduces CO_2 emissions. Among the possible initiatives, poly(L-lactic acid) (PLLA) has been proposed as an interesting option for the realization of automotive components, mainly due to its bio-based nature. However, PLLA is generally characterized by poor durability, high brittleness, and poor flexibility. The improvement of these properties employing additives presents limitations, as these can be released over time by the system. An interesting yet underexplored alternative is the combination of PLLA with thermosetting polymers, cross-linked polymer structures characterized by remarkable thermal, mechanical, and solvent resistance properties. Traditional thermosets have sustainability issues because they are petrol-based, not recyclable, and not repairable. These problems can be solved by designing thermosets derived from biomass that incorporate reversible covalent bonds, such as imine functional groups, within polymer chains. Thermosets of this type have been developed from resins based on vanillin[1], a bio-based molecule that has been properly functionalized to obtain polyfunctional monomers containing imine groups. Thanks to the presence of these groups, the resulting thermoset possesses reprocessibility and self-healing properties. In this work, we focused on the development of bio-based systems by mixing PLLA with a recyclable thermosetting polymer, to obtain an advanced lightweight material with good thermal and mechanical properties and that is both mechanically and chemically recyclable. The study was conducted on films produced by solvent casting, cured by UV lamp (Thorlabs UV lamp, $\lambda = 365$ nm) and thermally post-cured in the oven. The thermal stability and transitions of the resulting materials were studied using TGA and DSC analysis (TA Instruments, TGAQ500 and DSCQ2000). Solubility tests in dichloromethane were conducted to verify chemical stability. SEM characterizations were performed while mechanical properties were studied using DMA (TA Instruments, DMAQ800). The recyclability of the material has been ascertained through tests of mechanical reprocessing and chemical component separation. The results show that it is possible to produce such films and that their thermo-mechanical properties are related to their composition. Furthermore, the systems obtained are mechanically processable and the two components can be separated and chemically recycled.

Acknowledgments: Financed by the European Union - NextGenerationEU (National Sustainable Mobility Center CN00000023, Italian Ministry of University and Research Decree n. 1033 - 17/06/2022, Spoke 11 - Innovative Materials & Lightweighting). The opinions expressed are those of the authors only and should not be considered as representative of the European Union or the European Commission's official position. Neither the European Union nor the European Commission can be held responsible for them.

References

[1] Liguori A., Hakkarainen M. *Macromolecular Rapid Communications* 2022, **43**, 1-17.

Tuning the properties of graphene oxide by chemical functionalization

Leonardo Giaccari[1*], Francesco Amato[1], Alessandro Motta[1], Andrea Giacomo Marrani[1]

[1] *Department of Chemistry, Sapienza University of Rome, Rome, Italy*

**leonardo.giaccari@uniroma1.it*

Graphene oxide (GO) has attracted rising interest since the discovery of the wet chemical route to graphene. GO is a non-stoichiometric, bi-dimensional carbon nanomaterial composed of a graphitic sheet decorated with various oxygen functional groups (OFGs). It is easily produced in large quantities and of good quality by wet-chemical oxidation and exfoliation of bulk graphite. Amongst the most, Hummers' method is the most widely employed synthetic approach. The GO produced by these means is rich in OFGs such as islands of epoxides and hydroxyls in the basal plane and carbonyls, phenols, and carboxyl-groups on the edges and in the defects[1]. The coexistence of these groups makes GO prone to chemical functionalization through a plethora of synthetic pathways and to a wide range of electrostatic interactions. Furthermore, the presence of graphitic domains enables non-covalent functionalization through dispersive interactions such as $\pi - \pi$ stacking. Additionally, GO and GO-based materials can be reduced by both electrochemical and chemical means to restore the π-delocalized network obtaining a reduced graphene oxide (rGO) with similar properties to pristine graphene. Therefore, due to its quivering chemistry, graphene oxide can be regarded as a perfect starting point for the design of graphene-based functional materials[2].

This work aims to obtain graphene-based materials e.g. carboxyl-rich GO (GO-COOH) and reduced graphene oxide through different reaction approaches on previously synthesized GO. Respectively, these functionalized materials are obtained by exploiting O-acylation with succinic anhydride and reduction reaction with ascorbic acid and sodium ascorbate[3]. Furthermore, it will be explored the electrochemical reduction and concurrent deposition of GO and GO-based nanomaterials on different substrates. The materials obtained are characterized, step-by-step, by spectroscopy means e.g. XPS, Raman, and UV-Vis spectroscopies.

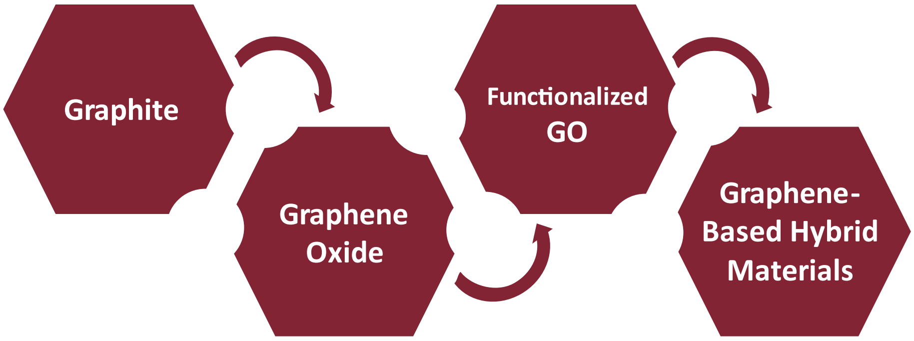


Figure 13: Schematic representation of the project

References

[1] Halbig C. A., Mukherjee B., Eigler S., Garaj S. *J. Am. Chem. Soc.*, 2024, **146**, 7431-7437.

[2] Guo S., Garaj S., Bianco A., Ménard-Moyon C. *Nat. Rev. Phys.*, 2022, **4**, 247-262.

[3] Amato F., Motta A., Giaccari L., Di Pasquale R., Scaramuzzo F. A., Zanoni R., Marrani A. G. *Nanoscale Adv.*, 2023, **5**, 893-906.

Additive Manufacturing of Polymer Composites with Printing-Direction-Independent Properties

Shani Ligati Schleifer[1*], Oren Regev[1,2]

[1]*Chemical Engineering, Ben Gurion University of the Negev, Beer Sheva, Israel*
[2] *Ilse Katz Institute for Nanoscale Science and Technology, Ben-Gurion University of the Negev, Beer-Sheva, Israel*

**ligati@post.bgu.ac.il*

The implementation of additive manufacturing techniques for thermal management applications necessitates the development of printable materials with enhanced properties. This study focuses on enhancing the thermal and mechanical properties of 3D-printed polymer composites (UV-based vat photopolymerization; VPP), starting by loading graphene nanoplatelets (GNP) as fillers into a monomer solution. GNP stabilization in the solution is achieved via the addition of sepiolite, a fiber-like clay, that traps them in dispersion[1]. However, the inherent GNP-induced UV blocking limits its concentration in the VPP-printed composite, yielding parts with undesired anisotropic properties. We overcome this GNP concentration limit by using the excluded volume approach, namely, adding micron-sized diamonds to increase the GNP effective concentration. This approach transforms the anisotropic VPP-printed composite into an isotropic structure, ensuring consistent thermal and mechanical enhancement regardless of the printing direction. Thermal conductivity (TC) and fracture toughness (FT) are enhanced by 180% and 100%, respectively (vs. the neat polymer), but the high electrical conductivity (EC) is undesirable in thermal management systems (risk of short-circuiting). Therefore, hexagonal boron nitride is added to reduce the EC, producing composites with enhanced TC and 140% FT enhancement. Our approach holds promise for various applications, especially in advanced heat management solutions, where enhanced TC, light weight, and low EC are imperative.

References

[1] S. Ligati Schleifer, O. Regev, *Additive Manufaturing*, **2023**, *70*, 103567.

Fluorescent biomass Carbon Dots: a convenient method for detecting nitrobenzene in water

Cinzia Michenzi[1*], Fabrizio Vetica[2], and Isabella Chiarotto[1]

[1]Department of Basic and Applied Sciences for Engineering (SBAI), Sapienza University of Rome, Via Castro Laurenziano, 7, 00161 Rome, Italy.
[2] Department of Chemistry, Sapienza University of Rome, Piazzale Aldo Moro, 5, 00185, Rome, Italy.

**cinzia.michenzi@uniroma1.it*

For three decades, nitroaromatic compounds have been recognized as hazardous substances, with nitrobenzene (NB) specifically known for causing multi-organ toxicity through various exposure routes and for its risks to aquatic environments and bioaccumulation. The significant presence of NB in these contexts is attributed to its extensive use in various industrial processes. Therefore, efficient probes for NB detection in water is introduced: biomass Carbon Dots (CDs). CDs have been obtained through an electrochemical bottom-up synthesis, free from organic solvents, using orange peel waste as the starting material. Subsequent characterization of the CDs revealed intriguing fluorescence properties. NB was detected at low concentrations using the CDs, without the need for any surface functionalization. The probes have demonstrated stability over time, with detection measurements unaffected by variations in pH and ionic strength conditions. Moreover, in the context of the circular economy, Process Efficiency Metrics (PEMs) were calculated for the electrochemical synthesis procedure, particularly focusing on mass intensity (MI), mass productivity (MP), reaction mass efficiency (RME), and environmental impact factor (E-factor). (Figure 1) [1]

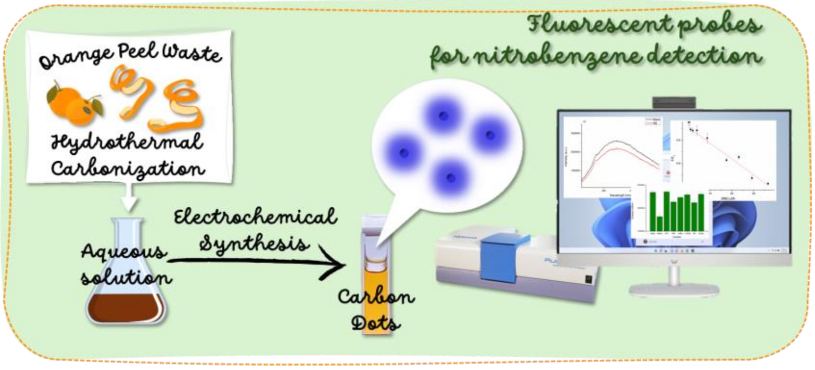


Figure 1. Recap of work objectives.

References

[1] C. Michenzi, A. Proietti, M. Rossi, C. Espro, V. Bressi, F. Vetica, B. Simonis, and I. Chiarotto, *RSC Sustainability*, **2024**, 2, 933-42.

Sustainable polymers with reversible shape-memory properties

Natali Daniele[1*], Michele Zanoni[2], Gualandi Chiara[2], Toselli Maurizio[1]

[1] *Department of Industrial Chemistry "Toso Montanari", University of Bologna.*
Viale Risorgimento 4, 40136 Bologna
[2] *Department of Chemistry "Giacomo Ciamician", University of Bologna.*
Via Selmi 2, 40126 Bologna.

**daniele.natali4@unibo.it*

Shape-memory polymers (SMPs) are stimuli-responsive materials that can be programmed to retain one or more temporary shapes and to switch from one to another with a reversible or irreversible mechanism when the right triggers are applied. SMPs present permanent and temporary netpoints in their structure and with the cleavage of the temporary netpoints the original shape is recovered. In SMPs, glassy or crystalline domains often represent the temporary netpoints; thus, SMPs usually exhibit thermo-sensitive features, and a temperature variation is the most common trigger. [1]
This proposal presents a novel SMP based on cross-linked block copolymers of sustainable and biodegradable polycaprolactone (PCL) and polybutylene succinate (PBS) starting from a methacrylate triblock copolymer PCL-PBS-PCL. The final polymeric network appears to be characterized by the presence of two distinct crystalline phases (with melting at about 50 and 85°C) near the thermal transitions of the two homopolymers. In this semicrystalline network, the chemical crosslinking between the chains act as permanent netpoints, PBS domain represents a skeleton for PCL's semicrystalline phase that acts as temporary netpoints. [2] After a thermo-mechanical programming cycle consisting of heating above the PBS domain's melting temperature, exerting external stress to deform the material and cool down, maintaining the stress applied, the material manages to show a reversible shape-memory effect, SME, (figure 1). When re-heated at the so-called activation temperature, the melting just of the PCL phase occurs, obtaining a contraction of the material (Melting-Induced Contraction, MIC); when cooled down, PCL-orientating crystallization is induced (Crystallization-Induced Elongation, CIE) by the stretched crystalline phase of PBS, further elongating the sample. A cycling variation in temperature between the melting and the crystallization of the PCL phase leads to a reversible change in the macroscopic shape of the sample.

.

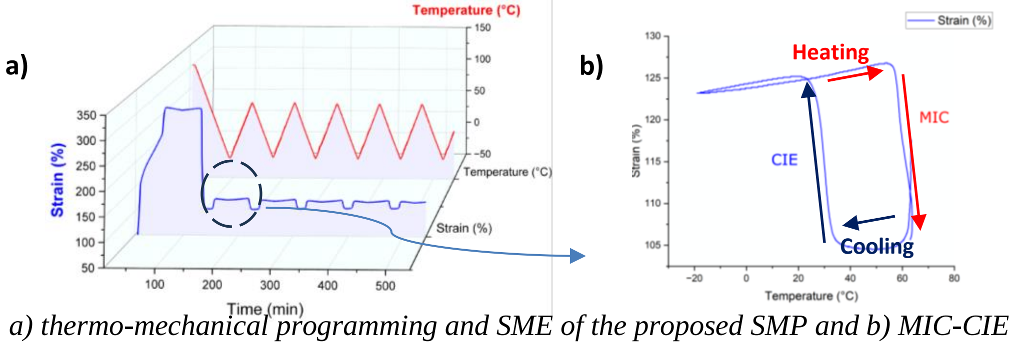


Figure 1, a) thermo-mechanical programming and SME of the proposed SMP and b) MIC-CIE mechanism

References

[1] M. J. Haskew et al. "*A Mini-Review of Shape-Memory Polymer-Based Materials.* Johnson Matthey Technol. Rev., 2020, 64, (4), 425–442.
[2] N. Invernardi et al. "*Stress-Free Two-Way Shape Memory Effect of Poly(ethylene glycol)/ Poly(ε-caprolactone) Semicrystalline"*. Macromolecules 2022, 55, 8533−8547.

The personalized nanoparticle-protein corona as an effective tool for early cancer detection

Erica Quagliarini[1*], Luca Digiacomo[1], Damiano Caputo[2], Tommaso Farolfi[2], Roberto Cammarata[2], Daniela Pozzi[1] and Giulio Caracciolo[1]
[1]Department of Molecular Medicine, University of Rome Sapienza, Rome, Italy
[2]Department of Surgery, University Campus Bio-Medico di Roma, 00128 Rome, Italy
**erica.quagliarini@uniroma1.it*

The application of nanotechnology in biomedical fields has made significant strides into the development of new cancer diagnostic technologies. Recently, the field of bio-nano interactions has offered new possibilities for cancer detection. Early investigations in this area revealed that nanoparticles (NPs) immersed in biological fluids develop a protein-enriched layer referred to as 'protein corona' (PC) [1]. Notably, it has been discovered that the PC is not merely a reflection of the human proteome but is instead personalized, varying for each individual and specific health condition [2]. This discovery has unlocked new pathways for isolating proteins present in low amounts, typically undetected by standard blood tests. Over the past decade, our research group has focused on designing, developing, and validating new technologies for early cancer detection based on the characterization of personalized PCs. These investigations have laid the groundwork for more extensive research in the field, establishing the principle of novel nanoparticle-enabled blood (NEB) tests for cancer detection [3,4]. NEB tests allow differentiation in the PCs formed on various NPs after exposure to healthy and oncological plasma samples (as depicted in **Figure 1**). In this study, we introduce a version of the NEB test tailored for pancreatic ductal adenocarcinoma (PDAC) and address the primary challenges in transitioning the NEB test into a reliable diagnostic tool for early detection, patient monitoring, and treatment management.

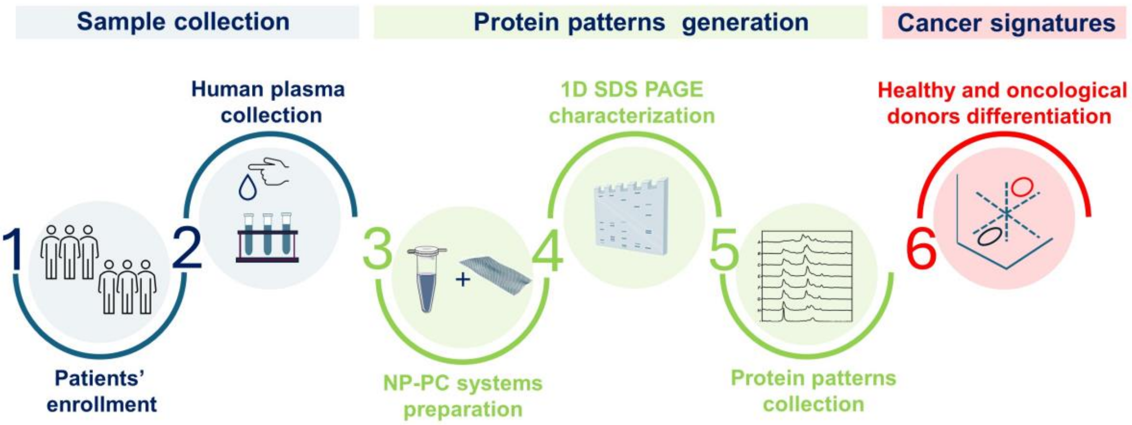


Figure 1. Nanoparticle-enabled blood test for cancer detection. Healthy and oncological donors are recruited (**point 1**) to provide human plasma (HP) samples (**point 2**). HP samples are then incubated with nanoparticles to create personalized protein coronas (PCs) (**point 3**). These personalized PCs undergo further characterization, including techniques such as 1D SDS-PAGE (**point 4**), to obtain protein profiles (**point 5**). Subsequently, the collected data are subjected to statistical analysis, such as principal component analysis (**point 6**), to identify cancer signatures capable of distinguishing between healthy and oncological donors.

Acknowledgements: The research leading to the results reviewed here has received funding from the AIRC foundation under IG 2017-ID. 20327 project–P.I. Caracciolo Giulio and IG 2020-ID. 24521 project–P.I. Pozzi Daniela. We couldn't have completed that project without the fundamental contribution of several coworkers.

References

[1] Quagliarini, E., et al., *Nano Today* 2022, 47, 101657.
[2] Colapicchioni, V., et al.,.*The international journal of biochemistry & cell biology* 2016, 75, 180-187.
[3] Caputo, D., et al., *Nanoscale* 2017, 9 (1), 349-354
[4] Papi, M., et al.,. *Nanoscale* 2019, 11 (32), 15339-15346.

Design of Novel PDMS-based magnetic Nanocomposites

Ibtissame Sidane[1*], Davide Peddis[1,2], Stefano Alberti[1], Sawssen Slimani[1,2]

[1] *Department of Chemistry and Industrial Chemistry (DCCI), University of Genova, Genova (GE), Italy*
[2] *Institute of Structure of Matter (ISM), National Research Council (CNR), Roma (RM), Italy*

**ibtissame.sidane@edu.unige.it*

Polymer-based magnetic nanocomposites (PMNCs) have attracted considerable interest in recent years as a new class of multifunctional materials. In this framework, the design of a suitable synthetic approach represents a key point to obtain a PMNCs with optimized physical properties[1] for biomedical and environmental applications[1][2]. A key step in the synthesis of PMNCs is definitively the molecular functionalization of magnetic nanoparticles (MNPs). This work focus on the investigation of morpho-structural and magnetic properties of 10 nm Fe_3O_4 and $CoFe_2O_4$ nanoparticles, bare (B-MNPs) and coated with oleic acid (OA-MNPs). Then PMNCs were synthetised embedding B-MNPs and OA-MNPs in a PDMS matrix using the electrospinning technique, in order to evaluate the effect of the coating in the PMNCs homogeneity. A complete characterization was carried out via a combination of morpho-structural (X-ray diffraction, XRD) and magnetic (Vibrating Sample Magnetometer, VSM) measurements, providing a detailed understanding of physical-chemical properties. Furthermore, additional techniques (Fourier Transform Infrared Spectroscopy, FTIR, Thermogravimetric Analysis, TGA, and Dynamic Light Scattering, DLS) were employed to confirm the magnetic nanoparticles coating and their stability in the working solvent. The magnetic investigation at room temperature of both particle and composites reveals the key role of the particles functionalization in tuning the morpho-structural properties of the PMNCs. The differences in morpho-structural and magnetic responses upon particles coating are due to the difference in the distribution of the magnetic particles within the PDMS matrix, resulting in a change of the magnetic properties (e.g. saturation magnetization) and the aging time of the PMNCs.

References

[1] Ma W, Zhang M, Li Y, Kang M, Huang C, Fu G. Flexible, durable and magnetic nanofibrous membrane with pH-switchable wettability for efficient on-demand oil/water separation. Environ Sci Nano. 2019;6(12):3699–711.

[2] Ai H. Layer-by-layer capsules for magnetic resonance imaging and drug delivery. Adv Drug Deliv Rev. 2011;63(9):772–88. Available from: http://dx.doi.org/10.1016/j.addr.2011.03.013

Tailoring the fluorescence of novel nitrogen doped carbon nanodots for imaging and biological applications

Elisa Sturabotti[1*], Lucia Cardo[1], Luca Comparini[1,2] and Maurizio Prato[1,3,4]

[1] Center for Cooperative Research in Biomaterials (CIC biomaGUNE), Basque Research and Technology Alliance (BRTA), Donostia-San Sebastian, Spain.
[2] University of the Basque Country, UPV-EHU, 20018 San Sebastián, Spain.
[3] Ikerbasque, Basque Foundation for Science, Bilbao, Spain.
[4] Dep. of Chemical and Pharmaceutical Sciences, Universitá Degli Studi di Trieste, Trieste, Italy.
** esturabotti@cicbiomagune.es*

Carbon Nanodots (CNDs) are a class of "zero" dimensional materials (size below 10 nm), mainly composed by carbon (followed by oxygen) and typically owning a spherical-like morphology and unique photoluminescence properties. Common approaches to synthetize CNDs involve pyrolysis or solvothermal treatment of selected molecular precursors, to obtain particle-like material through carbonization processes (bottom-up synthesis). By doing this, a great tunability of the nanoparticle's properties can be achieved. CNDs possess high water-solubility, due to the presence of functional groups on their surface (such as carboxylic acid, amines, and hydroxylic moieties), excellent biocompatibility, excitation-dependent photoluminescence, and outstanding photostability.[1] All these features enable the use of CNDs as tools for the fabrication of delivery systems, or theragnostic, bioimaging and engineered nano-agents for medical applications.[2]

We and others have developed CNDs with a typical size of 2-3 nm and doped with nitrogen, as a strategy to enhance fluorescence.[3] Here, we aimed to improve this aspect by increasing further the N-doping degree, thus obtaining CNDs with higher quantum yield (QY) and incorporating organic red-emissive dyes into CNDs frameworks, to red-shift CNDs fluorescence. The latter aspect is of pivotal importance when dealing with biological matrices, because of their blue autofluorescence and the severe photodamage that ultraviolet excitation light can provide.[4]

Upon screening a library of precursors and reaction parameters, we selected alanine and triethylenetetramine as starting materials to obtain new N-doped nano dots, named Blue-CNDs (**B-CNDs**) featured with surface amino groups and higher QY compared to parent materials. The positive polarization of the nanoparticles could be exploited to enlarge their field of applicability, considering the chemical and biological versatility of the amino rich nanomaterials.[5]

In addition, we incorporated a phenothiazine-based organic dye into B-CNDs, obtaining new dual blue and red-emissive nanomaterials, named Red-CNDs (**R-CNDs**). After careful characterization and purification, the B-CNDs and R-CNDs were visualized into biological environments, such as standard cell lines by confocal microscopy (at λ_{ex}= 405 nm and λ_{ex}= 640 nm, respectively). Finally, preliminary assays in cells show no cytotoxicity of both CNDs, fast cellular uptake, and good emissive properties, confirming their potential as safe-to-use fluorescent platforms for imaging and biological applications.

References

[1] De Medeiros T. V., Manioudakis J., Noun F. et al. *Journal of Materials Chemistry C,* 2019, **7(24)**, 7175-7195.
[2] Cardo L., Martínez-Parra L., Cesco M. et al. *Small*, 2023, **19(31)**, 2206442.
[3] Đorđević L., Arcudi F., Cacioppo M. et al. *Nature Nanotechnology*, 2022, **17(2)**, 112-130.
[4] Sun S., Zhang L., Jiang K. et al. *Chemistry of Materials*, 2016, **28(23)**, 8659-8668.
[5] Sturabotti E., Camilli A., Georgian Moldoveanu V. et al. *Chemistry–A European Journal,* 2024 e202303631N.

Ligand-binding directed cationic transport in nanoporous polymer membranes

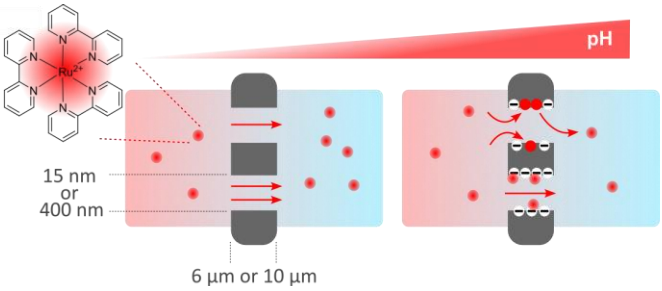
H.Samet Varol[1*], Matteo Cingolani[1], Francesco Casnati[1], Damiano Genovese[1]

[1]*Dipartimento di Chimica"Giacomo Ciamician", Università di Bologna, Bologna, Italy*

**samet.varol@unibo.it*

Selective binding between ions and their receptors at the cell membranes is the key mechanism for immune mechanism, cell signaling, and ion channel accessibility.[1] Inspired by such ligand-binding triggered nanopore activities, last year, our group showed a gradual chelation reaction between Ca^{2+} ions and negatively charged silica nanopores to neutralize nanopores and thus tune the ionic transport gradually towards using these hybrid membranes for diverse nM-sensitive ionic sensor applications.[2] Like our work, many nanoporous studies focus only on electrochemically triggered nanopore activities. However, other high-density nanoporous membranes, such as those used for reverse osmosis, ionic separation, and drug delivery, function without any external transmembrane potential; instead, their nanopore activities are tuned by other factors such as environmental pH, applied pressure, osmotic pressure, or membrane pore size and thickness. Moreover, the fundamental role of interaction between the ionic analyte molecules and charged nanopores and their impact on nanopore transport remains an open question for many of these high-pore density nanoporous systems.

In this contribution, we will show how the cationic luminescent analyte ($Ru(bpy)_3^{2+}$) interacts with negatively charged nanopores of polycarbonate ion track etched membranes during a concentration-driven (ΔC) transport and how this interaction regulates the pH-dependent nanopore transport. Our results show how (i) nanoconfinement – nanochannel diameter and length – (ii) environmental pH, and (iii) analyte concentration affect cation-nanopore interactions and ionic diffusion dynamics. Surprisingly, although higher electrostatic interactions exist between the cationic (+) analyte and deprotonated (-) nanopore at high pH, there is more limited cation diffusion from feed to permeate. Based on our confocal microscopy analysis, this is simply the consequence of stronger analyte and nanopore interactions while diffusion occurs at high pH. Confocal microscopy results also demonstrate how such ligand-binding could fluorescently stain the nanopores. We will also describe the role of (i) co-ligand (Ca^{2+} ion) presence and (ii) electron double layer (EDL) thickness on the analyte-nanopore interactions. Finally, we will also discuss the possibility of $Ru(bpy)_3^{2+}$– nanopore interactions when we apply a transmembrane potential to the system. We anticipate that the results of our work will provide a closer look at a widespread ionic analyte-nanopore interaction mechanism presumably happening in many micro and nanofluidic systems and clarify its impact on pH-dependent mass transport, selective nanopore fluorescent labeling and many more.



References

[1] D. C. Malaspina, G. Longo, I. Szleifer, *PLoS One* **2017**, *12*, e0185518.
[2] H. S. Varol, C. Förster, A. Andrieu-Brunsen, *Adv Mater Interfaces* **2023**, *10*, 2201902.

Theme L - Chemistry and Society

Sustainable corrosion inhibitors and carrier systems for the preservation of concrete heritage

Chiara Fratello[1,2*], Elena Messina[1], Francesca Boccaccini[1], Cristina Riccucci[1], Marianna Pascucci[1], Gabriella Di Carlo[1]

[1] Institute for the Study of Nanostructured Materials (ISMN), National Research Council (CNR), SP35d, 9, 00010 Montelibretti (Rome)
[2]Department of Chemical Engineering Materials Environment, Sapienza University of Rome, Via Eudossiana, 18, 00184 Rome

**chiara.fratello@uniroma1.it*

One of the major problems affecting the stability of reinforced concrete is the corrosion of the steel rebar. This is caused by the loss of the passivating oxide layer that occurs as carbonation proceeds and the pH in concrete matrix decreases, but can be also worsened by atmospheric and environmental factors such as the presence of chlorides.

The resulting structural damage indirectly affects both safety and economics [1]. Often corrosion, if in an advanced state, may even require invasive restoration interventions but, when dealing with concrete heritage, this is obviously not advisable and it is, therefore, even more important to preserve the integrity of the steel rebars to ensure the preservation of the cultural asset over time [2].

To date some organic and inorganic corrosion inhibitors exist that provide good protection, but they are not always effective and able to migrate into the concrete porosity up to rebars. Among them, there are amines, usually volatile, and heterocyclic compounds (i.e. BTA), harmful to operators and toxic to the environment. This research aims to seek increasingly *green* solutions that are not only effective but also safe to use, by identifying new inhibitors for steel in concrete.

In addition, as the inhibitor can only be applied on the surface, the chosen product has to be able to migrate into the innermost layers until it reaches the rebars. Part of this research is, therefore, also focused on the synthesis and validation of carrier systems that can deliver these inhibitors through the cement matrix and release them in a controlled mode upon environmental stimuli (pH change, presence of chlorides) such as layered double hydroxides[3].

The current research began with the validation of some corrosion inhibitors 5 years after their application, a particularly relevant analysis as these tests are usually conducted only over shorter timescales. To evaluate their efficacy, a multianalytical approach was chosen by means of optical and metallographic microscopy, as well as FTIR and SEM analysis of corrosion products present on the surface. At the same time, the synthesis of carriers that can contain the inhibitor is being carried out. The results of this ongoing research are promising: some of the inhibitors have been shown to provide good protection even over long timescales.

Acknowledgements:

This activity is carried out within the MUR PRIN2022 ECOforCONCRETE project (2022M4KCKP) which is kindly acknowledged for financial support.

References

[1] Poursaee, A. & Hansson, C. M. Potential pitfalls in assessing chloride-induced corrosion of steel in concrete. *Cement and Concrete Research* **39**, 391–400 (2009).

[2] Bertolini, L., Carsana, M., Gastaldi, M., Lollini, F. & Redaelli, E. Corrosion assessment and restoration strategies of reinforced concrete buildings of the cultural heritage. *Materials & Corrosion* **62**, 146–154 (2011).

[3] Giuliani, C. *et al.* On-Demand Release of Protective Agents Triggered by Environmental Stimuli. *Front. Chem.* **8**, 304 (2020).

Development of novel strategies for conserving stone monuments: application of biocidal hydrogels and hydrophobic coatings

Francesco Gabriele[1*], Cinzia Casieri[1], Ranaldi Roberta[2], Rugnini Lorenza[1,2], Spreti Nicoletta[1]

[1] Department of Physical and Chemical Sciences, University of L'Aquila Via Vetoio Coppito, I-67100, L'Aquila, Italy
[2] Department of Biology, Tor Vergata University of Rome, Via Cracovia 1, I-00133 Rome, Italy

**francesco.gabriele@univaq.it*

Biodeterioration is one of the most detrimental phenomena that affect the integrity of stone monumental cultural heritage. Environmental factors and water availability, combined with substrate bioreceptivity, favour the growth of biopatina, leading to both aesthetic, physical and chemical damage. Chemical treatments with aqueous solutions of biocides have proven to be the one of the most effective and widespread cleaning strategies, even if they often induce chromatic alterations as well as salt and by-product deposition [1]. For this purpose, the encapsulation of classical and alternative biocides in inert hydrogel matrices can overcome these drawbacks, allowing to reduce the amount of biocide and avoid dripping effects when applied on vertical surfaces [2]. Although the removal of biopatinas represents a critical step to preserve cultural heritage as long as possible, preventive actions must be aimed at protecting the substrate [3].

In the presented work we report the effective removal of biopatinas from stone substrates of different nature, both under controlled laboratory conditions and *in situ* applications, using alginate hydrogels encapsulating oxidant biocides or natural plant extracts [4-6]. In parallel with the removal of biopatinas, a laboratory comparison of classical silane-based and new acrylic hydrophobic coatings was carried out. SEM-EDS and micro-FTIR analyses, static contact angle measurements, and ^{1}H-NMR relaxometry demonstrate the ability of some protective agents to reduce water uptake without altering the appearance and the properties of highly bioreceptive stone substrates [7]. The application of these protectives after cleaning could prevent future microbial recolonization of the substrate, reducing the number of biocide treatments needed to preserve monumental cultural heritage.

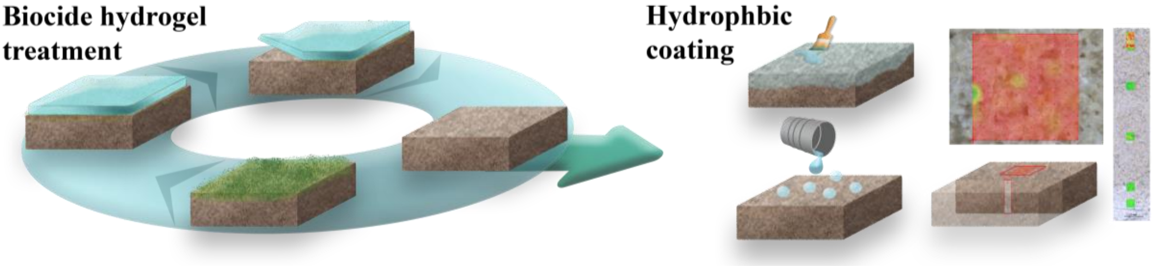


Fig.1: Schematic representation of the treatment of stone substrate with hydrogels encapsulating biocides and of the application and characterization of protective hydrophobic coatings.

References

[1] Pozo-Antonio J.S., Rivas T., López A.J., Fiorucci M.P., Ramil A. *Sci Total Environ*, 2021, **571**, 1017.
[2] Gabriele F., Tortora M., Bruno L., Casieri C., Chiarini M., Germani R., Spreti N. *J Cult Herit*, 2021, **49**, 106-114.
[3] Gherardi F., Conserving Stone Heritage: Traditional and Innovative Materials and Techniques, 2022, 5, 137-176, Springer, Cham, Switzerland.
[4] Gabriele F., Bruno L., Casieri C., Ranaldi R., Rugnini L., Spreti N. *Coatings*, 2022, **12**, 462.
[5] Gabriele F., Ranaldi R., Bruno L., Casieri C., Rugnini L., Spreti N. *Sci Total Environ.*, 2023, **870**, 161901.
[6] Bruno L., Casieri C., Gabriele F., Ranaldi R., Rugnini L., Spreti N. *Int Biodeterior Biodegr*, 2023, **183**, 105641.
[7] Gabriele F., Casieri C., Vetrano A., Spreti N. *Mater Chem Phys*, 2023, **307**, 128194.

Evaluation of element accumulation and oxidative stress in bees due to a landfill waste fire event

Marcello Messi[1*], Ottavia Giampaoli[2,3], Thomas Merlet[4], Fabio Sciubba[2,3], Silvia Canepari[2],
Mariangela Spagnoli[5], Maria Luisa Astolfi[1,6]

[1]*Department of Chemistry, Sapienza University of Rome, Piazzale Aldo Moro 5, 00185 Rome, Italy.*
[2]*Department of Environmental Biology, Sapienza University of Rome, P.le Aldo Moro 5, 00185 Rome, Italy.*
[3]*NMR-based metabolomics laboratory (NMLab), Sapienza University of Rome, 00185 Rome, Italy.*
[4]*Department of Chemistry, Toulouse INP - ENSIACET, 4 Allée Emile Monso, 31030 Toulouse, France.*
[5]*Department of Medicine, Epidemiology, Environmental and Occupational Hygiene, INAIL, via Fontana Candida 1, 00078 Monte Porzio Catone (RM), Italy.*
[6]*Research Center for Applied Sciences to the Safeguard of Environment and Cultural Heritage (CIABC), Sapienza University of Rome, P.le Aldo Moro 5, 00185 Rome, Italy*

**marcello.messi@uniroma1.it*

Landfill fires can contribute significantly to air pollution (1). Several pollutants can be emitted during waste combustion, such as toxic or potentially toxic elements (1,2). In particular, chemicals have environmental and health impacts that can also affect bee's health (2,3). The present study aimed to evaluate the impact of air pollution from waste fires on bee health, in terms of oxidative stress and metal accumulation, as well as the possible beneficial effect of feeding probiotics and *Quassia amara* to bees.

Six beehives were considered near the Malagrotta landfill, central Italy (41°51'49.9 N 12°19'46.5 E) before and after a landfill fire event on 15 June 2022. Bees were analyzed for elemental content by a quadrupole inductively coupled plasma mass spectrometry and cold vapor atomic fluorescence spectrometry (2,3), oxidative stress by hydrogen peroxide and protein carbonyl group contents (3), and metabolic profiles by ^{1}H-NMR (3).

Compared with control bees, lower concentrations of As, B, Ba, Cd, Co, Fe, Li, Mn, Ni, Pb, Sn, Ti, and U were found in probiotic-fed bees, and Ba, Be, Cd, Co, Fe, Li, Mn, Sn, Ti, and U in *Q. amara*-fed bees, indicating a possible protective action of probiotics and medicinal plants against the accumulation of toxic or potentially toxic elements (2,3). The administration of probiotics and *Q. amara* to bees has also shown a protective effect against the oxidative stress caused by the fire of landfill waste (3). The comparison of the metabolic profiles through pre- and post-event PCA analyses showed that bees treated with different feeds react differently to the environmental event. The greatest differences in metabolic profiles were observed between the placebo-fed bees compared to the others. This study can help to understand how some stress factors can affect the health of bees and to take measures to protect these precious insects.

Acknowledgements: The authors wish to thank Marco Papi, Marco Papi Azienda Agricola ed Apistica, Rome (Italy), for the study's precious support and all the sampling stages. We acknowledge the Ph.D. programs on green topics, PON Research and Innovation 2014–2020 project, funded by FSE REACT-EU.

References

[1] Dabrowska D., Rykala W., Nourani V. *Sustainability*, 2023, **15**(7), 5713. 10.3390/su15075713
[2] Astolfi M.L., Conti M.E., Messi M., Marconi E. *Chemosphere*, 2022, **308**, 136261. 10.1016/j.chemosphere.2022.136261
[3] Giampaoli O., Messi M., Merlet T., Sciubba F., Canepari S., Spagnoli M, Astolfi M.L. *Environmental Science and Pollution Research*, 2023, 1-17. 10.1007/s11356-023-31561-x

Poster Communications

List of Posters

N.	Name	Surname	Institution	Abstract Title
Theme A - Advances in Organic Chemistry				
P1	Biagio	Anderlini	University of Modena and Reggio Emilia	Lignin Depolymerization-Upgrading to Biomaterials
P2	Marianna	Bernardini	Sapienza University of Rome	Supramolecular catalysts for HAT reactions: site-selectivity in C-H bond functionalization
P3	Beniamin Emanuel	Birzu	Sapienza University of Rome	N-hydroxyphthalimide as mediator in the oxidations promoted by nonheme iron(IV)-oxo complexes
P4	Francesca	Blondelli	Sapienza University of Rome	Synthesis of space-grade polyimides using bio-based sustainable chemistry
P5	Luigi	Cirillo	Sapienza University of Rome	Selective oxidation of C-H bonds using bio-inspired confined catalysts
P6	Aurora	D'Arrigo	Sapienza University of Rome	Conductivity Variations in Water Solutions Induced by an Activated Carboxylic Acid
P7	Federica	Di Mascolo	Sapienza University of Rome	Derivatives of 2-(hydroxyimino)aldehydes as precursors of iminoxyl and alkyl radicals for antimicrobial and anticancer applications
P8	Beatrice	Di Mattia	Sapienza University of Rome	Liposomes of estrogenic soft-drugs to boost wound healing
P9	Laura	Loffredo	Sapienza University of Rome	Stereoselective Preparation of a Key Intermediate in the Synthesis of Orizalexin S Using Organocatalysts and Chiral Carbon Dots
P10	Micol	Mazzone	Sapienza University of Rome	Improved and greener syntheses of estrogenic soft drugs
P11	Roberta Maria	Nicolosi	Sapienza University of Rome	Evaluation of the cytotoxic activity of Lichen Roccella tinctoria DC. Extracts and major components
P12	Livia	Paolini	Sapienza University of Rome	Simultaneous Oxidative and Reductive C-S Bond Cleavage in t-Alkyl Aryl Sulfoxides Catalyzed by Tetrabutylammonium Decatungstate
P13	Dario	Possenti	Sapienza University of Rome	Fe-catalyzed aromatic C—H amination: mechanism and applications
P14	Francesco	Ranieri	Sapienza University of Rome	Artificial Molecular Pump
P15	Dario	Rendeli	Sapienza University of Rome	Enantioselective Norrish-Yang Photocyclization of 2-(Hydroxyimino)aldehydes
P16	Greta	Sandri	Sapienza University of Rome	Dissipative dynamic covalent chemistry of B-N bond
Theme B - Biomaterials				
P17	Gianluca	Ciarleglio	Sapienza University of Rome	Crosslinked PVA/HA Nanofibers Fabricated via Electrospinning for Potential Advanced Wound Management
P18	Mariangela	Clemente	CNR-Institute for Biological Systems (ISB)	Multicompartmental Janus Liposomes (MJL) as components of an innovative material for implant devices: how to convert bacteria-associated biofilm into a resource
P19	Marialourdes	Di Maio	Università degli Studi di Napoli Federico II	Sodium alginate eco-sustainable carriers in precision agriculture
P20	Ozge	Eslek	University of Rome "Tor Vergata"	Modification of Poly(vinyl alcohol) with Glicidyl Methacrylate: Characterization and Photo Polymerization of Poli(vinyl alcohol)-Methacrylate
P21	Silvia	Fanti	University of Bologna	BSA-nanoparticles sponge-like hydrogel as innovative biomaterial
P22	Chiara	Frezza	Università degli studi di Roma Tre	Ceria coating on nanostructured titanium surfaces enhance antibacterial and anti-infiammatory capabilities
P23	Hilal	Nasir	University of Naples Federico II, Italy	Development of ELISA assays based on advanced materials in lab-on-chip platforms for the detection of oncologic protein biomarkers
P24	Aurora	Patrizi	CNR-Institute for Biological Systems (ISB)	Development of Chitosan Nanoparticles for the delivery of antimicrobial peptides (AMPs)
P25	Fabio	Pizzetti	Politecnico di Milano	Decorated nanogels as promising tools for selective drug delivery in spinal cord injury treatment
P26	Davide	Principe	Sapienza University of Rome	Advancements in biomass valorisation: a new method for sustainable Poly-hydroxyalkanoates (PHAs) recovery

P27	Mattia	Stefano	Sapienza University of Rome	Progress of liposomes loaded with Resveratrol for delivery across the blood-brain barrier
P28	Riccardo	Tassoni	Alma Mater Studiorum - University Of Bologna	Synthesis and characterization of hyaluronic acid-based smart hydrogels
P29	Claudia	Vona	Sapienza University of Rome	Oxidative treatment for PHA recovery from Mixed Microbial Cultures cultivated in a continuous process
Theme C - Advances in Physical Chemistry				
P30	Josephine	Alba	University of Fribourg (Switzerland)	CryoEM architecture of a native stretch-sensitive membrane microdomain
P31	Alessandro	Azzali	Sapienza University of Rome	Deep learning force fields design for solid state electrolytes
P32	Federica	Borzelli	Sapienza University of Rome	Exploring Ochratoxin Binding Aptamer structure and binding via Molecular Dynamics
P33	Vittorio	Caprini	Sapienza University of Rome	Operando microRaman techniques and chemometric methods for the study of lithium-sulfur batteries.
P34	Davide	Carrea	Università degli studi di Genova	Alkaline copper electrodeposition from alanine-based baths
P35	Alessandro	Cingolani	Università Degli Studi di Genova	High efficiency eco-anodes obtained from an organic waste for lithium-ion batteries applications
P36	Gabriele	D'Aiuto	Sapienza University of Rome	Fluorescence micro-spectroscopy applied to Lithium-Oxygen Batteries
P37	Francesca	D'Ambrosio	Sapienza University of Rome	A computational approach to the study of carbon dots for the determination of their structure and properties
P38	Matteo	Daino	Sapienza University of Rome	New insights into the aromatic amination mechanism: a computational approach
P39	Irene	Matteucci	Sapienza University of Rome	Synthesis and characterization of composite polymer electrolytes added with functionalized graphene oxide.
P40	Carla	Palladini	Sapienza University of Rome	Nanocomposite Oxides from silicon-based MAX-phases: a novel approach for Negative Electrodes in Lithium-Ion Batteries
P41	Edoardo	Panzetta	Sapienza University of Rome	A computational study of N-methylacetamide amidic bond breaking in neutral and alkaline medium
P42	Riccardo	Testa	Sapienza University of Rome	Thermodynamic study of BaZrS3 and its two binary precursors BaS and ZrS2
P43	Francesco Iacopo	Travaglini	Sapienza University of Rome	Thermodynamic properties of urea/choline chloride deep eutectic solvent by Knudsen effusion mass spectrometry measurements
Theme D - Advances in Analytical Chemistry				
P44	Sara	Astolfi	Sapienza University of Rome	Characterization and quantification of flavonoids in functional products based on blueberries
P45	Maria Luisa	Astolfi	Sapienza University of Rome	Elemental content in hemp-based herbal teas by ICP-MS
P46	Beatrice	Beretta	Sapienza University of Rome	An untargeted analytical workflow based on Kendrick mass defect filtering reveals dysregulations in acylcarnitines in prostate cancer tissue
P47	Maria	Carbone	Sapienza University of Rome	Development of a monolithic column for the simultaneous online enrichment of glyphosate and other pesticides
P48	Federico	Cortese	Università degli Studi di Roma "Tor Vergata"	Overcoming challenges in urinary metabolomic profiling by computing NMR and UHPLC-HRMS: a novel approach to detecting synthetic opioids
P49	Martina	Croce	Sapienza University of Rome	Oral fluid multi-drug testing through magnetic dispersive solid phase extraction and HPLC-MS/MS
P50	Veronica	D'Eusanio	University of Modena and Reggio Emilia	Influence of Drying and Storage Conditions on the Volatile Organic Compounds Profile of Spirulina Platensis
P51	Gaia	Di Francesco	Sapienza University of Rome	Dried Saliva Spot and Parallel Artificial Liquid Membrane Extraction: a green combined design for microsampling and microextraction of drugs of abuse
P52	Davide	Filardi	Sapienza University of Rome	Cyclodextrin-based sustainable adsorbent polymers: synthesis, characterization and analytical application for solid phase extraction
P54	Nicholas	Kassouf	Alma Mater Studiorum University of Bologna	AF4 coupled to chemometrics for the analysis of protein fractions of milk

P55	Soo Suk	Lee	Soonchunhyang University	Simultaneous Detection of Exosomal microRNAs Isolated from Cancer Cells Using Surface Acoustic Wave Sensor Array
P56	Marta	Marchesini	Politecnico di Milano	Evaluation of salt concentration on the DNA melting temperature
P57	Eleonora	Oliva	Università degli Studi di Teramo	Determination of phytosterols in food samples base on molecurarly imprinted polymers (MIP) coupled with UPLC-MS/MS
P58	Maria Chiara	Paniccia	Sapienza University of Rome	In-depth characterization of lipids in hempseeds through photochemical cycloaddition reaction and high-resolution mass spectrometry (HRMS).
P59	Giordano	Putzolu	Sapienza University of Rome	Abundant protein depletion methods of Glioblastoma serum samples: a pilot investigation in the perspective of LC-MS proteomic profiling by top-down/bottom-up integrated platforms
P60	Elisa	Santoni	UNICAM	Analysis of Posidonia oceanica's stress factors in the marine environment of Tremiti Island
P61	Cecilia	Scandurra	University of Bari	Characterization and Sensing Applications of a Physisorbed Antibody Layer
P62	Lorenzo	Strani	University of Modena and Reggio Emilia	Optimizing LC-MS Methodology for Detecting Polar Emerging Contaminants in Reclaimed Water: Towards Sustainable Water Management
P63	Anna Laura	Tassi	Università Statale di Milano	Development and evaluation of the prolonged antifungal and antibacterial activity of an air cleaning system for indoor cultural heritage spaces
P64	Serena	Zampieri	Università di Roma "Tor Vergata"	Improving MASLD Diagnosis with 1H-NMR: Multivariate Analysis of Serum Metabolites Differentiating Disease Stages of Metabolic dysfunction-associated steatotic liver disease
Theme E - Advances in Coordination and Inorganic Chemistry				
P65	Matteo	Boattini	Sapienza University of Rome	Green Synthesis of CALF-20 for the separation of CO2/N2 mixtures
P66	Alessia	Fata	University of Rome Tor Vergata	N-methyl-corroles and their catalytic activity
P67	Rida	Nadeem	University of Salerno	Ruthenium olefin metathesis catalysts for transformations of renewables
P68	Pol	Pérez	Universitat de Barcelona	Non-Covalent Functionalization of Graphene Oxide with A Porphyrazine Macrocycle
Theme F - Colloids and Materials				
P69	Malak	Abo Alhija	The Hebrew University of Jerusalem	Shape and Morphology of Chiral Polyurea Nanocapsules Control Stereospecific Interactions with Albumins
P70	Junaid	Ali	University of Naples Federico II	Nanocomposites Derived from Polymers and Inorganic Nanoparticles with Promising Applications
P71	Eduardo	Annibali	Sapienza University of Rome	Synthesis and characterization of PNPs-AuNPs hybrids for drug delivery in nanomedicine
P72	Eleonora	D'Alessandro	Università Campus Bio-Medico di Roma	Design and optimization of in-batch and in-flow syntheses of silica-based nanomaterials
P73	Alessandra	Del Giudice	Sapienza University of Rome	Complex coacervation between sodium decanoate and cationic inulin: towards a structural understanding of more sustainable surfactant and polymer mixtures
P74	Tommaso	Gentili	Sapienza University of Rome	Metal Organic Frameworks: platforms for photonic up-conversion
P75	Angelica	Mallamo	Sapienza University of Rome	Characterization of sodium deoxycholate and poly-L-lysine catanionic mixtures
P76	Giorgio	Mandato	Sapienza University of Rome	Novel liposome-based multicomponent systems for gene and drug delivery
P77	Jean Pierre	Miranda Murillo	Università degli Studi di Genova	Synthesis of Fe Nanoparticles in Silica Matrix
P78	Sarah	Pavin	Sapienza University of Rome	Synthesis and characterisation of gold nanoparticles stabilised by organic and organometallic thiols
P79	Marco	Piccinni	Università degli Studi di Genova	Layered double hydroxides synthesised by coordination chemistry of citric acid
P80	Paula Stefana	Pintilei	Sapienza University of Rome	Peptide-based Magnetogels for the Removal of Organic Dyes from Water

P81	Marco	Ranaldi	Università degli Studi Roma Tre	Gold nanoparticles: from asymmetric shape to chirality
P82	Teresa	Varelli	Sapienza University of Rome	Graphene Oxide: A Versatile Material for Biomedical Applications
Theme G - Energy, Environment and Sustainability				
P84	Francisco	Abreu dos Santos	NOVA University Lisbon	Oil extracted from tomato pomace as feedstock for sustainable PHA production
P85	David	Albano	Sapienza University of Rome	Recovery of Ethylene Vinyl Acetate from end-of-life photovoltaic panels by a solvent/non solvent system
P86	Yana	Aleeva	University of Palermo	Novel hybrid composites containing lignin and polysiloxane derivatives
P87	Flavio	Catalano	Università degli studi di Genova	Effect of cathodic hydrogen charging on the fracture toughness of a X52 pipeline steel welds tested with SENT specimens
P88	Marta	Catalão	NOVA School of Science and Technology	Selection and characterization of microbiomes subject to identical environmental stress conditions for Polyhydroxyalkanoates (PHA) production
P89	Davide	Ceriotti	Politecnico di Milano	Magnetite functionalized with metal-organic frameworks (MOF) for perfluorooctanoic acid (PFOA) absorption
P90	Clarissa	Ciarlantini	Sapienza University of Rome	Efficient Chemical Recycling of Expanded Polystyrene Using Terpene-Based Green Solvents
P91	Raffaella	Salerno	Università di Roma “Tor Vergata”	Silicon/nanocrystalline-diamond cathodes for photon-enhanced thermionic emission
P92	Clarissa	Ciarlantini	Sapienza University of Rome	Circular economy in mussel farms: polypropylene recovery
P93	Marco	Colasanti	Sapienza University of Rome	An application of flow chemistry for co-precipitation of nickel rich NMC precursors using oxalic acid as precipitating agent
P94	Eleonora	De Santis	University of Naples Federico II	Evaluation of BioHydrogen Potential of agro-industrial waste using a mixed microbial culture.
P95	Maria	Di Pea	Sapienza University of Rome	C-S composites for Li-S battery applications
P96	Licia	Gaeta	University of Padova	Is it possible to obtain thermosetting materials from renewable sources which can be recycled at the end of their life?
P97	Davide	Gallo	University of Turin	Thermosetting polyurethane-based encapsulation of flexible perovskite solar cells: a step forward in devices stabilization in highly damp environment
P98	Maria	Gentile	University of Padova	Chemical recycling of poly(lactide) using (imidazol[1,5-a]pyrid-3-yl) phenolate Zn(II) catalysts
P99	Luna	Iacobini	Sapienza University of Rome	CeO2/rGO catalysts for PEMFCs
P100	Elisabetta	Lacolla	Sapienza University of Rome	Characterization of plastic wastes in Urban parks
P101	Michele	Leone	Sapienza University of Rome	Eco-sustainable regeneration of industrial catalysts
P102	Alyssa	Mancini	Sapienza University of Rome	Integrating LiFePO4 black mass into the hydrometallurgical route for re-synthesis of Nickel-Manganese-Cobalt cathodic materials from end of life lithium ion batteries
P103	Beatrice	Notari	ENEA	Evaluation of the controlled hydrodynamic cavitation as gas mass transfer system for biological hydrogen methanation
P104	Cecilia	Petitta	Sapienza University of Rome	Enhancing dark fermentation of cheese whey with Electrically Conductive Materials
P105	Valeria	Pierpaoli	Università degli Studi della Tuscia	Extraction and characterization of lignin from chestnut via hydrothermal treatment
P106	Maria	Presutti	Sapienza University of Rome	BIotechnologies for SUstainable REmediation – BISURE: Development of integrated chemical-physical-biological processes for the contaminated groundwater remediation
P107	Agnese	Ricci	Roma Tre University	Removal of Pharmaceuticals from Water Using Polyoxazoline-Functionalized Magnetic Iron Oxide Nanoparticles

P108	Tahreem	Saleem	University of Milano Bicocca	Lignin-based catalysts for hydrogen production
P109	Federico Maria	Scesa	Politecnico di Milano	Novel Solutions for Enhanced Performances in Fluoride-Ion Batteries
P110	Federico	Scopetti	Sapienza University of Rome	Hydrogen and methane production in a microbial electrolysis cell
P111	Beatrice	Simonis	CNR-Institute for Biological Systems (ISB)	Liposomes and lipoplexes for food safety in agriculture
P112	Eleonora	Stornelli	Sapienza University of Rome	CMC and Sodium Alginate as novel water-soluble binders for NMC cathodes
Theme H - Chemistry and Biology				
P113	Alessandro	Camilli	Sapienza University of Rome	Influence of Surface Functional Groups of Carbon Dots on the Inhibition of Candida albicans Biofilm
P114	Giulia	Fucile	University of Rome "Tor Vergata"	Mercury in benthos organisms: formalin fixation or freezing?
P115	Claudia	González Castro	University of Naples Federico II	Seleno-glycoconjugates for the prevention of oxidative stress
P116	Bruna	Matturro	IRSA-CNR	BISURE (BIotechnologies for Sustainable Remediation): A New Research Project Integrating Bioremediation of Multi-contaminated Sites within a Circular Economy Perspective
P117	Elena	Passarini	Sapienza University of Rome	Screening of synthetic molecules active towards Bacillus cereus group
P118	Adriano	Patriarca	Sapienza University of Rome	Pisum sativum L. ‘Eso’: Metabolic profiling of yellow seeds to define the optimal harvest time.
P119	Aki	Shibata	Tohoku University	Fabrication of intracellular releasing induced prodrug nanoparticles by hydrogen peroxide reaction
Theme I - Functional Materials				
P121	Marta	Cadeddu	University of Perugia/University of Sassari	Synthesis of Dual-Emitting Nonaromatic Fluorescent Polymers through Thermal Processing of L-Glutamic Acid and L-Lysine
P122	Matteo	Chimento	Sapienza University of Rome	Direct conjugation of TiO2 nanoparticles with carotenoids extracted from tomato peels
P123	Sara	Colecchia	Sapienza University of Rome	Investigating the electrochemical behavior of graphene oxide and its derivatives
P124	Alessio	Conti	Sapienza University of Rome	A multi-step synthesis of thiolated graphene oxide
P125	Laura	Costantini	Sapienza University of Rome	Bromine substitution in chloride hybrid perovskites
P127	Melania	Lettieri	Università della Calabria	Functionalization of PEEK for membrane preparation
P128	Fabrizio	Olivito	Università della Calabria	Effect of reaction conditions in PIM-1 synthesis
P129	Geraldo Augusto	Pereira	Fundaçao Oswaldo Cruz (FIOCRUZ-RJ-BRAZIL)	Enhancement and Analysis of Polyethylene Terephthalate Sulfonation: Technological Filtering Device
P130	Christian	Rossi	Università degli Studi di Genova	Citrate mediated chemical bath deposition of ZnMgO for Cu(In,Ga)Se2 solar cells
Theme L - Chemistry and Society				
P131	Donatella	Occhiuto	ARPA Lazio	LIFE SIRIUS project: A System for Integrated EnviRonmental Information in Urban areas
P132	Martina	Redi	University of Rome "Tor Vergata"	PVA Chemical hydrogels. A sustainable tool for Cultural Heritage Conservation.

Theme A - Advances in Organic Chemistry

Lignin Depolymerization-Upgrading to Biomaterials

Biagio Anderlini[1*], Antonio Lezza[1], Nicola Porcelli[1], Fabrizio Roncaglia[1,2]

[1] Department of Chemical and Geological Sciences, University of Modena and Reggio Emilia, Modena, Italy
[2] INSTM Research Unit of Modena, Via G. Campi 103, 41125 Modena, Italy.

** E-mail: biagio.anderlini@unimore.it*

Lignocellulosic biomass is primarily composed of the carbohydrates cellulose and hemicellulose, and of lignin, a complex phenolic polymer. While the carbohydrates are processed to high-value products, the lignin fraction is primarily burned for energy production. However, lignin is the main renewable resource of aromatic compounds. The native lignin present in biomass is a 3D amorphous macromolecule made up principally by the combination of three different phenylpropane monomer units: *p*-coumaryl alcohol, guaiacyl alcohol and syringyl alcohol, linked mainly by aryl ether bonds in a randomized way. Lignin is an abundant aromatic feedstock, but it is still largely considered as a source for heat and power from bio-refinery. The lack of well-established processes that add value to lignin can be largely attributed to its structural complexity and associated chemical inactivity. Lignin conversion to value-added products is governed by an interplay of three technological biorefinery aspects: (i) lignocellulosic biomass fractionation, (ii) lignin depolymerization, and (iii) upgrading towards targeted (intermediate or final) chemicals. Efficient lignin depolymerization could produce a wide range of fuels and chemicals (and/or their precursors). These molecules (especially alkylated phenols) could be used to produce chemicals and materials (polymers, antioxidants, resins, medicines, or pesticides) in substitution to fossil fuel resources.[1] One of the most promising routes is the disassembling of the lignin structure into its phenolic building blocks, to further transform them into targeted end products. These units are connected through various ether and carbon–carbon bonds and the *β-O-4* ether bond is the most abundant linkage, at least in native lignin.[2] Therefore, the oxidative conversion of lignin is of great interest because it enables the formation of highly functionalized, valuable compounds. Consequently, the design of more efficient and environmentally benign catalytic processes for the CC bond cleavage it's a topic of key importance. Oxovanadium complexes are among the most studied catalysts for the oxidation of dimeric lignin model compounds, using air or oxygen as oxidant. In particular, triphenolamines (TPAs) ligands seems to be the most active ones.[3] Catalyst's selectivity and reactivity can be tuned by changing ligand structure[2] and substituents.[3] In particular, during the first and second year, we focused on ligands synthesis in order to improve poor yields,[4] and obtain a greater variety of complexes.

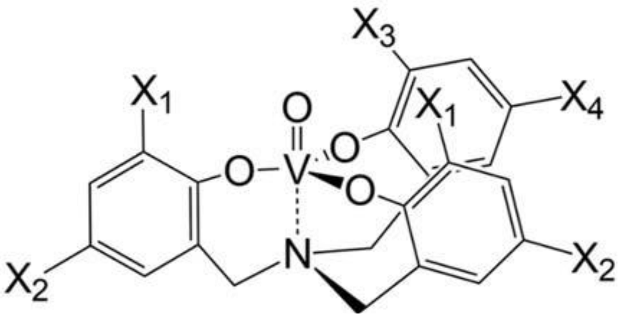


Figure 1. Generic triphenolamine oxovanadium

References

[1] Mussatto, S. I. (Ed.). (2016). Biomass fractionation technologies for a lignocellulosic feedstock based biorefinery. Elsevier.
[2] Vangeel, Thijs, et al. Lignin Chemistry (2020): 53-68.
[3] Amadio, Emanuele, et al. Advanced Synthesis & Catalysis 360.17 (2018): 3286-3296. [4] Groysman,
[4] Stanislav, et al. Advanced Synthesis & Catalysis 347.2-3 (2005): 409-415.

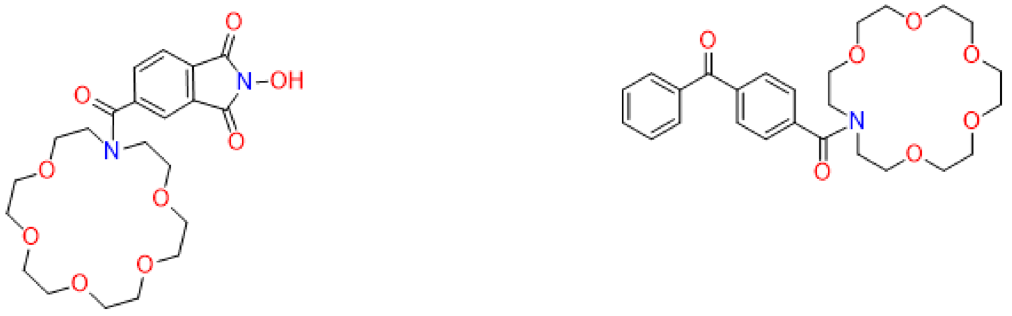
Supramolecular catalysts for HAT reactions: site-selectivity in C-H bond functionalization

Marianna Bernardini, Beniamin Emanuel Birzu, Federica Di Mascolo, Giorgio Olivo, Andrea Lapi,
Federico Frateloreto, Stefano Di Stefano, Osvaldo Lanzalunga

Dipartimento di Chimica e Istituto CNR per i Sistemi Biologici (ISB-CNR); Sezione Meccanismi di Reazione,
Università di Roma "La Sapienza", P.le A. Moro, 5, 00185, Roma, Italia.
marianna.bernardini@uniroma1.it

Selective functionalization of C-H bonds in hydrocarbons represents an outstanding challenge in synthetic organic chemistry. In this contest, catalysts that perform the C-H activation by hydrogen abstraction (HAT) have attracted increasing interest. The main challenge is the site-selectivity in the functionalization of C-H bonds with similar electronic and steric environments[1]. This is particularly true for the positions located far away from other functional or directing groups (remote sites). A supramolecular, geometric approach can provide a way to overcome these challenges.

In this context, we developed a series of catalysts containing a *N*-hydroxyphthalimide or benzophenone core functionalized with crown (1) or aza-crown (2) macrocyclic polyethers as supramolecular recognition sites (Figure1). The 18-crown-6 or the 1-aza-18-crown-6 receptors recognize the heads of primary, linear alkylammonium chains and, when coordinated to Ba^{2+} ions, can also establish electrostatic interactions with substrates containing carboxylates, sulfates, and sulfonates functional groups. By an intramolecular HAT, it should be possible to selectively abstract H atoms from specific C–H bonds that are properly oriented towards the active sites constituted by the phthalimide-*N*-oxyl radical or benzophenone triplet excited state.



Cat1 **Cat2**

Figure1

References

[1] G. Olivo, G. Capocasa, D. Del Giudice, O. Lanzalunga, S. Di Stefano, *Chem. Soc. Rev.*, 2021, **50**, 7681-7724.

N-hydroxyphthalimide as mediator in the oxidations promoted by nonheme iron(IV)-oxo complexes

Beniamin Emanuel Birzu, Marianna Bernardini, Marika Di Berto Mancini, Stefano Di Stefano,
Arianna De Santis, Daria Khaksar, Osvaldo Lanzalunga, Andrea Lapi, Giorgio Olivo

Dipartimento di Chimica e Istituto CNR per i Sistemi Biologici (ISB-CNR); Sezione Meccanismi di Reazione,
Università di Roma "La Sapienza", P.le A. Moro, 5, 00185, Roma, Italia.
birzu.1891061@studenti.uniroma1.it

Selective functionalization of unactivated aliphatic C-H bonds represents an important challenge in organic chemistry. In this context Hydrogen Atom Transfer (HAT) promoted by non-heme iron-oxo complexes, and by aminoxyl radicals have attracted a considerable attention. Recently, we have found that *N*-hydroxyphthalimide (NHPI), precursor of the phthalimide N-oxyl radical (PINO), acts as an efficient mediator in the oxidation of hydrocarbons and alcohols promoted by the nonheme iron(IV)−oxo complex, $[(N4Py)Fe^{IV}(O)]^{2+}$.[1] The presence of NHPI as a mediator determines a variation of the HAT selectivity displayed by the iron (IV)−oxo complex $[(N4Py)Fe^{IV}(O)]^{2+}$ in the oxidation of aliphatic alcohols and alkylaromatic substrates with the latter more reactive in the absence of the mediator and alcohols that are oxidized preferably in the presence of NHPI (Figure 1).[2]

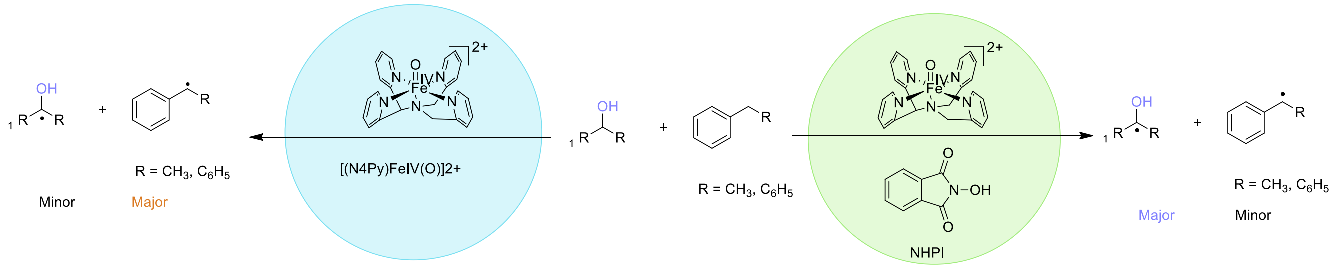


Figure 1

In the HAT vs S-oxidation chemoselectivity analysis of the oxidations of a series of aryl sulfides, alkylaromatic compounds and benzylic alcohols, sulfoxides are generally obtained as major products with $[(N4Py)Fe^{IV}(O)]^{2+}$ (Figure 2). In the presence of NHPI, HAT-derived products are obtained in higher yields leading to a reversed chemoselectivity.[3]

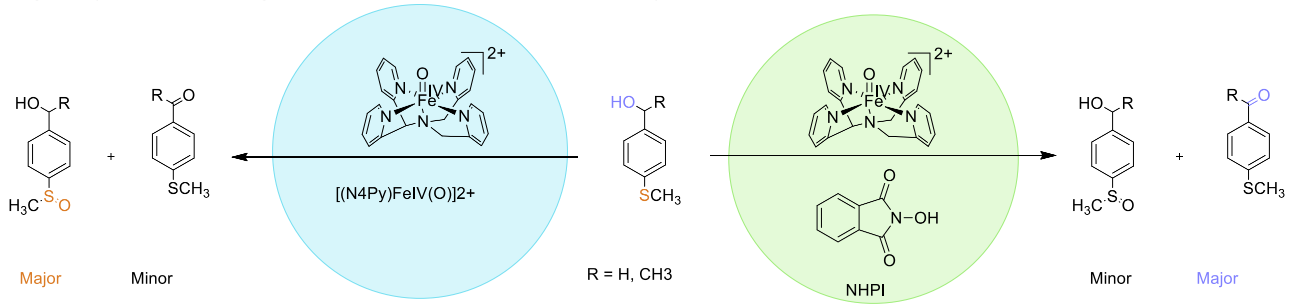


Figure 2

---

[1] A. Barbieri, O. Lanzalunga, A. Lapi, S. Di Stefano *J. Org. Chem.* **2019**, *84*, 13549−13556

[2] M. Di Berto Mancini, A. Del Gelsomino, S. Di Stefano, F. Frateloreto, A. Lapi, O. Lanzalunga, G. Olivo, S. Sajeva *ACS Omega* **2021**, *6*, 26428−26438

[3] M. Di Berto Mancini, M. Bernardini, B. E. Birzu, A. De Santis, S. Di Stefano, F. Frateloreto, D. Khaksar, A. Lapi, G. Olivo, O. Lanzalunga *Eur. J. Org. Chem* **2023**, *26*, e202300360

Synthesis of space-grade polyimides using bio-based sustainable chemistry

Francesca Blondelli[1*], Guido Saccone[2], Nunzia Favaloro[2], Elisa Toto[3], Maria Gabriella Santonicola[1]

[1]*Department of Chemical Engineering Materials Environment, Sapienza University of Rome, Rome, Italy*

[2]*CIRA, Italian Aerospace Research Centre Capua (CE), Italy*

[3]*Department of Astronautic, Electrical and Energy Engineering, Sapienza University of Rome, Rome, Italy*

**francesca.blondelli@uniroma1.it*

Polyimides (PIs) with imide and aromatic rings are widely used polymers in the space field. They possess outstanding properties such as excellent thermo-chemical stability and mechanical strength, which, combined with their light weight, make them ideal candidates for the realization of structures in space extreme environment. The synthesis of these materials is traditionally done using solvents (dimethyl acetamide, n-methyl pyrrolidone, tetrahydrofuran), that are toxic to workers and the environment. An advantage of our chemical strategy is to overcome the use of these solvents, by using greener alternatives, such as the bio-based dimethyl isosorbide (DMI). In this work, we focus on the molecular design and synthesis of polyimides with advanced properties for space applications, including for example the fabrication of lightweight self-healing materials for extra-terrestrial habitats.

Polyimides are synthetized in two steps, using dimethyl isosorbide (DMI), a non-toxic and bio-based solvent already used in our past work [1, 2]. First, aromatic dianhydride was added to a mechanically stirred solution of aromatic diamine in DMI. Then, poly(amic acid) (PAA) is converted to polyimide by thermal or chemical imidization. Selected additives, such as boric acid, are added during the synthesis to enhance the intrinsic self-repair ability. The dynamicity and reversibility of the chemical bonds, which is crucial for self-healing, are analysed by FTIR spectroscopy. Indeed, intrinsic self-healing is based on the mobility of chains. In addition, the ATR-FTIR spectra confirmed the presence of additives embedded in the polymer matrix. Further characterizations include measurement of the density of the polyimide-based materials by the hydrostatic weighing method, considering the guidelines of the ASTM D792 standard, and assessment of the thermal stability in a wide temperature range by differential scanning calorimetry (DSC).

References

[1] E. Toto, S. Laurenzi, R.C. Pellegrini, E. Cavallini, M.G. Santonicola, Eco-friendly synthesis of high-performance polyimide materials using bio-based greener solvents: Towards sustainable technologies in space environment, Mater. Today Sustain. 25 (2024) 100657, https://doi.org/10.1016/j.mtsust.2023.100657.

[2] E. Toto, M.G. Santonicola, S. Laurenzi, C. Circi, R.C. Pellegrini, E. Cavallini, E. Serra, S. Scaglione, D. Zola, UV–VIS-NIR optical properties of micrometric-thick polyimide membranes for lightweight devices in space, Opt. Mater. 146 (2023) 114604, https://doi.org/10.1016/j.optmat.2023.114604.

Selective oxidation of C-H bonds using bio-inspired confined catalysts

L. Cirillo[1]*, D. Possenti[1], A. Baidyuk,[3] C. Colomban,[3] G. Olivo,[1,2]

[1] *Dipartimento di Chimica, Università di Roma La Sapienza, P. le A. Moro 5, 00185 Roma, Italy*
[2] *Istituto CNR di Metodologie Chimiche (IMC-CNR), Sezione Meccanismi di Reazione, P. le A. Moro 5, 00185 Roma, Italy*
[3] *Facultè des Sciences St JEROME, Aix-Marseille University, 52 Avenue Escadrille Normandie Niement, 13013 Marseille, France*
**cirillo.1905420@studenti.uniroma1.it*

The conversion of C-H bonds, into C-O bonds of biological relevance is one of the major challenges in current organic synthesis[1], due to their abundance in organic compounds and their strength (BDE 80-110 kcal/mol). The development of a method for selective C-H oxidation would enable the rapid and mild condition preparation of a library of derivatives of a single molecule, such as a series of potential drug metabolites, facilitating the discovery and commercialization of new drugs and the functionalization of biomolecules. This would get chemists closer to metalloenzyme functionalities and it would give an alternative to current methodologies which require multi-step syntheses. However, the controlled insertion of C-O groups is particularly demanding.

In this research Fe/Mn-based catalyst chemistry is combined with supramolecular cage chemistry. By preparing encapsulated Fe and Mn catalysts, the project will offer a significant point of contact between these two research fields.[2] In addition, the preparation of bio-inspired models, trapping reactive species, and catalytic protocols are still underexplored in supramolecular chemistry.
The reaction mechanism involves a high-valence metal−oxo intermediate species that allows to achieve a good range of C-H oxidative reactivity: hydroxylation, olefin epoxidation, syn-dihydroxylation and desaturation[3], making cage catalysts chemistry relevant for a wide range of substrates.

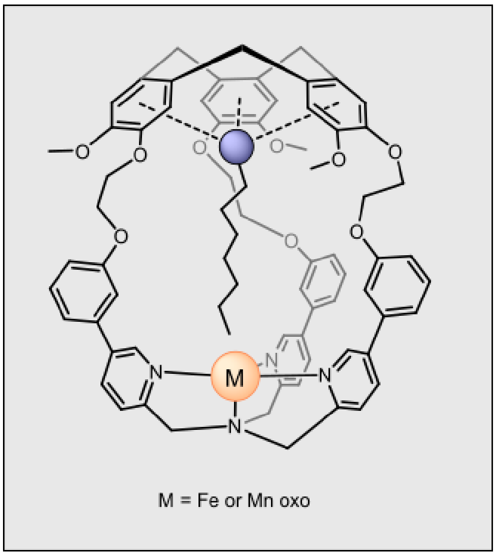


Figure 1. Example of Fe/Mn-based cage catalyst

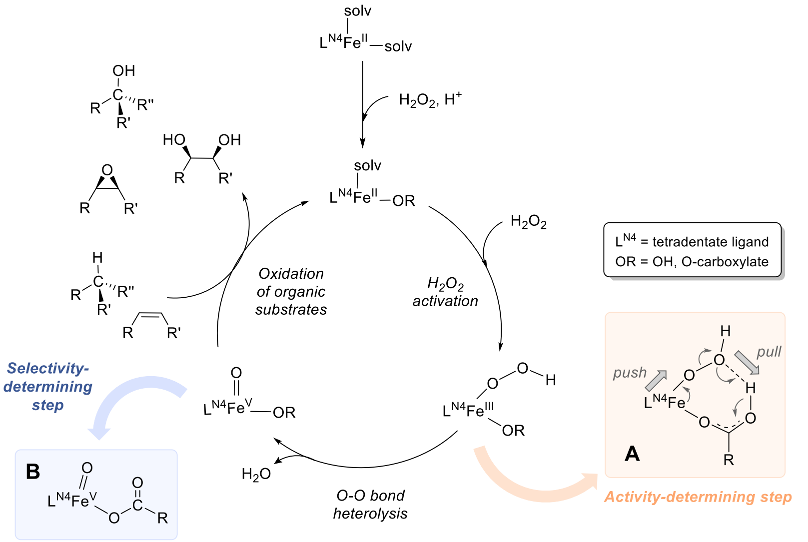


Figure 2. Catalytic cycle for the oxidation of C-H with N4 iron catalysts and H2O2,[3]

References

[1] T. Newhouse and P. S. Baran, Angew. Chem. Int. Ed Engl., 2011, 50, 3362-3374.
[2] G. Olivo, G. Capocasa, D. Del Giudice, O. Lanzalunga and S. Di Stefano, Chem. Soc. Rev., 2021, 50, 7681-7724.
[3] Laia Vicens, Giorgio Olivo, and Miquel Costas, ACS Catal. 2020, 10, 8611−8631

Conductivity Variations in Water Solutions Induced by an Activated Carboxylic Acid

A. D'Arrigo[1*], G. Capocasa[1], F. Frateloreto[1], M. De Angelis[1], S. Di Stefano[1]

[1]*Department of Chemistry, Università degli Studi di Roma "La Sapienza", 00185 Rome, Italy*

**darrigo.1853409@studenti.uniroma1.it*

The development of dissipative systems represents a hot topic in current chemical research. In a typical dissipative system, its components are initially found in a resting, equilibrium state. Exploiting the perturbation caused by a chemical or radiative stimulus (fuel), the system is driven from the initial equilibrium state to an out-of-equilibrium, functional state. When the fuel is dissipated (exhausted), the system spontaneously reverts to the initial equilibrium state (see Figure 1A). In this context, activated carboxylic acids (ACAs) have been extensively used as chemical stimuli to drive the operation of responsive, dissipative systems (see Figure 1B).[1] Until recently, ACAs had only been used as chemical fuels for acid-base-responsive dissipative systems.[2] However, amongst a number of applications, we recently showed that they can also be employed to control non-pH-responsive devices by using them in a concentration cell.[1]

Here, we investigated the possibility of using a particular water-soluble, activated carboxylic acid, named nitroacetic acid, to control and program, over time, the conductivity of a water solution containing a certain amount of a weak base. The initial water solution is characterized by a very low ion content, thus a low electrical conductivity. After the addition of nitroacetic acid, ions are formed in solution, drastically increasing its conductivity. Such a significant change in this chemical-physical property persists until all of the fuel is consumed by the system. The observation of this behavior paved the way for a series of applications, including interfacing this dissipative system with simple electrical devices.

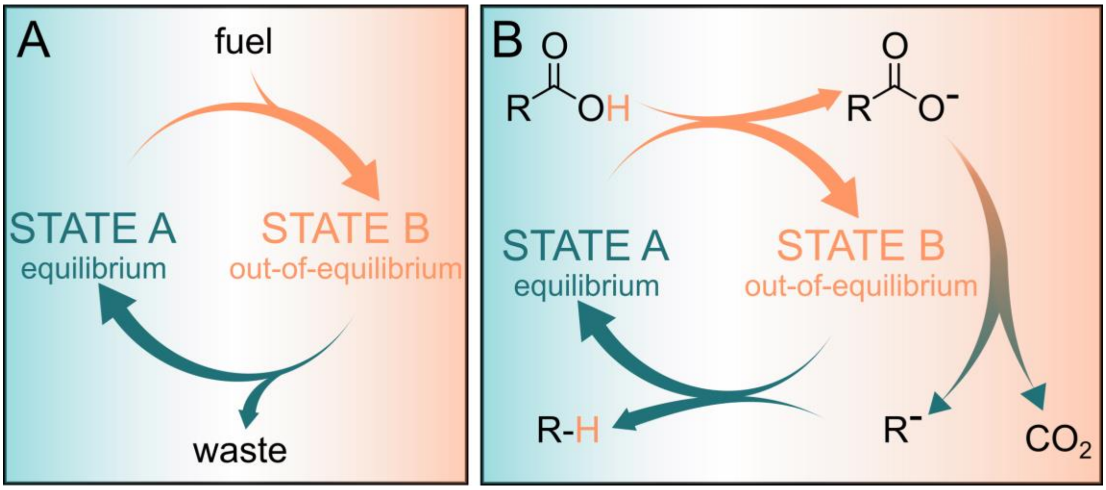


Figure 1. A) Operation of a generic dissipative system in the presence of a chemical stimulus. The fuel is converted to a waste product. B) An ACA driven dissipative system.

References

[1] G. Capocasa, F. Frateloreto, S. Correale Cavallari, M. Valentini, O. Lanzalunga, S. Di Stefano, Chem. Eur. J., 2024, 30, e202303897.

[2] D. Del Giudice, S. Di Stefano, Acc. Chem. Res., 2023, 56, 7, 889–899.

Derivatives of 2-(hydroxyimino)aldehydes as precursors of iminoxyl and alkyl radicals for antimicrobial and anticancer applications

F. Di Mascolo[1*], A. Argilli[1], F. D'Acunzo[2], T. De Simone[1], E. Passarini[3], M. Ragozzino[1], R. Remia[1], P. Gentili[1,2]

[1]Dipartimento di Chimica, Sapienza Università di Roma, Roma, 00185, Italia
[2]Instituto per i sistemi biologici (ISB), Consiglio Nazionale delle ricerche (CNR), Sezione Meccanismi di Reazione, c/o Dipartimento di Chimica, Sapienza Università di Roma, 00185 Roma, Italia
[3]Dipartimento di Biologia e Biotecnologie, Sapienza Università di Roma, Roma, 00185, Italia

**federica.dimascolo@uniroma1.it*

Oximes and their derivatives, such as oxime esters, have versatile uses in the medical sector and have been shown to exhibit anti-inflammatory, antimicrobial, antioxidant, and anticancer activity [1]. Oximes are also one of the most powerful antidotes to OP poisoning, while their esters have been proven to cleave DNA when photolyzed by UV light [2]. Our team has been obtaining new oxime derivatives by elaborating on the 2-(hydroxyimino)aldehyde RC=(NOH)CHO (HIA) structural platform (see Figure). The latter has been made accessible through α-oximation of a wide variety of aliphatic aldehydes, with good to excellent yields [3, 4]. The resulting general structure allows for a three-level variation (see Figure), i.e. of the R substituent, of the N-OH and of the aldehyde moiety, thus enabling the search for efficient drugs for different applications. We conducted the functionalization of the N-OH group to obtain oxime ethers and esters, thereby opening the possibility of generating, by photolysis or thermolysis, the iminyl and iminoxyl radical, both cytotoxic. We also introduced an imine function through the reaction between the CHO group and the amino acid tryptophan as a model for polypeptide binding and release. Interestingly, we were also able to exploit the CuAAC (click) chemistry as a convenient way to access variability in the R group. In fact, two of the resulting molecules, endowed with both the 1,2,3-triazole and HIA functionalities, are being tested as antimicrobial agents. Specifically, some bacteriostatic activity has been demonstrated on *Bacillus cereus TR22* for one of the tested structures.

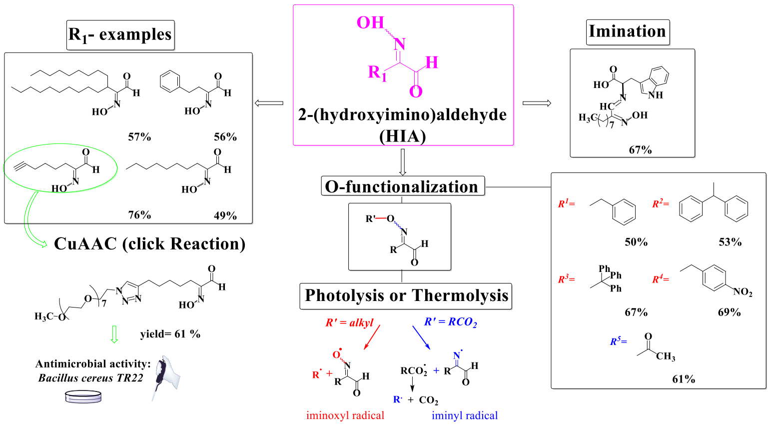


Figure 1: Three-level variation of 2-(hydroxyimino)aldehyde function.

References

[1] Surowiak A. K., Lochy ´ nski S., Strub D.J., *Symmetry* **2020**, *12*, 575.
[2] Hwu J. R., Tsay S. C., Hong S. C., Hsu M. H., Liu C. F., Chou S. S. P., *Bioconjugate Chem.* **2013**, *24*, 1778.
[3] Gentili P., Nardi M., Antignano I., Cambise P., D'Abramo M., D'Acunzo F., Pinna A., Ussia E., *Chem. Eur. J.* **2018**, *24*, 7683.
[4] D'Acunzo F., Carbonaro L., Dalla Cort A., Di Sabato A., Filippini D., Leonelli F., Mancini L., Gentili P., *Eur. J. Org. Chem.* **2021**, 289.

Liposomes of estrogenic soft-drugs to boost wound healing

Beatrice Di Mattia[1*], Micol Mazzone[1], Luigi Filocamo[2], Francesca Leonelli[1], Luciano Galantini[1],Francesca Ceccacci[3], Mariangela Clemente[3], Luisa Maria Migneco[1]

[1]Chemistry Department, Sapienza University of Rome, P.Le Aldo Moro 5, 00185, Rome, Italy,
[2] Department of Biochemistry Science "A. Rossi Fanelli", Sapienza University of Rome, P.Le Aldo Moro 5, 00185, Rome, Italy
[3]CNR-ISB-Secondary office of Rome, Reaction Mechanisms c/o Chemistry Department, Sapienza University of Rome, 00185, Rome, Italy

**dimattia.1920464@studenti.uniroma1.it*

Estrogens are steroid hormones known for having multiple biological activities, including their interesting involvement in the wound healing process. In this case, mitigation of typical systemic effects of these compounds is necessary. This goal is achieved by converting active molecules in soft drugs: active upon administration but rapidly inactivated by metabolic reactions, thus allowing solely topical action, and preventing systemic circulation. This study is aimed to prepare an efficient dermal nanovesicular carrier. Liposomes allow to increase drug accumulation at the target site and they have been chosen for their biocompatibility and non-toxicity characteristics. In our laboratory, two series of estrogenic soft drugs with hydrolysable ester group have been synthesized and, among all, **1**[1] and **2**[2] (Figure 1) resulted the most promising. In this work, we present preliminary studies on liposomes and transfersomes of **1** and **2**. Transfersomes have a more flexible structure than liposomes to enable penetration through the epidermis. Several nanovesicular carrier have been prepared using phosphocoline (dipalmitoylphosphatidylcholine, DPPC, or dimyristoylphosphatidylcholine, DMPC) as the main component in mixture with the estrogen derivative (**1** or **2**) and/or sodium cholate, the latter as the edge activator. The physicochemical properties have been analyzed by DELS and DLS.

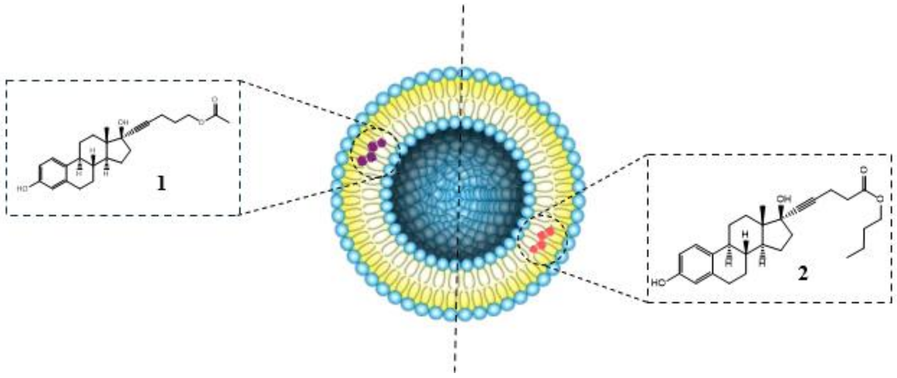


Figure 14: liposomes of estrogenic soft-drugs

References

[1] Brufani M., Ceccacci F., Filocamo L., Garofalo B., Joudioux R., La Bella A., Leonelli F., Migneco L.M., Marini Bettolo R., Farina P.M., Ashcroft G.S., Routley C., Hardman M., Meda C., Rando G., Maggi A. Molecular Pharmaceutics, 2009, **6**, 543

[2] Brufani M., Rizzi N., Meda C., Filocamo L., Ceccacci F., D'Aiuto V., Bartoli G., La Bella A., Migneco L.M., Marini Bettolo R., Leonelli F., Ciana P., Maggi A., Scientific Reports, 2017, **7**, 2510.

[3] Hua S., Lipid-based nano-delivery systems for skin delivery of drugs and bioactives, Frontiers in Pharmacology, 2015, **6**, 219.

Stereoselective Preparation of a Key Intermediate in the Synthesis of Oryzalexin S Using Organocatalysts and Chiral Carbon Dots

Laura Loffredo*[1], Chiara Codella[1], Marianna Mattei[1], Lorenzo Michelini[1], Fabrizio Vetica[1],
Francesca Leonelli[1], Luisa Maria Migneco[1]

[1]*Chemistry Department, Sapienza University of Rome, Piazzale Aldo Moro, 5, 00185 Rome, Italy*

* *loffredo.1835853@studenti.uniroma1.it*

Oryzalexin S (**1**) is a diterpenic phytoalexin produced by *Oryza Sativa L.*, i.e. the common rice plant, and first isolated by Kodama et al. in 1992 [1]. Considering its interesting activity and potential applications in agricultural and medicinal fields, its total synthesis, not yet reported, is underway. Following the strategic plan developed for **1** (Figure 1), key intermediate **6** was stereoselectively synthetized by means of organo-catalyst D-Tyrosine, and Carbon Dots (CDs) [2], chiral nano-particles that have recently gained attention for their eco-compatibility and applications in asymmetric synthesis. Preliminary results showed the higher efficiency of the organocatalytic approach (e.e.=88%) with respect to CDs approach (e.e.=18%) in the stereoselective cyclization leading to the synthesis of intermediate **6**.

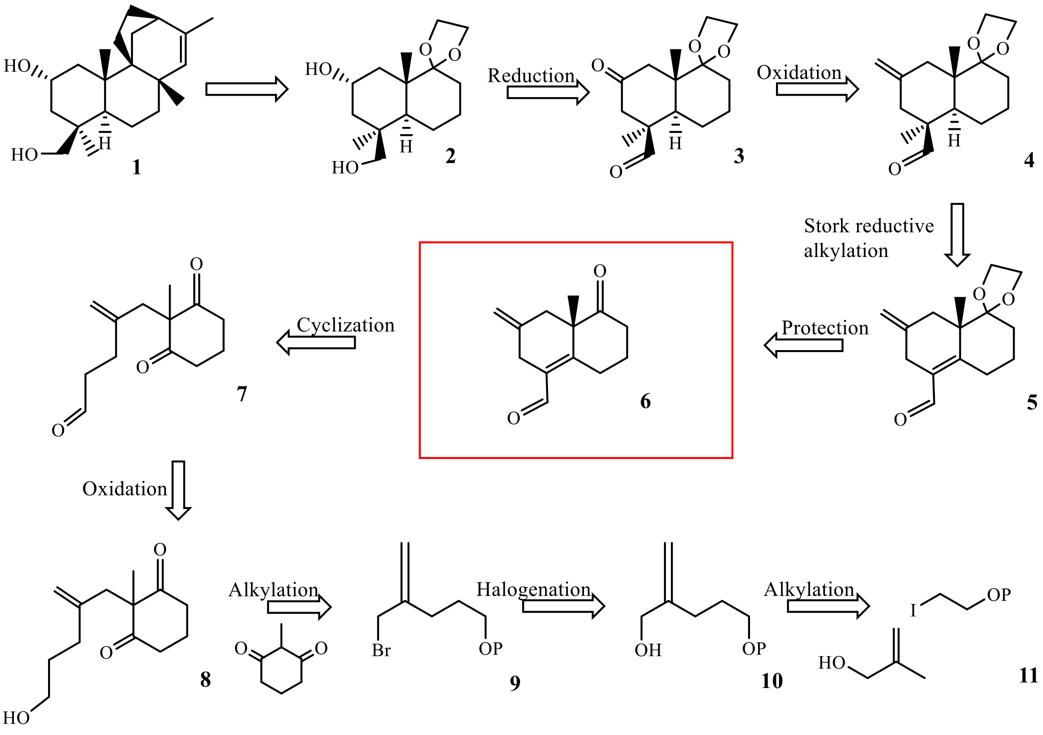


Figure 1: Retro-synthetic analysis of **1.** P=TBDMS

References

[1] Kodama O., Wen X. L., Tamogami S., Akatsuka T, *Bioscience, Biotechnology, and Biochemistry*, 1992, **56** (6), 1002-1003.

[2] Bortolami M., Bogles I.I., Bombelli C., Pandolfi F., Feroci M., Vetica F., *Molecules*, 2022, ***27*** (16), 5150.

Improved and greener syntheses of estrogenic soft drugs

Micol Mazzone*[1], Beatrice Di Mattia[1], Arianna Boldrini[1], Angiolina Servidio[1], Francesca Leonelli[1],
Luigi Filocamo[2], Francesca Ceccacci[3], Mariangela Clemente[3], Luisa Maria Migneco[1]

[1] *Chemistry Department, Sapienza University of Rome, P.Le Aldo Moro 5, 00185, Rome, Italy,*
[2] *Department of Biochemistry Science "A. Rossi Fanelli", Sapienza University of Rome, P.Le Aldo Moro 5, 00185, Rome, Italy*
[3] *CNR-ISB-Secondary office of Rome, Reaction Mechanisms c/o Chemistry Department, Sapienza University of Rome, 00185, Rome, Italy*

**mazzone.1862028@studenti.uniroma1.it*

Estrogens are a class of steroid hormones biologically relevant for their regulatory properties in many biological processes, among them, notably, wound healing. Estrogens generally exhibit systemic activity, however their formulations addressed to wound healing must exert only topical activity. To this end, estrogenic derivatives are designed as Soft Drugs (SD): pharmacologically active compounds that act solely at the site of application, minimizing systemic side effects in favor of increasing drug's therapeutic index. In light of this, in our laboratory several estrogenic derivatives have been conceived as soft drugs, carrying easily hydrolyzable ester groups that confer solely local, non-systemic activity to the molecule. So, we synthesized two classes of estradiol derivatives starting from estrone, with 3,17 β-Hydroxy-17α-(5'acetoxy-1'-pentyn-1'-yl)estra-1,3,5-(10)triene **1**[1] and 3,17 β-Hydroxy-17α-(4'carbobutoxy-1'-butyl-1'-yl)estra-1,3,5-(10)triene **2**[2] emerging as the most active compounds (Figure 1). In this work we present improved protocols for the syntheses of **1** and **2** focused on increasing efficiency and sustainability.

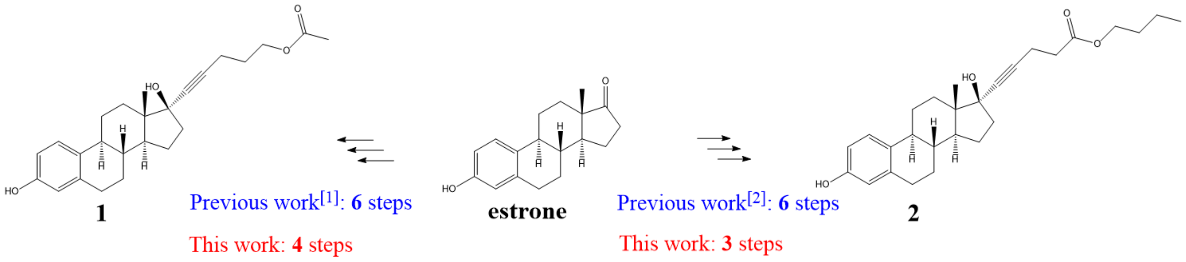


Figure 1 soft drugs synthesized from estrone.

References

[1] Brufani M., Ceccacci F., Filocamo L., Garofalo B., Joudioux R., La Bella A., Leonelli F., Migneco L.M., Marini Bettolo R., Farina P.M., Ashcroft G.S., Routley C., Hardman M., Meda C., Rando G., Maggi A. *Molecular Pharmaceutics*, 2009, **6**, 543.

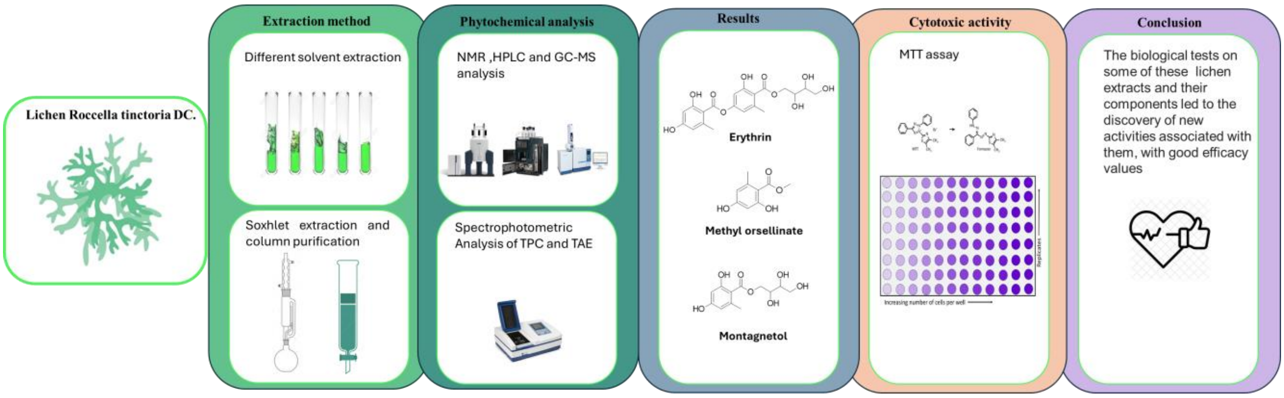
[2] Brufani M., Rizzi N., Meda C., Filocamo L., Ceccacci F., D'Aiuto V., Bartoli G., La Bella A., Migneco L.M., Marini Bettolo R., Leonelli F., Ciana P., Maggi A., *Scientific Reports*, 2017, **7**, 2510.

Evaluation of the cytotoxic activity of Lichen *Roccella tinctoria* DC. Extracts and major components

Roberta Maria Nicolosi[1*], Claudio Frezza[1], Dalia Rosa Fraioli[1], Paola Di Matteo[2], Silvia Di Giacomo[3,4], Antonella Di Sotto[3], Stefania Garzoli[5], Daniela De Vita[1]
[1] *Department of Environmental Biology, University of Rome 'La Sapienza', Piazzale Aldo Moro 5, 00185 Rome, Italy*
[2] *Department of Basic and Applied Sciences for Engineering, University of Rome "La Sapienza", Via Castro Laurenziano 7, 00161 Rome, Italy*
[3] *Department of Physiology and Pharmacology "V. Erspamer", University of Rome "La Sapienza", Piazzale Aldo Moro 5, 00185 Rome, Italy*
[4] *Department of Food Safety, Nutrition and Veterinary Public Health, Istituto Superiore di Sanità, 00161 Rome, Italy*
[5] *Department of Medicinal Chemistry and Technology, University of Rome 'La Sapienza', Piazzale Aldo Moro 5, 00185 Rome, Italy*
**robertamaria.nicolosi@uniroma1.it*

Lichens are a symbiotic association of a fungus defined as a mycobiont, that hosts photobiont inside it, that is either a green alga or a cyanobacterium [1]. *Roccella* DC. (Roccellaceae) is a genus of fruticose lichens that comprises more than 20 species, 7 of which are widespread in Europe, especially along the Mediterranean coasts. *Roccella tinctoria* DC. represents the most common species of this genus in Italy, characterized by a rigid fruticose brownish thallus, long smooth branches, a bark of hyphae anticlinally disposed, and, generally, the total absence of apothecia [2].

In this work, a phytochemical analysis was performed on different solvent extracts of *R. tinctoria* evidecing the presence of 20 volatile and 3 non-volatile components *i.e.*, erythrin (**1**), methyl orsellinate (**2**), and montagnetol (**3**). The methanolic extracts obtained from two different protocols were also studied for their TPC and TAE values. Lastly, these same methanolic extracts and the non-volatile compounds were tested for their cytotoxic activities on A549 and Mz-ChA-1 cancer cells and their tolerability in BEAS-2B and H69 noncancer cells, showing IC_{50} values from 94.6 µg/mL to 416.4 µg/mL [3].



The biological tests on some of these lichen extracts and their components led to the discovery of new activities associated with them, with good efficacy values

References

[1] Surridge, C. *Nature Plants*, *2016*, **2**, 16144
[2] Tehler, A., Irestedt, M., Wedin, M., & Ertz, D. *Systematics and Biodiversity*, *2010*, **8(2)**, 223–246.
[3] Frezza, C., Fraioli, D. R., Conti, F., Nicolosi, R. M., Scipione, L., Serafini, I., Petrucci, R., Di Matteo, P., Rocco, D., Di Giacomo, S., Di Sotto, A., Bonincontro, G., Simonetti, G., Garzoli, S., De Vita, D., & Foddai, S. *Pharmaceutics*, *2024*, **16(3)**, 331.

Simultaneous Oxidative and Reductive C-S Bond Cleavage in *t*-Alkyl Aryl Sulfoxides Catalyzed by Tetrabutylammonium Decatungstate

Livia Paolini, Marianna Bernardini, Osvaldo Lanzalunga

Dipartimento di Chimica e Istituto CNR per i Sistemi Biologici (ISB-CNR); Sezione Meccanismi di Reazione, Università di Roma "La Sapienza", P.le A. Moro, 5, 00185, Roma, Italia.

paolini.1806449@studenti.uniroma1.it

Tetrabutylammonium decatungstate, $(Bu_4N^+)_4W_{10}O_{32}^{4-}$, TBADT, is emerging as a powerful photocatalyst able to abstract hydrogen from several classes of organic compound including aliphatic hydrocarbons, aldehydes, amides and ethers. In the reaction of the excited state of decatungstate with thioethers, abstraction of the hydrogens α to the sulfur atoms of the substrates leading to dimers, $(R_2S[-H])_2$ is coupled with reduction of these substrates reduced form of the catalyst, $W_{10}O_{32}^{6-}$ generating the thioether anion radical. The latter than undergoes C-S bond cleavage to produce thiols, RSH and hydrocarbons, RH (Figure 1).[1]

$$W_{10}O_{32}^{4-} \xrightarrow{h\nu} W_{10}O_{32}^{4-*}$$

$$W_{10}O_{32}^{4-*} + R_2S \longrightarrow W_{10}O_{32}^{5-} + R_2S[-H]^{\bullet} + H^+$$

$$2\ W_{10}O_{32}^{5-} \longrightarrow W_{10}O_{32}^{4-} + W_{10}O_{32}^{6-}$$

$$2\ R_2S[-H]^{\bullet} \longrightarrow (R_2S[-H])_2$$

$$W_{10}O_{32}^{6-} + R_2S \longrightarrow W_{10}O_{32}^{5-} + R_2S^{\bullet -}$$

$$R_2S^{\bullet -} \longrightarrow R^{\bullet} + RS^-$$

$$R^{\bullet} + RSH \longrightarrow RH + RS^{\bullet}$$

Figure 1. Oxidation of thioethers photocatalyzed by decatungstate.

Oxidation of sulfoxide by the decatungstate excited state has received almost no attention, thus. in this study, we have investigated the TBADT photocatalyzed oxidation of *t*-alkyl aryl sulfoxides. In the absence of α to sulfur C-H bonds the sulfoxide radical cations is formed which undergoes a very fast C-S fragmentation process leading to a *t*-alkyl cation and the phenyl sulfinyl radical.[2] This step is followed by another C-S fragmentation reactions in the reductive process leading to a *t*-alkyl radical and a phenylsulfenate anion (Figure 2). An unprecedented two-sequential oxidative/reductive C-S bond cleavage processes are observed by excitation of the TBADT photocatalyst.

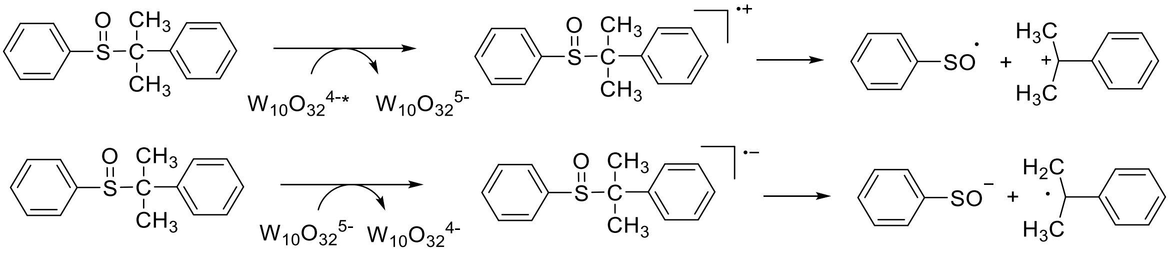


Figure 2. Oxidation of *t*-alkyl aryl sulfoxide photocatalyzed by decatungstate.

References

[1] R. C. Chambers, C. L. Hill, *J. Am. Chem. Soc.*, **1990**, *112*, 8427-8433.

[2] E. Baciocchi, T. Del Giacco, O. Lanzalunga, P. Mencarelli, B. Procacci, *J. Org. Chem.*, **2008**, *73*, 5675-5682.

Fe-catalyzed aromatic C—H amination: mechanism and applications

Dario Possenti[1,2*], Roberta Marino[1], Matteo Daino[1], Francesco Amato[1], Andrea G. Marrani[1],
Alessandro Motta[1], Giorgio Olivo[1,2]

[1]Dipartimento di Chimica, Università di Roma La Sapienza, Rome, Italy
[2]ISB-CNR Sede Secondaria di Roma - Meccanismi di Reazione

**dario.possenti@uniroma1.it*

Aromatic amines (anilines) is a widely spread functional group within both synthetic and natural organic scaffolds. The most common procedures rely on (*i*) functional group interconversion, requiring for a pre-functionalization, and, sometimes (*ii*) harsh reaction conditions. A direct method for the transformation of aromatic C—H bonds into C—NH_2 is therefore desirable.[1] Recently hydroxylamine derived salts have merged as a powerful reactant competent for the direct amination of aromatic C—H bonds in the presence of Fe salts or complexes.[1,2] This reaction has proved to be efficient for a broad substrate panel, however the mechanistic features remain unclear. Several pathways have been proposed as depicted in Figure 1, however a unifying mechanism needs to be established.[3]

To address this challenge we used a mean of reactivity experiments, spectroscopic characterization and computational data to distinguish among the possible pathways. This also help in the design of novel aminating reactants and methodologies to further broad the scope and selectivity of this reaction. Finally this protocol has been applied for the first time to graphene oxide (GO) and reduced graphene oxide (rGO), two very important carbon-based materials which can be successfully functionalized.

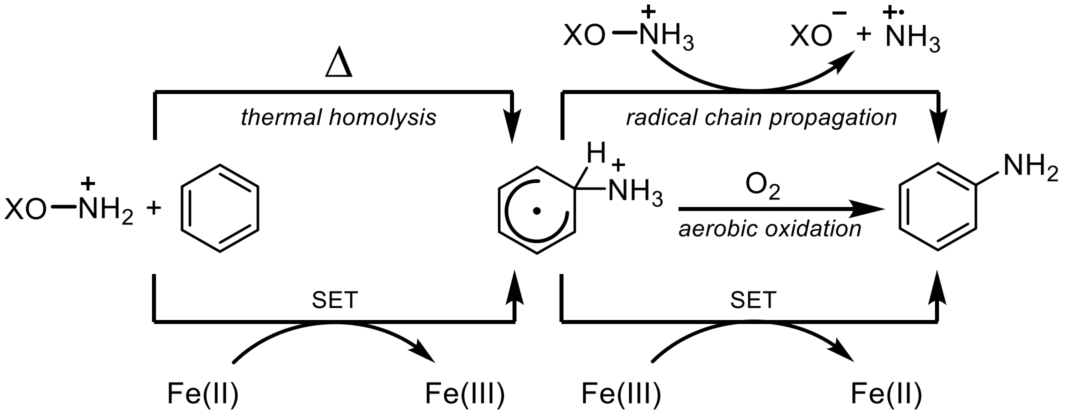


Figure 1. Reaction mechanisms proposed to occur in solution.

References

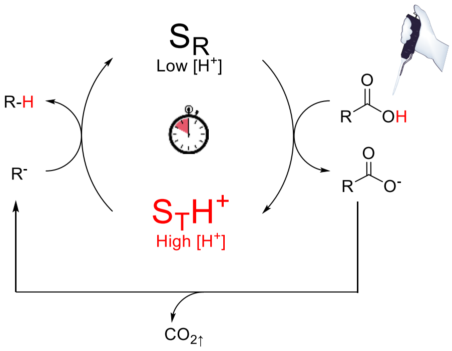
[1] Dario Possenti, Giorgio Olivo, *ChemCatChem* 2024, e202400353.
[2] Luca Legnani, Gabriele Prina Cerai, Bill Morandi, *ACS Catal.* 2016, 6, 8162-8165.
[3] Nicole Erin Behnke, Young-Do Kwon, Micahel T. Davenport, Daniel H. Ess, Làszlò Kürti, *J. Org. Chem.* 2023, 88, 16, 11847-11854.

Artificial Molecular Pump operated by unique Chemical Stimulus and based on Transimination Reaction

Francesco Ranieri[1*], Matteo Valentini[1], Daniele Del Giudice[1], Stefano Corrà[2], Alberto Credi[2], Brian Sachini[2], Stefano Di Stefano[1]

[1]*Department of Chemistry, University "La Sapienza", Rome, Italy*
[2]*Department of Industrial Chemistry, University "Alma Mater Studiorum", Bologna, Italy*

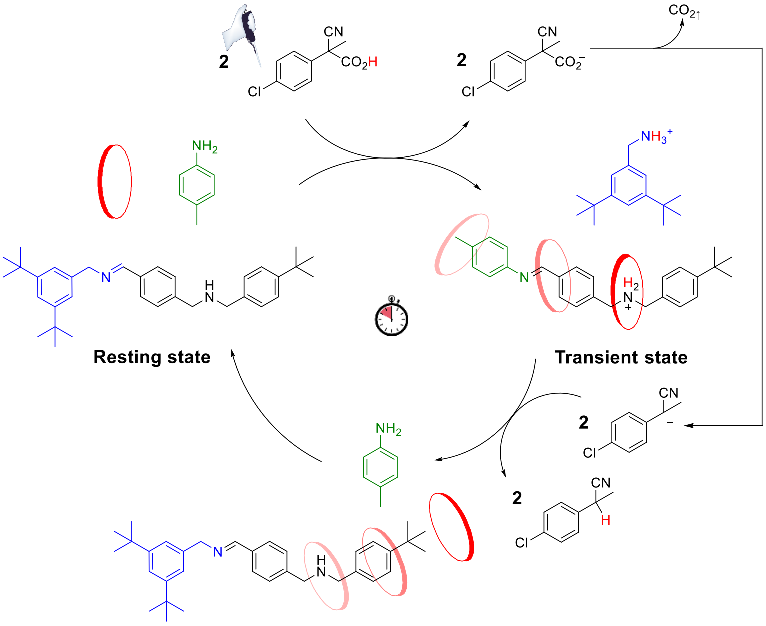
**francesco.ranieri@uniroma1.it*



In Dissipative Chemistry we are interested in moving a system from a Resting state, at the thermodynamic equilibrium, to a Transient out-of-equilibrium state and back again exploiting an appropriate stimulus. In this case we use an Activated Carboxylic Acid[1], which initially acts protoning the system and, and after the release of CO_2, generates *in situ* a carbanion. This strong base reverts the system to the initial state.

Aim of the project is to project and realize a molecular pump, i.e. a system able to perform unidirectional movement between its components. The idea we accomplished envisages a rotaxane based on transamination reaction and fuelled by a unique chemical stimulus, an activated carboxylic acid. The dibenzo-24-crown-8 behaves as the ring; the station of the axle is a protonable dibenzylic function; as entrance extremity there is an iminic moiety, while as leaving extremity there is a covalently bonded pseudostopper[2].

The fuel carries out two functions. In the dissipative phase of the cycle, protonates and subtract to the equilibrium the aliphatic amine (more basic), moving drastically the transamination towards the *p*-toluidine imine; in addition, protonates the station, so that the threading of the macrocycle becomes sterically accessible and thermodynamically favoured. After decarboxylation, with a back-proton-transfer, the equilibrium reverts, so the 3,5-di-tert-butyl-benzylamine imine is restored and the station is deprotonated, so that the dethreading from the covalent pseudostopper end is kinetically required and thermodynamically convenient.



The axle synthesis is already done and in following weeks we are interested in finding the best condition of solvent, amine relative amounts, type of fuel useful to operate the pump at the highest performance and following the process *via* NMR monitoring.

References

[1] Del Giudice D., Di StefanoS., *Acc. Chem. Res.*, 2023, **56**, 889-899.
[2] Corrà S., Credi A., M. Baronicini et al., *Chem. Eur. J.*, 2021, **27**, 11076-11083.

Enantioselective Norrish-Yang Photocyclization of 2-(Hydroxyimino)aldehydes

D. Rendeli[1]*, F. D'Acunzo,[2] A. Di Sabato,[1] E. Panzetta,[1] F. Vetica,[1] P. Gentili[1]

[1]*Department of Chemistry, Sapienza University of Rome, Rome, 00185, Italy*
[2]*Institute of Biological Systems (ISB), Italian National Research Council (CNR), Sezione Meccanismi di Reazione, c/o Department of Chemistry, Sapienza University of Rome, 00185 Roma, Italy*

**dario.rendeli @uniroma1.it*

Cyclobutanols, significant examples of heteroatom substitute four-membered rings, are prevalent in a variety of natural products and are used as intermediates in the total synthesis of sesquiterpenoids [1]. Belonging to this group, cyclobutanol oximes **(**CBO) are four-membered rings containing an oxime group in addition to alcoholic group. Within the framework of our continuing investigation of the 2-(hydroxyimino)aldehyde (HIA) functionality [2,3], recently we obtained CBOs through the Norrish-Yang's photocyclization of several HIAs (Figure 1) in DMSO-d_6 or CD_3CN as solvents. This photoisomerization takes full advantage of LED source (365 nm) to create a new C-C bond, with the concomitant formation of at least two new stereogenic center and, indeed, we obtained CBOs in high diastereomeric excess (up to 98%) and in good to excellent yields (up to 95%) [3]. Interestingly, when the reaction was carried out in DMSO, we observed the post-cyclization *E/Z* isomerization of C=NOH double bond, due to the strong H-bonding between the oxime-OH group and the solvent [3]. For this reason, we decided to exploit this strong interaction to develop an enantioselective version of Norrish-Yang reaction with the aid of chiral sulfoxides (or other chiral H-donor) as complexing agent. Therefore, we selected HIA **1a**, **1b** and **1c** as model substrates and we performed the reaction directly in CD_3CN in NMR tubes with LED source at -14°C, in the presence of a chiral complexing agent (Figures 1 and 2). The interaction between the chiral agent and the oxime-OH group was observed through NMR spectroscopy by the chemical shift's displacement of the proton of the oxime group. The reactions were monitored by NMR: in four hours CBOs were formed without any side products. Finally, after the purification of the crude by column chromatography, the enantiomeric ratio was analysed through HPLC analysis.

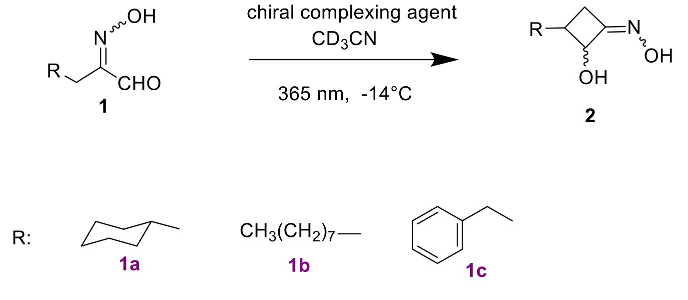


Figure 1: Synthesis of cyclobutanol oximes **(**CBO, **2**) by Norrish-Yang photocyclization of 2-(hydroxyimino) aldehydes (HIA, **1**)

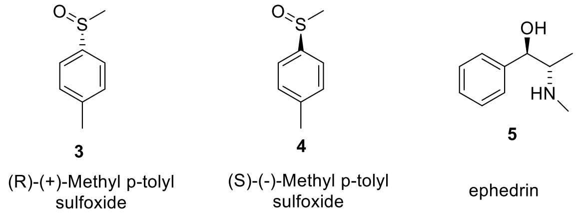


Figure 2: Chiral complexing agents

References

[1] Chen Y., Zhao J., Li S., Xu J., *Nat. Prod. Rep.*, 2019, **36**, 263

[2] Gentili P., Nardi M., Antignano I., Cambise P., D'Abramo M., D'Acunzo F., Pinna A., Ussia E.. *Chem. Eur. J.* 2018, **24**, 7683

[3] Di Sabato A., D'Acunzo F., Filippini D., Vetica F., Brasiello A., Corinti D., Bodo E., Michenzi C., Panzetta E., Gentili P., *J. Org. Chem.* 2022, **87**, 13803

Dissipative Dynamic Covalent Chemistry of B-N Bond

G. Sandri,[a] F. Frateloreto,[a] G. Capocasa,[a] M. de Angelis,[a] M. Valentini, S. Di Stefano,[a]

[a]*Dipartimento di Chimica, Università degli Studi di Roma "La Sapienza", 00185 Rome, Italy*

sandri.1846832@studenti.uniroma1.it

In the past decades, the field of dynamic covalent chemistry (DCC) has been largely developed and it played an important role in the design of complex molecular and supramolecular systems. The key idea in DCC systems is that the rapid equilibration of a mixture of reactants allows the coexistence of a variety of different product species, among which specific structures can be properly selected and overexpressed by the dynamic system. Quite recently, DCC has been expanded by coupling it with dissipative systems, thus paving the way for the developing of dissipative dynamic libraries (DDLs).[1]

Herein we report on a systematic investigation of the exchange reactions involving phenylboronic acid catechol ester and tertiary (aromatic) amines, that is formation/cleavage of the covalent B–N bond. Specifically, we measured, by means of 1H NMR spectroscopy, the association constants between the phenylboronic acid catechol ester and a homologous series of pyridines, also conducing experiments using two different pyridines competing for the same boronic ester, thus producing a dynamic covalent library (DCL) made of boronic ester-pyridine adducts. Finally, we combined this DCL with the dissipative cycle of tribromoacetic acid, promoting the dissipative interchange of the different pyridines driven by the decarboxylation of the activated carboxylic acid (see Figure 1).[2]

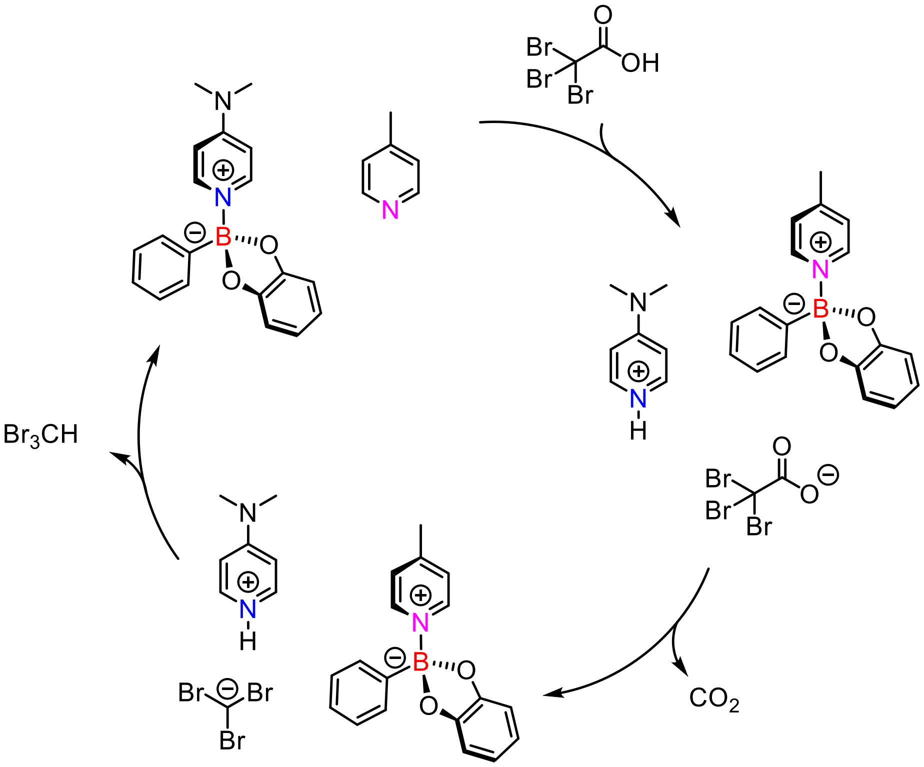


Figure 1. Dissipative exchange between 4-dimethylaminopyridine and 4-methylpyridine driven by the decarboxylation of the tribromoacetic acid.

[1] D. Del Giudice, E. Spatola, M. Valentini, G. Ercolani, S. Di Stefano, ChemSystemsChem 2022
[2] D. Del Giudice, S. Di Stefano, Acc. Chem. Res., 2023, 56, 889–899

Theme B - Biomaterials

Crosslinked PVA/HA Nanofibers Fabricated via Electrospinning for Potential Advanced Wound Management

Gianluca Ciarleglio[1*], Nicholas Capuccilli[1], Elisa Toto[2], Susanna Laurenzi[2], M. Gabriella Santonicola[1]

[1]*Department of Chemical Engineering Materials Environment, Sapienza University of Rome, Via Del Castro Laurenziano 7, 00161, Rome, Italy*
[2]*Department of Astronautical Electrical and Energy Engineering, Sapienza University of Rome, Via Salaria 851-881, 00138, Rome, Italy*

**gianluca.ciarleglio@uniroma1.it*

Electrospun polymeric nanofiber dressings represent an innovative approach to wound care due to their high surface area and three-dimensional structure, which mimics the natural extracellular matrix (ECM). In this study, we investigate the fabrication of bioactive nanofiber (NF) dressings based on polyvinyl alcohol (PVA) and hyaluronic acid (HA) using the electrospinning technique to improve wound healing. However, the high solubility of nanofibers (NFs) in aqueous environments limits their biological applications. To overcome this limitation, we propose a chemical crosslinking approach to stabilize PVA/HA nanofibers. We use thermal treatment at 150 °C and citric acid (CA) as a bio-based crosslinking agent without using organic solvents. The crosslinking process involves solid-state esterification, in which CA reacts with PVA and HA hydroxyl groups to form ester bonds.
Electrospinning parameters were optimized to obtain fibers with a diameter of 130 – 200 nm, without the use of organic solvents. The chemical structure of the nanofibers is investigated by FTIR spectroscopy, while their thermal behavior is evaluated by differential scanning calorimetry (DSC). The swelling kinetics and degradation of the nanofibers are analyzed in physiological solutions with different pH values. The results demonstrate the stabilizing effect of chemical crosslinking of PVA/HA/CA nanofibers by citric acid. These findings suggest that PVA/HA/CA could be used as promising and multifunctional wound dressings.

Acknowledgements:

This work was financially supported by Sapienza University of Rome grant n. AR1231888C51E137.

Multicompartmental Janus Liposomes (MJL) as components of an innovative material for implant devices: how to convert bacteria-associated biofilm into a resource

Mariangela Clemente [1*] , Davide Lanera [2] , Aurora Patrizi [1] , Diego Cotella [3] , Lia Rimondini [3] , Ilenia Viola [4] , Giovanna Mancini [5] , Francesca Ceccacci [1] , Cecilia Bombelli [1]

[1]CNR-ISB- Secondary office of Rome, Reaction Mechanisms c/o Chemistry Department, Sapienza University, 00185, Rome, Italy
[2] Chemistry Department, Sapienza University, 00185, Rome, Italy
[3] Department of Health Sciences and Center for Translational Research on Autoimmune and Allergic Diseases (CAAD), Università del Piemonte Orientale, 28100, Novara, Italy
[4]CNR-NANOTEC, c/o Physics Department, Sapienza University, 00185, Rome, Italy
[5]CNR-ISB, Rome 1 Research Area, 00015, Montelibretti (RM), Italy

**mariangela.clemente@cnr.it*

The advent of biomedical devices in surgery was certainly a revolutionary event that had a positive impact on the quality of life and life expectancy of the Western population. However, implant-associated infections are the flip side of the coin. The composition and characteristics of the implant surface promote colonization and biofilm formation by pathogens that take advantage of the tissue response to the presence of a foreign body at the surgical site. Current solutions to avoid fatal events are implant removal and replacement surgeries, or long-term systemic antibiotic therapies [1].

The driving idea behind our research work is to convert the threat posed by biofilm into a resource, by transforming bacteria present in the oral cavity or around percutaneous devices into a bio-factory for the production of therapeutic proteins, thereby promoting osteogenesis and tissue regeneration. This will be achieved by transfecting the bacteria with appropriate genetic sequences. To this end, innovative gene-loaded bio-hydrogels will be used: genetic sequences [3] encoding for the production of specific proteins will be complexed into lipoplexes and loaded into Janus (*i.e.* two-faced) liposomes [2] capable of adhering to both the hydrogel and the biofilm (to transfect bacteria by internal lipoplex). These innovative gene-loaded bio-hydrogels can be used as a coating for implants or as injectable material formulations for infection sites.

Acknowledgements: This research was supported by HORIZON-EIC-2022-PATHFINDEROPEN-01 through the project "Bioaction" PROT.N. 101098972.

We thank INsociety for the valuable contribution in producing the graphics.

References

[1] Azad, M. A. et al. *Clinical Microbiology Reviews,* 2024, e00104-23.
[2] Liu, Z. et al. *Soft Matter*, 2020, **16**, 2177-2184.
[3] Perri, V. et al. *PLoS One,* 2017, **12**, e0175784; Bombelli, C. et al. *Current medicinal chemistry,* 2009, **16**, 171-183.

Sodium alginate eco-sustainable carriers in precision agriculture

Marialourdes Di Maio[1,2*], Noemi Gallucci[1,2], Luigi Paduano[1,2], Irene Russo Krauss[1,2],
Gerardino D'Errico[1,2]

[1]*University of Naples Federico II, Department of Chemical Sciences, Italy,*
[2] *CSGI (Consorzio per lo Sviluppo dei Sistemi a Grande Interfase), Italy*

**marial.dimaio@studenti.unina.it*

Precision agriculture is a farming system based on the application of innovative technologies to effectively manage spatial and temporal variabilities related to the agricultural production [1]. The main goal of precision agriculture is to improve crop performance and environmental sustainability by reducing the amount of products (fertilizers, pesticides, biostimulants) used in the fields [2]. In this sense, a valid alternative to typical plant protection products are slow and controlled release products [3], based on the presence of carriers. In recent times, the interest in biocompatible and biodegradable carrier has grown, such as polysaccharides. A good example is sodium alginate, which forms versatile hydrogels through electrostatic interaction with Ca2+ ions.

In this perspective, we have designed and prepared carriers with different sizes: a macro-gel in the form of millimeter beads and a micro-gel in the form of a particle dispersion. Both carriers have been dimensionally characterized by optical microscopy, in the case of beads, and Dynamic Light Scattering (DLS) and Laser Scanning Confocal Microscopy (CLSM), in the case of micro-gel, obtaining monodisperse samples with beads with diameter of 2 mm and extremely polydisperse micro-gel with particle sizes in the µm range. Moreover, the process of micro-gel formation has been explored through DLS, identifying the optimal preparation procedure. These results have been confirmed by Electron Paramagnetic Resonance (EPR) measurements which show that alginate chains maintain large degrees of rotational freedom while engaged in polymer lattice formation and that the gels are better organized and dispersed when using the optimized procedure. UV-Vis spectroscopy has been used to evaluate the ability of the gel to encapsulate and release actives. The active chosen is a fusion protein, in which a toxin produced by some species of spiders acts as an insecticide. This peptide is bound with bovine serum albumin (BSA); in this way, the toxin manages to cross the epithelium of the intestine of the insect and get to the central nervous system where it is active. Loading capacity and encapsulation efficiency have been evaluated for both macro- and micro-carriers and the results are satisfactory, showing high capacity of encapsulation. Furthermore, release tests have been carried out in different conditions, showing promising release properties.

This study highlights the versatility of alginate hydrogel as an eco-sustainable platform for carrier design. Consequently, agronomic formulations based on its exploitation for active delivery are a valid alternative to traditional plant protection products in the framework of precision agriculture.

Acknowledgements: We acknowledge financial support under the National Recovery and Resilience Plan (NRRP), Mission 4, Component 2, Investment 1.1, Call for tender No. 1409 published on 14.9.2022 by the Italian MUR, funded by the European Union – NextGenerationEU – Project Title: Structure and flow dynamics of Concentrated AMphiphilic BIOmolecules (CAmBio) – CUP E53D23015540001 – Project Number P202229ME2 - Grant Assignment Decree No. 1386 adopted on 01/09/2023 by the Italian MUR.

References

[1] V. Gawande et al., *International Journal of Plant & Soil Science*, 2023, 35, 101-112.
[2] R. Bongiovanni et al., *Precision Agriculture*, 2004, 5, 359-387.
[3] I. M. S. Souza et al., *Journal of Environmental Chemical Engineering*, 2018, 6, 4171- 4177.

Modification of Poly(vinyl alcohol) with Glicidyl Methacrylate: Characterization and Photo Polymerization of Poli(vinyl alcohol)-Methacrylate

Ozge Eslek[1*], Fabio Domenici, Gaio Paradossi

[1] *Department of Chemical Science and Technologies, University of Rome Tor Vergata,Via della Ricerca Scientifica 00133, Rome, Italy*

**ozge.eslek@uniroma2.it*

Poly (vinyl alcohol) (PVA) is a synthetic, water soluble, and generally regarded as safe and biocompatible material, approved by Food and Drug Administration (FDA). PVA based hydrogels are three-dimensional cross-linked polymeric networks, able to absorb water and due to its mechanical properties have the potential to be deployed in a wide number of applications including drug delivery, tissue engineering, monitoring systems and contact lenses [1, 2].

The objective of this study was to modify the PVA backbone with glycidyl methacrylate (GMA), aiming to a PVA backbone grafted by methacrylic sidechains (Figure 1) [3]. PVA-MA network is then obtained by the free radical photo-polymerization of the acrylic moiety.

Following the modification process, PVA-MA was characterised by proton nuclear magnetic resonance (^{1}H NMR) spectroscopy, which demonstrated the successful modification protocol. Rheology, which is an important factor in understanding the mechanical properties of the material, was investigated. Viscoelastic properties such as the storage modulus (G') and loss modulus (G") were investigated in order to assess the gel behaviour of this material. PVA-MA based hydrogels showed G'> G" for strains sweeps ranging from 0.1% to 15% it is demonstrated that PVA-MA based hydrogels have gel behaviour. In this contribution we also show that inclusion of N-isopropyl acrylamide monomer in the network brings new thermoresponsive properties to the gel.

This work shows that PVA-MA dissolved in water can be UV-curable, transparent, yields a network structure and with good potential in biomedical applications.

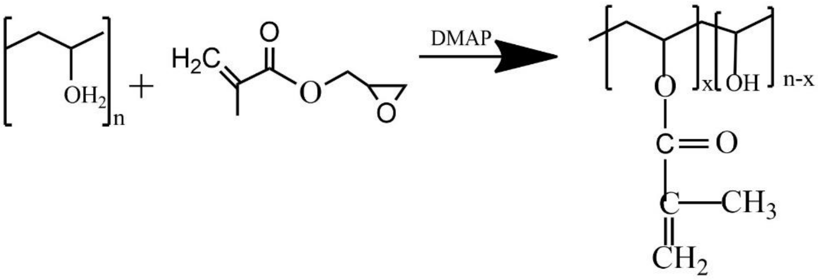


Figure 1 Synthesis of PVA-MA

References

[1] Y. Chen, J. Li, J. Lu, M. Ding, and Y. Chen, "Synthesis and properties of poly (vinyl alcohol) hydrogels with high strength and toughness," *Polymer Testing,* vol. 108, p. 107516, 2022.

[2] G. Paradossi, F. Cavalieri, E. Chiessi, C. Spagnoli, and M. K. Cowman, "Poly(vinyl alcohol) as versatile biomaterial for potential biomedical applications," *Journal of Materials Science: Materials in Medicine,* vol. 14, pp. 687-691, 2003.

[3] F. Cavalieri, F. Miano, P. D'Antona, and G. Paradossi, "Study of gelling behavior of poly(vinyl alcohol)-methacrylate for potential utilizations in tissue replacement and drug delivery," *Biomacromolecules,* vol. 5, pp. 2439-46, 2004.

BSA-nanoparticles sponges-like hydrogel as innovative biomaterial

Silvia Fanti[1*], Giuseppe Fazio[2] and Simona Fermani[2]

[1]*Department of Agricultural and Food Science (DISTAL), University of Bologna, Viale Giuseppe Fanin, 42, Bologna, Italy*
[2]*Department of Chemistry "Giacomo Ciamician", University of Bologna, Via Francesco Selmi, 2, Bologna, Italy*

**silvia.fanti5@unibo.it*

Albumin is the most abundant plasma protein in mammals, known for its versatility and easy availability as a biomaterial. It responds to changes in pH and temperature, dissolves at high concentrations, and readily gels under specific conditions. This versatility, combined with its cost-effectiveness and biocompatibility, makes albumin an attractive biomaterial for biomedical research and therapeutics[1]. Much of the albumin-based research has primarily focused on the use of albumin as a drug carrier or in nanoparticle form to improve drug pharmacokinetics and delivery to target sites[2]. In comparison, the study of albumin-based hydrogels is a relatively small but growing area of research, that has gained increasing interest in recent years.

In this context, our objective was to synthesize a new type of hydrogel formed by albumin nanoparticles using a simple and non-toxic approach, with the aim of studying its properties and characteristics.

For this purpose, bovine serum albumin nanoparticles (BSA-NPs) have been synthesized with a desolvation method and then, using a protein unfolding-chemical coupling (PNC) strategy[3], with a high excess of EDC, we developed a brand new hydrogel sponge-like biomaterial (Figure 1). This material is biodegradable, exhibits excellent swelling capabilities in water, and is synthesized in a completely non-toxic manner. Different initial concentrations of BSA-NPs and EDC were tested to investigate their influence on pore size and degradability over time. The material's ability to act as a heterogeneous nucleation agent for macromolecule crystallization was also studied, yielding promising preliminary results. Additionally, future work could easily functionalize BSA with fluorophores such as FITC or form complexes with gold (Au), endowing the resulting BSA-NPs sponge with distinctive properties.

Figure 15. A) BSA-NPs sponge-like hydrogel, B) SEM image of a BSA-NPs sponge-like hydrogel freeze-dried.

References

[1] Ong J., Zhao B., Justin AW., Markaki AE. *Biotechnology and Bioengineering*. 2019;116:3457–3468.
[2] Karami E., Behdani M., Kazemi-Lomedasht F., *Journal of Drug Delivery Science and Technology,* Volume 55, 2020, 101471, ISSN 1773-2247.
[3] Tang Z., He H., Zhu L.; Liu Z., Yang J., Quin G., Wu J., Tang Y., Zhang D., Chen Q., Zheng J., *Advanced science*, 2022, 9, 2102557.

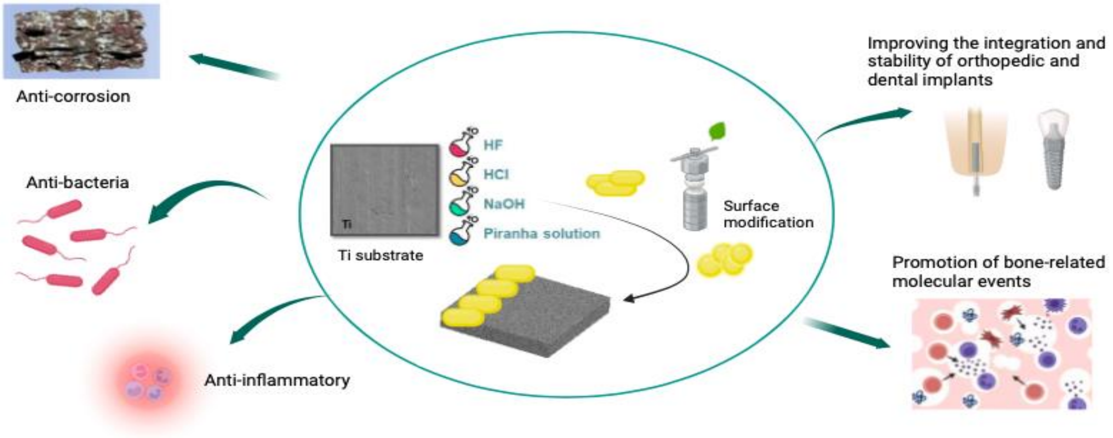
Ceria coating on nanostructured titanium surfaces enhance antibacterial and anti-infiammatory capabilities

Chiara Frezza[1], Monica Orsini[1], Susanna Romano[1], Benedetta Malvagna[1], Giovanni Sotgiu[1], Serena De Santis[1]

[1]*Department of Industrial, Electronic and Mechanical Engineering, Roma Tre University, Via Vito Volterra 62, 00146 Rome, Italy.*

Chiara.frezza@uniroma3.it

Despite the many advantages offered by titanium and its alloys as biomaterials for hard tissue replacement, poor osseointegration of the implants, bacteria adhesion, and excessive inflammatory response are some challenges that still need to be addressed. Nanoscale modifications and the activation of surfaces with multifunctional materials such as cerium oxide (ceria) can promote cell adhesion and the formation of a solid interface between bone and implant, while imparting antibacterial activity and improving corrosion resistance [1,2]. In the present work ceria nanoparticles (CeO_2NPs) with a rodlike morphology are synthesized by a green hydrothermal method. Active coating on titanium surfaces subjected to different etching treatments are realized exploiting a simple layer-by-layer drop casting technique. Surface composition, electrochemical response in simulated inflammatory conditions, and in vitro ability to induce hydroxyapatite (HA) precipitation are evaluated as a function of surface morphology an NPs distribution.



References

[1] Serena De Santis, Romualdo Varricchio, Anita Ceccucci, Giovanni Sotgiu, Alessandra Di Masi, Gabriele Magna, Simona Sennato, and Monica Orsini. *Cerium Coatings on Pristine and Nanostructured Ti and Ti6Al4V Surfaces: Bioactivity, Resistance in Simulated Inflammatory Conditions, and Antibacterial Performance.* ACS Biomaterials Science & Engineering **2023** 9 (6), 3262-3272, doi:10.1021/acsbiomaterials.2c01461

[2] De Santis S, Sotgiu G, Porcelli F, Marsotto M, Iucci G, Orsini M. *A Simple Cerium Coating Strategy for Titanium Oxide Nano-tubes*' Bioactivity Enhancement. Nanomaterials (Basel). 2021 Feb 10;11(2):445. doi: 10.3390/nano11020445.

Development of ELISA assays based on advanced materials in lab-on-chip platforms for the detection of oncologic protein biomarkers.

Hilal Nasir*, Filippo Causa, Edmondo Battista

Clinical and Translational oncology SSM, University of Naples Federico II, Italy
Interdepartmental Center for Research on Biomaterials (CRIB)

Hilalnasirgeneticist@gmail.com

The potential of microgels and miniaturized devices in targeted cancer therapies and diagnostic procedures is investigated in this work, with an emphasis on immunoglobulin identification—specifically, IgG identification. It emphasizes how cutting-edge fibre optic integration with small Lab-on-a-Chip (LoC) systems has revolutionized and accelerated scientific and medical diagnostics. This integration, which reduces sample sizes, expedites analysis, and enhances precision, is essential for developments in point-of-care testing, personalized healthcare, and environmental analysis. The study emphasizes the potential of microgels as adaptable drug delivery and biomarker identification vehicles in cancer therapy. Their surface chemistry and adjustable size improve the efficacy and specificity of treatment. The study shows enhanced targeting of cancer cells through conjugation of microgels with antibodies, improving treatment efficacy and safety. This strategy also uses ELISA techniques to identify biomarkers, with a focus on biomarkers such as CA 125 and CEA, to enable early and highly sensitive cancer detection. The study also explores the area of liquid biopsy techniques that are improved by these cutting-edge technologies. This method represents a major advancement in IgG detection, which is essential for the diagnosis and monitoring of numerous diseases. It does this by utilizing the inherent benefits of microfluidics and sophisticated materials. It provides biomolecular recognition that is quicker, more accurate, and less expensive than conventional IgG detection techniques. In the experimental part, microgels were conjugated onto surfaces for a new ELISA application. The concentration of the microgels in the feeding solution was adjusted to manipulate the microgel density. This study highlights the potential for numerous point-of-care applications and marks a significant advancement in medical diagnostics. It also highlights the potential benefits of utilizing multiplex assay techniques in the future.

Keywords: Microgels, Targeted Cancer Therapies, IgG Detection, Lab-on-a-Chip (LoC) Systems, Point-of-Care Testing, Biomarker Identification, ELISA Techniques, Cancer Detection, Liquid Biopsy.

Development of Chitosan Nanoparticles for the delivery of antimicrobial peptides (AMPs)

Aurora Patrizi[1*], Davide Lanera[2*], Mattia Stefano[2*], Federica Toma[2], Antonia Volpe[2], Fabiana Pandolfi[2], Beatrice Simonis[1], Stefano Borocci[1,4], Simona Sennato[5], Fernando Porcelli[4], Francesco Buonocore[4],Maura di Vito[3], Marco Mazzonna[7], Maurizio Sanguinetti[3,6], Francesca Bugli[3,6], Cecilia Bombelli[1], Francesca Ceccacci[1]

[1]CNR-Institute for Biological Systems (ISB), Secondary Office of Rome-Reaction Mechanisms c/o, Department of Chemistry, Sapienza University of Rome, 00185, Italy
[2]Sapienza, University of Rome, Rome, 00185, Italy
[3]Dpt di Scienze Biotecnologiche di Base, Cliniche Intensivologiche e Perioperatorie, UCSC, Rome, 00168, Italy
[4]Dpt for Innovation in Biological, Agrofood and Forest Systems, University of Tuscia, Viterbo, 01100, Italy
[5]CNR-Institute for Complex Systems (ISC) sede Sapienza, c/o Department of Physics, Sapienza, University of Rome, 00185, Italy
[6]Dpt di Scienze di Laboratorio e Infettivologiche, Fondazione Policlinico Universitario A, Gemelli IRCCS, Rome, 00168, Italy
[7]CNR-Institute for Biological Systems (ISB), Area della Ricerca di Roma 1, Via Salaria Km 29,300, 00015 Monterotondo, Italy

**aurora.patrizi@isb.cnr.it; lanera.1921318@studenti.uniroma1.it; stefano.1894126@studenti.uniroma1.it*

To combat multidrug resistance, particularly to antibiotics, systems are being developed to deliver natural and synthetic antimicrobial peptides (AMPs). Natural AMPs are extracted from several Antarctic fish species and have activity against ESKAPE bacteria (*E. faecium, S. aureus, K. pneumoniae, A. baumannii, P. aeruginosa, and Enterobacter sp.*) [1].

Encapsulation of AMPs in nanoparticle systems has many advantages: it preserves AMPs from degradation, increases their bioavailability, reduces their toxicity, and improves their interaction with bacteria. Chitosan, a natural polysaccharide obtained by the partial deacetylation of chitin, is a very good candidate for the development of AMP nanoparticles because of its mucoadhesive and antimicrobial properties [2].

The peptides used in our work are AMPs extracted from Antarctic fishes and their mutants. Preparation of the nanoparticles was conducted by ionotropic gelation technique. An HPLC protocol was developed to evaluate the amount of encapsulated peptide.

Acknowledgements:

This work was supported by the PRIN project 2022 "Fish-inspired antimicrobial peptide delivered by specific nanosystems to fight ESKAPE bacteria: a powerful weapon against antibiotic resistance" -FIDEANT (project n. 2022FKLKSY) funded by the European Union – Next Generation EU.

References

[1] Olivieri C., Buonocore F., Picchietti S. et al. *Biochimica et Biophysica Acta (BBA) –Biomembranes,* 2015, **6**, 1285-1293.
[2] Anuja Harugade, Atul P. Sherje, Anil Pethe, *Reactive and Functional Polymers,* 2023, **191**, 105634.

Decorated nanogels as promising tools for selective drug delivery in spinal cord injury treatment

Fabio Pizzetti[1*], Filippo Rossi[1], Pietro Veglianese[2]

[1]Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Politecnico di Milano, Via Mancinelli 7, 20131 Milano, Italy
[2]Department of Neuroscience, IRCCS Istituto di Ricerche Farmacologiche "Mario Negri", Milano, Italy

**fabio.pizzetti@polimi.it*

Spinal cord injury (SCI) is an invalidating disease that involves the damage of the spinal cord or the nerves connecting the spine to the central and peripheral nervous system [1]. This pathology is characterized by the primary SCI, that is the consequence of the traumatic event, and by the subsequent inflammatory response, characterized by the activation of microglia/macrophages/astrocytes, that leads to an aggravation of the pathology and to neurodegeneration [2]. A possible therapeutic approach is represented by the possibility to modulate the inflammatory response through the release of drugs in the damaged zone selectively within different cell lines. Recent advances in polymer science and nanotechnologies showed an increased interest for the nanogels (NGs), a new class of colloidal systems that, if properly functionalized, can be used as carriers of drugs to treat SCI. Nanogels were synthesized using polyethylene glycol (PEG) and linear polyethylenimine (PEI), after having functionalized PEI with a chromophore using a "click" reaction [3, 4]. This PEI functionalization is essential for being able to constantly trace the nanogels during the biological assays. Many different coating strategies of the nanogels were analyzed: in fact, the surface functionalization is essential to tune the characteristics, and the biological behavior, of the final system. The NGs underwent characterization through dynamic light scattering analyses and drug release tests together with *in vitro* and *in vivo* biological assays. Biological tests proved that functionalized nanogels were able to be selectively internalized in mouse microglia or astrocytes depending on their surface decoration, that their degradation promoted drug release and the use of anti-inflammatory molecules as delivered drug were able to mitigate the pain state [5, 6]. *In vivo* subsequent assays on diseased mouse confirmed the result obtained *in vitro* and the potentiality of this kind of surface functionalization.

References

[1] S. Thuret, L. D. F. Moon, F. H. Gage. Therapeutic interventions after spinal cord injury. 2006, 7, 628-643.
[2] S. Papa, V. Veneruso, E. Mauri, G. Cremonesi, X. Mingaj, A: Mariani, M. De Paola, A. Rossetti, A. Sacchetti, F. Rossi, G. Forloni, P. Veglianese. *J. Control. Release*, 2021, **330**, 218-228.
[3] F. Pinelli, F. Pizzetti, A. Rossetti, Z. Posel, M. Masi, A. Sacchetti, P. Posocco, F. Rossi. *Coll. Surf. A*, 2021, **614**, 126164.
[4] F. Pinelli, M. Saadati, A. Rossetti, F. Rossi, A. Sacchetti. *Coll. Surf. A*, 2023, **658**, 130623.
[5] I. Vismara, S. Papa, Valeria Veneruso, E. Mauri, A. Mariani, M. De Paola, R. Affatato, A. Rossetti, M. Sponchioni,D. Moscatelli, A. Sacchetti, F. Rossi, G. Forloni, P. Veglianese. *ACS Nano*, 2020, **14**, 360-371.
[6] S. Papa, F. Rossi, R. Ferrari, A. Mariani, M. De Paola, I. Caron, F. Fiordaliso, C. Bisighini, E. Sammali, C. Colombo, M. Gobbi, M. Canovi, J. Lucchetti, M. Peviani, M. Morbidelli, G. Forloni, G. Perale, D. Moscatelli, P. Veglianese. *ACS Nano*. 2013, **7**, 9881-9895.

Advancements in biomass valorisation: a new method for sustainable Poly-hydroxyalkanoates (PHAs) recovery

Davide Principe[1*], Sara Alfano[1], Lionel Nguemna Tayou[1], Claudia Vona[1], Luca Di Leva[1], Marianna Villano[1], Andrea Martinelli[1]

[1]*Department of Chemistry, University of Rome La Sapienza, Rome, Italy*

* *principe.1891610@studenti.uniroma1.it*

In recent years, the problems associated with solid waste management and the dependence on petroleum-based plastics have created great interest, mainly focused on biomass valorisation to develop bio-derived and biodegradable polymers. One of the most promising class of biopolymers that can be used as a fossil plastic substitute is the polyhydroxyalkanoates family (PHAs). PHAs are polyesters that can be naturally accumulated as intracellular granules by many prokaryotic microorganisms. The stored copolymer is a biodegradable thermoplastic material suitable for several applications, including packaging and biomedical devices. PHAs granules can be recovered and purified from the surrounding biomass. All the activities focused on biomass separation and polymer recovery and purification constitute the downstream processing of PHA. It is a crucial stage and contributes to the entire PHAs production cost. In this scenario, the choice of an appropriate extraction method strongly impacts the economy of the whole process. Furthermore, the downstream process is the major factor affecting the ecological footprint of microbial polyesters. PHAs can be recovered by direct solubilization of granules or by chemical digestion of Non-Polymeric Cellular Material (NPCM). Alternatively, extraction by polymer granule solubilization involves the use of chlorinated solvents since PHAs are soluble at room temperature only in chlorinated hydrocarbon (e.g. $CHCl_3$). On the other hand, for NPCM digestion the most effective oxidant is sodium hypochlorite (NaOCl) which generates hazardous intermediates.

In this work, an alternative and safer extraction process is proposed. The illustrated method is based on the mechanical homogenization of the biomass in ethyl acetate (EtOAc), a non-toxic solvent that could be produced in a biorefinery context. The process is conducted at 70 °C to favour the swelling of PHA granules. Then, the polymer suspended in the organic phase is effectively separated from the biomass by adding a water solution of hydroxyethyl cellulose (HEC) as a thickening agent. The EtOAc PHA-rich phase is recovered, centrifuged and dried under a fume hood overnight. The effect of different HEC concentrations as well as swelling and homogenization time on PHAs recovery, purity and molecular weight are investigated. Additionally, given a cascade approach for biomass valorisation, the possibility of recovering proteins from the aqueous biomass-rich phase is under investigation.

Acknowledgements

This project has received funding from the European Union's Horizon Europe research and innovation programme under the grant agreement No. 101081776, the UK Research and Innovation (UKRI) fund under the UK government's Horizon Europe funding guarantee, the Swiss State Secretariat for Education, Research and Innovation (SERI) and from the National Key Research and Development Program of China (NKRDPC). Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of neither of the aforementioned Funding authorities. Neither the European Union, the United Kingdom, the Swiss Confederation or the People's Republic of China nor the European Commission, UKRI, SERI or NKRDPC can be held responsible for them.

Progress of liposomes loaded with Resveratrol for delivery across the blood-brain barrier

Mattia Stefano[1*], Matteo Saraceno[2], Beatrice Simonis[3], Mariangela Clemente[3], Enrica Donati[4], Marco Mazzonna[4], Domenico Vignone[5], Odalys Gonzalez Paz[5], Annalise Di Marco[5], Simona Sennato[6], Francesca Santangeli[1], Sara Marcoccia[7], Giovanna Mancini[4], Cecilia Bombelli[3], Francesca Ceccacci[3]

[1]*Chemistry Department, Sapienza University, 00185, Rome, Italy*
[2]*Biology Department, Sapienza University, 00185, Rome, Italy*
3CNR-ISB- Secondary office of Rome, Reaction Mechanisms c/o Chemistry Department, Sapienza University, 00185, Rome, Italy
4CNR-ISB, Rome 1 Resarch Area, 00015, Montelibretti (RM), Italy
5Experimental Pharmacology, IRBM SpA, via Pontina Km 30.600, 00071 Pomezia (RM), Italy
[6]*CNR-ISC- Secondary office of Rome c/o Physics Department, Sapienza University,*
[7]*Department of Physiology and Pharmacology, Sapienza University00185, Rome, Italy - IRCCS Santa Lucia Foundation, 00179, Rome Italy*

**stefano.1894126@studenti.uniroma1.it*

The development of new drugs for the central nervous system (CNS) is one of the major challenges of our time, as the effective defensive action of the blood brain barrier (BBB) is an obstacle in the treatment of CNS diseases. The most promising approach to overcome this problem are drug delivery systems, particularly liposomes.

Here we report on the preparation and characterization of liposomes functionalized with different ligands that should promote crossing of the BBB [1]. The liposome formulations used are mainly composed of a phosphocoline (DPPC or DOPC) and cholesterol in mixture with synthetic cationic gemini and/or glycosylated amphiphiles. Gemini should promote crossing of BBB *via adsorption-mediated transcytosis* whereas the glycosylated amphiphiles should in principle facilitate crossing *via GLUT1 carrier-mediated transcytosis*. Another amphiphile used to functionalized liposome formulations is Fenlip, which is characterized by the presence of a phenylalanine residue on the headgroup. The presence of phenylalanine on the surface of liposome should facilitate crossing as phenylalanine is recognized by *LAT1* transporters, which are overexpressed in the BBB. *Trans*-resveratrol (RSV) was included in the liposomes as tracer in transport assays on *in vitro* barrier model [2].

The most promising formulations loaded with RSV have been subjected to biological *in vitro* experiments on BBB models to assess the crossing ability of liposomes.

Acknowledgements: this work was supported by Ministero dell'Università e della Ricerca through the project ‘‘*CNCCS-Centre for rare, neglected and poverty related diseases*”.

References

[1] I. Posadas, S. Monteagudo, V. Ceña, *Nanomedicine*, 2016, **11**, 833-849.
[2] Simonis, B., et al. *Journal of Colloid Interface Science,* 2022, **627**, 283.

Synthesis and characterization of hyaluronic acid-based smart hydrogels

Riccardo Tassoni[1]*, Cecilia Velino[1], Lucia Ferrazzano[1], Alessandra Tolomelli[1], Walter Cabri[1], Giovanna Desando[2], Chiara Gualandi[1], Maria Letizia Focarete[1]

[1]*Department of chemistry Giacomo Ciamician, Alma Mater Studiorum – University of Bologna, Bologna, Italy*
[2] *RAMSES Laboratory, Rizzoli RIT - Research, Innovation & Technology Department, Istituto di Ricerca Codivilla Putti, IRCCS, Istituto Ortopedico Rizzoli, Via di Barbiano, 1/10, 40136 Bologna, Italy*
*riccardo.tassoni4@unibo.it

The advantage of smart hydrogels over classic hydrogels lies in their dynamic behavior based on the environment in which they are located.

The synthesis and characterisation of hyaluronic acid (HA)-based pH responsive smart hydrogels functionalized with thiol groups are here presented. HA smart hydrogels were obtained through functionalization with either lipoic acid (LA) or N-acetyl-L-cysteine (NAcCys).

The synthesis of HA functionalized with LA was conducted by activating LA with 1,1′-carbonyldiimidazole to obtain lipoyl imidazolide, which reacted with HA in formamide under basic conditions [1]. Subsequently, the intramolecular disulfide bridge present in the final product was reduced using sodium borohydride ($NaBH_4$). The successful formation of the final adduct was confirmed by H-NMR, which yielded a degree of substitution (DS) of 74%. The synthesis of HA functionalized with NAcCys was carried out following the Stenglich esterification procedure [2]. Initially, NAcCys was activated with N,N′-Dicyclohexylcarbodiimide (DCC), which reacted with HA in formamide under basic conditions [3]. The successful formation of the final adduct was confirmed by H-NMR, which yielded a degree of substitution (DS) of 72%. Various characterizations were performed on the final products, with rheological analyses being among the primary tests conducted. The purpose of these characterizations was to gain a detailed understanding of the material's behavior under stress or deformation. Moreover, the rheological analyses were conducted under different pH conditions. The goal was to provide a comprehensive understanding of the material's response to cross-linking at both neutral and alkaline pH.

Acknowledgements.

This work was supported by the Italian Ministry of Health (Grant Number: GR-2019-12370030 “A novel functionalized NUTraceuticals-laden hyaluronic hydrogel for gender-based PERsonalized treatment for osteOArthritis care: a novel proof-of-concept in viscosupplementation – NUTperOA).

References

[1] Picotti F., Fabbian M., Gianni R., Sechi A., Stucchi L., Bosco M. *Carbohydr Polym*, 2013, **93**, 273.
[2] Neises B., Steglich W. *Angewandte Chemie International Edition in English*, 1978, **17**, 522.
[3] Jin X., Asghar S., Zhang M., Chen Z., Huang L., Ping Q., Xiao Y. *Colloids Surf B Biointerfaces*, 2018, **172**, 655.

Oxidative treatment for PHA recovery from Mixed Microbial Cultures cultivated in a continuous process

Claudia Vona[1*], Luca di Leva[1], Lionel Nguemna Tayou[1], Gaia Salvatori[1], Sara Alfano[1], Andrea Martinelli[1], Marianna Villano[1]

[1] *Department of chemistry, Sapienza University of Rome, Rome, Italy*

**claudia.vona@uniroma1.it*

Polyhydroxyalkanoates (PHA) are a family of biodegradable polyesters naturally produced by microorganisms under stress conditions, typically due to unbalanced nutrient growth conditions (e.g. limiting concentration of essential nutrients like nitrogen and phosphorus). PHA production using mixed microbial cultures (MMC) is being implemented in a multi-stages process involving: i) the acidogenic fermentation of waste organic substrates to produce carboxylic acids, ii) the microbial selection of PHA-storing microorganisms from an activated sludge, iii) the PHA accumulation, and iv) the PHA recovery [1]. The last stage represents the bottleneck of the multi-stage process. Indeed, the most common PHA recovery processes, usually include solvent extraction, which often deals with high costs and environmental and safety risks due to the use of non-green solvents, such as chloroform or dichloromethane. The chemical solubilization of non PHA cell matrix (NPCM) with strong oxidant agents has lately been investigated as a more sustainable alternative for PHA recovery [2].

More specifically, in this work, chemical solubilization of NPCM using an alkaline non-toxic solution of sodium hydroxide, NaOH has been applied to a PHA-rich biomass coming from a continuous flow multi-reactors process. Different pre-treatment methods (thermal quenching at 4°C and acid quenching with sulfuric acid) and NaOH concentration (0.2 and 0.4 M during 4 hours of contact) were investigated. Also, after the treatment with NaOH, an extra-treatment with a solution of hydrogen peroxide (H_2O_2), was tested in order to increase the purity of the final extracted polymer. The thermal quenching was investigated with two different NaOH concentrations (0.2M and 0.4M) that demonstrated a polymer purity of 63% and 40% (wt/wt), respectively. The oxidative treatment with NaOH 0.2 M was then implemented with the acid pre-treatment, which resulted in a significant improvement of the polymer purity (80%, wt/wt). On the other hand, the use of H_2O_2 as an extra-step of the downstream process, did not significantly affect the polymer purity. In conclusion, the oxidative treatment with NaOH joined to the acid pretreatment represents an efficient and more sustainable alternative for PHA recovery from a continuous feeding process, although further investigations are still ongoing.

Acknowledgements: The authors want to tank AGRILOOP (2022-2026). This project was funded by European Union's HEU research and innovation programme, the UK Research and Innovation fund under the UK government's HEU funding guarantee (GA n. 101081776) and The National Key Research and Development Funds of China. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union. Neither the European Union nor the granting authority can be held responsible for them.

References

[1] Kourmentza, C., Plácido, J., Venetsaneas, N., Burniol-Figols, A., Varrone, C., Gavala, H. N., & Reis, M. A., *Recent advances and challenges towards sustainable polyhydroxyalkanoate (PHA) production*, 2017, **4**, 55.

[2] Salvatori, G., Alfano, S., Martinelli, A., Gottardo, M., Villano, M., Ferreira, B. S., ... & Lorini, L. *Chlorine-free Extractions of Mixed-Culture Polyhydroxyalkanoates Produced from Fermented Sewage Sludge at Pilot Scale*,2023, **62**, 17400

Theme C - Advances in Physical Chemistrys

CryoEM architecture of a native stretch-sensitive membrane microdomain

J. Alba[1*], J. M. Kefauver[2], M. Hakala[3], L. Zou[2], J. Espadas[3], M. G. Tettamanti[2,3], L. F. Estrozi[4], S. Vanni[1], A. Roux[3], A. Desfosses[4], R. Loewith[2]

[1]*Dept. of Biology, University of Fribourg, Fribourg, Switzerland*
[2]*Dept. of Molecular and Cellular Biology, University of Geneva, Geneva, Switzerland*
[3]*Dept of Biochemistry, University of Geneva, Geneva, Switzerland*
[4]*Institut de Biologie Structurale, Univ Grenoble Alpes, CEA, CNRS, IBS, Grenoble, France*

**josephine.alba@unifr.ch*

Biological membranes are partitioned into functional zones containing specific lipids and proteins, termed membrane microdomains. Their composition and organization remain controversial owing to a paucity of techniques that can visualize lipids in situ without disrupting their native behavior [1-2]. The yeast eisosome, a membrane compartment scaffolded by the BAR-domain proteins Pil1 and Lsp1, senses and responds to mechanical stress by flattening and releasing sequestered factors[3– 5]. Here, we isolated native eisosomes as helical filaments of Pil1/Lsp1 lattice bound to plasma membrane lipids and solved their structures by helical reconstruction. We observe remarkable organization within the lipid bilayer density from which we could assign headgroups of PI(4,5)P2 and phosphatidylserine bound to Pil1/Lsp1 and a pattern of membrane voids, signatures of sterols, beneath an amphipathic helix. We verified these assignments using in vitro reconstitutions and molecular dynamics simulations. 3D variability analysis of the native eisosomes revealed a dynamic stretching of the Pil1/Lsp1 lattice that affects functionally important lipid sequestration, supporting a mechanism in which membrane stretching liberates lipids otherwise anchored by the Pil1/Lsp1 coat. Our results provide mechanistic insight into how eisosome BAR-domain proteins create a mechanosensitive membrane microdomain and, more globally, resolve long-standing controversies about the architecture and nature of lipid microdomains [5].

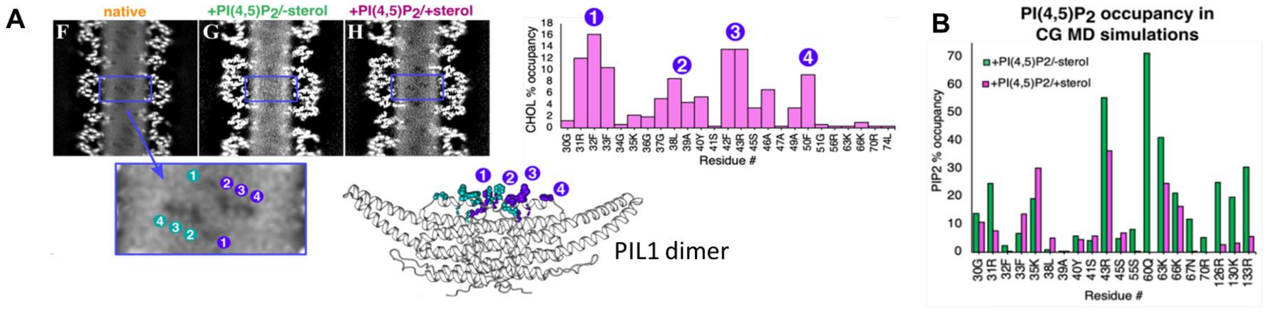


Figure1. Sterols are stabilized by the Pil1/Lsp1 amphipathic helix within the eisosome membrane microdomain. **A**. Membrane voids pattern within the cytoplasmic leaflet in native (F), "+PI(4,5)P2/-sterol" reconstituted (G), and "+PI(4,5)P2/+sterol" reconstituted eisosomes (H) **.** In the centre**,** cholesterol occupancy in +PI(4,5)P2/+sterol system in CG-MD simulations. **B.** PI(4,5)P2 occupancy.

References

[1] Levental, I., Levental, K. R. & Heberle, F. A., 2020, Trends in Cell Biology 30, 341–353
[2] Sezgin, E., Levental, I., Mayor, S. & Eggeling, C, 2017, Nat Rev Mol Cell Biol, 18, 361–374
[3] Malinsky, J., Opekarová, M. & Tanner, W., 2010, Yeast, 27, 473–478
[4] J.M. Kefauver, M. Hakala, L. Zou, J.Alba, J. Espadas, […] L.F. Estrozi, S.Vanni, A. Roux, A. Desfosses, R. Loewith, biorxiv https://doi.org/10.1101/2023.08.25.554800 **- under review on Nature**

Deep learning force fields design for solid state electrolytes

A. Azzali*[1], E. Bodo[1]

[1]*Department of chemistry, Sapienza, università di Roma, Rome*

**alessandro.azzali@uniroma1.it*

All-solid state (ASSB) batteries are one of the most promising alternatives of Li-ion liquid technology. ASSB have several advantages[1], such as greater stability, better safety, and higher energy density[2], but also an intrinsic, and still unsolved, problem caused by their solid nature, the low ion mobility. Amorphous Lithium thiophosphates, LPS (xLi_2S-$(1-x)P_2S_5$) and their oxidised form LPSO (with Li_2O and/or P_2O_5) are among the most promising[3] electrolytes. Optimizing their performances by tuning their composition in order to achieve high ion conductivities (at least 10^{-3} S/cm to be competitive with liquid electrolytes) is an extremely complicated task because we do not yet know the structure-properties relation and the optimization process require laborious trial-and-error laboratory procedures. Using molecular modelling we can help making this process much quicker. Typically, computational approaches to electrochemistry involve ab-initio molecular dynamics (AIMD) methods, that, despite their accuracy, are very slow and computationally intensive, compared to classical molecular dynamics (MD), that instead relies on parametric force fields (FF). Classical MD calculations on LPS and LPSO are, at the moment, difficult to perform because they would need the development of a suitable FF whose analytical form is complicated due to the different states of chemical coordination that Li^+ assumes in the amorphous solid. Nevertheless, it is important for the electrochemical community to have access to a quick and efficient way to model electrolytes such as LPS and LPSO.

We have used deep learning molecular dynamics[4], to generate the FF. The deep neural network[5] has been trained using accurate ab-initio data and a deep learning force field (DLFF)[7-8] has been produced. The FF has the high accuracy[6] of the ab-inito level chosen for the training set and, being parametric, a high efficiency (classical MD level). Using this DLFF we have performed fast ed accurate simulations on model systems beyond the actual limits of AIMD. This approach will be crucial to determine electrochemical properties of LPS and optimize their composition to make this technology competitive in a large-scale industry environment.

References

[1] Sun, Y.-K., ACS Energy Lett. 2020, 5, 3221–3223.
[2] Zhang, Z. et al., Energy Environ. Sci. 2018, 11, 1945–1976
[3] Grady, Z. A. et al., Front. Energy Res. 2020, 8.
[4] Unke, O. T. et al., Chem. Rev. 2021, 12, 10142–10186.
[5] Mo, Y. et al., Chem. Mater. 2012, 24, 15–17.
[6] He, X. et al., npj Comput Mater 2018, 4, 1–9.
[7] Wang, H. et al., Comp Phys. Comm. 2018, 228, 178–184.
[8] Zhang, L. et al., Phys. Rev. Lett. 2018, 120, 143001.

Operando microRaman techniques and chemometric methods for the study of lithium-sulfur batteries.

Vittorio Caprini[1*], Maria Di Pea[1], Thamara Ruellas[2], Eugenio Sandrucci[1], Arcangelo Celeste[1],
Sergio Brutti[1], Federico Marini[1]

[1]*Department of Chemistry, University La Sapienza, Rome, Italy*
[2]*Department of Chemistry, Federal University of Sao Carlos, Sao Carlos, Brazil*

caprini.1801329@studenti.uniroma1.it

Lithium-sulfur batteries (LSBs) are electrochemical devices consisting of a metallic lithium anode, a sulfur-based cathode along with a so-called "host material", a separator, and an aprotic electrolyte.
These batteries offer several advantages over lithium-ion batteries (LIB), such as higher specific capacity at both the cathode and anode. However, due to the formation of reaction intermediates (lithium polysulfides or LiPS), their commercialization is challenging as they give rise to the so-called "shuttle effect".
The aim of this work is to focus on exploring analytical methods and experimental setups to carry out reliable in situ/operando experiments on LSBs, aimed at understanding electrochemical and chemical reactions occurring during a discharge/charge cycles by using micro-Raman spectroscopy on various cell types. The goal is to identify experimental strategies to optimize the analytical method and to understand which experimental conditions allow for the acquisition of reliable and traceable measurements either form the electrochemical or the spectroscopic points of view. All datasets obtained from the operando Raman experiments have been analysed using chemometric algorithms to process the acquired information, enabling a more accurate interpretation of the results. In this study, the iterative MCR-ALS algorithm has been employed to decouple the hidden information in the Raman spectra sequence recorded during the operando test in a commercial optical electrochemical cell.

References

[1] L. Xue., Y. Li., A. Hu., M. Zhou., W. Chen., T. Lei., Y. Yan., J. Huang., C. Yang., X. Wang., Y. Hu., J. Xiong. *Small Structures*, 2022, **3**, 2100170
[2] R. Tauler., A. de Juan. *Data Handling in Science and Technology*, 2015, **29** 247-287.

Alkaline copper electrodeposition from alanine-based baths

Davide Carrea[1*], Marco Piccinni[1,2], and Diego Colombara[1,2].

[1]Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Genova, Via Dodecaneso 31, 16126 Genova Italy.
[2]Istituto Italiano di Tecnologia, Graphene Labs, via Morego 30, 16163 Genoa, Italy.

S4649175@studenti.unige.it

The deposition of copper is pivotal in industry, e.g. for the fabrication of integrated circuits and $Cu(In,Ga)Se_2$ (CIGS) photovoltaic devices [1]. The state-of-the-art processes from acidic baths display low faradaic efficiency due to hydrogen evolution, whereas alkaline baths use cyanide as a complexing agent, raising safety concerns [2]. We formulated and characterized a Cu alkaline bath for thin films electrodeposition, by exploiting alanine as complexing agent. By means of hydrodynamic kinetic studies, we gained deeper understanding of the deposition mechanism. These studies allowed us to identify diffusion coefficients and Langmuir's adsorption constants, as well as the hydrodynamic radius of the coordination compounds.

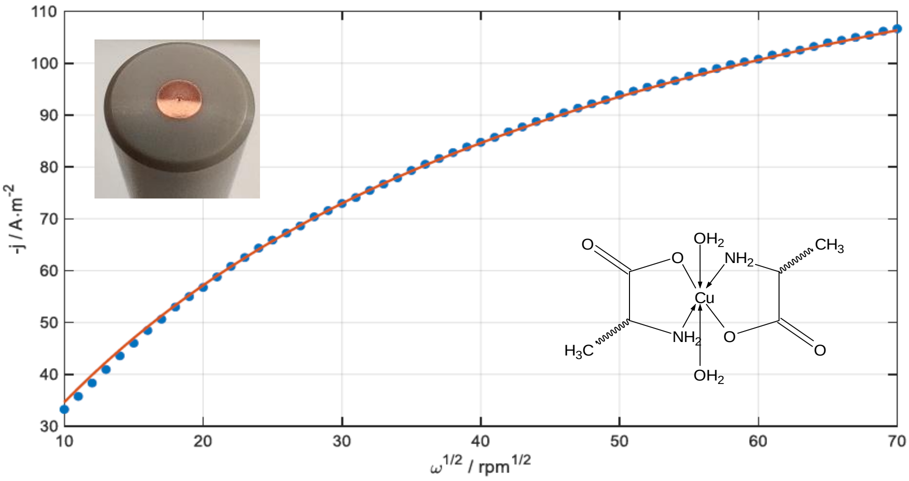


Figure 1. Levich plot of $Cu(Ala)_2$ reduction at -0.3V fitted Scharifker model [3]. Copper film (top-left), structure of the $Cu(Ala)_2$ complex (bottom-right).

Acknowledgements:
This work was supported in part by the Italian Ministry of Foreign Affairs and International Cooperation (grant No. US23GR17), and in part by the European Commission under the PathFinder Open programme (REMAP project, grant No. 101046909). Funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or European Innovation Council and SME Executive Agency (EISMEA). Neither the European Union nor the granting authority can be held responsible for them.

References

[1] Zhou J. and Li C., in *E3S Web of Conferences*, 2021, 267.
[2] Yli-Pentti A., in *Comprehensive Materials Processing*, 2014, **4**, 277–306.
[3] Vargas R., Borrás C., , Mostany J., and Scharifker B. R., *Electrochim Acta*, 2012, **80**, 326–333.

High efficiency eco-anodes obtained from an organic waste for lithium-ion batteries applications

Alessandro Cingolani[1*], Roberto Spotorno[1], Paolo Piccardo[1]

[1]*Department of Chemistry and Industrial Chemistry, University of Genoa, Genoa, Italy*

**alessandro.cingolani@edu.unige.it*

Lithium-ion batteries have an irreplaceable combination of high energy and power density, making them the best technology of choice for portable electronics, power tools, and hybrid/full electric vehicles. In particular, the research in this field in the last years, due the climate change, has shown a rapid increase to find better materials for raising the batteries' efficiency. One of the most sought-after solutions lies in using silicon as the anode because of its very high capacity, 3400 mAh/g versus 372 mAh/g for graphite [1]. The problem in using silicon as an anode lies in its instability during charge and discharge cycles due to its volumetric expansion. Lithiation of silicon leads to an increase in the volume of the anode that causes the cell rupture. Owing to the fact of increasing interest in green energy production using green materials, this work is focused on the production of an eco-graphite, obtained by the pyrolysis of Si-rich organic waste, where the Si should increase consistently the capacity of the electrode. The green chemistry behind this process is evident, since the botanic waste material is converted into a functional graphite through heat treatment. Hard carbon/graphite hybrid system with increased gravimetric capacity compared to that of commercial graphite is the final product. These materials are certified by manufacturing half cells with metallic lithium as the second electrode. Therefore the maximum gravimetric capacity for the eco-anode can be evaluated. These materials were also characterized via SEM-EDXS, XPS, XRD, and electrochemical charge and discharge tests. The electrochemical tests were performed on coin cells at a low C rate and a high C rate, to evaluate the behavior of the eco-anode both in standard testing conditions and high-stress conditions of cycling. The material produced resulted in anodes (eco-anodes) with 34% higher capacities than commercial graphite, a coulombic efficiency of 98%, and great cycling stability, thus highlighting that the developed process is highly promising for the production of eco-batteries.

References

[1] J. R. Szczech, S. Jin. *Energy & Environmental Science, Nanostructured silicon for high capacity lithium battery anodes*, 2011, **4**, 56.

Fluorescence micro-spectroscopy applied to Lithium-Oxygen Batteries

Gabriele D'Aiuto[1,*], Sergio Brutti[1], Francesco Vitucci[2]

[1] Department of Chemistry, University of Rome La Sapienza, P.le Aldo moro 5, 00136 Roma, Italy
[2] Crisel Instrument Srl, Via Mattia Battistini, 177, 00167 Roma RM
[*]*gabriele.daiuto@uniroma1.it*

Fluorescence micro-spectroscopy is an underestimated characterization technique in battery science. Here we demonstrate the capabilities of this techniques to investigate Lithium-Oxygen Batteries (LOBs) electrodes collected post mortem after cycling. The goal is to highlight the ability of this technique to disclose new experimental information, coupling morphological data with chemical discrimination.

The instrument used in this study is capable of coupling visible/fluo-microscopy with fluorescence spectroscopy on sample's micrometric portions, allowing to obtain very precise chemical-morphological maps of the sample surfaces.

Overall this technique proved itself to be complementary to the traditional microscopy ones (scanning electron miscroscopy, SEM, shite light optical microscopy, LOM) in delivering combined chemical-morphological information, and also spectroscopical promising in the selective recognition of chemical species.

To validate this technique, we used two LOBs post-mortem positive electrodes (GDL) submitted to a prolonged discharge-charge cycle, together with reference samples of five of the most probable lithium-containing species originating from the electrolyte degradation: $Li_2C_2O_4$, CF_3COOLi, CH_3COOLi, Li_2CO_3, $LiNO_3$.

All the samples showed good fluorescence micrographies (figure 1), in particular, compared to traditional imaging techniques like LOM, fluo-microscopy allows to visualize emission originating below the insulating Whatman fibers inevitably present on post mortem electrodes. Furthermore, fluorescence spectra integrated on selected spots of the surface of the electrodes, proved the precipitation of Li_2CO_3[1] at the nanoscale in line with the evidence from FTIR microscopy.

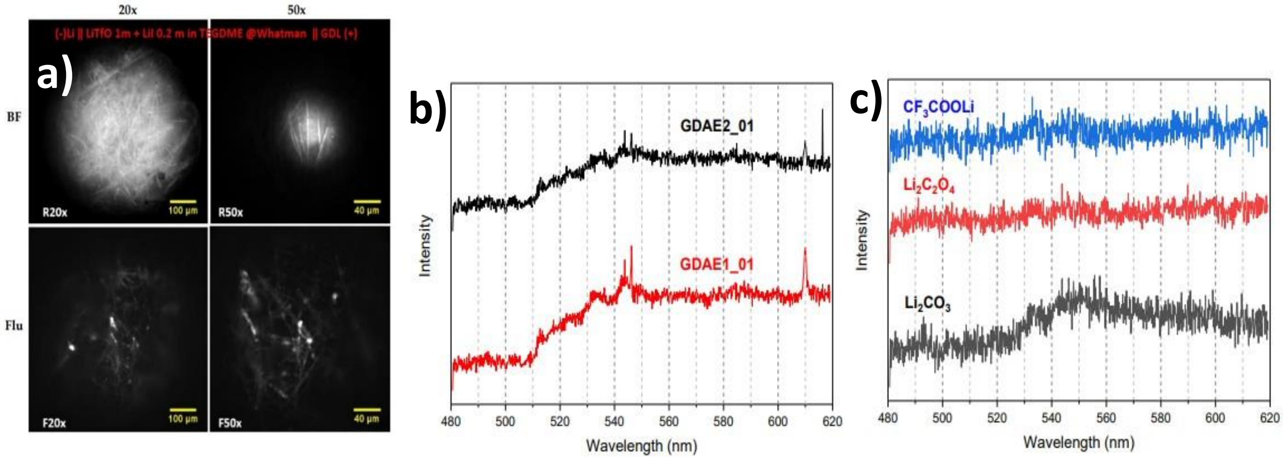


Figure 16: a) Micrography comparison between LOM (upper) and Fluorescence (lower). b) Fluorescence spectra of the two post-mortem samples and c) 3 of the 5 references.

References

[1] Jenkins, M., et al. "The Accumulation of Li2CO3 in a Li–O2 Battery with Dual Mediators." Faraday Discussions, Royal Society of Chemistry, 2023

A computational approach to the study of carbon dots for the determination of their structure and properties

Francesca D’Ambrosio, Enrico Bodo

Chemistry Department, University of Rome “La Sapienza”, Piazzale Aldo Moro 5, 00185, Rome, Italy

francesca.dambrosio@uniroma1.it

Recently, carbon dots (CDs) have emerged in the family of carbon-based nanoparticles due to their unique properties such as intense photoluminescence, low toxicity, excellent biocompatibility, and easy surface functionalization[1]. In addition, they involve simple synthetic approaches, including bottom-up and top-down methods[2], which in turn determine the surface functional groups, their size, and their photoluminescence response. For all these reasons, CDs have found applications in various fields, most notably in biological and biomedical applications[3]. To date, a detailed understanding of the atomic-level structure of these compounds and the relationship between the structure and their properties has only been partially established[4]. Therefore, it is necessary to develop an efficient computational method to fill these gaps. Preferably, this approach should maintain an explicit description of the electronic degrees of freedom in order to evaluate the optical properties from first principles and to investigate the electron density and, ultimately, the surface charge of the nanoparticle.

We present results on the application of a computational multiscale approach based on ab-initio DFT (Density Functional Theory) and semi-empirical (TB-DFT, tight binding density functional theory) methods to the class of carbon dots. The advantage lies in the reduction of time and cost of research compared to experimental methods, while considering a wide range of structures and maintaining a good level of accuracy. Our study begins with CDs with an amorphous carbogenic core, the less studied variant in literature. Several model structures based on amorphous carbon functionalized with nitrogen or oxygen atoms, with a number of atoms ranging from 20 to 200, have been studied and will be presented.

References

[1] Ozyurt D., Al Kobaisi M. *Carbon Trends*, 2023, **12**, 100276.
[2] Yao B., Huang H. *Trends in Chemistry*, 2019, **1(2)**, 235–246.
[3] Liu J., Li R. *ACS Central Science*, 2020, **6(12)**, 2179–2195.
[4] Mintz K. J., Bartoli M. *Carbon*, 2021, **173**, 433–447.

New insights into the aromatic amination mechanism: a computational approach

Matteo Daino*, Leonardo Giaccari, Francesco Amato, Andrea Giacomo Marrani, Dario Possenti, Giorgio Olivo, Alessandro Motta

Department of Chemistry, Sapienza University of Rome, Rome, Italy

**daino.1837708@studenti.uniroma1.it*

Arylamines are important and useful intermediates for several applications, such as the synthesis of organic functional materials, pharmaceuticals, or biologically active molecules. Various strategies were developed to achieve the amination under several conditions, such as cross-coupling reactions, or ferrocene-catalyzed aminium radicals reactions[1]. These several syntheses aim to achieve the most chemoselective and efficient way to obtain arylamines, avoiding methods based on the reduction of nitroarenes or transition-metal-catalyzed methods that require the pre-introduction of halogen atoms[2]. The knowledge of the mechanism involved in the aryl amination processes is fundamental to improve the performance of the reaction in terms of rate and selectivity. In this perspective, our proposal is the modeling of a prototypical aryl amination using ferrocene as the starter agent/catalyst, benzene and its derivates as substrates and $MsONH_3OTf$ as the aminating agent. We modelized this pathway using the DFT method, supported by experimental results, on various substrates and in different solvents. Optimization and frequency calculations were conducted using M06 functional and 6-311+G** basis set. The proposed mechanism sheds new light on the behavior of ferrocene (a much-debated issue in the literature[3]), whose role is the formation of $[NH_3]^{\bullet+}$. After the C-N bond-forming step, $[Ar\text{-}NH_3]^{\bullet+}$ and $MsONH_3^+$ are involved in the propagation cycle.

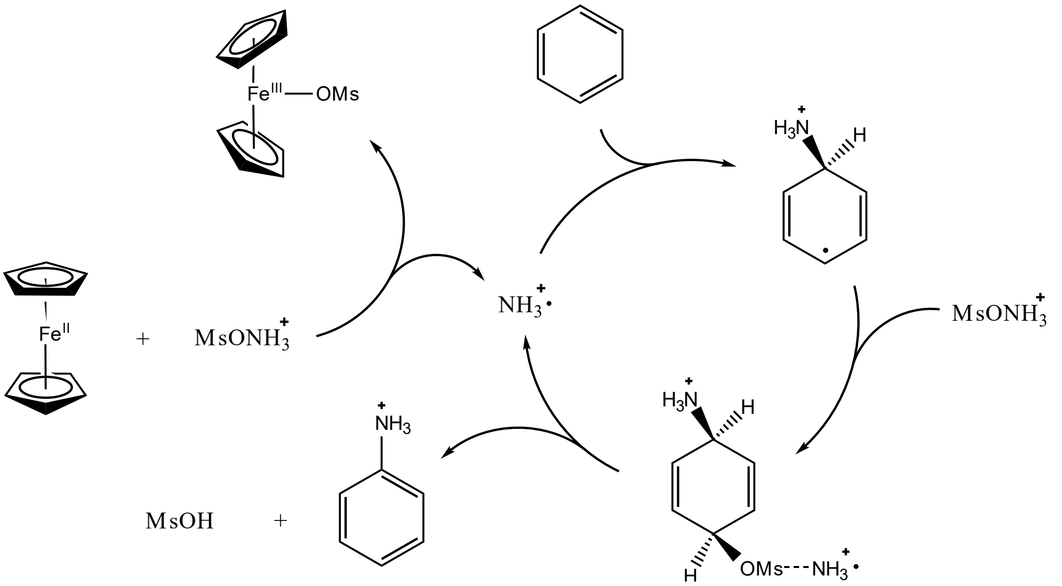


Figure 1: Schematic representation of the propagation cycle

References

[1] Legnani L., Cerai G. P., Morandi B. *ACS Catalysis,* 2016, **6**, 8162-8165.
[2] Morofuji T., Shimizu A., Yoshida J. *J. Am. Chem. Soc.*, 2013, **135**, 5000– 5003.
[3] Behnke N. E., Kwon Y. D., Davenport M. T., Ess D. H., Kürti L. *J. Org. Chem.,* 2023, **88**, 11847– 11854.

Synthesis and characterization of composite polymer electrolytes added with functionalized graphene oxide.

Irene Matteucci[1*], Nicholas Carboni[1], Maria Assunta Navarra[1]

[1]*Dipartimento di Chimica, Università di Roma "La Sapienza", Piazzale Aldo Moro 5, 00158 Rome, Italy*

matteucci.1764715@studenti.uniroma1.it

Electrochemical devices such as polymer electrolyte membrane (PEM) fuel cells (FCs) and PEM water electrolyzers (WEs) play an important role in the development of a hydrogen based economy [1]. They both use a proton-conducting solid polymer membrane as the electrolyte and the state-of-the-art outlines those based on perfluorosulfonic acid, like Nafion, as the most used. Nafion provides proton conduction thanks to the presence of terminal sulfonic acid groups ($-SO_3^-$). PEM ionic conductivity depends on the hydration level and on the amounts of acid sites. However, high material costs, chemical stability and limited ionic conductivity under low relative humidity values limits the commercialization of PEM devices on a large scale. In order to improve the hydration level and the ionic conduction of Nafion based electrolytes, in this work, the strategy of adding functionalized nanoparticles to the polymer matrix was adopted. Synthesis by modified Hummer's method [2] and functionalization of graphene oxide (GO) by Arbuzov reaction, used as an additive, was carried out. [3] Then, Composite Nafion membranes with phosphonated graphene oxide (PGO), added in different amounts (NF-PGO1%, NF-PGO 3%, NF-PGO5%), one with graphene oxide (NF-GO3%) and one without additive as benchmark (NF recast) were prepared by a solvent casting method.
The Ion Exchange Capacity (IEC) and Water Uptake (WU), fundamental parameters for the functionality of the proposed electrolytes were evaluated: the composite membranes showed WU and IEC values increasing with the amount of PGO, thanks to the presence of hydrophilic and phosphonic acid groups. To evaluate the application of the membranes in the devices of interest (PEMWEs ad PEMFCs) electrochemical characterization were conducted by performing ionic conductivity tests through the four-probe method. The measurements were carried out at increasing temperatures (T=30-50-60-80°C) and a relative humidity (RH) of 100%. The NF-PGO 3% membrane showed a higher proton conductivity compared to that of NF recast, reaching a maximum value of 0.273 S/cm at 80°C, confirming that the addition of the acidic phosphonic groups contributes to the increase in proton conductivity. However, the NF-PGO 5% membrane, despite having the highest IEC value, showed a decrease in proton conductivity: this was attributed to the formation of additive aggregates that obstructed the polymer ion channels available for proton conductivity; this was confirmed by SEM-EDX analysis. Upon the results obtained in this work, the positive effect of PGO additive for PEMs was confirmed and the optimal range, among those evaluated, was found to be around 3 wt.%.

References

[1] Y. Wang, Y. Pang, H. Xu, A. Martinez, K. S. Chen, *Energy and Environmental Science*, 2022, **15**, 2288-2328.

[2] N. Carboni, L. Mazzapioda, A. Caprì, I. Gatto, A. Carbone, V. Baglio, M. A.Navarra, *Electrochimica Acta*, 2024, **486**, 144090.

[3] B. Barik, Y.Yun, A. Kumar, H. Bae, Y. Namgung, J.Y. Park, S.J. Song, *International Journal of Hydrogen Energy*, 2023, **48**, 11029-11044.

Nanocomposite Oxides from silicon-based MAX-phases: a novel approach for Negative Electrodes in Lithium-Ion Batteries

C. Palladini[1*], N. Vallana[2], A. Gentile[3], S. Marchionna[3], R. Ruffo[2], A. G. Marrani[1]

[1]Dipartimento di Chimica, Università degli Studi di Roma "La Sapienza", Piazzale Aldo Moro 5, Roma 00185, Italy
[2]Dipartimento di Scienze dei Materiali, Università di Milano Bicocca, Via Cozzi 55, Milano 20125, Italy
[3]Ricerca sul Sistema Energetico – RSE S.p.A., Via R. Rubattino 54, Milano 20134, Italy

**palladini.1873466@studenti.uniroma1.it*

Significant progress has been made in recent years through the use of lithium-ion batteries (LIB) due to their electrochemical capacity.

As an alternative to graphite, the use of lithium alloy systems such as Li-Sn and Li-Si as negative electrodes in LIBs deserves further investigation, thanks to their high capacity. However, the practical implications of significant volume changes during cycling remain a sticking point.[1]

Volume variations are critical even when considering the adoption of corresponding conversion oxides such as SnO_2 and SiO_2.[2]

A potential solution to address the aforementioned issues and achieve a robust structure is to use solid solutions of conversion oxides with intercalation oxides such as TiO_2. Specifically, experimentation has focused on using MAX-phase systems with thermal treatment to produce nanostructured solid solutions of oxides.[3]

The work proposes, in the study of possible alternatives to graphite for negative electrodes in LIBs, to start with Si-based MAX phases, both $Ti_3Al_{1-x}Si_xC_2$ and $Ti_3Al_xSi_ySn_zC_2$ (with x+y+z=1), and then oxidize them to obtain both SiO_2 (with SnO_2) and TiO_2 embedded in the MAX-phase structure, similarly to what is reported for the corresponding Sn-based materials. These materials were investigated depending on the MAX-phase composition, the elements involved, and the thermal protocol. The physical-chemical properties of the obtained oxides were analyzed from a morphological (SEM), structural (XRD) and chemical composition (XPS) point of view. Finally, their electrochemical performances were evaluated as possible new negative electrodes for LIBs, achieving encouraging perspectives in this field.

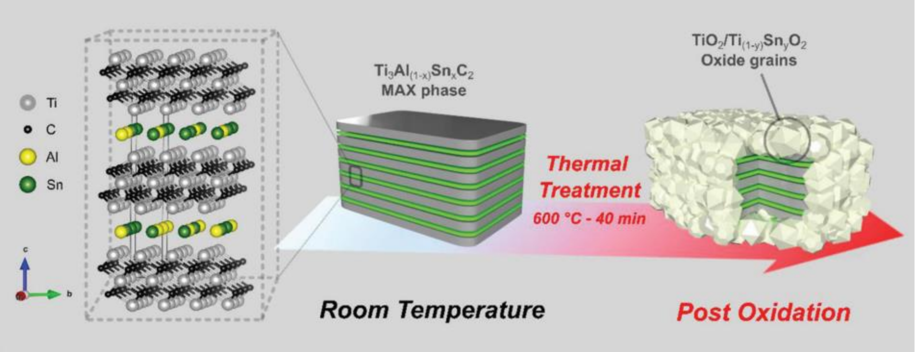


Figure 1. MAX phase crystal structure and scheme of the materials before and after the thermal treatment.[3]

References

[1] M. Peng, K. Shin, L. Jiang, Y. Jin, K. Zeng, X. Zhou, Y. Tang, Angewandte Chemie International Edition 2022, 61 (33), e202206770.

[2] T. Autthawong, C. Yodbunork, N. Ratsameetammajak, O. Namsar, Y. Chimupala, T. Sarakonsri, ACS Applied Energy Materials 2022, 5 (11), 13829-13842.

[3] I. Ostroman, C. Ferrara, S. Marchionna, A. Gentile, N. Vallana, D. Sheptyakov, R. Lorenzi, R. Ruffo, Small Methods 2023, 2300503

A computational study of N-methylacetamide amidic bond breaking in neutral and alkaline medium

Edoardo Panzetta[1*], Maria Laura De Sciscio[2], Marco D’Abramo[2]

[1]*Institute of Molecular Biology and Pathology, CNR c/o Dep. Chemistry, Sapienza University of Rome, Rome, Italy*
[2]*Department of Chemistry, Sapienza University of Rome, Rome, Italy*

**panzetta.1757273@studenti.uniroma1.it*

Peptide bond is at the base of the protein chemistry, it is not surprising that its nature regulates different biochemical processes. Although they are very stable in usual conditions, with a lifetime of year or month depending on the specific bond, its cleavage can be accelerated by orders of magnitude acting on temperature and pH. To date, no clear mechanism for the peptide bond cleavage reaction has been reported in the literature, either in neutral or alkaline media, and whether any type of intermediate is involved[1]. As the effect of time cannot be reproduced in laboratory experiments, we apply here a computational approach able to reconstruct the free energy profile of the peptide bond cleavage and the associated kinetic constants in solutions. We start by studying the mechanism in neutral and alkaline mediums and its effect on the kinetics of this reaction through a computational approach.: That is, we apply the Perturbed Matrix Method, a theoretical-computational approach that considers a system divided into two parts: the quantum center (QC) in which are described the atoms involved in the reaction treated with quantum mechanics calculations and the environment, treated with classical Molecular Dynamics simulations which furnish the perturbation acting on the QC. This study starts with a small model system with an amide bond, N-methylacetamide (NMA), thus neglecting the effect of lateral chains of amino acids and conformational effects present in proteins. We model the entire water-mediated mechanism and by means of PMM, we estimate the reaction kinetics at 300 K, through Eyring equation. Our results, (k_1=3.6×10^{-12} and k_2=1.6×10^{-9} and the corresponding half-life at 363 K is 113 days;) are within the statistical error in reasonable agreement with data reported in the literature[2]. The next steps will be studying a larger system like di- or tripeptide with different compositions to understand the role of flanking peptides as well as of the side chains on the kinetics of this reaction.

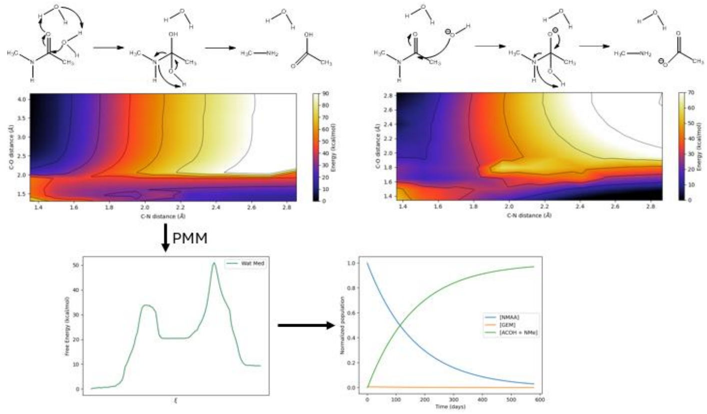


Figure 1. General scheme of this computational study.

References

[1] Pan B., Ricci M.S., Trout B.L. *J. Phys. Chem. B*, 2011, **115**, 5958-5970.
[2] Sun Y., Frenkel-Pinter M., Liotta C.L., Grover M.A. *Phys. Chem. Chem. Phys.*, 2020, **22**, 107-113.

Thermodynamic study of $BaZrS_3$ and its binary precursors BaS and ZrS_2

Riccardo Testa[*], Lorenza Romagnoli, Alessandro Latini, Andrea Ciccioli

Department of Chemistry, Sapienza University of Rome, Rome, Italy

* *testa.1788226@studenti.uniroma1.it*

Recently, chalcogenide perovskites such as $BaZrS_3$ have emerged as a possible alternative to the more studied lead halide perovskites for photovoltaic applications[1]. The reasons are multiple: *in primis*, they present a much higher tolerance to physical and chemical agents and a much lower toxicity. Unfortunately, there is a severe lack of experimental studies regarding the physical and chemical properties of these materials, due in part to the very harsh conditions required for their synthesis, that often requires temperatures up to 1100 °C and dangerous reagents such as H_2S or CS_2 requiring special equipment to be handled. Our first aim being to fill this gap, a milder synthesis process has been recently developed by our team[2], thus allowing us to study the decomposition behaviour at high temperatures of these compounds more easily. The purpose of this work is to determine the thermodynamic properties and decomposition behaviour of the perovskite and its two binary precursor BaS and ZrS_2 by a multitechnique approach.

By means of Knudsen effusion mass spectrometry experiments we were able to study the sublimation/decomposition processes in a wide range of temperatures, up to 1700 °C, by determining the partial pressure at equilibrium of the released species. BaS was found to sublimate congruently, giving BaS(g) as the most abundant gas species and the dimer Ba_2S_2, the latter about two order of magnitude less abundant. ZrS_2 decomposes by releasing $S_2(g)$ and, to a much lesser extent, S(g), forming the Zr-richer solid phase Zr_3S_4, whose thermodynamic properties were determined from the equilibrium $ZrS_2(s) \rightleftharpoons Zr_3S_4(s) + S_2(g)$. Finally, in the vapor phase produced by the $BaZrS_3$ perovskite, the Ba_2S_2 and BaS molecules have been detected in the gas phase, besides S, S_2. The following gaseous equilibria were thus analysed:

$BaS(g) \rightleftharpoons Ba(g) + S(g)$
$BaS(g) + S(g) \rightleftharpoons S_2(g) + Ba(g)$
$Ba_2S_2(g) \rightleftharpoons 2\ BaS(g)$

and subjected to thermodynamic analysis with the assistance of coupled cluster *ab initio* calculations to determine the dissociation energies of BaS(g) and $Ba_2S_2(g)$.

References

[1] Sopiha K.V., Comparotto C., Márquez J.A., Scragg J.J.S. *Adv. Optical Mater.,* 2021, 2101704.
[2] Romagnoli L., Ciccioli A., Dale P.J., Yetkin H.A., Panetta R. *J. Am. Ceram., Soc.* 2024, **107**, 698–703.

Thermodynamic properties of urea/choline chloride deep eutectic solvent by Knudsen effusion mass spectrometry measurements

F. I. Travaglini, L. Romagnoli, M. Busato, G. Mannucci, P. D'Angelo, A. Ciccioli

Department of Chemistry, Sapienza University of Rome, Piazzale Aldo Moro 5, 00185 Rome, Italy

travaglini.1746634@studenti.uniroma1.it

Deep eutectic solvents (DES) have been among the most important chemical systems studied in recent years due to their ease of synthesis and a variety of potential applications. Many DESs exhibit favorable distinctive properties such as low toxicity, affordability of precursors, low volatility, and good thermal stability. DES find applications in numerous fields, including energy storage, catalysis and separation processes, making them very interesting subjects for research in both organic and inorganic chemistry.

The 2:1 urea/choline chloride mixture (also known as reline) is one of the most studied among DES, which was demonstrated to have a very low freezing point in the earlier work of Abbott et al. [1] Since then, many DES involving choline chloride were presented in the literature. However, very few studies are available on the determination of the basic thermodynamic properties, one exception being the recent work of van den Bruinhorst et al.,[2] in which thermodynamic mixing properties of some DESs containing choline chloride and several partners (excluding urea) were measured using a combined calorimetry and molecular dynamics approach.

The measurement of vapor pressure is one of the most direct ways to determine thermodynamic properties of solutions. In this respect, only two studies conducted by thermogravimetry are reported[3,4] for reline, showing significant discrepancies. No data on this property measured by effusive methods are available. This prompted us to conduct vapor pressure measurements under thermodynamic equilibrium conditions, using Knudsen effusive mass spectrometry. In our experiments, the time-dependent mass spectrometric signal of gaseous urea, the most volatile component in the mixture, was monitored over a temperature range of 320-360 K while remaining close to the eutectic composition. The objective was to calculate the activity of urea in the mixture as a function of temperature, given by the ratio of the partial pressure of urea in reline to that of pure urea. Finally, from measuring the activity, we could to calculate thermodynamic mixing properties such as Gibbs free energy, enthalpy, and entropy.

References

[1] A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed, V. Tambyrajrajah, *Chem. Commun.* 2003, 70-71.

[2] van den Bruinhorst, C. Corsini, G. Depraetère, N. Cam, A. A.H. Padua and M. Costa Gomes, *Faraday Discuss.*, 2024, accepted manuscript.

[3] K. Shahbaz, F. S. Mjalli, G. Vakili-Nezhaad, I. M. AlNashef, A. Asadov, M. M. Farid, *J. Mol. Liq.* 2016, 222, 61-66.

[4] S. Ravula, N. E. Larm, M. A. Mottaleb, M. P. Heitz, G. A. Baker, *ChemEngineering* 2019, 3, 42.

Theme D - Advances in Analytical Chemistry

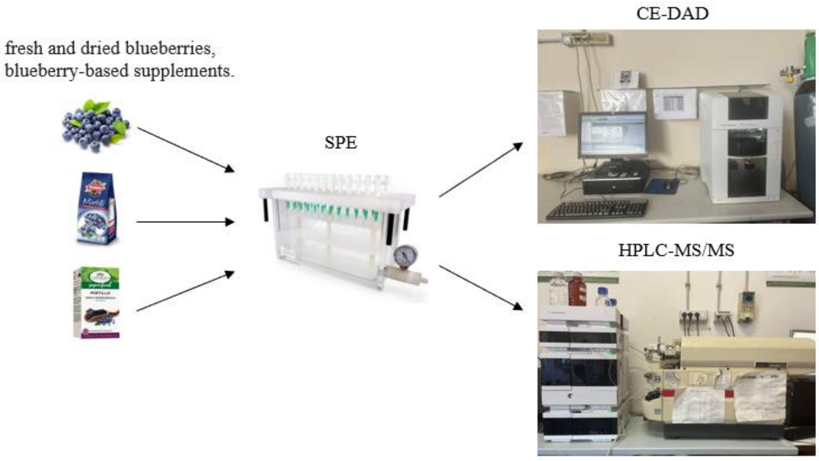
Characterization and quantification of flavonoids in functional products based on blueberries

Sara Astolfi[1*], Maria Presutti[1], Andrea Fricano[1]

[1]*Department of Chemistry, Sapienza University of Rome, Piazzale Aldo Moro, 5, 00185 Rome, Italy*

**astolfi.1892843@studenti.uniroma1.it*

Flavonoids, compounds belonging to the class of phytochemicals, are secondary plant metabolites. They are biologically and pharmacologically active molecules, showing beneficial effects on human health, such as antioxidant, anti-inflammatory, antimutagenic, anticarcinogenic, antithrombotic and antimicrobial properties. The aim of this study, in line with the growing interest of the scientific community, is the optimization of an analytical method for the qualitative and quantitative characterization of the profile and content of flavonoids in samples such as fresh and dried blueberries, blueberry-based supplements, and herbal teas (mainly based on blueberry, berries and rose hips). Before performing the instrumental analysis, preliminary tests were carried out, on the real samples, in order to evaluate the actual presence of polyphenols and flavonoids, as well as the related antioxidant activity. The *Total Phenolics Content* (TPC) and the *Total Flavonoids Content* (TFC) tests were conducted and, subsequently, two tests such as DPPH (*2,2-diphenyl-1-picrylhydrazyl*) and ABTS (*2,2′-azino-bis (3-ethylbenzothiazoline-6-sulfonic acid*)) were carried out to evaluate the antioxidant activity in these samples. The quali-quantitative analysis was carried out using Zonal Capillary Electrophoresis (CZE) with *Diode Array Detector* (DAD) as the analytical separation technique. All samples were subjected to *Solid Phase Extraction* (SPE) purification method. This procedure brought to a drastic reduction of interferences, eventually simplifying the electropherograms and making them more interpretable. CE-DAD was proved to be a suited analytical technique for the qualitative evaluation of the profile of the flavonoids of interest. Although, a correct quantitative analysis was not achieved, due to co-elution phenomena of the flavonoids with interfering species, as shown by the "Peak Purity function". These analytical limitations were overcome by using high-performance liquid chromatography coupled to triple quadrupole tandem mass spectrometry (HPLC-MS/MS), in a multiple reaction monitoring (MRM) acquisition mode quantitative analysis. The results obtained confirmed the CE qualitative analyses results, and allowed to quantitatively assess the flavonoid content in the real samples. In overall, this work showed the analytical approach proposed, to be fit for purpose. In addition, to have a more complete nutritional picture, some evaluations were made to assess the daily intake of polyphenols from fresh and dried blueberries, as well as blueberry-based supplements.



Elemental content in hemp-based herbal teas by ICP-MS

Maria Luisa Astolfi[1*], Elodie Enri[2], Viviana Chiappini[1], Roberta Giorgione[3], Anna Maria Girelli[1]

[1] Department of Chemistry, Sapienza University of Rome, Rome, Italy
[2] École nationale supérieure de chimie de Rennes (ENSCR), Rennes, France
[3] Department of Environmental Biology, Sapienza University of Rome, Rome, Italy

**marialuisa.astolfi@uniroma1.it*

Cannabis sativa L. is one of the earliest and most widely cultivated herbaceous plants. It is known for its medicinal and healing properties, thanks to cannabinoids, but it has applications in various industrial and edible hemp products. Recently, it has found widespread use as a herbal tea, especially among young people (Fig. 1). However, contaminants, including toxic or potentially toxic metals, can accumulate in the cannabis plant and are a potential source of risk for human health and for the safety of marketed food products [1,2].

This study reports an analytical method to miniaturize the sample digestion for hemp-based herbal teas by inductively coupled plasma mass spectrometry (ICP-MS) in order to achieve accurate and reproducible results with low detection limits for the analyzed elements. The best sample preparation procedure was evaluated using different reagent mixtures and four food standard reference materials (NIST1515, NIST1547, INCT-TL-1 and BCR482). The use of a 3 mL reagent mixture consisting of HNO_3 and H_2O_2, 2:1 (v/v) was found to produce satisfactory results in all cases. The optimized method was subsequently applied to real commercially available samples. The detected levels of the most toxic elements were below the prescribed limits established by the WHO. This method can be used for routine analysis and food quality control applications.

Fig. 1. Hemp-based herbal teas.

Acknowledgements: This work was funded by the project 2021 RM12117A5D872C39 (Principal Investigator M.L. Astolfi) financed by Sapienza University of Rome.

References

[1] Zafeiraki E., Kasiotis K.M., Nisianakis P., Machera K. *Frontiers in Chemistry*, 2021, **9**, 654308.
[1] Placido D.F., Lee C.C. *Plants,* 2022, **11,** 595.

An untargeted analytical workflow based on Kendrick mass defect filtering reveals dysregulations in acylcarnitines in prostate cancer tissue

Beatrice Beretta[1*], Andrea Cerrato[1], Sara Elsa Aita[1], Carmela Maria Montone[1], Enrico Taglioni[1], Anna Laura Capriotti[1]

[1]*Department of Chemistry, Sapienza University of Rome, Piazzale Aldo Moro 5, 00185, Rome, Italy*

**beretta.2077172@studenti.uniroma1.it*

Metabolomics is nowadays considered one of the most powerful analytical approaches for the discovery of metabolic dysregulations associated with the insurgence of cancer, given the reprogramming of the cell metabolism to meet the bioenergetic and biosynthetic demands of the malignant cell. Notwithstanding, several challenges still exist regarding quality control, method standardization, data processing, and compound identification. Therefore, there is a need for effective and straightforward approaches for the untargeted analysis of structurally related classes of compounds, such as acylcarnitines, that have been widely investigated in prostate cancer research for their role in energy metabolism and transport and β-oxidation of fatty acids.

Results: In the present study, an innovative analytical platform was developed for the straightforward albeit comprehensive characterization of acylcarnitines based on high-resolution mass spectrometry, Kendrick mass defect filtering, and confirmation by prediction of their retention time in reversed-phase chromatography. A customized data processing workflow was set up on Compound Discoverer software to enable the Kendrick mass defect filtering, which allowed filtering out more than 90 % of the initial features resulting from the processing of 25 tumoral and adjacent non-malignant prostate tissues collected from patients undergoing radical prostatectomy. Later, a partial least square–discriminant analysis model validated by repeated double cross-validation was built on the dataset of 74 annotated acylcarnitines, with classification rates higher than 93 % for both groups, and univariate statistical analysis helped elucidate the individual role of the annotated metabolites.

Significance: Hydroxylation of short- and medium-chain minor acylcarnitines appeared to be a significant variable in describing tissue differences, suggesting the hypothesis that the neoplastic growth is linked to oxidation phenomena on selected metabolites and reinforcing the need for effective methods for the annotation of minor metabolites.

Development of a monolithic column for the simultaneous online enrichment of glyphosate and other pesticides

Maria Carbone*, Sara Elsa Aita, Andrea Cerrato, Carmela Maria Montone, Enrico Taglioni, Anna Laura Capriotti

Department of Chemistry, Sapienza Università di Roma, Piazzale Aldo Moro 5, 00185 Rome, Italy

**carbone.1912462@studenti.uniroma1.it*

Multicomponent reactions offer efficient and environmentally friendly strategies for preparing monoliths suitable for applications in analytical chemistry. In the described study, a multicomponent reaction was utilized for the one-pot miniaturized preparation of a poly(propargyl amine) polymer inside commercial silica-lined PEEK tubing. The reaction involved only small amounts of reagents and was characterized by atom economy. The resulting monolithic column was incorporated into an autosampler system for the online extraction and cleanup of glyphosate and other pesticides from beer samples.

The sample pretreatment was minimized to only include degassing and acidification of the sample before analysis. The resulting platform incorporated LC-MS analysis in monitoring multiple reactions for the quantitative analysis of the analytes under investigation. The method was validated in unaltered beer samples, demonstrating applicability for monitoring both polar and non-polar pesticides. The recoveries were over 87%. To our knowledge, the developed platform is the only one that allows the simultaneous determination of glyphosate and its metabolites, as well as non-polar pesticides commonly present in beer samples. The environmental impact of the process was assessed as acceptable due to the miniaturization of the monolith synthesis and the automation of the extraction. This work demonstrates that multicomponent reactions are versatile, cost-effective, and potentially an eco-friendly methodology to produce reversed-phase and mixed-mode adsorbents, enabling the miniaturization of the entire analytical procedure from the preparation of extraction adsorbents to the analysis.

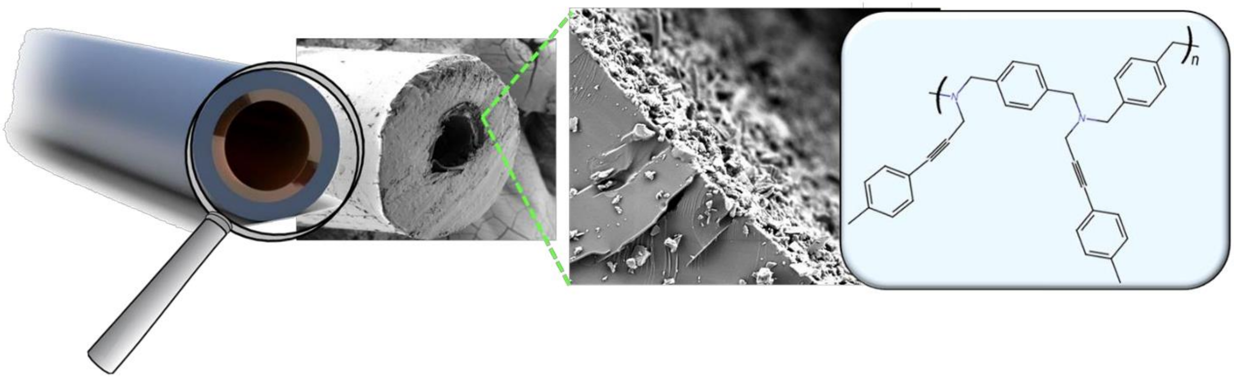


Figure. High-resolution SEM image of the inside of functionalized PEEK-sil capillary.

References

[1] Cerrato A., Aita S. E., Cavaliere C., Laganà A., Montone C. M., Piovesana S., Taglioni E., Capriotti A. L., *Analytical Chemistry,* 2024, **96**, 11, 4639–4646

Overcoming challenges in urinary metabolomic profiling by computing NMR and UHPLC-HRMS: a novel approach to detecting synthetic opioids

F. Cortese,[1*] G. Petrella,[2] G. Ciufolini,[2] C. Montesano,[3] G. Di Francesco,[3] M. Sergi,[3] M. Marti,[4] D.O. Cicero[2]

[1]Department of Electronic Engineering, University of Rome "Tor Vergata," Via del Politecnico, 00133, Rome, Italy
[2]Department of Chemical Science and Technology, University of Rome "Tor Vergata," Via della Ricerca Scientifica, 00133, Rome, Italy
[3]Department of Chemistry, University of Rome "La Sapienza," Piazzale Aldo Moro, 00185, Rome, Italy
[4]Department of Experimental and Clinical Medicine, University of Ferrara, Via Fossato di Mortara 44121, Ferrara, Italy
**cortese@ing.uniroma2.it*

Metabolomics is a rapidly expanding field that requires continuous improvement in analytical techniques to enhance our understanding of the human metabolome. However, the most used techniques in metabolomics, Nuclear Magnetic Resonance (NMR) Spectroscopy and Liquid Chromatography coupled with Mass Spectrometry (LC-MS), present some limitations [1]. LC-MS is highly sensitive and can detect thousands of compounds across a wide range of concentrations, providing detailed metabolic profiles with just a small sample. However, compound identification in MS can be complex. Additionally, some LC-MS methods may lack reproducibility in quantifying metabolites. In contrast, NMR is non-destructive and requires minimal sample preparation. It can quickly and accurately identify compounds with a single analysis but has lower sensitivity compared to MS. A possible way to overcome these limitations could be found in combining the data obtained separately with NMR and LC-MS [2]. We employed a novel approach called SYNHMET (Synergic use of NMR and HRMS for METabolomics), which follows an iterative process to increase the number of quantified metabolites and the accuracy of that quantification [3].

SYNHMET was used in the context of a novel approach for detecting New Psychoactive Substances (NPS), specifically focusing on New Synthetic Opioids (NSOs). NPS are a wide range of new drugs in the illicit market that can evade standard drug tests. They have diverse structures, change quickly in the drug scene, and have largely unknown metabolic profiles, presenting evolving challenges for detection. This approach focuses on developing an indirect screening method for NSOs, by measuring changes in endogenous urinary metabolites that occur after these substances' exposure [4].

We analyzed 63 mice urine samples using NMR and UHPLC-HRMS techniques and identified and quantified 82 metabolites using SYNHMET. The combination of these two techniques enabled us to create a more robust and complete database with fewer missing values. This matrix served as the starting point for statistical analyses aimed at identifying a common endogenous metabolic signature to the intake of both fentanyl and morphine, regardless of their chemical structure.

References

[1] Wishart D.S., Cheng L.L., Copié V. et al. Metabolites 2022, **12(8)**, 678.
[2] Bhinderwala F., Wase N., DiRusso C., Powers R., J. Proteome Res. 2018, **17**, 4017–4022.
[3] Petrella G., Montesano C., Lentini S. et al. Molecules 2021, **26(14)**, 4167.
[4] Di Francesco, G., Montesano, C., Vincenti, F. et al. Sci Rep 2024, **14**, 9432.

Oral fluid multi-drug testing through magnetic dispersive solid phase extraction and HPLC-MS/MS

Martina Croce[1,2*], Gaia Di Francesco[2], Ilenia Bracaglia[1,2], Francesco Bartolini[2], Gianmarco Pezzuti[2], Alessandro Ciccola[2], Camilla Montesano[2], Manuel Sergi[2]

[1]*Department of Public Health and Infectious Diseases, Sapienza University of Rome, Rome, Italy*
[2] *Department of Chemistry, Sapienza University of Rome, Rome, Italy*

**martina.croce@uniroma1.it*

The rapid spread of new psychoactive substances (NPS) has become a topic of interest for researchers, healthcare professionals and law enforcement. NPS are defined as new narcotic drugs that are not controlled by the United Nations Conventions on Narcotic Drugs (1961) or Psychotropic Substances (1971), but which may pose a comparable threat to public health[1]. In recent years, the interest in so-called "alternative" matrices for toxicological analysis is growing sharply. Among these, oral fluid (OF) offers a series of advantages that justify its use in different fields of application. OF is a relatively clean matrix, collection is simple, non-invasive, no special skills are required for sampling which can be supervised without violation of privacy, while reducing the possibility of specimen adulteration or substitution. The aim of the present work is to develop a new method for the determination of several substances of abuse and NPS in OF. Magnetic solid phase extraction (mSPE) was applied as a sample clean-up technique and subsequently an HPLC-MS/MS analysis was performed for the determination of the analytes of interest. In this work, C_{18}-SiO_2@Fe_3O_4 functionalized MNPs were synthesized[2]. Their dimensional distribution and functionalisation degree were subsequently verified using FT-IR, DLS and microscopic techniques. The clean-up through mSPE was performed by three subsequent steps, i.e. loading, washing and elution; in each step the magnetic adsorbent was isolated from the eluent by using an external magnetic field. The final extract was analyzed by HPLC-MS/MS in scheduled MRM by including two MRM transitions for each analyte, and one for the internal standards. The proposed procedure was then validated according to the SWGTOX international guidelines showing good results in terms of recoveries and matrix effect, proving the efficiency of the clean-up step. Low limits of quantification and identification, in the pg/mL range, were attained for almost all the analytes, thanks to the enrichment factor in pretreatment and the sensitivity of the HPLC-MS/MS analysis. In conclusion, MSPE was shown to be effective for extraction and clean-up, and at the same time less time-consuming and laborious than conventional cartridge SPE. It also had advantages of low consumption of organic solvent, ease of operation, relatively low cost, and no requirement of filtration or centrifugation.

References

[1] United Nations Office on Drugs and Crime. *World Drug Report*, 2014
[2] Yu X., Lim C.Y., Dong B., Hadinoto K. *LWT – Food Science and Technology*, 2000, 127, 109410

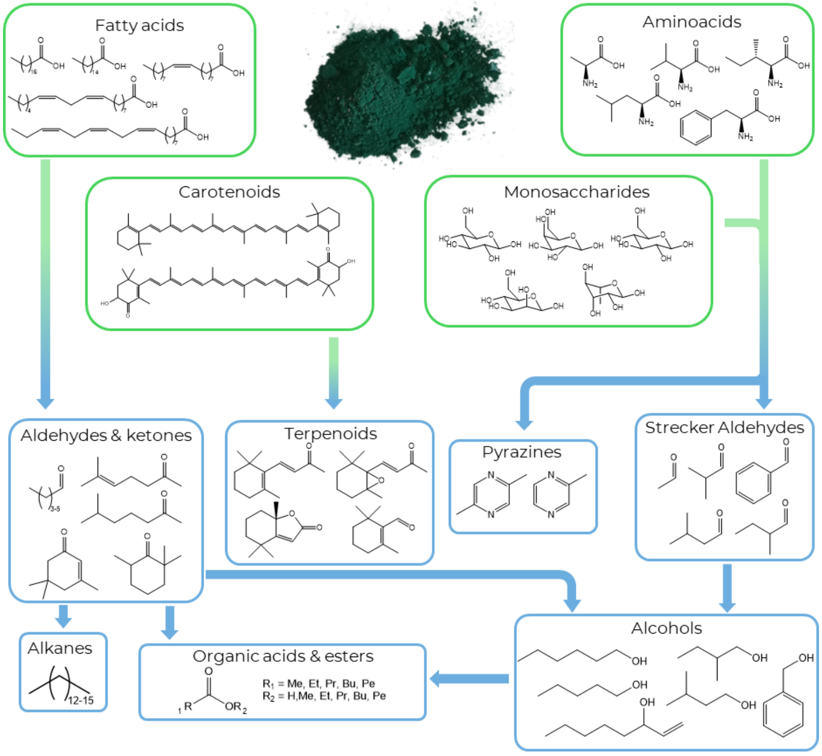
Influence of Drying and Storage Conditions on the Volatile Organic Compounds Profile of Spirulina Platensis

Veronica D’Eusanio[1*], Alberto Ughetti[1]*

[1] *Department of Chemical and Geological Sciences, University of Modena and Reggio Emilia, Via Campi 103, 41125 Modena, Italy*

**veronica.deusanio@unimore.it; alberto.ughetti@unimore.it*

Spirulina has gained a lot of popularity in the last few years due to its remarkable nutritional properties. Its applications span various industrial sectors, including pharmaceuticals, animal and/or human feed, and biofuel production, all of which continue to be subjects of rigorous investigation. Furthermore, it shows the potential as a hypothetical solution for low-space high efficiency CO2 sequestering crops. The chemical composition of Spirulina is profoundly influenced by diverse factors such as cultivation methods, harvesting techniques, and drying and storing conditions. Throughout these processes, Spirulina generates an array of volatile organic compounds (VOCs) that serve as indicative biomarkers for growth and preservation quality. In this work, we analyzed the VOCs profile of eight different Spirulina samples using HS-SPME-GC-MS. These samples were subjected to different drying and storing conditions. Specifically, the samples were dried through oven drying, air drying and spray drying techniques. Additionally, principal component analysis (PCA) was used as a multivariate technique to discern similarities and differences among the samples. The volatile profile is characterized by a variety of compounds including aldehydes, ketones, alcohols, organic acids, pyrazines, and esters. The main difference observed among the samples is that the air-dried samples showed higher quantities of organic acids after storage, indicating fermentative processes and a strong modification of the aroma profile. Moreover, some analytes are related to carotenoid degradation, such as ionones, while others are strictly related to lipid oxidation, such as hexanal or other linear aldehydes. Additionally, we detected Strecker aldehydes, which are associated with protein degradation. Our findings underscore the significant impact of drying methods and storage conditions on the volatile organic compounds profile of Spirulina.



Dried Saliva Spot and Parallel Artificial Liquid Membrane Extraction: a green combined design for microsampling and microextraction of drugs of abuse

G. Di Francesco[1*], A. Leone, M. Croce[1,2], F. Bartolini[1], I. Bracaglia[1,2], G. Pezzuti[1], C. Montesano[1], M. Sergi[1]

[1]Department of Chemistry, Sapienza University of Rome, Rome, Italy
[2] Department of Public Health and Infectious Disease, Sapienza University of Rome, Rome, Italy

**gaia.difrancesco@uniroma1.it*

Novel Psychoactive Substances (NPS) are a wide group of substances, principally of synthetic production, characterised by harmful pharmacological and toxicological properties. They can be grouped into different classes, according to their biological activities (e.g., hallucinogens, psychostimulants, sedatives, hypnotics) or to their chemical structures (e.g., cathinones, synthetic cannabinoids, synthetic stimulants, phenethylamines, and synthetic opioids). Oral fluid (OF) is a useful alternative biological matrix for forensic toxicology due to its correlation with blood concentration[1] and the advantages in terms of sample collection. The dried matrix spots (DMS) sampling approach is acknowledged as a useful collection technique, simplifying transport and storage, since a liquid matrix is dried on a filter paper. DMS typically involve blood samples, while there is a reduced number of studies which consider alternative matrices. Parallel artificial liquid membrane extraction (PALME) is a recent approach for liquid-phase microextraction based on a multiple-well filter plate that divides the acceptor and the donor solution by a hydrophobic polymeric flat and porous membrane. In this study, dried saliva spot (DSS) sampling and PALME were combined to develop a new method for multi-class illicit drug analysis in OF exploiting LC-MS/MS as detection technique. For the microsampling step a volume of 20 μL of fortified OF were deposited on a Whatman® 903 protein saver cards and let dry for ten minutes. Subsequently the spot was cut and inserted into the PALME 96-well plate for microextraction; the acceptor solution consisted of 40 μL of 0.1% formic acid while carbonate/bicarbonate buffer (pH 10,5) was used as donor solution. The addition of 0.4 g NaCl to the donor solution was useful to increase the recovery by influencing the partition of the analytes between the donor solution and the organic solvent membrane (dihexyl ether with 1% of trioctylamine). The results showed that PALME allowed to obtain a good clean-up removing the interferences of the matrix, enhancing the accuracy and the precision of the method. The method was validated according to SWGTOX guidelines by evaluating stability, precision, accuracy, recoveries, and matrix effect. This new approach could expand the possible application and combination of microsampling and microextracting strategies, promoting the transition to greener procedures, in the forensic toxicology field.

References

[1] K. F. da Cunha, K. D. Oliveira, M.A Huestis, J. L. Costa, Journal of Analytical Toxicology, 2020, Volume 44 697-707.

Cyclodextrin-based sustainable adsorbent polymers: synthesis, characterization and analytical application for solid phase extraction

Davide Filardi[1*], Nina Felli[1], Riccardo Sergi[1], Massimo Giuseppe De Cesaris[1], Luisa Maria Migneco[1], Iolanda Francolini[1], Alessandra Gentili[1]

[1] Department of Chemistry, Sapienza University of Rome, Piazzale Aldo Moro 5, 00185 Rome, Italy

**filardi.1839665@studenti.uniroma1.it*

In recent years, a particular interest has aroused towards the synthesis of green, biodegradable, biocompatible and inexpensive sorbent materials for analytical applications. Cyclodextrins are cyclic oligosaccharides well known for their capability to form inclusion complexes with molecules of appropriate shape and size. Already known in the literature for their wide use in separation science and in pharmaceutical field [1], they can also be employed as polyfunctional monomers in the synthesis of CD-NS.

In this work, the sorbent properties of different cyclodextrin-based cross-linked polymers, called cyclodextrin nanosponges (CD-NS), were investigated. Nanosponges were obtained using alpha (□-CD), beta □□-CD□□□gamma (□-CD□□and 2-hydroxypropyl-beta □□-HP-□-CD□□cyclodextrins as monomers, citric acid as cross-linking agent and sodium dihydrogen phosphate (NaH_2PO_4) as catalyst [2]. The obtained polymers were used for the dispersive solid phase extraction (d-SPE) of several xenobiotics, belonging to different families such as drugs, hormones, herbicides, and pesticides, from environmental water samples. Experiments carried out by disperding 150 mg of sorbent material in each samples, evidenced as the □-CD-based nanosponges (□-CD-NS) permitted the best recoveries. The latter nanosponge was, therefore, characterized by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) to verify the occurrence of cross-linking, and by scanning electron microscopy (SEM) to observe the morphology of the material.

The materials developed, in particular □-CD-NS, were found to be safe, easy to produce and use, and versatile in the analysis of different classes of environmental pollutants. The good recoveries obtained demonstrate that nanosponges are effective adsorbents in the field of trace analysis and are potentially promising in the field of water remediation. Other applications on different matrices, such as food or biological samples, will be investigated in the future.

References

[1] Gentili A., *Journal of Chromatography A.*, 2020, **1609**, 460654.

[2] Bednarz S., Lukasiewicz M., Mazela W., Pajda M., Kasprzyk W., *Journal of Applied Polymer Science*, 2011, **119(6)**, 3511-3520.

AF4 coupled to chemometrics for the analysis of protein fractions of milk

Nicholas Kassouf[1], Pierluigi Reschiglian[1,2], Alessandro Zappi[1], Pietro Morozzi[3], Dora Melucci[1]
Valentina Marassi[1,2]

[1] *Dipartimento di Chimica G. Ciamician, Università di Bologna, Bologna, Italy*
[2] *byFlow srl, Bologna, Italy*
[3] *COOP ITALIA Soc. Cooperativa, 40033 Casalecchio di Reno, Bologna, Italy*
nicholas.kassouf2@unibo.it

In this work, the Asymmetric Flow Field Flow Fractionation (AF4) analysis was applied to the characterization of the colloidal fraction of milk samples. By AF4, it was possible to evaluate the protein fraction of milk with the aim of discriminating samples based on the production method, geographical origin, and production manufacturer.

Forty-nine commercial milk samples were considered; thirty-seven of them were produced by the Ultra High Temperature (UHT) procedure, and twelve were not-UHT. For all of them the geographical origin and the manufacturing plant were known. The discrimination was performed using Principal Component Analysis (PCA), applied to the full fractograms. By evaluating PCA scores plot, as a first result, it was possible to discriminate UHT and not-UHT milks, as reported in Figure 1: two well-discriminated clusters are present, the red one composed of UHT samples, and the blue one, the not-UHT samples. [1]

A second PCA model was calculated for the UHT milk samples only. Such model was able to discriminate samples based on their geographical origin and producer. The geographical origin discrimination was less strong than the producer plant one, because it is known that milk can be transported also for long distances before being bottled. Therefore, the effect of the treatment to which the milk is subjected to in the production plant covers the information derived from its geographical origin. This preliminary work underlines how different production methods influence the protein content of milk, and shows that AF4 is a very suitable method for protein separation and characterization. Coupling this separative technique with chemometrics, it was possible to use the protein fingerprint of milk samples to evaluate the differences due to production method (UHT and not-UHT) and to the origin of the product.

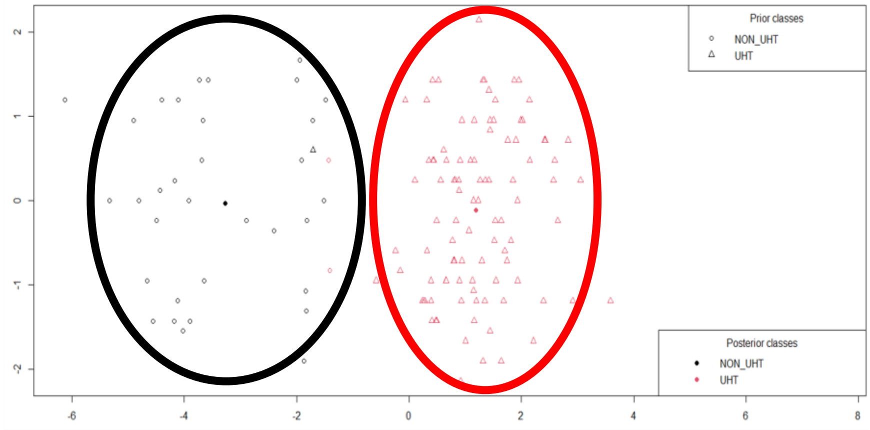


Figure: Discriminant plot between UHT and not-UHT classes

References

[1] Zappi, A., et al., *Extracting Information and Enhancing the Quality of Separation Data: A Review on Chemometrics-Assisted Analysis of Volatile, Soluble and Colloidal Samples.* Chemosensors, 2023. **11**(1).

Simultaneous Detection of Exosomal microRNAs Isolated from Cancer Cells Using Surface Acoustic Wave Sensor Array

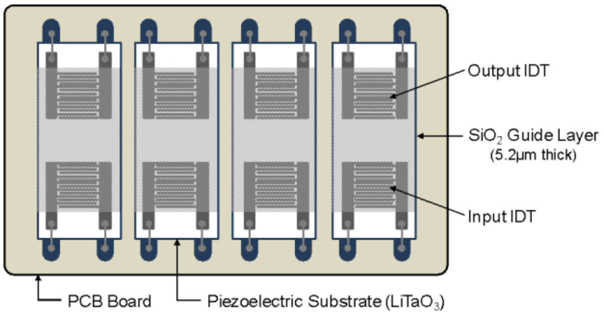
Soo Suk Lee*, Su Bin Han

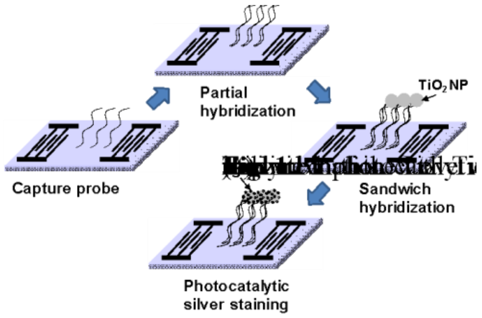
Department of pharmaceutical Engineering, Soonchunhyang University, Asan, Republic of KOREA

**sslee0810@sch.ac.kr*

We present a surface acoustic wave (SAW) sensor array for microRNA (miRNA) detection that utilizes photocatalytic silver staining on titanium dioxide (TiO_2) nanoparticles as a signal enhancement technique for high sensitivity with an internal reference sensor for high reproducibility. SAW sensors adopt the principle that when mass is loaded on the sensor surface, a change in surface acoustic velocity occurs, which can be detected as a frequency shift or phase shift of the surface acoustic wave.

A sandwich hybridization was performed on working sensors of the SAW sensor array that could simultaneously capture and detect three miRNAs (miRNA-21, miRNA-106b, and miRNA-155) known to be upregulated in cancer. MicroRNAs (miRNAs) are small (21–25 nucleotides in length) endogenous non-coding, and naturally occurring single-stranded RNA molecules. They can be used as biomarkers for early detection of cancer and various diseases. Sensor responses due to signal amplification varied depending on the concentration of synthetic miRNAs. It was confirmed that normalization (a ratio of working sensor response to reference sensor response) screened out background interferences by manipulating data and minimized non-uniformity in the photocatalytic silver staining step by suppressing disturbances to both working sensor signal and reference sensor signal. Finally, we were able to successfully detect target miRNAs in cancer cell-derived exosomal miRNAs with performance comparable to the detection of synthetic miRNAs.





Acknowledgements: This work was supported by Soonchunhyang University and the Basic Science Research Program through the National Research Foundation of Korea (NRF-2022R1F1A1067428).

References

[1] Han S.B., Kim M.J., Lee S.S. *Electroanalysis*, 2023, **35**, e202300011.
[2] Han S.B., Lee S.S. *Micromachines*, 2024, **15**, 249.

Evaluation of salt concentration on the DNA melting temperature

Marta Marchesini[1*], Maria Laura Costantino[1], Nina Bono[1], Gabriele Candiani[1]

[1]Department of Chemistry, Materials and Chemical Engineering "G. Natta", Politecnico di Milano, Via Mancinelli 7, 20131 Milan, Italy.

**marta.marchesini@polimi.it*

As the fundamental building block of life, DNA has long been the focus of close scientific investigation. One interesting aspect of DNA is the impact of salt concentration on its melting temperature (T_m), a phenomenon that holds significant implications in various fields, including molecular biology, biotechnology, and genomics. The T_m of a DNA stretch is the temperature at which 50 % of the double-stranded DNA (dsDNA) molecules split apart into two single-stranded molecules (ssDNA), a process known as denaturation. The T_m is influenced by various factors, including the nucleotide composition of the stretch, the sequence length, and the ionic environment in which the DNA is dissolved. Recent studies have shed some light on the intricate relationships between the salt concentration and the DNA melting temperature[1–3]. Researchers have employed statistical models and numerical calculations to explore the stability of the dsDNA under a wide range of salt concentrations[1]. As the salt concentration increases, this stabilizes the DNA double helix, and the melting temperature of the DNA rises. In this context, the goal of the present work was to evaluate the impact of salt concentration on T_m through the fluorescent signal of SYBR Green I, which intercalates the dsDNA. To control the temperature of the process, this experiment was performed using a thermocycler applying a temperature sweep from 20 °C to 100 °C. The samples were composed of 10 µM of each one of the 21 nt-long complementary ssDNA stretch, NaCl buffer with increasing concentrations from 0.1 mM to 1 M and 50× SYBR Green I initially diluted in PBS and dH_2O. It is worth noting that the T_m trends when SYBR Green I was initially diluted in PBS and dH_2O were very similar, but when SYBR Green I was diluted dH_2O induced a general decrease in T_m (*Figure 1*). This difference becomes more noticeable at low NaCl concentrations, suggesting that dsDNA is not as stable as at higher NaCl concentrations. Overall, the presence of PBS increases the stability of the dsDNA, and the T_m in all the conditions tested. According to the literature, the results confirm that as the salt concentration increases the stability of dsDNA is enhanced, which implies higher T_m.

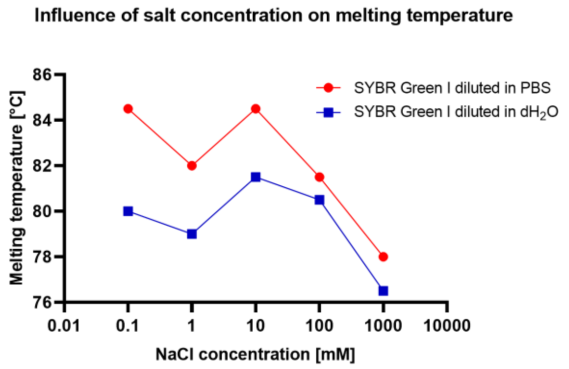


Figure 1. Dependence of T_m on the salt concentration. The red curve represents the samples prepared with SYBR Green I diluted in PBS, while the orange one represents the samples with SYBR Green I diluted in dH_2O. For each dilution of SYBR Green I were tested at different NaCl concentrations of the buffers from 0.1 mM to 1 M.

References

[1] Maity A., Singh A., Singh N. *European Biophysics Journal* **2017**, *46* (1), 33–40.
[2] Rui-Xin D., Xun-Ling Y., Xiao-Feng P., Shan J., Sheng-Gang L. *Commun. Theor. Phys.* **2004**; Vol. 41.
[3] Meunier-Prest R., Raveau S., Finot E., Legay G., Cherkaoui-Malki M., Latruffe N. *Nucleic Acids Res* **2003**, *31* (23).

Determination of phytosterols in food samples base on molecurarly imprinted polymers (MIP) coupled with UPLC-MS/MS

E. Oliva[1*], S. Palmieri[1], F. Eugelio[1], F. Fanti[1], M. Sergi[2], D. Compagnone[1], M. Del Carlo[1]

[1] *Department of Bioscience and Technology for Food, Agriculture and Environment, University of Teramo, Teramo, Italy.*
[2] *Department of Chemistry, Sapienza University of Rome, Rome, Italy.*

eoliva@unite.it

Phytosterols (PSs) are bioactive compounds structurally and functionally similar to cholesterol. They contain an extra methyl, ethyl group, or double bond, and most of their side chains contain 9-10 carbon atoms. PSs have been classified as 4-desmethyl sterols of the cholestan series, which all have double bonds at the C_5 position of the B-ring[1]. These molecules are particularly known for widely range of properties including reduced intestinal cholesterol absorption and potential contributions to the prevention of cardiovascular diseases[2]. PSs are generally classified into three groups based on the number of methyl groups on carbon-4, two (4-dimethyl), one (4-monomethyl), or none (4-desmethyl). Moreover, 4-dimethyl esters and 4-monomethylsterols are metabolic intermediates in the biosynthetic pathway leading to the final product, 4-desmethyl phytosterols, but are usually present at low levels in most plant tissues. These compounds are present in plants, such as seeds, grains and legumes, both in free and conjugated form and they can be found in the form of fatty acyl esters, glycosides and fatty acyl glycosides. The selectivity issue in plant matrices is a challenging task, and classic approach such as solvent or solid phase extraction (SPE) are expensive and not always give the needed selectivity. In this scenario a low cost molecularly imprinted polymers (MIPs) approach for the selective of extraction these compounds was not fully explored. In this work, a fast chemical MIPs synthesis approach for selective extraction of PSs was performed, using cholesterol as a dummy template. The MIPs were used as an adsorbent phase for SPE and combined with a targeted approach using liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS) with atmospheric pressure chemical ionization (APCI). The results showed high selectivity with significant extraction performances and low matrix effect, a principal goal in complex plant matrices. The proposed strategy can be consider as fast and effective method to produced MIPs as extraction tool for the determination of these target compounds.

References

[1] Moreau R.A., Nystrom L., Whitaker B.D., Winkler-Moser J.K., Baer D.J., Gebauer S. K., Hicks K.B., *Prog. Lipid Res.*, 2018, **70**, 35–61.
[2] Othman R.A., Moghadasian M.H., *Nutr. Rev.*, 2011, **69**, 371–382.

In-depth characterization of lipids in hempseeds through photochemical cycloaddition reaction and high-resolution mass spectrometry (HRMS).

Maria Chiara Paniccia*, Sara Elsa Aita, Andrea Cerrato, Carmela Maria Montone, Anna Laura Capriotti

Department of chemistry, University of Rome "La Sapienza", Rome, Italy

**paniccia.1796985@studenti.uniroma1.it*

Recently, the consumption of hempseeds and its derivatives is rapidly increasing for the high nutritional value of its bioactive compounds, including their high content of polyunsaturated fatty acids (PUFA) belonging to the omega-3 (ω-3) and omega-6 (ω-6) classes. These essential fatty acids (FA) cannot be synthesized by mammals and are converted to very long-chain PUFA (e.g., arachidonic acid, ω-6, and eicosapentaenoic acid, (ω-3) [1]. Within the human body, ω-3 and ω-6 very-long-chain PUFA are well-known to exert primary albeit opposite functions, with the former responsible for anti inflammatory and vaso-dilatory activities [2] and the latter capable of promoting inflammation and constriction of blood vessels [3]. As such, absolute content and proportions of the dietary intake of ω-3 and ω-6 PUFA play a significant role in regulating body homeostasis [4], and hempseeds are known to contain a unique and balanced FA composition, with a ratio ω-6/ω-3 around 3 [5]. Despite their importance for the human health, the overall lipid composition is largely unknown at present. In this study, we initiated the development of an analytical platform for extraction, untargeted analysis using HRMS, and detailed annotation of lipid species. The first step involved comparing and refining five single-phase and two-phase solid-liquid extraction protocols using a pooled hemp seed sample. The objective was to identify the most suitable method to achieve maximum overall efficiency and facilitate easy coupling with lipid derivatization via photochemical cycloaddition [2+2] with 6- azauracil. Subsequently, lipid species were annotated using a data processing workflow in Compound Discoverer software, typically employed in polar lipidomics. Furthermore, examination of MS/MS spectra of lipid derivatives following the aza-Paternò-Büchi reaction enabled the detection of the regiochemistry of carbon-carbon double bonds.[6] Ultimately, a total of 184 lipids were identified, comprising 26 fatty acids and 158 phospholipids, along with minor subclasses containing N acylphosphamididiletanolamines. Following the establishment of the platform, lipid extracts from nine hemp seed samples, obtained from different hemp strains, were characterized, providing insight into the regiochemistry of free and conjugated fatty acids. The characterization of the polar lipidome of nine of the hempseeds that are cultivated in the EU demonstrated the rich content in biologically active free and conjugated PUFA, as well as significant intra-strain differences in terms of both lipid composition and minor regioisomer content.

References

[1] Saini R.K., Keum Y.-S., *Life Science*, 2018, **203,** 255–267,
[2] Adkins Y., Kelley D.S, *The Journal of Nutritional Biochemistry*, 2010, **21**, 781–792,
[3] Dennis E.A., Norris P.C., *Nature Reviews Immunology*, 2015, **15,** 511–523
[4] Kang J.X., Liu A., *Cancer and Metastasis Reviews*, 2013, **32,** 201–210,
[5] Lopez C., Novales B., Rabesona H., Weber M., Chardot T., Anton M., *Food Research International Journal*, 2021, **150**, 110759
[6] Cerrato A., Capriotti A. L, Cavaliere C., Montone C. M, Piovesana S., Laganà A., *Analytical Chemistry* , 2022, **94,** 13117-13125.

Abundant protein depletion methods of Glioblastoma serum samples: a pilot investigation in the perspective of LC-MS proteomic profiling by top-down/bottom-up integrated platforms

Giordano Putzolu[1*], Alexandra Muntiu[2], Federica Vincenzoni[2,3], Diana Valeria Rossetti[4], Alessandro Olivi[3,5], Andrea Urbani[2,3], Giovanni Sabatino[3,5], Francesca Buiarelli[1], Claudia Desiderio[4]

[1]*Department of Chemistry, Sapienza University of Rome, Rome, Italy*
[2]*Dipartimento di Scienze Biotecnologiche di Base, Cliniche Intensivologiche e Perioperatorie, Università Cattolica del Sacro Cuore, 00168 Rome, Italy;*
[3]*Fondazione Policlinico Universitario A. Gemelli IRCCS, Catholic University 00168 Rome, Italy;*
[4]*Istituto di Scienze e Tecnologie Chimiche "Giulio Natta", Consiglio Nazionale delle Ricerche, 00168 Rome, Italy;*
[5]*Institute of Neurosurgery, Fondazione Policlinico Universitario A. Gemelli IRCCS, Catholic University, 00168 Rome, Italy.*

**Putzolu.1855586@studenti.uniroma1.it*

Glioblastoma Multiforme (GBM) is the most common primary malignant brain tumor characterized by poor prognosis and average one-year survival rate of 41.4% [1]. The lack of rapid and effective diagnostic methods presents a major challenge in GBM treatment, aggravated by the absence of effective pharmacological interventions. Therefore, the identification of diagnostic biomarkers in biofluids holds paramount importance in improving patient survival rates. Proteomics is an essential tool to investigate the molecular mechanisms of disease onset and progression as well as to identify potential biomarkers in biological fluids and tissues. Compared to other biological fluids, the proteomic analysis of serum is challenging due to the presence of high abundant proteins which need to be depleted to prevent their signal from masking that of potentially significant smaller, low-abundant proteins. In the perspective to explore potential GBM serum biomarkers by mass spectrometry proteomic analysis, either investigating the digested as well as the intact proteome by bottom-up/top-down integrated platforms, our study aimed to develop and compare different cost-effective pretreatment procedures for most abundant protein depletion. Our pretreatment methods utilize small volumes of organic solvents offering an economical, easy, and fast approach. We have therefore modified an optimized method from the literature [2] with the introduction of formic acid, to improve protein and peptide solubilization after depletion, and of chloroform, to remove the acetonitrile not compatible with the FASP (Filter Aided Sample Pretreatment, with filter cut-off of 10 kDa) protocol applied for sample digestion and fractionation and compared the data of total protein content obtained by Bradford assay. We tested four different procedures on GBM serum sample and commercial control human serum, which yielded a protein depletion in the range 65-99 %. The effect of the different procedures will be evaluated comparing the number of identifications of proteins and peptides by proteomic analysis of the depleted serum samples following FASP filtration and digestion to provide a comprehensive insight into the serum proteome.

References

[1] Tan AC, Ashley DM, López GY, Malinzak M, Friedman HS, Khasraw M. *CA Cancer J Clin*. 2020, **70**, 299.
[2] de Jesus JR, da Silva Fernandes R, de Souza Pessôa G, Raimundo IM Jr, Arruda MAZ. Talanta. 2017, **170**, 199.

Analysis of *Posidonia oceanica*'s stress factors in the marine environment of Tremiti Island

Elisa Santoni[1*], Martina Fattobene[1], Paolo Cognigni[2], Raffaele Emanuele Russo[1], Adelmo Sorci[3], Mario Berrettoni[1], Silvia Zamponi[1]

[1]*School of Science and Technology, Chemistry Division, University of Camerino, Camerino (MC) 62032, Italy.*
[2] *Department of Engineering "Enzo Ferrari", University of Modena and Reggio Emilia, Modena*
[3]*Laboratorio del Ma.Re, Isole Tremiti (FG) 71040, Italy*

**elisa.santoni@unicam.it*

Posidonia oceanica significantly contributes to the health of oceans and coastal areas; however, its progressive decline is becoming an increasing source of concern. The present study aims to assess the chemical parameters that describe the state of preservation of the aforementioned plant meadows located in the Tremiti Islands archipelago. To better understand the plant's response to external factors, the emission of Biogenic Volatile Organic Compounds (BVOCs) was investigated using Posidonia oceanica as a biological indicator. Subsequently, heavy metal concentrations in sediments, rhyzomes, leaves, and seawater were determined and the DMSP to DMSO ratio was calculated to evaluate oxidative stress levels in the meadows.

BVOCs analysis revealed dimethyl sulphide (DMS) as the most abundant molecule. Significant findings included the presence of tribromomethane in one site and the higher sesquiterpene abundance and diversity at another. No significant differences were observed among leaf types for our goal.

Morphological features led to variations in metal concentrations across sampling sites, with sheltered bays displaying a higher metal content. Essential nutrients (Ca, Mg, K) show no significant variability across leaf types while for heavy metals there is a correlation between leaf categories and significant differences between sampling sites. The content and sampling depth of DMSP analysis were shown to be inversely related; degradation is indicated by a greater DMSO content in the outer leaves. In accordance with the metal content, the bioindicator ratio confirms greater degradation on the south side, which aligns with increased oxidative stress, and metal content confirms itself as the only factor that gives us confirmation about stress conditions.

Characterization and Sensing Applications of a Physisorbed Antibody Layer

Cecilia Scandurra[1*], Lucia Sarcina[1], Cinzia Di Franco[2], Maria Pia Caputo[3], Michele Catacchio[3], Paolo Bollella[1,4] , Gaetano Scamarcioe[6], Eleonora Macchia[3,4,6] and Luisa Torsi[1,4,6]

[1] *Dipartimento di Chimica, Università degli Studi di Bari Aldo Moro, Via E. Orabona 4, 70125 Bari, Italy*
[2] *CNR – Institute of Photonics and Nanotechnologies, 70126 Bari, Italy*
[3] *Dipartimento di Farmacia-Scienze del Farmaco, Università degli Studi di Bari Aldo Moro, 70126 Bari, Italy*
[4] *CSGI (Centre for Colloid and Surface Science), Via E. Orabona 4, 70125 Bari, Italy*
[5] *Dipartimento Interateneo di Fisica "M. Merlin", Università degli Studi di Bari Aldo Moro, 70126 Bari, Italy*
[6] *The Faculty of Science and Engineering, Åbo Akademi University, 20500 Turku, Finland*
**cecilia.scandurra@uniba.it*

The phenomenon of antibody physisorption at a solid interface is a captivating area of research with significant implications for various applications, including the development of modified interfaces for biosensor devices.[1] The performance of a device can be determined by the immobilization strategy of the biorecognition element.[1] Notably, the physical adsorption approach is the simplest[2], being cost-effective, fast, and compatible with printing techniques.[3] Physisorption, despite the huge advantages, is not widely used due to a prevailing belief that it does not result in optimal performance. The lack of uniformity and long-term stability in physisorption have not been studied systematically, particularly in the case of bilayers of capturing antibodies.

Herein, the homogeneity and stability of an antibody's layer against SARS-CoV-2-Spike1 (S1) protein physisorbed onto a gold surface have been investigated by means of a multi-parameter Surface Plasmon Resonance (SPR).[4] The evaluation of figures of merit, such as the limit of detection of 2 nM and the selectivity ratio between the negative control and sensing experiment as low as 0.04, proved the high performance of the sensing. This SPR S1 protein assay is, to the best of our knowledge [5,6], highly performing. The elicited figures of merit outmatch those measured with more sophisticated biofunctionalization procedures involving the chemical bonding of the capturing antibodies to the gold surface. The present study opens interesting new pathways toward the achievement of a cost-effective and scalable biofunctionalization protocol, which could guarantee prolonged stability of the biolayer and easy handling of the biosensing system.

References

[1] Kim, K., Son, T., Hong, J.S., Kwak, T.J., Jeong, M.H., Weissleder, R., & Im, H., *ACS Applied Materials & Interfaces*, 2022, **23**, 26548-26556.

[2] Zhang, L., Mazouzi, Y., Salmain , M., Liedberg, B., Boujday, S., *Biosens Bioelectron* 2020, **165**, 112370.

[3] Juste-Dolz, A., Avella-Oliver, M., Puchades, R., Maquieira, A.,*Sensors*. 2018, **18**, 3163.

[4] Sarcina L., Scandurra C., Di Franco C., Caputo M., Catacchio M., Bollella P., Scamarcio G., Macchia E., Torsi L., *Journal of Materials Chemistry,* 2023, **27**, 9039–9368

[5] Saada, H., Pagneux, Q., Wei, J., Live, L., Roussel, A., Dogliani, A., Die Morini, L., Engelmann, I., Alidjinou, E. K., Rolland, A. S., Faure, E., Poissy, J., Labreuche, J., Lee, G., Li, P., Curran, G., Jawhari, A., Yunda, J. A., Melinte, S., Legay, A., Gala, J.-L., Devos, D.R., Boukherroub and Szunerits, S., *Sensors & Diagnostics*, 2022, **1**, 1021–1031.

[6] Pandey, P. S., Raghuwanshi, S. K., Shadab, A., Ansari, M. T. I. U. K. Tiwari & S. Kumar, *IEEE Sens.* 2022, **22**, 13800–13810.

Optimizing LC-MS Methodology for Detecting Polar Emerging Contaminants in Reclaimed Water: Towards Sustainable Water Management

Lorenzo Strani[1*], S. Pellacani[1], M. Battisti[1], B. Benedetti[2], M. Cocchi[1], C. Durante[1]

[1]*Department of Chemical and Geological Sciences, University of Modena and Reggio Emilia, via Campi 103, 41125 Modena, Italy*
[2]*Department of Chemistry and Industrial Chemistry, University of Genova, Via Dodecaneso 31, Genova, 16146, Italy caterina.durante@unimore.it*

**lostrani@unimore.it*

Food and agriculture are major contributors to the global demand for water, given the substantial quantities needed for crop cultivation and livestock rearing. Approximately 70% of water usage across agricultural, municipal, industrial and energy sectors is attributed to farming activities. Effective management of available water resources is imperative to meet the increasing need for food production [1]. Consequently, exploring the potential utilization of reclaimed water for irrigation presents a significant opportunity for water conservation and aligns with principles of the circular economy.

This study focuses on optimizing an analytical method utilizing liquid chromatography-mass spectrometry (LC-MS) to detect 33 polar emerging contaminants in wastewater. These contaminants encompass a range of classes, including pharmaceuticals, personal care products, and other emerging pollutants.

Given the high polarity of the analytes, hydrophilic interaction liquid chromatography (HILIC) employing a zwitterionic stationary phase was utilized. To improve analysis efficiency, response surface methodology (RSM) employing a Fractional Factorial Design [2] was employed to optimize experimental parameters. Several factors influencing chromatographic separation in HILIC, such as initial mobile phase percentage, gradient time, column temperature, salt type and concentration and flow rate, were investigated to achieve optimal separation and sensitivity for the target analytes. Subsequently, the optimized method was integrated with appropriate sample pre-treatment and applied to diverse reclaimed water samples. This enabled the evaluation of method performance in real-world matrices and the investigation of the presence of the considered contaminants in treated water.

References

[1] UNESCO, 2012. https://unesdoc.unesco.org/ark:/48223/pf0000215644.
[2] Box, G.E, Hunter, J.S., Hunter,W.G., *Statistics for Experimenters: Design, Innovation, and Discovery, 2nd Edition*, 2005, Wiley, Hoboken, NJ, USA

Development and evaluation of the prolonged antifungal and antibacterial activity of an air cleaning system for indoor cultural heritage spaces

Anna Laura Tassi[1*], Pilar Bosch-Roig[2], Andrea Bernardos[3], Marìa Cebriá-Mendoza[3], Daniela Pinna[4], Vittoria Guglielmi[1], Alessia Santiglia[1], Paola Fermo[1]

[1]*Department of chemistry, University of Milan, Milan, Italy*
[2]*Instituto de Restauracion del Patrimonio, Universitat Politecnica de Valencia, Camino de Vera s/n, 46022, Valencia, Spain*
[3]*Instituto Interuniversitario de Investigacion de Reconocimiento Molecular y Desarrollo Tecnologico, Universitat Politecnica de Valencia, Camino de Vera s/n, 46022, Valencia, Spain*
[4]*Dipartimento di Chimica "Giacomo Ciamician" Via Selmi 2, Bologna*

**Annalaura.tassi@unimi.it*

Biological air contamination inside cultural heritage indoor spaces is an issue that needs to be solved since microbial deposition on artistic surfaces can cause mechanical and esthetical damages, leading to unfeasible access of the artworks. To prevent this, introducing an air-cleaning system is helpful to reduce the presence of microorganisms in the air. This project began with the work of a research group from the *Universitat Politècnica de Valencia* that has already applied tea tree essential oil cold diffusion as an active air cleaning system for this purpose in a small space in Los Santos Juanes Church in Valencia [1]. As a next step, this work purposes to encapsulate the tea tree essential oil inside the pores of mesoporous silica support to elongate the period of activity of the oil, enhance its performance and prevent unwanted side reactions between the artistic material and the essential oil components. To obtain the simplest device, it has been designed to be a part of a passive-release air cleaning system.

Once synthetized, the silica mesoporous support has been characterized through diffuse/specular reflectance and ATR-IR/Raman spectroscopy, electron microscopy (SEM-EDX), porosimetry and X-ray diffraction and the amount of essential oil charged has been evaluated through thermogravimetric analysis (TGA) [2].

Afterwards, this pioneer air cleaning system has been tested in test rooms and compared with the performance of the free oil system. Inside both the two test rooms, a complete air monitoring (temperature and relative humidity measurement plus microbial and particulate matter assay) has been performed and it reported that the essential oil encapsulated in the microparticles (as a passive release system) keeps its biocidal activity for a longer time than the free one. This difference became more evident especially after the third week for the bacteria and from the fourth for the fungi. The new cleaning system has also been applied in vitro [3].

These promising results do the groundwork for future research projects that will focus on combining microparticles and essential oils to have a high immediate and long-term biocidal effect, by applying them, for instance, in air filtration system.

References

[1] J. Díaz-Alonso, A. Bernardos, J. L. Regidor-Ros, R. Martínez-Máñez, and P. Bosch-Roig, ‘Innovative use of essential oil cold diffusion system for improving air quality on indoor cultural heritage spaces’, Int. Biodeterior. Biodegrad., vol. 162, p. 105251, Aug. 2021, doi: 10.1016/j.ibiod.2021.105251.

[2] A. Bernardos et al., ‘Antifungal effect of essential oil components against Aspergillus niger when loaded into silica mesoporous supports’, J. Sci. Food Agric., vol. 95, no. 14, pp. 2824–2831, 2015, doi: 10.1002/jsfa.7022.

[3] A. Winkler, T. Contardo, V. Lapenta, A. Sgamellotti, and S. Loppi, ‘Assessing the impact of vehicular particulate matter on cultural heritage by magnetic biomonitoring at Villa Farnesina in Rome, Italy’, Sci. Total Environ., vol. 823, p. 153729, Jun. 2022, doi: 10.1016/j.scitotenv.2022.153729.

Improving MASLD Diagnosis with ^{1}H-NMR: Multivariate Analysis of Serum Metabolites Differentiating Disease Stages of Metabolic dysfunction-associated steatotic liver disease

Serena Zampieri[1*], Greta Petrella[1], Elisa Nagni[1], Stefania Basili[2], Francesca Maiorca[2], Ludovica Lombardi[2], Annamaria Sabetta[2], Lucia Stefanini[2], Daniel Oscar Cicero[1]

[1] Department of Chemical Science and Technology, University of Rome "Tor Vergata," 00133, Rome, Italy.
[2] Department of Translational and Precision Medicine, Sapienza University of Rome, 00185, Rome, Italy.
**serena.zampieri@students.uniroma2.eu*

Metabolic dysfunction-associated steatotic liver disease (MASLD), formerly known as non- alcoholic fatty liver disease (NAFLD) is a spectrum of liver diseases ranging from simple hepatic steatosis (MASL) to non-alcoholic steatohepatitis (MASH), all characterized by an excessive accumulation of fat in the liver.[1] Today, it is one of the most common liver diseases in the world, able to progress towards cirrhosis and/or towards hepatocellular carcinoma (HCC).[2] At present, the most reliable method to diagnose MASLD is through liver biopsy. This technique is the only one that can differentiate between various stages of disease progression, providing an accurate assessment of hepatic steatosis, hepatocellular damage, inflammation, and early stages of fibrosis. However, metabolomics could offer a new way of discovering potential non-invasive biomarkers for the MASLD prognosis. To this end, we conducted a metabolomic analysis of the serum metabolic composition of MASLD patients enrolled at the Hospital Umberto I (Ethic Committee Approval date: 31.03.2021- Rif. 6216 - Prot. 0297/2021; NCT05128253). The 88 serum samples were obtained from four different groups of patients with progressively worsening prognosis of liver disease, namely controls, MAFL, MASH, and Metabolic dysfunction-associated cirrhosis. The polar fraction of the samples was analyzed by ^{1}H-NMR. Through a manual deconvolution process, it was possible to identify and quantify 62 metabolites. A multivariate analysis was conducted to investigate the relationship between the systemic metabolic profile and the progression of the disease. Three Orthogonal Partial Least Square Discriminant Analyses (OPLS-DAs) were used to compare the serum metabolic profile of controls with those of MASL, MASH, and MASH/cirrhotic patients. This approach was used to qualitatively identify the specific metabolic fingerprints of each stage of the disease. Additionally, we analyzed whether the common part of the altered metabolism, compared to controls, showed a progressive increase or decrease over the stages of the disease. To investigate this correlation, an OPLS was used to study the relationship between metabolite levels and MAFLD progression. Many of the metabolites that were found to be altered in the serum of MAFLD patients are consistent with previous studies on this liver illness. However, no current research focuses on the relationship between metabolism and the disease course. These results can help in the future to improve our understanding of the biochemical mechanisms underlying the progression of MAFLD and to identify possible new therapeutic avenues.

References

[1] De, A.; Duseja, A.; Natural History of Simple Steatosis or Nonalcoholic Fatty Liver. *J Clin Exp Hepatol*. 2020, **10(3)**, 255-262.
[2] Li, B.; Zhang, C.; Zhan, Y-T.; Nonalcoholic Fatty Liver Disease Cirrhosis: A Review of Its Epidemiology, Risk Factors, Clinical Presentation, Diagnosis, Management, and Prognosi. *Can J Gastroenterol Hepatol*. 2018, **2784537**.

Theme E - Advances in Coordination and Inorganic Chemistry

Green Synthesis of CALF-20 for the separation of CO_2/N_2 mixtures

Matteo Boattini[1*], Benedetta Brugnoli[1], Alessandro Latini[1], Maria Chiara Di Gregorio[1], Mariangela Bellusci[2], Francesca Varsano[2], Iolanda Francolini[1]

[1]*Department of Chemistry, Sapienza University of Rome, Rome, Italy*
[2]*ENEA, Casaccia Research Centre, Via Anguillarese 301, 00123, Roma, Italy*

**boattini.1917402@studenti.uniroma1.it*

In addition to the rapid growth of global population, energy consumption has been increasing significantly. Fossil fuels have currently gained worldwide attention and demand as the main sources of energy notwithstanding the emission of huge amounts of CO_2 into the atmosphere.

Metal organic frameworks (MOFs) represent a valid alternative in the production of a new class of materials for CO_2 capture and separation, thanks to their high specific surface area and their tunable chemical and structural characteristics [1]. The rationale behind the selection of their building units and the modification of their composition by post-synthetic functionalization allows the fine-tuning of the affinity of the pores internal surface with CO_2 for the specific conditions of use [2]. Among the different MOFs, a zinc-triazole-oxalate-based MOF, named Calgary Framework (CALF-20), has emerged as a promising candidate for large scale CO_2 capture owing its durable sorption performance under industrially relevant conditions [3]. Commonly, CALF-20 is synthesized by solvothermal methods, which require high temperatures and pressures.

In this study, a novel liquid and green synthetic procedure was set up for the preparation of CALF-20. Specifically, ethanol and water were used as solvents for oxalic acid dihydrate (OXA) and 1,2,4-triazole (TRZ). OXA and TRZ were mixed with stirring at room temperature obtaining a cloudy suspension. Then, solid basic zinc carbonate was added, producing effervescence. A physico-chemical and structural characterization was carried out to confirm CALF-20 obtainment. ATR-FTIR spectroscopy confirmed the characteristic functionalities of CALF-20. To examine the stability of CALF-20, thermogravimetric analysis (TGA) was carried out. CALF-20 showed a weight loss of 7% in the temperature range of 50-100 °C, due to water molecule adsorption. A following weight loss of 33% at 370 °C, which corresponds to two-stage collapse of the CALF-20 skeleton, thus confirming its thermal stability as an adsorbent. Powder X-Ray Diffractions (PXRD) showed the typical peaks at 11°, 13° and 14°, should be assigned to the (100), (011), and (110) diffractions of the CALF-20 framework.

Currently, experiments are ongoing to remove oxides impurities by washings using four different acids (chloridric acid, nitric acid, acetic acid and citric acid). In addition, post-synthetic functionalization using specific linkers is being set up to improve the hydrophobicity of CALF-20 and, so, reduce water adsorption which may compete with CO_2 capture.

Funds: PIANO TRIENNALE DI REALIZZAZIONE 2022-2024 DELLA RICERCA DI SISTEMA ELETTRICO NAZIONALE, TEMA DI RICERCA 1.6 Efficienza energetica dei prodotti e dei processi industriali

References

[1] Ghanbari T., Abnisa F., Wan Daud WMA. Science Of The Total Environment, 2020, **707,** 135090
[2] Bellusci M et al. Microporous and Mesoporous Materials, 2021, **328**, 111458
[3] Chen Z et al. ACS Materials Letters, 2023, **5(11),** 2942-2947

N-methyl-corroles and their catalytic activity

Alessia Fata*, Francesco Pizzoli, Roberto Paolesse and Sara Nardis.

Department of Chemical Science and Technologies, University of Rome Tor Vergata, Italy.

*alessia.fata@students.uniroma2.eu

Corroles are one of the most intriguing classes of compounds in the porphyrinoid family, thanks to their peculiar chemistry. They highlight a notable coordinative versatility with the possibility to introduce different metals allowing the expansion of the so-called Periodic Table of Metallocorroles.[1] Moreover, their unique reactivity and photophysical behavior allow their use as sensing materials in the field of chemical sensors for optical, electrochemical, and conductometric transducers. [2]

Their catalytic activity has been also investigated in several literature studies; iron corroles, for example, were found to be more selective catalysts than analogous porphyrins for the aziridination of olefins [3] and specific functionalizations on their *meso* positions can be studied to apply them in electrocatalysis.[4] Furthermore the use of metallocorroles together with TBAX (tetrabutylammonium chloride or bromide), resulted in a very powerful cooperative catalytic system for CO_2 fixation with epoxides.[5]

In this work, we studied the catalytic activity of meso-arylcorrole complexes and their N-methyl analogs (see Figure below): in particular, we used the N-substituted macrocycles to introduce an interesting dimension, considering their relatively unexplored chirality in catalysis. Investigation of their performances in CO_2 insertion reactions with epoxides for cyclic carbonate synthesis, as well as in the insertion of diazo compounds into N-H bonds of amines for amino ester synthesis, could provide valuable insights into their potential as enantioselective catalysts and also contribute to the development of greener synthetic methodologies.

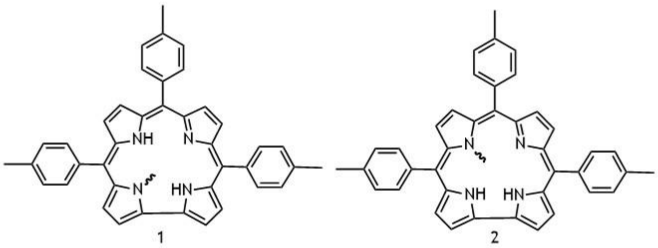


Figure. Structures of N-methyl derivatives of 5,10,15-tri-p-tolylcorrole.

References

[1] S. Nardis, F. Mandoj, M. Stefanelli, R. Paolesse, *Coordination Chemistry Reviews*, 2019, 388, 360–405.

[2] R. Paolesse, S. Nardis, D. Monti, M. Stefanelli, and C. Di Natale. *Chemical reviews*, 2017, 117(4), 2517-2583.

[3] L. Simkhovich, Z. Gross, *Tetrahedron Letters*, 2001, 42, 8089–8092.

[4] W. Sinha, A. Mahammed, N. Fridman, Z. Gross, *ACS Catal*., 2020, 10, 3764−3772.

[5] M. Tiffner, S. Gonglach, M. Haas, W. Schçfberger, M. Waser, *Chem. Asian J.*, 2017, 12, 1048–1051.

Ruthenium olefin metathesis catalysts for transformations of renewables

Rida Nadeem, Assunta D’Amato, Fabia Grisi

[1] *University of Salerno, Department of Chemistry and Biology “A. Zambelli”, Via Giovanni Paolo II 132, I-84084 Fisciano, SA, Italy.*

**rnadeem@unisa.it*

Olefin metathesis is a metal-catalyzed transformation through which pairs of carbon-carbon double bonds are rearranged allowing simple molecules to easily transform into more complex and precious compounds. The synthesis of a huge number of natural products, polyfunctional biologically active products as well as polymers by olefin metathesis has been achieved to date.[1] As petrochemical resources become increasingly scarce and expensive, much research attention has been focused on renewable resources as green alternatives for producing chemicals. Catalytic olefin metathesis is a powerful tool to transform bio-sourced structural motifs, containing carbon–carbon double bonds (e.g. phenylpropenoids, terpenes, unsaturated fatty acid esters), in valuable compounds for the chemical industry. In this view, easy-handling, stable ruthenium-based catalysts supported by *N*-heterocyclic carbene (NHC) ligands are considered as excellent candidates. The appropriate choice of the NHC ligand architecture is one of the key issues for the development of highly active and selective catalysts.[2] The introduction of unsymmetrical NHCs (uNHCs), modulated by different substituents at the nitrogen atoms of the NHC ring, has led to important effects on the reactivity and selectivity of the resulting catalysts, thus allowing for significant advancements in some challenging or specific olefin metathesis reactions.[3] With the aim of increasing catalyst efficiency in olefin metathesis reactions involving renewable substrates of both academic and industrial relevance, herein we report the synthesis and the catalytic behaviour in specific metathesis applications of new ruthenium complexes bearing uNHCs combining different backbone configurations (*syn* or *anti)* with *N*-alkyl/*N*-aryl substituents of variable bulkiness.

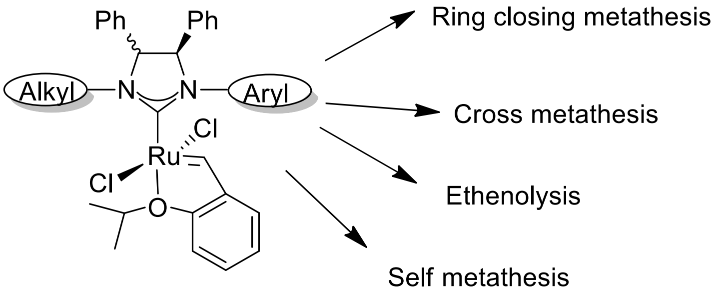


Figure 1: New ruthenium catalysts for metathesis applications.

Acknowledgements:

This study was supported by funding from University of Salerno (*FARB grants*).

References

[1] Grela K., Olefin Metathesis: Theory and Practice, 2014, 1, 3-5, John Wiley & Sons, New Jersey, United States of America.
[2] Bruneau C., Fischmeister C., *Organometallics for Green Catalysis*, 2019, 77-102.
[3] Paradiso V., Costabile C., Grisi F., *Beilstein J. Org. Chem.,* 2018, **14,** 3122-3149.

Non-Covalent Functionalization of Graphene Oxide with A Porphyrazine Macrocycle

Perez Quer P.[1,2*], Amato F.[2], Donzello M. P. [2], Giustini M. [2], Motta A.[2], Marrani A. G. [2], Viola E. [2]

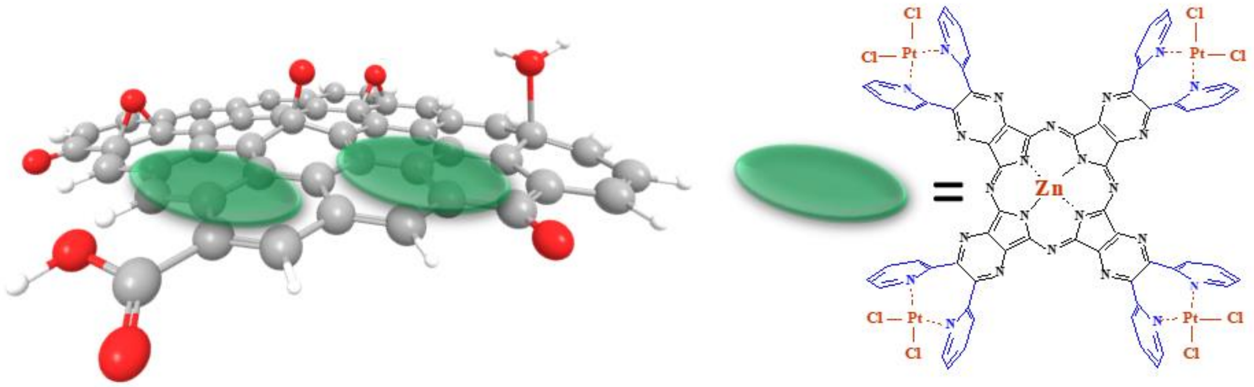
[1]*Department of Chemistry, University of Barcelona, Diagonal 645, Catalonia, Barcelona, Spain*
[2]*Department of Chemistry, Sapienza University of Rome, P.le A. Moro 5, Rome, Italy*

**pperezqu22@alumnes.ub.edu*

Graphene Oxide (GO) possesses a large and rigid π-conjugated planar structure, coupled with oxygen-containing groups on the edges and in the basal plane, which provides the material with several amazing physicochemical properties, such as excellent water dispersibility, surface modifiability, biological compatibility, and so on.[1] For these reasons, it is considered among the most promising nanomaterials for biological imaging or sensing, drug delivery, composite materials, and luminescent devices.[2]

This contribution presents a comprehensive study carried out within an Erasmus Programme on the non-covalent functionalization of graphene oxide (GO) with a pentanuclear porphyrazine macrocycle (Pz), exactly $[(PtCl_2)_4LZn]$ where L = tetrakis-2,3-[5,6-di(2-pyridyl)-pyrazino]porphyrazinato dianion, an active photosensitizer for $^1O_2$ production,[3] which was aimed at obtaining a stable hybrid nanostructure with unique physico-chemical properties.

The novel porphyrazine-graphene oxide hybrid material (Pz@GO) was characterized by UV-visible, infrared and Raman spectroscopy and photoluminescence measurements. A preliminary investigation on the photosensitizing efficiency of Pz@GO in the production of the $^1O_2$ was also carried out. Worth of notice, the hybrid Pz@GO shows better water solubility than pure porphyrazine, which is of great interest for potential biomedical applications in the field of Photodynamic Therapy and in other multimodal therapies.



References

[1] Georgakilas V., Otyepka M., Bourlinos A. B., Chandra V., Kim N., Kemp K. C., Hobza P., Zboril R., Kim K. S. *Chem Rev*, 2012, **112 (11)**, 6156–6214.

[2] Jiříčková A., Jankovský O., Sofer Z., Sedmidubský D. *Materials*, 2022, **15 (3)**, 920.

[3] Donzello M. P., Viola E., Ercolani C., Fu Z., Futur D., Kadish, K. M., *Inorg Chem*, 2012, **51 (22)**, 12548–12559.

Theme F - Colloids and Materials

Shape and Morphology of Chiral Polyurea Nanocapsules Control Stereospecific Interactions with Albumins

Malak Abo Alhija [1*], Amani Zoabi [1], Adan Sultan [1] , Anna Radko [2] , KatyMargulis[1].

[1]The Institute for Drug Research, the School of Pharmacy, the Faculty of Medicine, The Center for Nanoscience and Nanotechnology, The Hebrew University of Jerusalem, Jerusalem 9112192, Israel.
[2]The Unit for Nanoscopic Characterization, The Center for Nanoscience and Nanotechnology, The Hebrew University of Jerusalem, Jerusalem 91904, Israel.

**Malak.aboalhija@mail.huji.ac.il*

Hypothesis: This study aims to investigate interactions between chiral polyurea nanocapsules and albumins from various sources. It is suggested that the interactions are stereospecific and that morphology of nanocapsules may influence albumin adsorption and their cellular internalization. Further, control over interaction strength may be achieved by combining opposite chiralities in one capsule.

Experiments: Chiral polyurea nanocapsules with reproducible sizes and neutral surface potentials were synthesized. Synthesis optimization was introduced to reduce the capsule size. Also, capsules with regions of opposite chiralities were formed. Enantioselective interactions with albumins were evaluated by effects on size, fluorescence quenching, and surface charge. Biocompatibility, stability and cellular internalization were next explored. Additionally, scanning transmission electron and atomic force microscopies were carried out to assess particle shape and morphology.

Findings: It was uncovered that D-nanocapsules exhibited a 2.1-2.6 times greater adsorption of albumins compared to L-counterparts. This difference can be attributed to a distinct morphology of D-nanocapsules characterized by a more concave shape, central depression effect and rougher surface. The extent of adsorption could be finely tuned by adjusting the ratio of D- and L-lysine monomers during synthesis. Both chiral configurations demonstrated biocompatibility and stability, with D-nanocapsules showing a 2.5-fold increase in cellular internalization.

Nanocomposites Derived from Polymers and Inorganic Nanoparticles with Promising Applications

Junaid Ali [1,2], Noemi Gallucci [1,2], Alessandro Cangiano [1,2], Irene Russo Krauss [1,2], Alessandro Vergara [1], Gerardino D'Errico [1,2], Luigi Paduano [1,2]

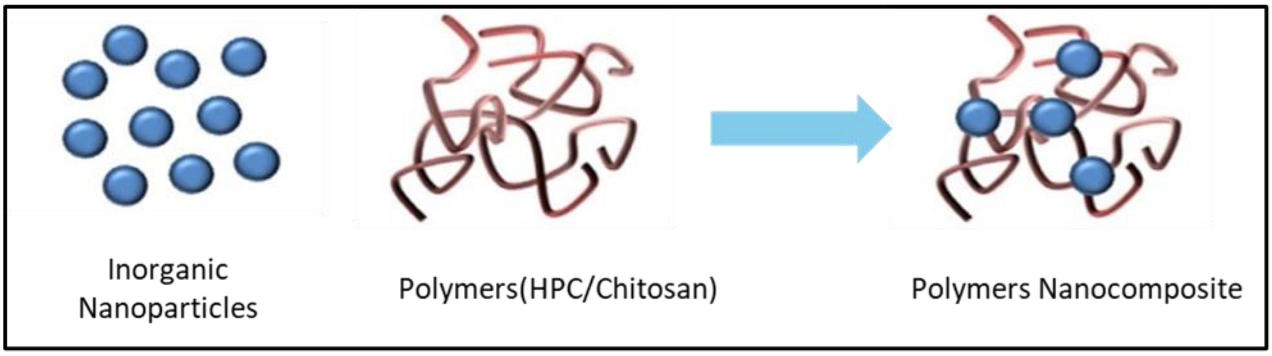
[1] *Department of Chemical Sciences, University of Naples Federico II, 80126 Naples, Italy*
[2]*CSGI, Centre for Colloid and Surface Science, Via della Lastruccia 3, Sesto Fiorentino, FI, Italy*[4]

junaid.ali@unina.it

The development of novel materials with superior properties and applications in diversified fields boost momentum towards modern-day science. The evolution of hybrid materials, resulting from the combination of polymers (HPC and Chitosan) with inorganic nanoparticles (such as ZnO and carbon dots) presents the captivating field of research. Because of its ability to be easily tailored, polymers are widely regarded as ideal host matrices for composite materials, providing a diverse array of bulk physical properties and possessing long-term stability and good processability while Inorganic nanoparticles possess outstanding optical, catalytic, electronic, and magnetic properties.

The nanocomposites derived by the combination of mechanical and biocompatibility properties of polymers with well-defined physico-chemical properties of inorganic nanoparticles (optical, thermal, electrical, and magnetic) display synergistically improved properties and potential capabilities for drug delivery, wound healing, tissue engineering, cancer treatment, and even food packaging.

Keywords: nanocomposites; polymers; inorganic nanoparticles



References

[1] Jeon, I. Y., & Baek, J. B. (2010). Nanocomposites are derived from polymers and inorganic nanoparticles. Materials, 3(6), 3654-3674.
[2] Das, D., Kar, T., & Das, P. K. (2012). Gel-nanocomposites: materials with promising applications. Soft Matter, 8(8), 2348-2365.
[3] Braun, P. V. (2003). Natural nanobiocomposites, biomimetic nanocomposites, and biologically inspired nanocomposites. Nanocomposite science and technology, 155-214.
[4] Sanchez, C., Julián, B., Belleville, P., & Popall, M. (2005). Applications of hybrid organic–inorganic nanocomposites. Journal of materials chemistry, 15(35-36), 3559-3592.

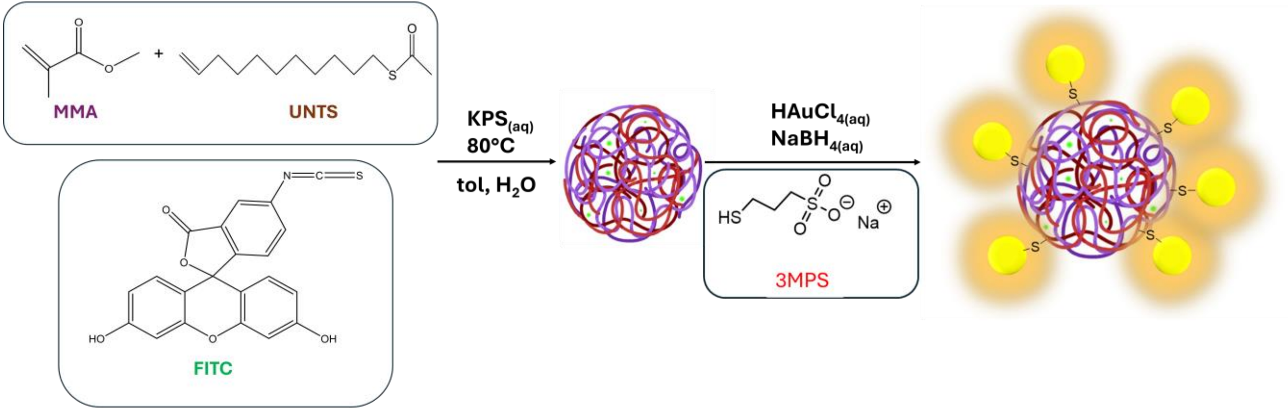
Synthesis and characterization of PNPs-AuNPs hybrids for drug delivery in nanomedicine

Eduardo Annibali*[1], Tommaso Salamone[1], Sara Cerra[1], Beatrice Pennacchi[1], Martina Mercurio[1], Ilaria Fratoddi[1]

[1] *Dipartimento di Chimica, Università di Roma La Sapienza, P. le A. Moro 5, 00185 Roma, Italy*

**annibali.1891546@studenti.uniroma1.it*

During the last years, noble metal and polymeric nanoparticles have been the object of a renewed academic interest, due to their optoelectronic properties, a very high surface to volume ratio and their excellent behaviour as nanocarriers of drugs, antibodies or other biologically active molecules [1, 2]. The aim of this work is to synthetize functionalized co-polymeric nanoparticles and characterize them to develop a biocompatible technology for drug delivery and theranostic uses. The first step is the synthesis of spherical co-polymeric nanoparticles (PNPs), starting from two monomers: MMA (methyl methacrylate) and UNTS (10-undecenyl-1-thioacetate), exploiting surfactant-free radical emulsion polymerization [2]. In addition, a fluorescent molecule, FITC (fluorescein isothiocyanate) is intercalated during the synthesis for optical imaging [2]. Monodispersity and a small diameter (up to a few hundreds of nanometers) are essential for their biological functions; in order to fine tune these properties, reaction time, solvent/co-solvent ratio, and monomers ratio must be controlled. Subsequently, the co-polymeric nanoparticles are decorated with gold nanoparticles, covalently linked by a S-bridge with UNTS exploiting an *in-situ* reduction of a gold precursor ($HAuCl_4$) with sodium borohydride, thus obtaining a multi-component nanostructured system suitable for biomedical applications. Gold nanoparticles in this system are further stabilized with a thiol ligand, 3MPS (sodium-3-mercapto-1-propanesulfunate) and can be loaded with diagnostic probes or biologically active drugs, which, together with the fluorescent dye in the PNPs, can give rise to a multimodal imaging or theranostic probe. The obtained systems are studied with UV-Vis, DLS, FT-IR, NMR, TEM and FESEM.



References

[1] Salamone T. A., Rutigliano L., Pennacchi B., Cerra S., Matassa R., Nottola S., Sciubba F., Battocchio C., Marsotto M., Del Giudice A., Chumakov A., Davydok A., Grigorian S., Canettieri G., Agostinelli E. and Fratoddi I., J. *Colloid Interface Sci*., 2023, 649, 264 —278.

[2] Cerra S.; Dini V.; Salamone T.A.; Hajareh Haghighi F.; Mercurio M.; Cartoni A.; Del Giudice A.; Marsotto M.; Venditti I.; Battocchio C.; et al. *Acrylates-Based Hydrophilic Co-Polymeric Nanobeads as Nanocarriers for Imaging Agents. Colloids Surf*. A Physicochem. Eng. Asp. 2023, 674, 131829.

Design and optimization of in-batch and in-flow syntheses of silica-based nanomaterials

Eleonora D’Alessandro[1*], Emanuele Limiti[1,2], Sara Maria Giannitelli[1], Alberto Rainer[2], Francesco Basoli[1], Marcella Trombetta[1]

[1]*Department of Science and Technology for Sustainable Development and One Health, Università Campus Bio-Medico di Roma, Roma, Italy*
[2]*Department of Engineering, Università Campus Bio-Medico di Roma, Roma, Italy*

*e.dalessandro@unicampus.it

Among the variety of nanomaterials, silica-based nanoparticles (SiO_2 NPs) are promising delivery systems for biomedical applications. To date, conventional NPs syntheses hinder the potential transposition of nanocarriers into clinical applications mainly due to low batch-to-batch reproducibility and limited scalability. Microfluidics has emerged as a potential tool for the in-flow production of NPs, providing platforms for highly reproducible syntheses [1,2]. The aim of the present work is the design of inorganic nanomaterials, i.e., mesoporous bioactive glass (MBG NPs) and SiO_2 NPs, through the optimization of in-batch and in-flow syntheses. MBG NPs were synthesized *via* traditional sol-gel reaction based on a hydrothermal approach, meanwhile the in-flow synthesis was performed in a microfluidic chip, conceived as sol-gel reaction device (Fig.1A and 1B). The resulting MBG and SiO_2 NPs were characterized in terms of size, polydispersity index and morphology through dynamic light scattering, transmission and scanning electron microscopy (TEM and SEM). The obtained MBG NPs showed a size distribution below 200 nm, with good polydispersity index (PDI=0.2), and the presence of a porous structure, which is a desirable feature for nanomaterials in clinical and biomedical applications. In contrast, the fluidically formulated SiO_2 NPs were found to be of a larger dimension (size>1 µm) but with a narrower size distribution and with a smooth shape. In conclusion, the tested processes ensured the production of silica-based nanomaterials with favorable characteristics, in terms of size and PDI. Moreover, the microfluidic approach has demonstrated great potential due to its ease of control and versatility in the implementation of different synthesis conditions, which give great expectations for its future development as one of the leading technologies in the production of bio-nanomaterials.

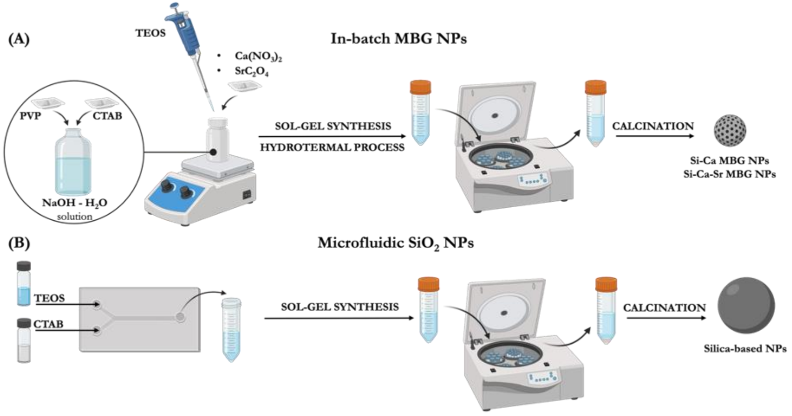


Fig. 1: (A) Experimental set-up of MBG NPs *via* traditional sol-gel reaction based on a hydrothermal approach; (B) Experimental set-up of SiO_2 NPs obtained through microfluidic sol-gel reaction device.

Acknowledgements: This work is funded by the European Union - Next Generation EU - NRRP M4.C2 - Investment 1.5 Establishing and strengthening of Innovation Ecosystems for sustainability (Project n. ECS00000024 Rome Technopole).

References

[1] Deshmukh K., et al., *RSC advances*, 2020, **10**, 33782-33835.
[2] Hao N., et al., *Biomaterials science*, 2019, **7**, 2218-2240.

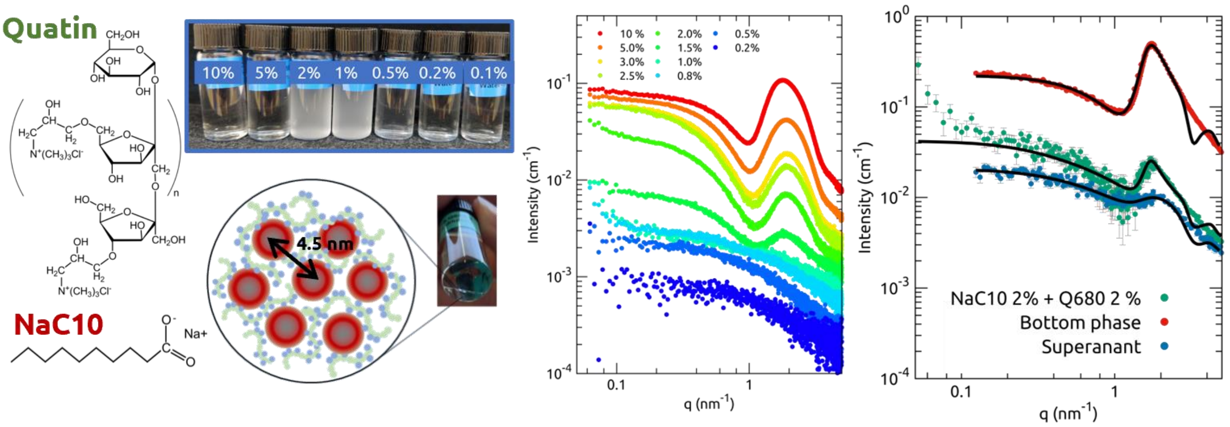
Complex coacervation between sodium decanoate and cationic inulin: towards a structural understanding of more sustainable surfactant and polymer mixtures

A. Del Giudice,[1] M. Gubitosi,[2] T. Nylander,[3] T. Halthur[2]

[1] *Department of Chemistry, Sapienza University of Rome, Rome, Italy*
[2] *CR Competence AB, Lund, Sweden*
[3] *Division of Physical Chemistry, Lund University, Lund, Sweden*

**alessandra.delgiudice@uniroma1.it*

Oppositely charged polymer-surfactant systems are expected to interact to form coacervate complexes near charge neutrality composition. Such behavior has applications in formulated products where the deposition or encapsulation of target substances can be triggered by dilution.[1] A transition towards the study and the use of more sustainable and potentially edible ingredients is occurring. However, they often show more complex bulk and interfacial properties: e.g. pH-, counterion-, temperature- dependence for fatty acid salts, and less controlled chemical composition for bio-based polymers. We studied as a model system mixtures of sodium decanoate (NaC10) and hydroxypropyl trimonium inulin, a fructan with varying degree of cationic substitution ("Quatin") and found that the formation of coacervates occurs when the surfactant concentration approaches the cmc (3-1 wt%), as seen by instantaneous turbidity development and eventual separation of a denser liquid phase. The mixtures were characterized by bulk DLS and SAXS to estimate size and internal structure of the aggregates present at different nominal composition. For high surfactant concentration Quatin seems partially embedded in the micelles' shell, coacervate samples showed an enhanced contribution from micelles clustered within concentrated droplets that eventually macro-phase-separate, while below a threshold surfactant concentration only the oligosaccharide scattering can be seen. Variability observed between direct preparation, bulk and in-situ dilution experiments suggested dependence on the mixing protocol and container, characteristic of kinetically trapped systems.[2]



Acknowledgements: Vinnova – Swedish Governmental Agency for Innovation Systems (Proposal 2021-03835), BM29 (ESRF experiment MX2464) INTER (ISIS Neutron and Muon Source, experiment RB2220526), PON Research and Innovation 2014–2020 DM1062/2021 RTD-A contract 26-G-15245-1.

References

[1] Lindman B., Antunes F., Aidarova S., Miguel M., Nylander T., *Colloid Journal*, 2014, **76**(5), 585.
[2] Del Giudice, A.; Gubitosi, M.; Sthoer, A.; Köhler, S.; Ayscough, S.; Skoda, M. W. A.; Nylander, T.; Halthur, T. Colloids Surfaces A Physicochem. Eng. Asp. 2024, 134365. https://doi.org/10.1016/J.COLSURFA.2024.134365.

Metal Organic Frameworks: platforms for photonic up-conversion

Tommaso Gentili[1*], Valerio La Gambina[1], Francesco Amato[1], Andrea Giacomo Marrani[1],
Alessandro Latini[1], Luciano Galantini[1], Maria Chiara di Gregorio[1]

[1]*Department of Chemistry, Sapienza University, P.le A. Moro 5, 00185, Rome, Italy*

**gentili.1842930@studenti.uniroma1.it*

Metal-Organic Frameworks (MOFs) are crystals forming from the self-assembly of organic molecules and metal ions through coordination bonds. Known for about 25 years, these structures have largely dominated the scene of modern materials chemistry due to their high porosity and the resulting applications (e.g. gas storage, catalysis, etc.).

The combination of erbium and ytterbium ions is known in the literature to give up-conversion phenomena when inserted into inorganic crystalline structures. However, the use of MOFs as supporting platforms for this phenomenon is largely unexplored; the very first studies appeared only in very recent years [1, 2].

Here, we report the synthesis of new MOFs using as building blocks 1,2,3,4-butanetetracarboxylic acid, erbium and ytterbium salts. Thanks to the presence of lanthanides nodes, these MOFs are able to emit higher energy photons in the visible upon irradiation by an IR laser ($\lambda = 980$ nm). Different synthesis parameters of MOFs have been explored to obtain different structures and tune the emissions thereof (Figure).

Furthermore, it was observed that the synthesized MOFs show a strong tendency to evolve over time if left in the reaction solution. Through various microscopy and spectroscopy techniques, we attempted to obtain information on the crystal growth mechanism, highlighting non-classical crystallization mechanisms (e.g. fusion processes).

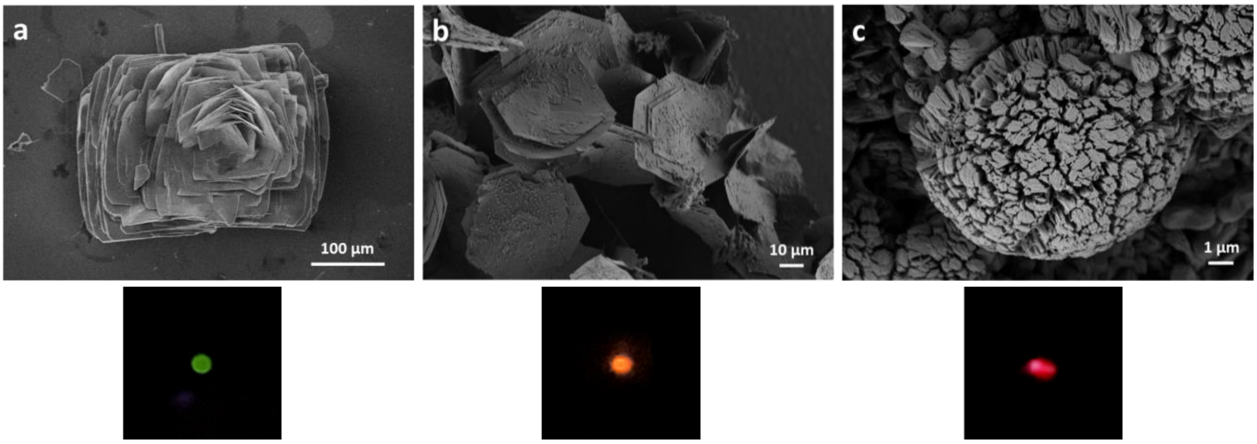


Figure. Scanning Electron Microscopy images of the synthesized MOFs (top) and emitting MOF powders under irradiation at 980 nm (bottom)

References

[1] Xie Y.; Sun G.; Li J.; Sun R.; Sun L., Er^{3+}-Sensitized Upconversion/Down-Shifting Luminescence in Metal−Organic Frameworks. J. Phys. Chem. Lett., 2023, 14, 10624−10629.

[2] Xie Y.; Sun G.; Li J.; Sun L., Multimode Emission from Lanthanide-Based Metal-Organic Frameworks for Advanced Information Encryption. Adv. Funct. Mater, 2023, 33, 2303663.

Characterization of sodium deoxycholate and poly-L-lysine catanionic mixtures

Angelica Mallamo[1*], Benedetta Brugnoli[1], Giacomo Di Matteo[2], Luisa Mannina[2], Alessandra Del Giudice[1], Anita Scipioni[1], Iolanda Francolini[1] Luciano Galantini[1]

[1]Department of Chemistry, Sapienza University of Rome, Rome, Italy
[2]Department of Chemistry and Technology of Drugs, Sapienza University of Rome, Rome, Italy

** mallamo.1809485@studenti.uniroma1.it*

High cholesterol levels, or hypercholesterolemia, is a major risk factor for heart disease. Liver plays a key role in managing cholesterol by converting it into bile acids (Bas), which act as detergents due to their amphiphilicity, helping to break down fats in human digestive system. Lately, polymeric BA sequestrants (BASs) have been proposed as potential drugs to manage hypercholesterolemia or dyslipidemia [1-3]. The basic requirements for polymeric BASs include suitable swelling properties in the intestine and appropriate density of cationic charges providing enhanced BA sequestration.

In this study, the interaction of a bile salt, sodium deoxycholate (NaDC), with a cationic polypeptide, poly-L-lysine (PLL), was studied. Catanionic mixtures at different NaDC/PLL charge ratios (CR), from 0 to 4, were prepared and the influence of CR on PLL self-assembly in water was investigated by using a combined approach of different complementary techniques, including dynamic light scattering (DLS), circular dichroism (CD), turbidimetry, nuclear magnetic resonance (^{1}H-NMR) and small angle X-ray (SAXS).

Results confirmed the interactions between PLL and NaDC. Upon the addition of NaDC, the PLL/NaDC mixture became opalescent at a charge ratio as low as 0.3. This opalescence was accompanied by a significant decrease in transmittance. Further increasing the CR to values above 0.75 resulted in the precipitation of the catanionic complex. DLS analysis showed that the PLL/NaDC interaction initially reduced the size of PLL, forming nanoaggregates approximately 200 nm in diameter. The size of these aggregates increased at CR values greater than 1. Additionally, the zeta potential shifted from positive values for pure PLL to negative values for the PLL/NaDC mixture. Circular Dichroism (CD) analysis revealed no change in the random coil conformation of PLL, but a decrease in the intensity of the characteristic band at 197 nm, indicating that PLL was sequestered from the solution by NaDC interaction. These findings suggest that PLL and, more broadly, cationic peptides could serve as BA sequestrants, with potential applications in designing functional foods to reduce cholester levels. Moreover, the PLL/NaDC catanionic complexes could be used as systems for encapsulating or delivering nutrients in food products.

Acknowledgements: Project funded under the National Recovery and Resilience Plan (NRRP), Mission 4 Component 2 Investment 1.3 - Call for tender No. 341 of 15 March 2022 of Italian Ministry of University and Research funded by the European Union – NextGenerationEU. Project code PE00000003, Concession Decree No. 1550 of 11 October 2022 adopted by the Italian Ministry of University and Research, CUP D93C22000890001, Project title “ON Foods - Research and innovation network on food and nutrition Sustainability, Safety and Security – Working ONFoods”.

References

[1] Islam M.S., Sharif A., Kwan N., Tam K.C. *Mol Pharm.* 2022,**19(5)**,1248.
[2] Heřmánková E., Žák A., Poláková L., Hobzová R., Hromádka R., Širc J. *Eur J Med Chem.* 2018, **144**, 300.
[3] Bellesi F.A., Pilosof A.M.R. *Food Hydrocoll.* 2021, **118**, 106766
[4] Lopez-Pena C., Arroyo-Maya IJ, McClements DJ, *Food Hydrocolloids,* 2019, **87,** 352-259.

Novel liposome-based multicomponent systems for gene and drug delivery

Giorgio Mandato[1*], Nadia Felli[2], Federica Felicetti[2] , Michela Flego[2], Roya Binaymotlagh[1], Laura Chroopoulou[1,3] and Cleofe Palocci[1,3]

[1]Department of Chemestry, University of Rome La Sapienza, Rome, Italy
[2]National Center for Global Health, Istituto Superiore di Sanità, Viale Regina Elena 299, 00161 Rome, Italy.
[3]Research Center for Applied Sciences to the safeguard of Environment and Cultural Heritage (CIABC)
**Giorgio.mandato@uniroma1.it*

The role that nanobiotechnology plays in the pharmaceutical field is expanding. These are not just technologies that exploit basic biological processes and new technologies for the production of innovative materials but they also contribute to the development of novel drugs for the treatment of various diseases, including those with a genetic basis. These innovative approaches are leading to the emergence of new models of personalized medicine in order to obtain more effective drugs and sometimes aimed at the treatment of a specific population, if not of individual patients.

As well known melanoma is a tumor with high metastatic potential if not diagnosed early [1]. In recent years, microRNAs have taken on an increasingly important role in the panorama of cancer therapies. In this context, our group has demonstrated a tumor-suppressive role of microRNA-126 (miR126) in advanced and therapy-resistant melanoma [2]. On this basis, we considered it of great scientific interest and potential application in therapy to study a system that will allow us to directly and specifically deliver miR126 into target cells, while at the same time allowing us to protect this RNA oligo from enzyme-induced degradation. To this aim, different phospholipids, all approved by the FDA, were selected for the production of liposomes with high stability and high encapsulation efficiency. A microfluidic system was used to produce the liposomes, that will be functionalized with an antibody specific for the melanoma marker chondroitin sulfate proteoglycan 4 (CSPG4). After *in vitro* evaluations, the efficacy of this treatment will be assessed through an *in vivo* experiment using mice bearing resistant human melanoma.

References

[1] Situm, M., Buljan, M., Kolic, M., and Vucic, M. (2014). Melanoma--clinical, dermatoscopical, 668 and histopathological morphological characteristics. Acta Dermatovenerol Croat 22, 1-12.
[2]Arasi M.B., De Luca G., Chronopoulou L., Pedini F., Petrucci E., Flego M. et al., *Molecular Therapy* 2024, **32**,

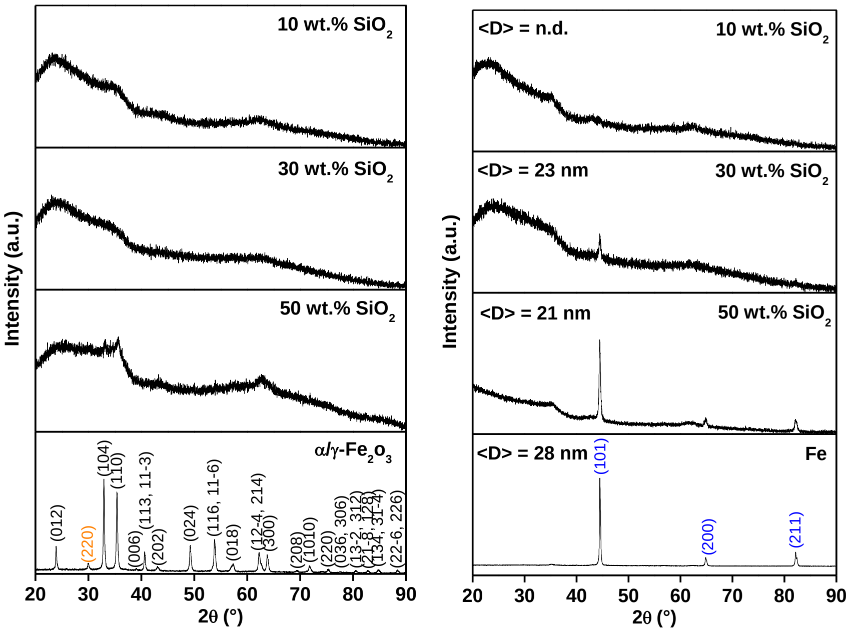
Synthesis of Fe nanoparticles in silica matrix

Jean Pierre Miranda Murillo[1*], Pierfrancesco Maltoni[1] and Davide Peddis[1-2]

[1]Department of Chemistry and Industrial Chemistry, University of Genova, Via Dodecaneso 31, 16164 Genova, Italy & UdR INSTM Genova, Italy
[2]Institute of Structure of Matter, National Research Council, Nm2-LAB, Research Area Roma 1, Monterotondo Scalo, Roma, 00015 Italy

**Jeanpierre.mirandamurillo@edu.unige.it*

Magnetic nanoparticles (MNPs) are promising for applications in various fields of nanotechnology, such as medicine, catalysis and permanent magnets, owing to the enhanced magnetic properties below specific critical sizes at the nanoscale[1]. Magnetic properties are size-dependent, and strictly correlated to the crystal structure, and, in turn, the magnetic moment generated by each atom in specific sites of the cell[2]. This configuration becomes rather complex when the size of the material approaches a critical diameter (D_c), below which the transition from multi- to mono-domain occurs for the nanoparticles[2]. This work focuses on the synthesis of Fe MNPs, with a size approaching the D_c (i.e., ~20 nm)[2], embedded in a SiO_2 matrix at different metal wt.% (41, 23 and 7.2). The MNPs are the result of a self-combustion sol-gel synthesis followed by annealing in a controlled H_2/N_2 atmosphere: the powder diffraction patterns confirm the expected single-phase Fe NPs with a $Im\bar{3}m$ spacegroup for all the samples (a ~ 2.9 Å) with an average crystallite size of ~20 nm.



XRPD pattern of the samples obtained from the self-combustion sol-gel (left) and after double annealing (500°C, 1h, air + 500°C, 1h, H_2/N_2). The miller index of the α-Fe_2O_3 ($R\bar{3}c$), γ-Fe_2O_3 ($Fd\bar{3}m$) and Fe ($Im\bar{3}m$) phase are reported in black, orange and blue, respectively.

References

[1] D. L. Huber. *Small*, 2005, **1**, 482.
[2] J. M. D. Coey, Magnetism and Magnetic Material, 2010, 633, Cambridge University Press, Cambridge, United Kingdom.

Synthesis and characterisation of gold nanoparticles stabilised by organic and organometallic thiols

Sarah Pavin[1*], B. Pennacchi[1], S. Cerra[1], T. A. Salamone[1], M. Mercurio[1], I. Fratoddi[1]

[1] *Dipartimento di Chimica, Sapienza University, P.le A. Moro 5, 00185 Rome, Italy*

**pavin.1864020@studenti.uniroma1.it*

Nanomaterials and nanocomposites, with their multiple applications, have been centre of much attention during the last years of research [1,2]. Among the variety of organic compounds, fluorene (9,9-didodecyl-2,7-dibromofluorene) and their organometallic thiol derivates are of interest due to the presence of extended π-conjugation, optical properties, and charge transfer mechanisms due to the presence of heteroatoms [3,4]. These characteristics make them a good choice to functionalise metal nanoparticles to obtain interconnected nanoparticles network. The aim of this work is to optimise the synthesis of functionalised gold nanoparticles (AuNPs) stabilised by commercial thiol ligands, such as 1-dodecanethiol (DDT), 4-bromobenzenethiol (4BBT), synthetic bifunctional 9,9-didodecyl-2,7-bis(acetylthio)fluorene (FL), and related platinum(II)-containing derivatives (using FL and 4,4'-diethynylbiphenyl, DEBP as rigid spacers). Such kind of stabilising agents will be used in mixture to obtain both single (DDT/4BBT pair), and interconnected AuNPs networks (DDT/FL, DDT/Pt-FL, DDT/Pt-DEBP pairs), stable in organic media (**Figure 1**). Extensive characterisation of thiol-stabilised AuNPs will be carried out by UV-Vis and FTIR spectroscopy, Dynamic Light Scattering (DLS), Field Emission Scanning Electron Microscopy (FESEM), ^{1}H and ^{31}P Nuclear Magnetic Resonance (NMR), and X-Ray Photoelectron Spectroscopy (XPS). Then, AuNPs/P3HT (poly-3-hexylthiophene-2,5-diyl) blends will be obtained in different AuNPs/P3HT weight ratios to study their electrical properties and exploit potential applications in various fields, such as optoelectronics, catalysis, and sensing.

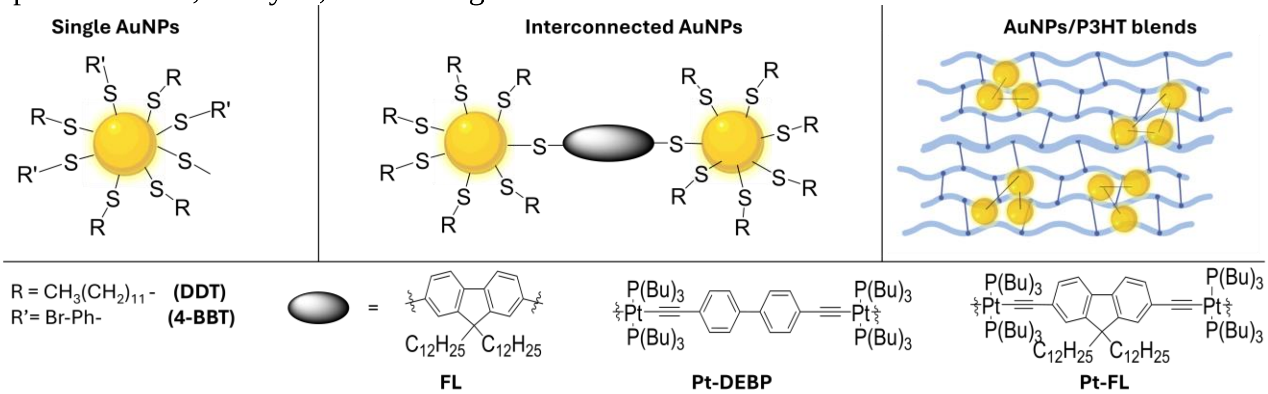


Figure 1. AuNPs functionalised with thiol ligands used in this work.

References

[1] Ghobashy M. M., Alkhursani Sh. A., Alqahtani Haifa A., El-damhougy T. K., Madani M., *Mater. Sci. Eng. B.*, 2024, **301**, 117191

[2] Dai J., Ashrafizadeh M., Aref A. R., Sethi G., Y. N. Ertas, *Drug Discov. Today*, 2024, 103981,

[3] S. Grigorian, Fontana L., Cerra S., Pietsch U., Scaramuzzo F. A., Fratoddi I., *Synth. Met.*, 2022, **283**, 116973

[4] Cerra S., Fontana L., Rossi E., Bassetti M., Battocchio C., Venditti I., Carlini L., Matassa R., Familiari G., Fratoddi I., *Inorg. Chim. Acta*, 2021, **516**, 120170

Layered double hydroxides synthesised by coordination chemistry of citric acid

Marco Piccinni[1,2*], Christian Rossi[1], Marco Fortunato[1], Anna Maria Cardinale[1], Francesco Bonaccorso[2,4], Diego Colombara[1,2]

[1]Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Genova, via Dodecaneso 31, 16146 Genoa, Italy.
[2]Istituto Italiano di Tecnologia, Graphene Labs, via Morego 30, 16163 Genoa, Italy.
[3]Institute of Condensed Matter Chemistry and Technologies for Energy, CNR, Via de Marini 6, 16149 Genoa, Italy.
[4]BeDimensional Spa., via Lungotorrente Secca 30R, 16163 Genoa, Italy.

**marco.piccinni@edu.unige.it*

Layered double hydroxides (LDHs) are a class of two-dimensional materials that find many applications (*e.g.*, catalysis, concrete additives, energy storage) since the last century [1]. Nowadays, nanostructured LDHs are mainly obtained as inks by liquid phase exfoliation [2] of their bulk counterpart in formamide [3]. Here, we propose a green, aqueous-based, synthetic route to produce nanostructured NiAl, NiFe and ZnAl-LDHs intercalated with citrate anions. The coordination chemistry-based mechanism of LDH formation is supported by pH-potentiometric titrations and electronic spectroscopy. The layered morphology of citrate intercalated LDHs is partially retained after pyrolysis, yielding metallic alloy nanosheets for future applications in catalysis.

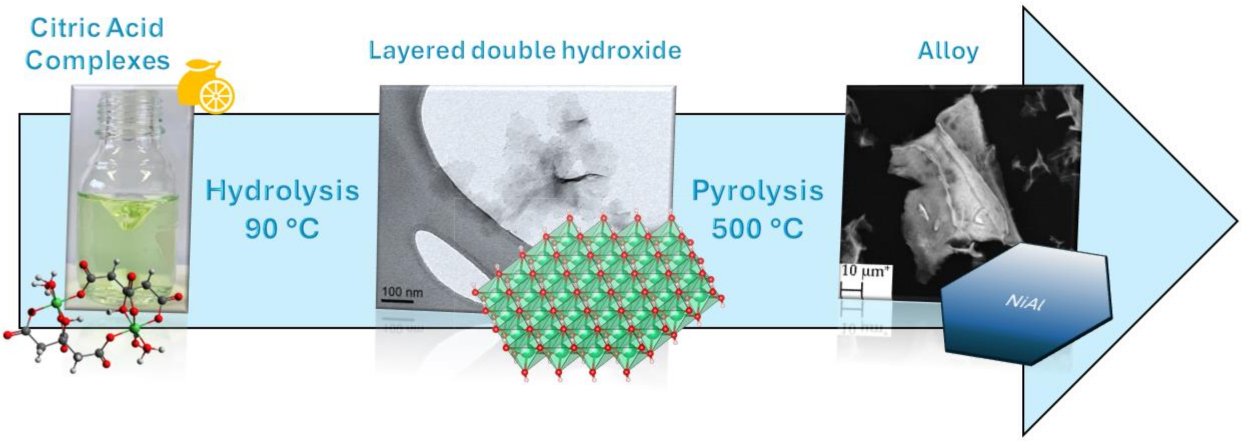


Figure 1. Synthetic procedure of LDHs nanosheets and related alloys.

Acknowledgements:

Part of this research was enabled by the University of Genova and Compagnia di San Paolo through the Curiosity Driven and Promoting Competitiveness schemes.

References

[1] Cavani F., Trifirò F., Vaccari A. *Catalysis Today*, 1991, **11**, 2, 173-301.
[2] Bonaccorso F., Bartolotta A., Coleman J.N., Backes C. *Advanced Materials*, 2016, **28**, 29, 6136-6166.
[3] Wang Q., O'Hare D. *Chemical Reviews*, 2012, **112**, 7, 4124-4155.

Peptide-based Magnetogels for the Removal of Organic Dyes from Water

Pintilei Paula Stefana[1*], Farid Hajareh Haghighi[1], Roya Binaymotlagh[1], Laura Chronopoulou[1,2] and Cleofe Palocci[1,2]

[1]Department of Chemistry, Sapienza University of Rome, Piazzale Aldo Moro 5, 00185, Rome, Italy;
[2]Research Center for Applied Sciences to the Safeguard of Environment and Cultural Heritage (CIABC)
Sapienza University of Rome, Piazzale Aldo Moro 5, 00185, Rome, Italy

* *pintilei.1794298@studenti.uniroma1.it*

As well known, water pollution by organic dyes is a major environmental concern, threatening both human and animal health. The disposal and/or treatment of these wastes generally require expensive and complex processes to implement. For this reason, scientific research is exploring new low-cost absorbent materials, simple to synthesize and easy to use. We have prepared magnetogels combining peptide hydrogels, made of short self-assembling peptides, and Fe_2O_3-based magnetic nanoparticles (γ-Fe_2O_3NPs) [1]. The ability of different hydrogel preparations to remove model dyes (Methylene Blue (MB), Rhodamine 6G (Rh6G) and Methyl Orange (MO)) was investigated in the presence and in the absence of an external magnetic field, by calculating the percentage of removal effectiveness (RE%) for each system. As part of this study, two experimental set-ups: a "static" one and a "dynamic" one were developed. Overall, the magnetogels demonstrated good adsorbent ability towards the selected synthetic dyes under the experimental conditions used. The magnetogels used in dynamic experimental set-ups, as expected, were overall more effective because of the interaction with the whole gel volume, compared with the interfacial interaction of the static set-up.

References

[1] F Hajareh Haghighi, R Binaymotlagh, PS Pintilei, L Chronopoulou, C Palocci. Preparation of Peptide-Based Magnetogels for Removing Organic Dyes from Water. Gels 2024, 10 (5), 287

Gold nanoparticles: from asymmetric shape to chirality

Marco Ranaldi[1*], D. Lipani[1], M. Parisi[1], I. Gianani[1], M. Barbieri[1], G. Iucci[1], S. Amatori[1], F. Bertelà[1], C, Battocchio[1], A. Palma[2], S. Grande[2], I. Venditti[1].

[1]Science Department, Roma Tre University, Via della Vasca navale 79, 446, Rome (IT)
[2]National Center for Innovative Technologies in Public Health, Istituto Superiore di Sanità, Rome 00161

**marco.ranaldi@uniroma3.it*

Gold nanoparticles (AuNPs) are nanomaterials showing unique chemical and physical properties which differ from their bulk state due to quantum effects. One of the most peculiar properties of AuNPs is the localized surface plasmon resonance phenomenon (LSPR) which allows their use in optoelectronics, sensing and imaging [1,2]. The possibility of differentiated surface functionalization allows, at the nanostructure, to obtain additional optical properties, due to the presence of capping agent, e.g. chiral or fluorescent molecules. Some studies have described the transfer of molecular chirality in micrometer-sized helical ceramic crystals, this technique has yet to be implemented for metal nanoparticles with dimensions of tens or hundreds of nanometers [3]. This work focus on the synthesis and characterization of AuNPs with different shape: spheres (symmetric), rods (asymmetric) and chiral (helicoid) using a chiral molecule as capping agent, the L-Cysteine. Spectroscopic characterizations were carried out using UV-Vis, FT-IR, X-ray photoelectron spectroscopy (XPS), circular dichroism (CD) and ^{1}H NMR, verifying the functionalization of the gold surface. Furthermore, Dynamic Light Scattering and ζ-potential studies confirmed the colloidal stability in aqueous solution. These preliminary studies encourage the use of these systems in the field of chirality-based optical biosensors.

Acknowledgements: The Grant of Excellence Departments 2023–2027, MIUR (ARTICOLO 1, COMMI 314–337 LEGGE 232/2016), and Rome Technopole Project (CUP:F83B22000040006) are gratefully acknowledged by authors of Roma Tre University.

References

[1] S. Grigorian, L. Fontana, S. Cerra, U. Pietsch, F. A. Scaramuzzo, and I. Fratoddi, *Synth. Met.*, 2022, **273**, 116973.
[2] I. Venditti, G. Iucci, I. Fratoddi, M. Cipolletti, E. Montalesi, M. Marino, V. Secchi, and C. Battocchio, *Nanomaterials*, 2020, **10**, 1898.
[3] H. E. Lee, R. M. Kim, H.Y. Ahn, Y. Y. Lee, G. H. Byun, S. W. Im, J. Mun, J. Rho and K. T. Nam, *Nat. Comun*, 2020, **11**, 263.

Graphene Oxide: A Versatile Material for Biomedical Applications

Teresa Varelli[1*], Leonardo Giaccari[1], Francesco Amato[1], Alessandro Motta[1], Andrea Giacomo Marrani[1]

[1] *Department of Chemistry, Sapienza University of Rome, Rome, Italy*

**varelli.1798494@studenti.uniroma1.it*

Graphene Oxide (GO) is the oxidized form of graphene. It's a bidimensional nanomaterial constituted of oxygen-rich regions and graphitic networks. This material exhibits excellent properties, including electrical and thermal conductivity, mechanical strength, and general versatility. These properties can be further enhanced by functionalizing the compound. Indeed, GO can be easily functionalized through both non-covalent and covalent approaches, exploiting π-π stacking interactions and the reactivity of its oxygen functional groups, respectively[1]. Additionally, oxygenated functional groups (OFGs), such as epoxides and hydroxyls within the basal plane, and carbonyls, phenols, and carboxyls at the edges and defect sites, allow for diverse functionalization strategies[2]. OFGs are abundantly obtained through the modified Hummers method for synthesis. This study focuses on non-covalent interactions that open intriguing research prospects for biomedical applications. Our work specifically aims to establish a chemical coupling between GO and laminin, a crucial glycoprotein in the extracellular matrix, contributing to the structure and function of tissues[3], through a multi-step functionalization process. Each step is meticulously characterized using various spectroscopic techniques, including circular dichroism, UV-Vis spectroscopy, X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and cyclic voltammetry. The resulting compound is expected to possess properties suitable for coating biomedical devices, such as sensors, implants, or tissue regeneration scaffolds, enabling chiral selectivity as an additional advantageous feature. In summary, GO's unique features and facile functionalization make it a promising candidate for advancing biomedical applications.

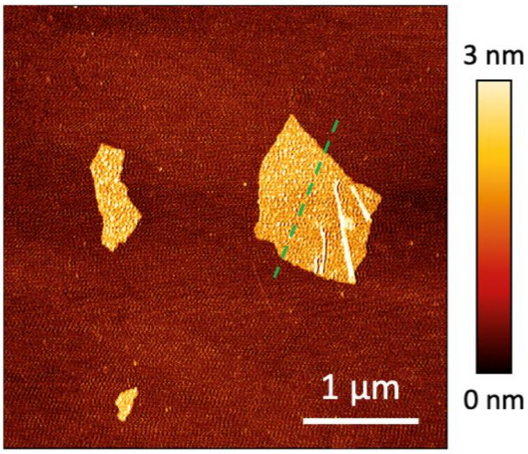


Figure 17: AFM image of a single layer of GO.

References

[1] Georgakilas V., Tiwari J. N., Kemp K. C., Perman J. A., Bourlinos A. B., Kim K. S., Zboril R. *Chem. Rev*., 2016, **116**, 5464−5519.
[2] Guo S., Garaj S., Bianco A., Ménard-Moyon C. *Nat. Rev. Phys*., 2022, **4**, 247-262.
[3] Durbeej M. *Cell Tissue Res*, 2010, **339**, 259–268.

Theme G - Energy, Environment and Sustainability

Oil extracted from tomato pomace as feedstock for sustainable PHA production

Francisco Santos[1,2*], Cristiana Torres[1,2], Anouk F. Duque[1,2], Filomena Freitas[1,2], Maria Reis[1,2]

[1] *i4HB, Institute for Health and Bioeconomy, School of Science and Technology, NOVA University Lisbon, Caparica, 2829-516, Portugal*
[2] *UCIBIO—Applied Molecular Biosciences Unit, Department of Chemistry, School of Science and Technology, NOVA University Lisbon, Caparica, 2829-516, Portugal*
**fra.santos@campus.fct.unl.pt*

Polyhydroxyalkanoates (PHAs) are biodegradable aliphatic polyesters produced via microbial cultivation, increasingly recognized as sustainable alternatives to petroleum-based plastics. These biopolymers exhibit a diverse range of mechanical properties, from brittle and rigid thermoplastics to flexible elastomers, making them suitable for a wide range of applications including packaging and medical devices [1, 2]. However, the commercial viability of PHAs is limited by their high production costs compared to traditional, non-biodegradable plastics, which primarily stem from the expenses associated with the fermentation substrates, accounting for up to 50% of production costs [3]. As such, an emerging solution is the utilization of low-cost substrates such as agricultural wastes [2]. Tomato pomace (TP), a byproduct of the tomato processing industry, comprising skins, seeds, and a small amount of residual pulp, represents a significant annual global waste stream, estimated at 5.4–9.0 million tonnes [4]. Its abundant availability and low cost make it an excellent candidate for sustainable PHA production. This study reports the feasibility of using oil extracted from TP as a novel substrate for PHA synthesis.

Herein, TP oil was utilized as the sole feedstock to produce PHAs. Ten different bacterial strains were screened and the highest polymer content in the biomass was obtained for *Cupriavidus necator* DSM 428 (73.4 ± 2.2 wt.%) and *Burkloderia thailandensis* E264 (72.5 ± 4.9 wt.%), both producing a homopolymer of poly(3-hydroxybutyrate) (PHB). Additionally, *Pseudomonas resinovorans* NRRL B-2649 produced a medium-chain-length PHA, mainly composed of hydroxyoctanoate and hydroxydecanoate, reaching a polymer content of 42.0 ± 2.4 wt.%. *C. necator* was also tested in a 2 L scale bioreactor (Bionet F1, Spain) setting, achieving an impressive accumulation of 79.3 ± 4.9 wt.% PHB on a total cell dry weight of 6.49 g/L, underscoring the efficacy of TP oil in supporting high PHA yields. Overall, this study shows, for the first time, that TP oil is a suitable substrate for PHA production since it sustains high polymer yields and allows for the synthesis of different PHAs by selection of the adequate strains. Furthermore, the utilization of TP oil enhances environmental sustainability of PHA production and contributes to advancing circular bioeconomy strategies by transforming a low-value waste into high-value biodegradable plastics.

Acknowledgements:

This project has received funding from the European Union’s Horizon Europe research and innovation programme under the grant agreement No. 101081776, the UK Research and Innovation (UKRI) fund under the UK government’s Horizon Europe funding guarantee, the Swiss State Secretariat for Education, Research and Innovation (SERI) and from the National Key Research and Development Program of China (NKRDPC). Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of neither of the aforementioned Funding authorities. Neither the European Union, the United Kingdom, the Swiss Confederation or the People’s Republic of China nor the European Commission, UKRI, SERI or NKRDPC can be held responsible for them.

References

[1] M. V. Cruz *et al.*, *New Biotechnology*, vol. 33, no. 1, pp. 206–215, 2016, doi: 10.1016/j.nbt.2015.05.005.
[2] P. Zytner, D. Kumar, A. Elsayed, A. Mohanty, B. V. Ramarao, and M. Misra, *RSC Sustainability*, vol. 1, no. 9, pp. 2120–2134, 2023, doi: 10.1039/D3SU00126A.
[3] R. G. Saratale, S. Cho, G. D. Saratale, A. A. Kadam, G. S. Ghodake, M. Kumar, R. N. Bharagava, G. Kumar, D. S. Kim, S. I. Mulla, H. S. Shin. Bioresource Technology, vol 325, 124685, 2021.
[4] Z. Lu, J. Wang, R. Gao, F. Ye, and G. Zhao, *Trends in Food Science & Technology*, vol. 86, pp. 172–187, Apr. 2019, doi: 10.1016/j.tifs.2019.02.020.

Recovery of Ethylene Vinyl Acetate from end-of-life photovoltaic panels by a solvent/non solvent system

David Albano[1*], Loris Petrelli[2], Iolanda Francolini[1], Antonella Piozzi[1]

[1]*Department of Chemistry, Sapienza University of Rome, Italy*
[2]*Legambiente, Via Salaria 403, Rome, Italy*

**david.albano@uniroma1.it*

Photovoltaic technology plays a fundamental role in the production of clean energy as it is one of the most mature and widespread technologies for electricity production from solar energy [1]. In the coming decades, a significant increase in installed PV capacity is expected due to the growing energy demand. The recovery and reuse of materials (glass, silicon, metals) and polymers from end-of-life photovoltaic panels (EoLPV) is very important to reduce the use of resources that are running out or the use of these materials in other production chains. Generally, PV modules consist of about 70-75% glass, 10% Al (chassis), 7% of encapsulant (EVA polymer film), 4% Tedlar (conductive backsheet), 4% silicon cells Cu and other components. By shredding the panel, it is possible to obtain the screening separation between the glass powder and the other materials. The plastics are quite difficult to recover due to the presence of the metal components. In this work, the Nike s.r.l industrial process concerning the recycling of end-of-life photovoltaic panels was studied and improved. Particular attention was paid to recovery of EVA polymer present into the EoLPVs. The process involved manual removal of the junction box and cables (2% by weight of PV) and frame removal by a framing machine and a blade crusher to obtain the aluminium fraction (about 9%). Then, the photovoltaic panels were subjected to a new mechanical operation, which allowed the selective removal of the backsheet, the obtaining of a glass with a light layer of Ethylene-Vinyl Acetate (EVA, 73.9% wt) and a powder composed of EVA, cells and electrical contacts (10% wt). A tumbling machine was used to remove the EVA layer from the glass, thus obtaining high-quality pure glass (73 % by weight). Hence, the crushed material containing EVA, cells and metals was sieved (< 1 mm) to separate the electrical contacts (0.4% wt) from the rest of the fraction. This fraction consisted of 5.8% of EVA and 3.8% of Si and metals used in the cell (Al, Ag, Zn, Pb, Sn, Cu, Fe). Finally, the solvent/non solvent system (dissolution/reprecipitation method) was used to recover EVA from the powder fraction. Different solvents (2-ethylhexyl acetate, cyclohexane, heptane, hexane), recovery times and temperatures were used. The experimental results showed that there were no relevant differences in polymer recovery using the chosen solvents. Therefore, 2-ethylhexyl acetate was selected due to its high GSK score (7.4). Finally, to precipitate EVA ethanol was used (2% wt), subsequently recovered by distillation [2,3].

References

[1] Sajan P., Stefan Thor S., *Journal of Cleaner Production*, 2024, 448, 141661
[2] Rubino A., Pier Giorgio S., Pietro A., Francesca P., *Waste Management*, 2021, 122, 89-99
[3] Dina Magdy A., Teresa M., Franco M., Luigi P., *Processes*, 2023, 11, 1848

Novel hybrid composites containing lignin and polysiloxane derivatives

Yana Aleeva[1*], Elena Piacenza[1], Delia Francesca Chillura Martino[1]

[1]Department of Biological, Chemical and Pharmaceutical Sciences and Technologies, University of Palermo, Palermo, Italy

**yana.aleeva@unipa.it*

Recent rise of a circular bioeconomy requires innovation in technologies and the complete valorization of various feedstocks in an environmentally friendly manner along with the full product life cycles from feedstock provisioning to materials production and end-of-life recyclability and degradability. In this perspective, lignin is the most abundant natural biopolymer with about 300 billion tonnes globally available in the biosphere, however, it is the least utilized biomass resource due to its inherent heterogeneity and recalcitrance [1]. Nonetheless its complex and heterogenous structure, the abundance of chemical linkages and hydroxyl (-OH) groups paths the way for a wide variety of chemical functionalization and application as a major aromatic source and renewable substrate for polymers [2]. The aim of present study was to solubilize kraft lignin in green solvents and subsequently use it for coupling with polymethylhydrosiloxane . After ultrasound sonication, 10 % wt. kraft lignin (KL) was mostly soluble in PEG-200 followed by PEG-400 < PEG-600 < Ethanol< Butyl acetate solvents. Solubilized lignin fractions were mixed with polymethylhydrosiloxane (PMHS) at various weight ratios (30:70, 50:50, 70:30 wt.%/wt.%). The solutions were drop casted onto glass slides and left at room temperature or further annealed at 60 and 100°C to obtain films or foams. The chemical structures of as-deposited coatings were confirmed by ATR-FTIR. Notably, the absorption peak from the Si-H stretching vibration at 2156 cm^{-1}, characteristic of PMHS before the functionalization, decreased significantly after the reaction with KL-PEG in all systems studied, suggesting the formation of network-based coatings. This low-cost synthetic method for lignin-based composites offers new opportunities for better utilization of lignin as a crosslinking additive in silicones.

Acknowledgements:

The Project MICS - “Made in Italy Circolare e Sostenibile - MICS”, tematica “11. Circular and sustainable Made-in-Italy” (CUP B73C22001270006) is acknowledged for funding.

References

[1] Shorey R., Gupta A., Mekonnen TH. *Ind. Crops Prod*, 2021, **174**, 114189.
[2] Bass G., Epps T., Mekonnen TH. *Polym. Chem.*, 2021, **12**, 4130.

Effect of cathodic hydrogen charging on the fracture toughness of a X52 pipeline steel welds tested with SENT specimens

Flavio Catalano[1*], Marco Palombo[2], Marco De Marco[2], Michelangelo Mortello[2], Paolo Piccardo[1], Roberto Spotorno[1]

[1] Department of Chemistry and Industrial Chemistry, University of Genoa, Via Dodecaneso 31, 16146 Genoa, Italy
[2] Istituto Italiano della Saldatura, Lungobisagno Istria 15A, 16141 Genoa, Italy

* *flavio.catalano@edu.unige.it*

In recent times, the ecological transition has increased attention to the environment and clean energy sources. As far as industrial activity and transport are concerned, hydrogen appears to be the best candidate for replacing fossil fuels, because it can be burned or introduced into a fuel cell to obtain electricity. The fastest and cheapest solution is to convert the current pipeline network to hydrogen [1]. However, hydrogen can diffuse inside metallic materials, worsening their toughness to the point of obtaining unexpected breakages since the phenomenon, known as hydrogen embrittlement (HE) [2], does not show macroscopic effects while it is taking place. Microstructure plays a key role in HE because hydrogen atoms are attracted to lattice discontinuities such as inclusions, grain boundaries and notches. Furthermore, the pipes welding process adds a further criticality because it induces the creation of residual stresses and microstructural defects. Although API 5L medium strength steels have the highest resistance to HE among pipeline steels, the production and welding quality standards of the past may not be suitable for a hydrogenated environment. It has then become necessary to evaluate the several types of steel commonly used for the construction of gas pipelines for service in the presence of hydrogen. In this study, we analyse the correlation between the microstructure of the circumferential welded joint of a 70s Italian API 5L X52 pipeline steel and the amount of hydrogen that could be electrolytically introduced into it. Base material (BM), heat affected zone (HAZ) and fused zone (FZ) were subjected to ½, 1, 2 and 4 hours of continuous charging with a current density $J = -10$ mA/cm^2 in a solution composed of [H_2SO_4] = 0,05 and 2,00 g/L of CSN_2H_4. For our tests, we recreated the HAZ from the BM through an appropriate heat treatment and characterized microstructurally and mechanically to verify its similarity to the original one. The electrolytic test revealed the FZ to be the material that can absorb the most hydrogen, followed by BM and HAZ. The BM absorbs high concentrations of hydrogen due to the characteristic higher concentration of non-metallic inclusions. Afterward, the materials underwent fracture mechanics tests with single edge notch tension (SENT) specimens. The tests took place both in air and under electrolytic charging to record the change in fracture toughness calculated as the J integral at the maximum force (in accordance with BS 8571 standard). BM is the most sensitive material to a hydrogenated environment; it presents the highest drop in toughness between the test in air and the test in hydrogen ($J_{MAX\ H}/J_{MAX\ Air} = 0.590$) compared to HAZ ($J_{MAX\ H}/J_{MAX\ Air} = 0.690$) and FZ ($J_{MAX\ H}/J_{MAX\ Air} = 0.686$).

References

[1] Chatzidouros EV, Papazoglou VJ, Tsiourva TE, Pantelis DI. Hydrogen effect on fracture toughness of pipeline steel welds, with in situ hydrogen charging. International Journal of Hydrogen Energy 2011; 36: 12626-12643.
[2] Nagumo M. Fundamentals of Hydrogen Embrittlement. 1st ed. Springer; 2016.

Selection and characterization of microbiomes subject to identical environmental stress conditions for Polyhydroxyalkanoates (PHA) production

M. Catalão[a,b], Cristiana A.V. Torres[a,b], Juan F. Martínez-Blanch[d], Filomena Freitas[a,b], Rui Oliveira[c], Maria A.M. Reis[a,b]

[a]Associate Laboratory i4HB - Institute for Health and Bioeconomy, School of Science and Technology, NOVA University Lisbon, Caparica 2825-149, Portugal.
[b]UCIBIO – Applied Molecular Biosciences Unit, Department of Chemistry, School of Science and Technology, NOVA University Lisbon, Caparica 2825-149, Portugal
[c]LAQV-REQUIMTE, NOVA Science and Engineering School, NOVA University of Lisbon, Caparica 2825-149, Portugal
[d]ADM-Biopolis S.L., University of Valencia Science Park, Carrer del Catedràtic Agustín Escardino Benlloch 9, Edificio 2, 46980, Paterna, Valencia, Spain
**m.catalao@campus.fct.unl.pt*

In nature, microorganisms thrive within complex ecosystems called microbiomes, where their collective capabilities surpass those of individual populations. Through bacterial communication, involving metabolite exchanges and molecular signalling, microbial consortia achieve a division of labour, enhancing productivity and resilience against environmental fluctuations. Over time, this communal living fosters stability within consortia, making them robust in diverse environmental conditions. Leveraging these attributes, natural microbiomes from various ecosystems can be tailored to produce commercially valuable metabolites, such as biopolymers. Polyhydroxyalkanoates (PHAs), biocompatible and biodegradable polyesters synthesized by select microbial species, offer sustainable alternatives to conventional plastics. The feast-and-famine (F/f) strategy is utilized to cultivate consortia enriched in PHA-producers, involving alternating periods of carbon excess (feast) and deprivation (famine). This induce PHA-producers to utilize resources efficiently, while non-PHA-storing organisms are eliminated [1]. In a study aimed at enriching microbiomes in PHA-producers, natural samples from diverse habitats across Portugal underwent F/f cycling. Over a month, these microbiomes evolved into PHA-enriched mixed microbial consortia (MMCs), characterized by quantification of biomass, nutrients, PHA and microbial composition profiling. While all tested microbiomes transitioned into PHA-enriched MMCs within 33 days, their original compositions significantly influenced the final consortia. Common phyla included Bacteroidetes, Proteobacteria, and Actinobacteria, with variations based on geographic and environmental conditions. Notably, Proteobacteria predominated in most cases, while Actinobacteria became dominant in specific environments. Remarkably, microbiomes from Corroios Marshland and moss collected from olive trees exhibited the highest PHA yields. This study sheds light on the evolutionary trajectories of microbiomes under standardized conditions, offering insights into engineering and predicting the evolution of PHA-producing consortia from natural sources. Such knowledge paves the way for sustainable biopolymer production through microbiome manipulation.

Acknowledgements: This project receives funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101000733. This work is financed by national funds from FCT - Fundação para a Ciência e a Tecnologia, I.P., in the scope of the project UIDP/04378/2020 and UIDB/04378/2020 of the Research Unit on Applied Molecular Biosciences – UCIBIO, the project LA/P/0140/2020 of the Associate Laboratory Institute for Health and Bioeconomy - i4HB and within the Associated Laboratory for Green Chemistry (LAQV)

References

[1] Cardoso de Oliveira, Silva, C.E., Carvalho, G. and Maria A.M. Reis (2017). Strategies for efficiently selecting PHA producing mixed microbial cultures using complex feedstocks: Feast and famine regime and uncoupled carbon and nitrogen availabilities. New Biotechnology, 2017, 37, pp.69–79

Magnetite functionalized with metal-organic frameworks (MOF) for perfluorooctanoic acid (PFOA) absorption

D. Ceriotti[a*], M. Pedrazzoli[a], L. Magagnin[a,b], M. Sansotera[a,b]

[a] *Dipartimento di Chimica, Materiali e Ingegneria Chimica, Politecnico di Milano, via Mancinelli 7, 20131 Milano*
[b] *Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali, via G. Giusti, 9, 50121 Firenze*
**davide.ceriotti@polimi.it*

Poly- and Per-fluoroalkyl substances (PFAS) are hazardous and bioaccumulative compounds that negatively affect the environment and human health[1]. The presence of perfluoroalkyl acids (PFAAs) in drinking water, especially perfluorooctanoic acid (PFOA) in Northern Italy[2], is an increasing concern. Over the past decade, various degradation techniques have been developed to address this issue[3], but they often result in the release of additional environmentally toxic molecules or short-chain PFAS[4]. Some adsorption methods, like activated carbon[5] and ion exchange resin filters[6], have been explored; however, they tend to be non-selective, saturate quickly, or are costly. An innovative solution involves using magnetic particles coated with metal-organic frameworks, which can selectively adsorb PFOA without requiring filtration steps or generating unwanted byproducts.
In this work, zirconium-based (UiO-66) and iron-based (Fe-MIL-100) metal–organic frameworks have been synthetized and employed to functionalize magnetic particles.
The resulting magnetic powders demonstrated impressive adsorption capabilities, capturing up to 99% of dissolved PFOA in water. This approach not only offers a sustainable and efficient solution to PFAS contamination but also represents a significant advancement in the development of selective and high-capacity adsorption materials for environmental remediation.

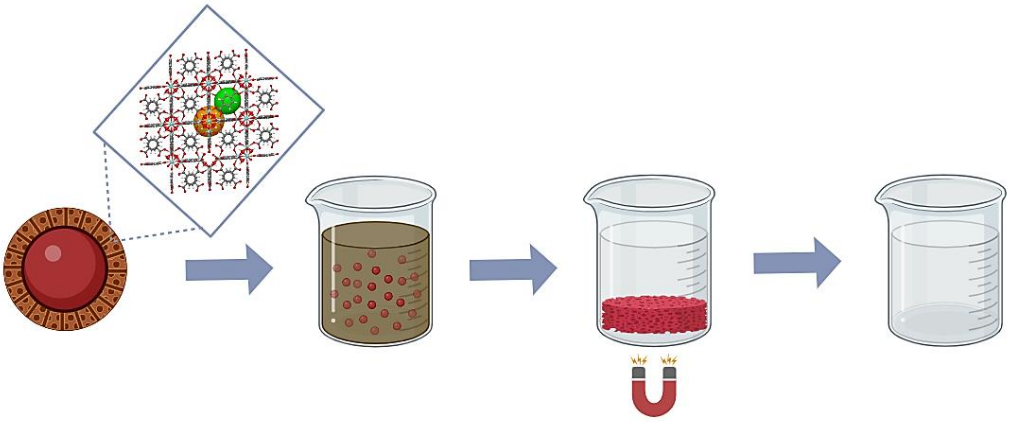


Figure 1: Magnetic particles with metal-organic frameworks functionalization and subsequent PFAS adsorption

References

[1] Brown JB, Conder JM, Arblaster JA and Higgins CP. *Environ. Sci. Technol.* 2020; **54**: 15202-15214.
[2] Ingelido AM, Abballe A, Gemma S, Dellatte E, Iacovella N, De Angelis G, Zampaglioni F, Marra V, Miniero R, Valentini S, Russo F, Vazzoler M, Testai E and De Felip E. *Environ. Int.* 2018; **110**: 149-159.
[3] Mirabediny M, Sun J, Yu TT, Åkermark B, Das B and Kumar N. *Chemosphere* 2023; **321**: 138109.
[4] Sharma S, Shetti NP, Basu S, Nadagouda MN and Aminabhavi TM. *Chem. Eng. J.* 2022; **430**: 132895.
[5] Liu W, Lin T, Zhang X, Jiang F, Yan X and Chen H. *Chemosphere* 2022; **309**: 136733.
[6] Woodard S, Berry J and Newman B. *Remediation* 2017; **27**: 19-27.

Efficient Chemical Recycling of Expanded Polystyrene Using Terpene-Based Green Solvents

Clarissa Ciarlantini[1*], Iolanda Francolini[1], Antonella Piozzi[1], Loris Pietrelli[2]

[1]Chemistry Department, Sapienza University of Rome, Italy
[2]Legambiente, Rome, Italy

**clarissa.ciarlantini@uniroma1.it*

Expanded polystyrene (EPS) finds extensive applications across diverse sectors, from construction to packaging, due to its excellent thermal and acoustic insulation properties. However, the widespread use of EPS has led to significant environmental concerns regarding its disposal. Indeed, the poor EPS recycling is mainly due to its low density (12-15 kg/m^3), significantly increasing transport costs. Furthermore, since EPS may contain brominated flame-retardants, incineration is problematic as the combustion process can produce toxic gases (dioxins). Only compacted EPS foam (in this case the volume reduction is about 30 times) can be recycled in some applications. In this study, we aim to address these concerns by developing an efficient EPS recycling process that enhances both recovery rates and the quality of recycled products (polystyrene), utilizing environmentally friendly and cost-effective solvents.

Specifically, various terpene-based green solvents [1] were evaluated for EPS solubilization and compared with conventional solvents such as cyclohexane, chloroform, and toluene. Among terpenes, limonene and p-cymene emerged as the most efficient solvents, achieving EPS solubilization rates comparable to toluene while demonstrating higher solubility (approximately 1 g/mL) and faster polymer dissolution, particularly for limonene. Physico-chemical characterization of the recycled EPS revealed properties such as molecular weight, purity, and mechanical strength similar to those of virgin EPS, indicating the high quality of the recycled polymer. A comprehensive mass and economic balance analysis underscored the significant economic advantages of the developed recycling process, which hinges on the developed process as a sustainable solution for EPS waste management.

References

[1] Janicka P., Płotka-Wasylka J., Jatkowska N., Chabowska A., Fares M.Y., Andruch V., Kaykhaii M., Gębicki J. *Current Opinion in Green and Sustainable Chemistry*, 2022, **37**, 100670.

Silicon/nanocrystalline-diamond cathodes for photon-enhanced thermionic emission

Raffaella Salerno[1,2], Veronica Valentini[2], Eleonora Bolli[2], Matteo Mastellone[2,3],
Alessandro Bellucci[2], Riccardo Polini[1], and Daniele M. Trucchi[2]

[1] *Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma "Tor Vergata", 00133 Roma, Itala*
[2] *ISM-CNR, DiaTHEMA Lab, Via Salaria km 29.300, 00015 Monterotondo, Roma, Italy*
[3] *ISM-CNR, FemtoLAB, Contrada S. Loia, 85050 Tito Scalo, Potenza, Italy*

**raffaella.salerno@students.uniroma2.eu*

Photon-enhanced thermionic emission (PETE) harnesses photon absorption by a semiconducting material and electron thermalization energy in order to thermionically emit electrons from a low electron affinity material in a highly efficient process, holding significant promise for enhancing concentrated solar energy conversion[1].

The PETE cathodes which were examined consisted of hydrogen terminated nanocrystalline diamond thin films deposited onto heavily-doped p-type silicon[2] (Figure A) that displayed low electron affinity value (~ 0.4 eV). The electron emission properties of the cathodes, while exposed to concentrated solar radiation, were studied as a function of the diamond film thickness (from 40 nm to 1.4 µm). These measurements as well as Raman spectra and Kelvin-Probe Force Microscopy maps of the diamond films highlight the importance of grain-boundaries whose presence correlates with a higher emission current density, notably observed with the 80 nm-thick diamond emitter. Finally, photon absorption by the silicon layer was optimized through surface microstructuring with femtosecond pulsed laser treatments (Figure B), resulting in a tenfold increase in emission current density.

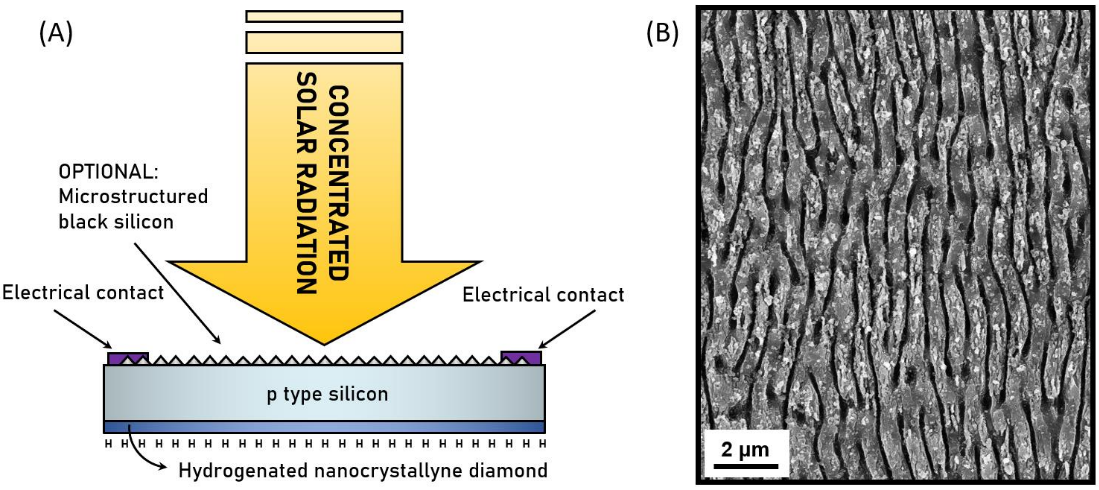


***Figure A**: Scheme of the PETE cathode structure.* ***Figure B**: Microstructured silicon surface.*

References

[1] J. W. Schwede, I. Bargatin, D. C. Riley, B. E. Hardin, S. J. Rosenthal, Y. Sun, F. Schmitt, P. Pianetta, R. T. Howe, Z.-X. Shen and N. A. Melosh *Nature Materials*, 2010, **9**, 762–767.
[2] R. Salerno, V. Valentini, E. Bolli, M. Mastellone, V. Serpente, A. Mezzi, L. Tortora, E. Colantoni, A. Bellucci, R. Polini, D. M. Trucchi *ACS Omega*, 2023, **8**, 25496–25505.

Circular economy in mussel farms: polypropylene recovery

Clarissa Ciarlantini[1*], Antonella Piozzi[1], Iolanda Francolini[1], Stefania Di Vito[2], Fabrizio Soddu[2], Elisa Scocchera[2], Marzia Mattioli[2], Loris Pietrelli[2]

[1]*Chemistry Department, Sapienza, Rome, Italy*
[2]*Legambiente, Rome, Italy*

* *clarissa.ciarlantini@uniroma1.it*

Mussels represent an important source of low-cost protein for many people [1]. Mussel production is an environmentally friendly and sustainable activity; as mussels feed by filtering nutrients from sea water (0.252 kg CO_2 eq. per 1 kg of mussel produced against over 20 kg CO_2 eq. per 1 kg of beef produced). Nevertheless, the accidental dispersion on the seabed and along beaches of plastic “socks” used for their farming represents a significant environmental problem. Mussel farming can be really considered as a simple bio-based strategy to provide an efficient method to remove nutrients from eutrophic waters. Basically, for each kg of mussels produced, about 1 linear meter (20 g/m) of polypropylene (PP) net is used. Therefore, in face of the Mediterranean Sea production (320 ktonnes), about 6400 tonnes of plastic waste could be produced (European Waste Code, CER 020104). Considering the landfill disposal cost (0.25–0.30 €/kg), it is plausible to hypothesize that a certain number of mussel farmers usually abandon used socks at sea contributing significantly to marine litter. The recovery and recycling of the polymer material can represent a proper solution for the management of the plastic waste produced by mussel farming. However, the presence of organic materials, algae and biofouling on the surface of mussel socks makes PP not easily recyclable with traditional systems. The LIFE MUSCLES project, funded by the EU, was established to develop a newly treatment method for recovering polypropylene from mussel nets [2]. Through experiments performed on a laboratory scale, it was verified that it is possible to effectively remove biofilm (93%) from the polymeric material using the Fenton reaction (30% H_2O_2 solution, t=40 min, pH=2, T=25°C and $FeSO_4$ as catalyst). However, to simplify the process and reduce costs, further experiments were carried out with pressurized water (25-30 bar) and in the absence of oxidizing agent (H_2O_2). The results showed excellent biofilm removal (98%) after 30 minutes. Moreover, process costs could be further reduced by recycling the washing water after filtration. The spectroscopic, thermal and mechanical characterization of the socks shredded and washed for 30 minutes demonstrated that the treatments undergone by the polymer had a non-significant impact on the PP physical properties, thus allowing its reuse in the same supply chain. In particular, the regenerated PP had an elastic modulus value (0.697±0.058 GPa) comparable to that of pristine PP (0.758±0.069 GPa). Therefore, as the Life MUSCLES project fully embraces the circular economy as a production model, prioritizing material recycling, to demonstrate the feasibility of this treatment process, a mobile recycling pilot plant capable of processing 300 kg of mussel nets per day was constructed. This approach will effectively lower expenses associated with new mussel nets while mitigating environmental damage.

References

[1] Matarazzo Suplicy F., *Reviews in Aquaculture* 2020, **12**, 204–223
[2] Pietrelli L., *Polymers*, 2022, **14**, 3469.

An application of flow chemistry for co-precipitation of nickel rich NMC precursors using oxalic acid as precipitating agent

Colasanti Marco*,[1], Giona Massimiliano[1], Schiavi Pier Giorgio[2], Altimari Pietro[2], Pagnanelli Francesca[2]

[1]*Department of chemical,materials and environmental engineering, Sapienza University of Rome, Rome,Italy*
[2]*Department of chemistry, Sapienza University of Rome, Rome, Italy*

**marco.colasanti@uniroma1.it*

Nowadays, several studies focus on the energy transition. Many topics are coming out, but only few of them can be effectively used soon, and lithium-ion batteries belong in this class. Among all of them, nickel rich NMC (with cathode materials made of mixed oxides of nickel, cobalt and manganese) are acquiring prestige because of their high capacity and low necessity of cobalt (which is a critical raw material), although they easily degrade. It was proved that degradation mechanisms can be reduced producing NMC precursors as spherical particles having diameter of 10 μm and the closer possible to single crystal structure. These properties are obtained using recipes or trials and error approach, because growth mechanisms are not understood. This gap reduces the possibility to move to continuous productions or alternative chemistries (NMC precursors are mainly obtained as mixed crystals of nickel, manganese and cobalt hydroxides, produced through co-precipitation reaction). Particles precipitation as oxalates instead of hydroxides is acquiring importance because it allows an easier scalability, since it is safer and easier to control. The main drawback this proposal have is the lack of knowledge in the field, which is faced using recipes for hydroxides precipitation. The study here presented looks for a better understanding of oxalate precipitation analysing how operating conditions can affect precursor characteristics. Flow chemistry is used to put in evidence the kinetic mechanism. The reactor body is made of pipes having diameter of 1÷2 mm and length from 50 cm to 10 m; diameter and length are combined in dependence on the residence time invested. The reactor is fed with two solutions injected using a T-junction, one is a mixture of nickel, cobalt and manganese, the other is oxalic acid. The outcomes showed that the reaction kinetic is so fast that makes nucleation phenomena undetectable. Therefore, the growth mechanism is mainly influenced by agglomeration and aggregation phenomena. Comparing the obtained results with the ones taken from stirred tank reactors, it can be observed a large fluid dynamics influence; particles' structure changes a lot moving from laminar to turbulent regime. In addition, the reaction kinetics is different respect the hydroxide ones, this makes many operating conditions usually taken from recipes useless.

Acknowledgements:

This work is carried out within the project PNRR CN4 National Center for Sustainable Mobility Spoke 13 Electric Traction System and Batteries Task 3.3 Support the adoption of circular economy solutions.

References

[1] Mathew L., Jun L., Zhongwei C., Khalil A., *Advanced Materials*, 2018, **30**, 1800561.
[2] Taehoon K., Wentao S., Dae-Yong S., Luis K. O., Yabing Q. , *Journal of Materials Chemistry A*, 2019, **7**, 2942-2964.
[3] Yuqing W., Qing Z., Ruoyang W., Wenhua X., Mengke Z., Yao L., Benhe Z., Yang S., Xiaodong G., *Chemical Engineering Science*, 2024, **284**, 119459.
[4] Xu Y., Zemin X., Weijie C., Hongcai G., Qiang Z., Jingze L., Aijun Z., *Materials Today Communications*, 2019, **19**, 262-270.

Evaluation of BioHydrogen Potential of agro-industrial waste using a mixed microbial culture

Eleonora De Santis[1*], Silvia Rosa[2], Antonella Marone[2], Massimiliano Fabbricino[1]

[1]Department of Civil, Building and Environmental Engineering (DICEA), University of Naples "Federico II", Via Claudio 21, 80125, Naples, Italy
[2]Department of Energy Technologies, Italian National Agency for New Technologies, Energy and Sustainable Economic Development (ENEA), Via Anguillarese 301, 00123, Rome, Italy

**eleonora.desantis@unina.it*

Biohydrogen (BioH_2) production via dark fermentation (DF) is widely considered as a promising strategy for clean energy generation. On an industrial scale, continuous bioH_2 production requires the use of renewable feedstock such as agro-industrial waste (AIW), with a high organic content and preferably, rich in carbohydrates. The efficiency of DF process is influenced by many parameters, including the composition of organic substrates, the type and the source of inoculum, the methods of substrate and inoculum preparation and the process conditions. Due to their high morphological and functional diversity, mixed microbial cultures (MMCs) are preferred for AIW valorization [1]. In order to develop a DF process using a stable and efficient MMC, the initial step of this study involved the selection of different substrates, representative of the Italian agro-industrial sectors. The AIW were: orange processing waste (OPW), confectionery waste, mainly biscuits (BW), sheep cheese whey (CW) and crude glycerol (CG). To evaluate the BioH_2 potential, also allowing H_2 yields comparison, a standardized protocol for glucose as model substrate, was used [2]. According to this protocol, the experiments were carried out using an automatic BHP system with continuous biogas release and standard operating conditions (37±1 °C; 17.5mM MES buffer; 5gVS/L of substrate; Substrate/Inoculum ratio (S/I)=2.7; starting pH 7.5). A heat pretreated digestate from a mesophilic digester treating agricultural waste and cattle manure was used as inoculum. In the current study, glucose fermentation showed H_2 yields of $1.67\pm 0.41 \text{mol}_{H2}/\text{mol}_{gluc}$, attesting the protocol reproducibility. The BHP results of AIW showed that the applied conditions were able to identify the H_2 potential of OPW (100 ± 24 Nml/gVS_{added}) and BW (165 ± 25 Nml/gVS_{added}), substrates with a carbohydrate content above 70% dry matter. In contrast, more complex substrates such as CW and CG showed inhibition. This was probably due to the presence of different impurities (acetate for CG and lactate for CW), but also to the presence of the indigenous lactic acid bacteria (LAB) community in CW. Therefore, different standard operating conditions were tested. CW showed a positive response in terms of H_2 yield (80 ± 21 Nml/gVS_{added}), at 2.5 gVS/L, S/I=1.3 and starting pH = 9, demonstrating that, adopting tailored operating conditions, it was possible to balance the inhibitoin due to the presence of lactate and LAB. In contrast, even lowering substrate concentrations to 1.5gVS/L was not possible to evaluate BHP for CG. We hypothesized that dry inoculum could be the main limiting factor. In conclusion, these results showed that the standard BHP protocol is applicabile and reproducible with substrates rich in carbohydrates (OPW and BW). At the same time, for more complex substrates, it was a rapid screening for adapting the operating parameters to the substrates properties, also allowing a comparison among the respective yields of bioH_2 potential production.

References

[1] Ghimire, A.; Frunzo, L.; Pirozzi, F.; Trably, E.; Escudie, R.; Lens, P.N.L.; Esposito, G. (2015). A Review on Dark Fermentative Biohydrogen Production from Organic Biomass: Process Parameters and Use of by-Products. *Appl. Energy*, *144*, 73–95

[2] Carrillo-Reyes, J., Buitrón, G., Moreno-Andrade, I., Tapia-Rodríguez, A. C., Palomo-Briones, R., Razo-Flores, E., *et al.* (2020). Standardized protocol for determination of biohydrogen potential. *MethodsX*, *7*.

C-S composites for Li-S battery applications

Maria Di Pea[1*], Vittorio Caprini[1], Thamara Ruellas[2], Marco Agostini[3], Sergio Brutti[1]

[1]Department of Chemistry, University La Sapienza, Rome, Italy
[2]Department of Chemistry, Federal University of São Carlos, São Carlos, Brazil
[3]Department of Chemistry and Pharmaceutical Technologies, University La Sapienza, Rome, Italy

dipea.1812435@studenti.uniroma1.it

Li-S batteries are rechargeable batteries that exploit lithium as anode and sulfur as cathode active materials. The most important advantage is in the use of non-toxic and cheap materials: sulfur is very abundant on the earth crust; its production is industrially simple and environmentally friendly. However, the insulating character of sulfur requires the use an host material that can increase the electronic conductivity and allow the redox reaction. In our case amorphous meso-porous carbons, i.e. an *hard carbon*, are used ad host material for the sulfur [1]. A biomass has been treated in an autoclave following different types of digestions: acidic routes exploiting citric acid at different concentrations; and an alkaline one using LUDOX (a suspension of nanometric silica particles in a NaOH aqueous solution). The resulting hydro-chars have been pyrolyzed at 1000C under Ar/H_2 flow to form hard carbons. All hard carbons have been mixed with sulfur to obtain C-S composites, by means of an infiltration process at 165C using an autoclave.

All prepared hard carbons and C-S composites have been characterized by a combination of techniques such as X-ray diffraction (XRD), Raman spectroscopy and thermogravimetric analysis (TGA). To comprehensively understand the carbons' atomic structure and morphology the XRD [2] and Raman [3] experimental patters have been simulated by using physically-funded models for quasi-molecular carbons.

The electrochemical characterization of samples has been carried out on coin cells using an aprotic electrolyte. To optimize the performances different types of separators and different volume of electrolyte have been tested in galvanostatic cycling (GC) experiments.

References

[1] Li Zhen et al. «Status and prospects in sulfur–carbon composites as cathode materials for rechargeable lithium–sulfur batteries», *Carbon* 92, 2015, pp. 41–63, doi: https://doi.org/10.1016/j.carbon.2015.03.008.

[2] Wilhelm Ruland, Bernd Smarsly, «X-ray scattering of non-graphitic carbon: An improved method of evaluation», *Journal of Applied Crystallography, v.35, 624-633, 2002*, doi: 10.1107/S0021889802011007.

[3] A.C. Ferrari et al., «Quantifying defects in graphene via Raman spectroscopy at different excitation energies», *Nano letters*, 2011, url: https://doi. org/10.1021/nl201432g.

Is it possible to obtain thermosetting materials from renewable sources which can be recycled at the end of their life?

Licia Gaeta[1,2*], Annalisa Pace[1], Claudio Pellecchia[1]
[1]*Department of Chemistry and Biology, "A. Zambelli", University of Salerno, via Giovanni Paolo II, 132, Fisciano, SA 84084, Italy*
[2]*Department of Industrial Engineering, University of Padova, via Gradenigo, 6/a, Padova, PD 35131, Italy*
** licia.gaeta@phd.unipd.it*

The increasing amount of plastic waste derived from fossil fuels that is contaminating our environment is one of the most critical issues of our time.[1] While for thermoplastic materials recycling and reprocessing can be carried out with relative ease, thermosets are classified as the most difficult materials to recycle due to the presence of cross-links which make them stable and resistant to temperature and solvents. Thermosets can display superior mechanical and chemical properties, making them ideal for use in various fields; therefore, the introduction of these materials in a circular economy context is necessary. An interesting approach is the use of polymer networks crosslinked with dynamic covalent bonds, named "covalent adaptable networks" (CANs and/or "vitrimers"). These materials are designed to behave as the commonly available thermosets under service conditions but, owing to the presence of weaker bonds in the crosslinks, they are potentially able to flow and thus to be reprocessed as thermoplastics under trigging stimuli and also to be chemically recycled at the end of their life. Additionally, the starting monomers used for the synthesis of these polymers can be obtained from renewable sources. We have pursued the synthesis of thermosets based on poly(lactic acid) (PLA), the most commercially important bio-based polymer.[2]

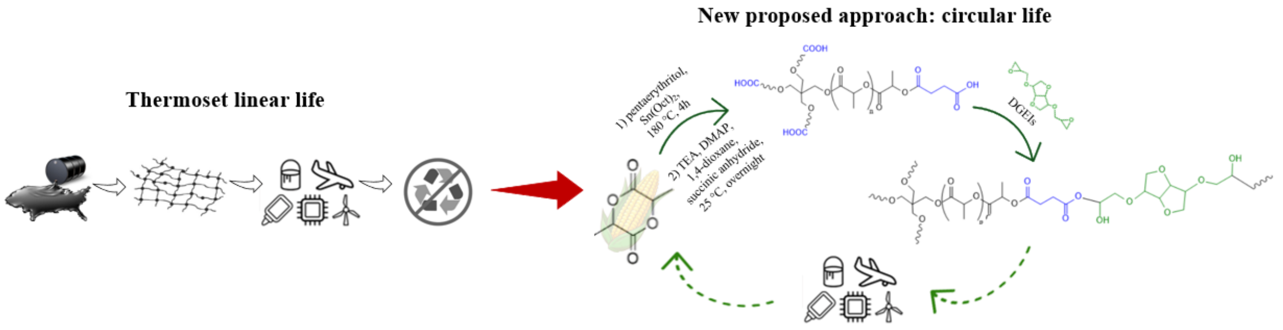


Figure 18 - New proposed approach for biobased and recyclable thermosets

Star-PLA oligomers end-capped with carboxylic groups were prepared by Ring Opening Polymerization of L-lactide using pentaerythritol as the initiator and Sn(II) 2-ethylhexanoate as the catalyst, followed by treatment with succinic anhydride. The prepolymers were then crosslinked using isosorbide diglycidyl ether (DGEIs),[3] a bis epoxide obtainable from sugars like sorbitol, under different curing conditions. The obtained materials are insoluble with high gel fractions (>90%), and were characterized via DSC, TGA and DMA.

Acknowledgements:
This study was carried out within the PRIN 2022-PNRR P2022K9XN3 "New recyclable thermosetting and elastomeric polymeric materials based on bio-renewable feedstocks", CUP D53D23017130001.

References

[1] Post W., Susa A., Blaauw R., Molenveld K., Knoop R. J., *Polymer reviews*, 2020,**60**(2), 359-388.
[2] Brutman J. P., Delgado P. A., Hillmyer M. A., *ACS Macro letters*, 2014, **3**(7), 607-610.
[3] Chrysanthos M., Galy J., Pascault J. P., *Polymer*, 2011, **52**(16), 3611-3620.

Thermosetting polyurethane-based encapsulation of flexible perovskite solar cells: a step forward in devices stabilization in highly damp environment

*Davide Gallo *, Francesca De Rossi #, Luca Bonandini §, Giulio Koch #, Alberto Menozzi §, Matteo Bonomo*, Francesca Brunetti #, Gabriele Viada*, Ana Yancy Segura Zarate*, Simone Galliano*, Claudia Barolo*♦,*
**: Department of Chemistry, NIS Interdepartmental Centre and INSTM Reference Centre, University of Turin, Via Gioacchino Quarello 15/a, 10135 Turin, Italy*
#: CHOSE (Centre for Hybrid and Organic Solar Energy), Department of Electronic Engineering, University of Rome Tor Vergata, Via del Politecnico 1, 00133 Rome, Italy
§: Demak Polymers S.r.l., Strada del Cascinotto, 163, 10156 Torino, Italy
♦: Istituto di Scienza, Tecnologia e Sostenibilità per lo sviluppo dei Materiali Ceramici (ISSMC-CNR), Via Granarolo 64, 48018, Faenza, RA, Italy
**d.gallo@unito.it*

Perovskite solar cells (PSC) have experienced an unprecedented improvement in their power conversion efficiency (PCE) in just a couple of decades, equalling monocrystalline silicon at 26.1% and thus surpassing all thin film technologies [1]. These results, combined with the outstanding optoelectronic features of perovskite and the ease of device fabrication have fuelled further research into this technology, whose road to commercialisation is slowed down by stability issues, mainly due to the interaction of the active layer with oxygen and moisture [2]. This contribution aims to develop polyurethane (PU) formulations tailored for encapsulating flexible perovskite solar cells (f-PSCs). Six formulations were engineered by combining various diisocyanates and polyols, with a preference for aliphatic PUs due to their superior thermal stability and flexibility [3], crucial for accommodating the flexible substrates. Among the tested resins, DG4 resin was chosen for its high transparency, thermal and UV resistance, refractive index matching, and flexibility. Implementing DG4 as encapsulant on f-PSCs did not significantly affect cell performance or flexibility. Double-side encapsulation (both back and front) was found to be the most effective strategy for protecting the device from medium-high humidity levels (RH = 40%) in simulated indoor environments, extending device lifetime (T80) to over 2300 hours. This strategy also proved crucial in highly damp environments (RH ≈ 80%), increasing device lifetime by almost one hundred times compared to unencapsulated f-PSCs. The immersion of encapsulated devices in water reveals a vulnerability in the proposed strategy: the exposed electrical contacts serve as entry points for external agents such as water, moisture, and oxygen, leading to irreversible degradation. By relocating the electrical contacts using wires, we can achieve complete coverage of the device, including the contact areas, thereby enhancing protection from the external environment and reducing the risk of lead (and other contaminants) leakage in case of device failure.

Acknowledgements:

This contribution has been funded by the Italian Space Agency (ASI) project, PEROSKY Perovskite and other printable materials for energy application in space (no. 2018-1-R.0). D.G., M.B. and C.B. acknowledge support from Project CH4.0 under the MUR program “Dipartimenti di Eccellenza 2023–2027” (CUP D13C22003520001). DG acknowledges Decreto-Legge 6 maggio 2021, n. 59 (PNRR) for funding the PhD scholarship. The authors gratefully acknowledge Demak Polymers S.r.l. for providing the PU precursors.

References

[1] NREL, Best Research-Cell Efficiency Chart | Photovoltaic Research | NREL. Best Res. Effic. Chart | Photovolt. Res.
[2] J. Y. Kim, J.-W. Lee, H. S. Jung, H. Shin, N.-G. Park, Chem. Rev. 2020, 120, 7867
[3] M. F. Sonnenschein, Polyurethanes: Science, Technology, Markets, and Trends; 2014; Vol. 9781118737.

Chemical recycling of poly(lactide) using (imidazol[1,5-a]pyrid-3-yl) phenolate Zn(II) catalysts.

Maria Gentile[1,2]*, Licia Gaeta[1,2], Giuseppe Gravina[1], Claudio Pellecchia[1]
[1]*Department of Chemistry and Biology "A. Zambelli", University of Salerno, via Giovanni Paolo II, 132, Fisciano, SA 84084, Italy*
[2]*Department of Industrial Engineering, University of Padova, via Gradenigo, 6/a, Padova, PD 35131, Italy*
**maria.gentile.2@studenti.unipd.it*

Poly(lactide) (PLA) is a highly relevant bio-based polymer in commercial applications and stands out as one of the most promising materials for sustainable plastic use in a circular economy [1]. Despite the green credentials of PLA, currently its recycling is not planned, as the end-of-life option for post-consumer PLA waste is the collection with the organic fraction for composting. However, since PLA global production and use are expected to grow significantly in the next years, it is necessary to establish more sustainable options for its end-of-life management, including chemical recycling [2].

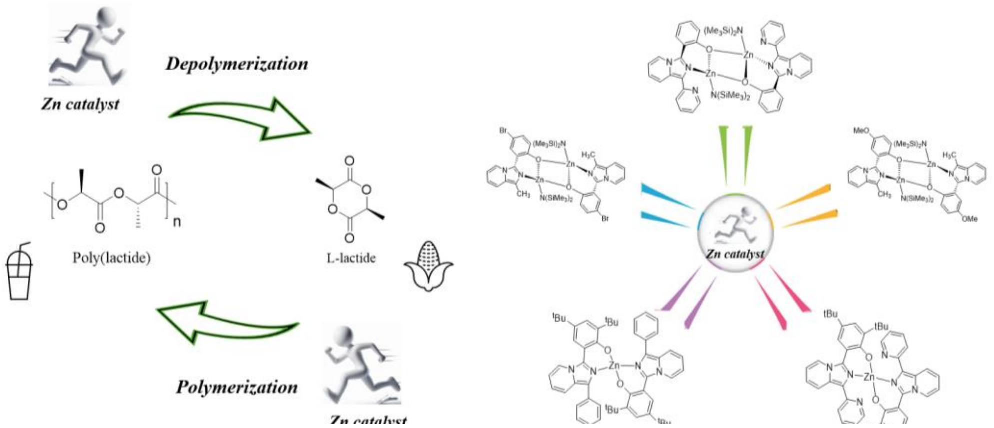


Figure 1: Polymerization and depolymerization promoted by new Zn catalysts

In this work we report a series of (imidazol[1,5-a]pyrid-3-yl)phenolate Zn(II) catalysts, previously tested in the polymerization of L-lactide [3].These catalysts were employed to facilitate the closed-loop recycling of polylactic acid in accordance with circular economy principles. Specifically, they enabled the chemical recycling to monomer (CRM) through thermal depolymerization to L-lactide in bulk under vacuum in the presence of an alcohol. Additionally, they allowed to obtain alkyl lactates with high conversion and selectivity by alcoholysis under mild conditions and without solvents.

Acknowledgements:
This study was carried out within the Agritech National Research Center and received funding from the European Union Next-GenerationEU (PIANO NAZIONALE DI RIPRESA E RESILIENZA (PNRR) – MISSIONE 4 COMPONENTE 2, INVESTIMENTO 1.4 – D.D. 1032 17/06/2022, CN00000022). This manuscript reflects only the authors' views and opinions, neither the European Union nor the European Commission can be considered responsible for them.

References

[1] Pretula J., Slomkowski S., & Penczek S., *Advanced drug delivery reviews*, 2016, **107**, 3-16.
[2] Farah S., Anderson D. G., & Langer R., *Advanced drug delivery reviews*, 2016, **107**, 367-392.
[3] D'Alterio M. C., D'Auria, I., Gaeta L., Tedesco C., Brenna S., & Pellecchia C., *Macromolecules* 2022, **55**, (12), 5115–5122

CeO_2/rGO catalysts for PEMFCs

L. Iacobini[1*], N. Carboni[1], J. Montero[1], V. Naticchioni[2], M.A. Navarra[1,3]
[1]*Dept. of Chemistry, Sapienza University of Rome, Rome, 00185, Italy*
[2]*ENEA, CR-Casaccia, Via Anguillarese 301, 00123, Rome, Italy*
[3]*hydro-Eco Research Center, Sapienza University of Rome, Via A. Scarpa,16, 00161, Rome, Italy*

**luna.iacobini@uniroma1.it*

Hydrogen has become, especially during the recent years, one of the protagonists on the continuous race towards sustainable and clean energy sources. Following this trend, proton-exchange membrane fuel cells (PEMFCs) are electrochemical devices able to directly convert chemical energy into electricity by the total reaction $H_2(g) + \frac{1}{2}O_2 \rightarrow H_2O\ (g/l)$, producing only water as by-product. The very high efficiency of these systems (~60%) compared to combustion systems (~30%) encourages their study and their development. Anyways, PEMFCs have some problems to overcame, the main one is related to the low kinetics of the oxygen reduction reaction (ORR) that occurs on the cathode side and that requires the employment of a catalyst to enhance the kinetics and at the same way reduce the overpotential of the process. The best choice in terms of catalytic activity for this type of fuel cells is Platinum, but it is very expensive (~$28.95 per gram) due to its low abundance and it suffers, like other noble metals, for very easy passivation and contamination. For this reason, the demand for a cheaper alternative is of paramount importance. Here, CeO_2/rGO (reduced-Graphene Oxide) is proposed as a promising additive to the commercial Pt/C catalyst, aimed to reduce the Platinum loading and enhance the catalyst efficiency [2]. The CeO_2 has been synthetized generating oxygen vacancies (namely, $CeO_{2-\delta}$) that act as catalytic centers where the reduction of the oxygen can take place [1]. Moreover, thanks to its hygroscopicity, CeO_2 can help in the cell water management and reduce flooding effects. This non stoichiometric compound acts also as an oxygen radical scavenger, thanks to the Ce_{3+}-to-Ce_{4+} conversion consuming unwanted peroxides of the complex ORR [1]. Despite all these good qualities, it is known that cerium ions may become soluble in water, migrating from the electrode towards the membrane in which they can form ionic interaction with the anionic sulfonic groups of the acidic polymer, thus reducing the proton conductivity. The rGO is found to be a good choice to get a better stability of the ceria and, according to its reduction degree, it can promote good electrical conductivity and provide high surface area for a more efficient catalyst deposition. Synthesis, physical-chemical characterizations, and electrochemical tests, both ex-situ by rotating disk electrode analysis and in-situ by FC performances evaluation, will be presented in this work, proving the effect of the CeO_2/rGO on the ORR kinetics.

Acknowledgements:

The financial support of ENEA within the PNRR POR H2 - Mission 2 – Component 2 – Investment 3.5, is gratefully acknowledged (Project title: “Synthesis and characterization of low-cost alternative catalysts for low-temperature fuel cells.

References

[1] L. Mazzapioda, G. Moscatelli, N. Carboni, S. Brutti, M.A. Navarra, ChemElectroChem, Volume 10, (2023) 9.

[2] P. Salarizadeh, M.B. Askari, H. Beydaghi, M. Rastgoo-Deylami, S. M. Rozati, JPhysChemSolids, Volume 159 (2021) 8.

Characterization of plastic wastes in Urban parks

Elisabetta Lacolla[1*], Antonella Piozzi[1], Stefania Di Vito[2], Elisa Scocchera[2], Loris Pietrelli[2]

[1]Chemistry Department, Sapienza University, Rome, Italy
[2]Legambiente, Rome, Italy

**e-mail address of the presenting author*

Urban parks (UPs) represent a “natural” space in the urban context for many people, especially resident citizens [1]. Although municipalities prohibit littering in public places, inviting people to use containers provided for garbage disposal, in urban parks littering and cleanliness is an ongoing worry. In general, waste represents a significant public and environmental health concern and can appropriately be considered a sanitation hazard. In this study, waste present in many Italian urban parks was collected, characterized and quantified to understand its composition in order to help determine measures and encourage visitors to keep an urban park clean by regularly using containers. The monitoring campaigns for the collection and characterization of urban park litter were carried out annually (2018-2023) by Legambiente (the most widespread environmental association in Italy). A total of 274 urban parks were monitored in 108 cities and small towns (from 745 inhabitants to 2.7 million). An adaptation of the sampling protocol proposed by the Marine Strategy Framework Directive (MSFD) Technical Group on Marine Litter (2008/56/CE) was applied. Using Fourier Transformed Infrared Spectroscopy (FTIR) 19 different polymers were identified. The most common were cellulose acetate (cigarette butts) polyethylene (PE) and polypropylene (PP). However, an interesting aspect concerned the heterogeneity of materials, as the waste was composed not only of traditional polymers such as PE, PP, PET and PS, but also polyamides, polyurethanes and some copolymers such as acrylonitrile butadiene styrene (ABS). Following the application of recent SUP (single-use plastics) regulations, blended biopolymers of polylactic acid (PLA) and starch were also found (till 0.33%). The presence of highly degraded polymers by thermo-oxidative phenomena, UV exposure or mechanical abrasion was also observed. In particular, many of the plastic pieces (till 27.8 items/100m^2) derive from the degradation of low-density polyethylene (LDPE) used for shopping bags employed until 2017, the year which biodegradable/compostable bags (according to UNI EN 13432 standard) were introduced on the market. By FTIR spectroscopy, the degradation of the polymers was also evaluated by observing the changes in the carbonyl band (Carbonyl Index, C.I.=Abs_{1720}/Abs_{2020}) [2]. In some polyethylene samples, for example, C.I. reached rather high values (0.06 - 0.29), justifiable only with a long stay in the park.
The category list obtained by these monitoring campaigns can be useful to support the policy actions in the best way. In fact, it emerged that in addition to people's lack of civic responsibility, the parks also appear dirty due to a lack of support from the public administration.

References

[1] N. Torabi, J. Lindsay, J. Smith, L.A. Khor, O. Sainsbury. *Cities*, 2020, 98, 102527.
[2] P.K. Roy, P. Surekha, C. Rajagopal, S.N. Chatterjee, V. Choudhary. *Polym. Degrad.Stab*. 2007, 92, 1151-1160.

Eco-sustainable regeneration of industrial catalyst

Leone Michele[1*], Mario Martinez[2], Ida Pettiti[1], Antonella Piozzi[1], Daniela Pietrogiacomi[1]

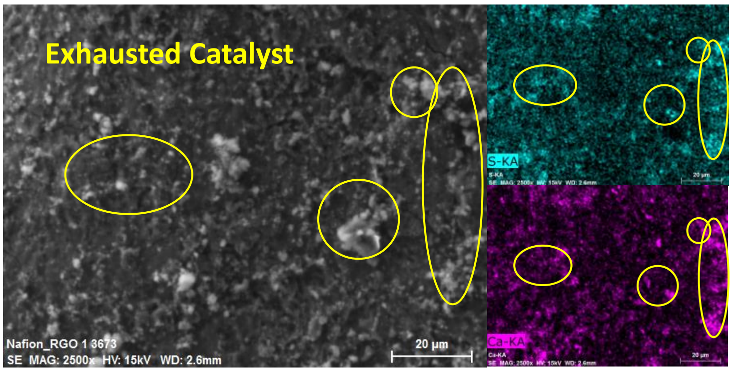
[1]Chemistry Department, Sapienza University of Rome, Rome 00155, Italy
[2] Bio Protect Group srl, Fabrica di Roma (VT), 01034, Italy

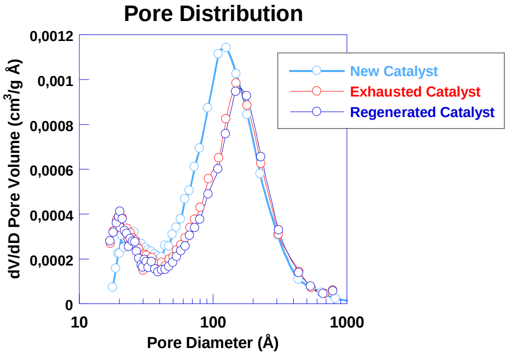
**michele.leone@uniroma1.it*

In power plants, the production of energy through combustion of various fuels (like oil, solid urban waste, industrial waste, natural gas, etc.) produce a large amount of atmospheric pollutants. As for the abatement of NOx, that are the main products in the fumes emitted by power plants and are responsible for photosmog and acid rains, well-defined V_2O_5/TiO_2 catalysts achieve the DeNOx process, i.e. the selective catalytic reduction with ammonia as reductant (NH_3-SCR). The increase in the use and diffusion of these catalysts, that suffer for deactivation and whose main fate is to be disposed of in landfills for hazardous materials, has led to develop regeneration methodologies [1] and our interest in the research of an eco-sustainable regeneration processes from a circular economy vision.

For this purpose, a series of deactivated catalytic modules arising from application in different power plants was studied in collaboration with Bio Protect Group s.r.l.. Characterization studies of solid surface (N_2 physisorption for specific surface area and pore distribution, FESEM-EDX for the mapping and elemental analysis, Raman spectroscopy for species revelation) and of solid bulk (XRD diffraction for crystallographic phases) were conducted on the new, exhausted and regenerated catalysts to understand the nature, extent and conditions of poisoning.

Preliminary results showed that the deactivated catalysts undergo both fouling and poisoning of the active sites. The first is due to deposition on the surface of various species such as calcium sulphate (Figure on the right) and carbonaceous species, which decreased both the total volume of the mesoporous structure (Figure on the left) and the specific surface area. The poisoning of active sites occurred probably *via* the interaction between ammonium sulphate and active terminal vanadyls, blocking their catalytic activity. A first attempt of regeneration applied to the used catalyst recovered the surface active site, restoring the catalytic activity up to 85-90%, without restoring its specific surface area. Further studies are needed to improve and optimize the regeneration process with the aim to remove all the deposits and to make regeneration feasible multiple times on the same catalyst.





References

[1] Ferella F. *Journal of Cleaner Production*, 2020, **246**, 118990.

Integrating LiFePO4 black mass into the hydrometallurgical route for re-synthesis of Nickel-Manganese-Cobalt cathodic materials from end of life lithium ion batteries

Alyssa Mancini*, Ludovica D’Annibale, Pier Giorgio Schiavi, Pietro Altimari, Francesca Pagnanelli

Department of Chemistry University La Sapienza of Rome

* *mancini.1854544@studenti.uniroma1.it*

Lithium-Ion-Batteries (LIB) are crucial components of the green transition in renewable energy stationary accumulation systems and e-mobility [1]. The lack of European raw materials for LIB manufacturing and current regulations for environment protection push towards the development of recycling processes of end of life LIB. Due to the complexity of the structure and the chemical heterogeneity, recycling process of LIB is facing different obstacles in scaling-up to industrial field. As for chemical heterogeneity, NMC cathodic materials used in LIB are composed of oxides of Nickel, Manganese and Cobalt with different stoichiometries. These metals are critical and strategic raw materials of interest for the manufacturing sector. While LFP ($LiFePO_4$) cathodic materials are made of low-value materials and then not susceptible to dedicated hydrometallurgical processes, but mainly sent to cheaper direct recycling process for the recovery of LFP cathodes without dissolution. Nevertheless, LFP is also used as a blending material in NMC cathodic material, making the separation of these two types of black masses not feasible.

To address this issue and treat mixed powders (LFP-NMC), modifications have been made to the hydrometallurgical process for re-synthesis of NMC cathodic materials from NMC black masses recovered by end of life LIB as developed within the LIFE DRONE project [2].

The developed process includes different stages.

The first is the mechanical stage, where pre-treatment of LIB batteries occurs treating NMC and LFP, separately or together according to the sorting system available in the treatment plant.

The second stage is the hydrometallurgical stage where leaching with H_2SO_4 (1.5 M) and H_2O_2 as a reducing agent occurs to bring the target metals (Ni, Co, Mn) in solution. In this stage, the addition of LFP black masses to NMC ones allows to eliminate the use of hydrogen peroxide thus reducing the environmental impact of the developed process.

The third stage is product recovery including FePO4 precipitation and NMC precursors precipitation.

In this poster the results concerning leaching of mixed black masses and FePO4 recovery are reported.

References

[1] Jedrzej P., Semih A, TetyanaM.B., Serhiy B., Mika H. S.Adam S. *Adv. Energy Matter*. **2021**,11,2003456

[2] LIFE DRONE “Direct production of New Electrode materials from battery recycling” (LIFE19 ENV/IT/000520) https://www.lifedrone.eu/it

Evaluation of the controlled hydrodynamic cavitation as gas mass transfer system for biological hydrogen methanation

Notari Beatrice[1,2*], Vicinanza Andrea[3], Audi Mohamed [4], Giuliano Antonio[1]

[1]*SSPT-USER-T4W, ENEA Research Center, Bologna, Italy*
[2]*DICEA, University of Naples Federico II, Italy*
[3]*DISTAL Alma Mater Studiorum, University of Bologna, Italy*
[4]*DICAM Alma Mater Studiorum, University of Bologna, Italy*

**beatrice.notari@unina.it*

Biomethane obtained from biogas upgrading plays a crucial role in leading the energy transition. Among the different biogas upgrading technologies, biological hydrogenotrophic methanation (BHM) through methanogenic archaea represents a promising alternative to the traditional ones, since it allows the direct conversion of CO_2 contained in the raw biogas using exogenous green H_2 [Fig.1] [1]. Despite the relevant potential application, one of the main technical constraints that limits the global efficiency of BHM is represented by the poor solubility of H_2 into the liquid media [2]. Among the different approaches to improve the gas solubilization, an attractive solution is represented by the hydrodynamic cavitation (HC), due to the low power requirement and scale-up potential [3]. The main goal of this study is to evaluate the potential use of a novel HC reactor as a gas-liquid mass transfer system in the BHM process. A comparison between the novel HC system and two venturi tube ejectors (V4 and V6), having different nozzle sizes, in terms of gas solubilization capacity was assessed by calculating the global volumetric mass transfer coefficient (k_La) in a tubular bioreactor implemented in a closed loop circuit by adopting different inlet gas flow rate (Q_{in}) and internal liquid recirculation rate (Q_r). This study verified that gas sparging through the novel HC device can efficiently transfer gas into the liquid phase reaching k_La values of 13-192% and 13-170% higher than those of V4 and V6, respectively, in accordance with the specific operating conditions applied. The effectiveness of the controlled HC as gas-to-liquid mass transfer system in the BHM process and its long-term effects on biological process stability are evaluated in ongoing experimental pilot trials.

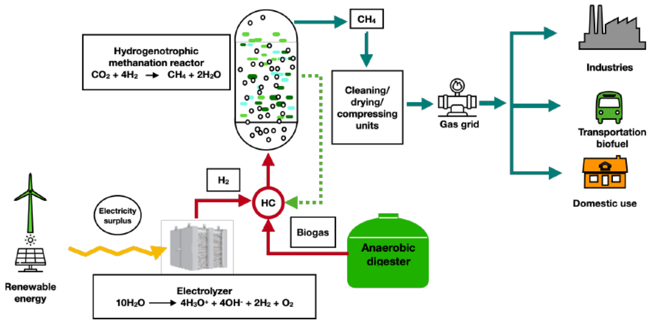


Fig. 1 – Schematic representation of the biological hydrogen methanation for biomethane production

References

[1] Antukh T., Lee I., Joo S., and H. Kim, "Hydrogenotrophs-Based Biological Biogas Upgrading Technologies" *Front. Bioeng. Biotechnol.*, 2022, **10**, 833482

[2] Jensen M.B., Ottosen L.D.M., Kofoed M.V.W., H_2 gas-liquid mass transfer: A key element in biological Power-to-Gas methanation, *Renewable and sustainable energy rev.* 2021, **147**, 111209

[3] Giuliano A., Cellamare C.M., Chiarini L., Tabacchioni S., Petta L., *Evaluation of the controlled hydrodynamic cavitation as gas mass transfer system for ex-situ biological hydrogen methanation, Chem. Engin. Jou*. 2023, **471**,144475

Enhancing dark fermentation of cheese whey with Electrically Conductive Materials

Cecilia Petitta[1,2*], Matteo Tucci[1], Matteo Daghio[3], Chiara Capelli[3], Carlo Viti[3], Alessandra Adessi[3], Federico Aulenta[1], Maria Presutti[4], Carmela Riccardi[5], Luca di Palma[2], Carolina Cruz Viggi[1]

[1] *Water Research Institute (IRSA), National Research Council (CNR), Montelibretti (Rome), Italy*
[2] *Department of Chemical Engineering Materials Environment, Sapienza University of Rome, Italy*
[3] *Department of Agriculture, Food, Environment and Forestry (DAGRI), University of Florence, Firenze, Italy*
[4] *Department of Chemistry, Sapienza University of Rome, Rome, Italy*
[5] *DIT, INAIL, Rome, Italy*
*cecilia.petitta@uniroma1.it

Cheese manufacturing companies typically rely on high-energy consumption (e.g., for refrigeration). Therefore, the development of innovative strategies for *in-situ* energy generation using alternative fuels could enhance their competitiveness and promote more sustainable production practices. Cheese whey (CW) is a residue that remains after the recovery of the curd from the clotting of milk. CW production accounts for approximately 9–10 liters per kilogram of cheese manufactured and poses significant environmental challenges due to its remarkably high chemical oxygen demand (COD), often exceeding 100 gCOD/L. Dark fermentation offers a promising solution for treating CW, converting sugars (e.g., lactose) and other compounds into volatile fatty acids (VFAs) and H_2. Notably, the produced H_2 can be used for *in-situ* electrical energy generation using conventional fuel cells. Furthermore, the generated VFAs can also be further exploited for chemicals production or for additional H_2 production using bio-electrochemical systems, like microbial electrolysis cells.

In this context, the main objective of this study was to assess the effectiveness of different electrically conductive materials (ECMs) in enhancing the rate and yield of hydrogen (H_2) and VFAs production during the dark fermentation of cheese whey (CW).

To this aim, undiluted CW (total COD of 73 g/L; soluble COD of 56 g/L) was fermented at 35°C in 250-mL, stirred anaerobic bioreactors, in presence of different ECMs (namely biochar, magnetite, and graphite) supplied at a final concentration of 10 g/L. Throughout the fermentation process, the concentrations of volatile fatty acids (VFAs), lactic acid, and H_2 were monitored over time. Additionally, upon completion of the fermentations, the bacterial communities were analyzed through high-throughput sequencing of 16S rRNA gene amplicons.

Remarkably, dark fermentation experiments conducted with CW revealed a significant enhancement in the production of H_2 and VFAs (up to ten-fold) in presence of ECMs, where biochar exhibited the most promising outcomes. This stimulating effect caused by ECMs is likely due to the promotion of direct interspecies electron transfer (DIET) processes among the syntrophic partners engaged in cheese whey fermentation.

This work was co-financed by the Italian Ministry of University and Research during the research program PRIN 2022 PNRR "Valorization of cheese whey by hydrogen production in bio-electrochemical systems catalyzed with purple bacteria (WHISPER)"

Extraction and characterization of lignin from chestnut via hydrothermal treatment

Valeria Pierpaoli[1*], Giorgio Tofani[2], Miha Grilc[2,3], Jasmina Jusic[1,4], Manuela Romagnoli[1],

[1]Department for Innovation in Biological, Agro-Food and Forest Systems (DIBAF), University of Tuscia,
Via S. Camillo de Lellis, snc, 01100 Viterbo, Italy
[2] Department of Catalysis and Chemical Reaction Engineering, National Institute of Chemistry, Hajdrihova 19, 1001 Ljubljana, Slovenia
[3]Center of Excellence for Low Carbon Technology, Hajdrihova 19, 1000 Ljubljana, Slovenia
4Fraunhofer Italia, Via Alessandro Volta 13A, 39100, Bozen, Italy

**valeria.pierpaoli@unitus.it*

Castanea sativa plays a significant role in the Italian forestry sector, due to its widespread presence for nearly 2.6% of Italy's total land (1). This biomass' resource includes significant volumes of residues from wood processing (2): over the years there has been a change in its exploitation, from being a fuel source to high-value applications considering the fractionation of lignocellulosic biomass to obtain biopolymers,. In particular, lignin has aroused special attention as it is the most abundant aromatic biopolymer (3). Among chemical treatments, thermochemical ones such as hydrothermal treatment or pyrolysis are alternatives to generate energy and chemicals at the same time: many studies (4) have investigated the potential of the fractions obtained from these processes (bio-oil, water-soluble fraction, water-insoluble fraction), but have never focused on the lignin nanomaterials production and application.

The main goal of this study is to identify the composition of the hydrochar obtained from the hydrothermal treatment of chestnut to understand if the contained lignin can be further used for high-valued applications, such as the synthesis of nanoparticles, mainly aimed at drug delivery.
Three types of chestnut biomass were used: virgin wood waste (VW, which has not undergone any alteration or treatment), chestnut wood bark (B) and detannized wood waste (DT, which has undergone the tannin extraction process at the industrial level). The wood materials were air dried for several weeks and resulted in a 0.25 mm wood powder that was put into the 250 mL hydrothermal reactor at 200 °C. The extracted fractions were isolated and characterised.
The resulting hydrochar was analyzed via FTIR to provide information about the presence of functional groups and molecular structures, via HPSEC to provide information about size and via TGA to study its thermal stability and decomposition behaviour. The observation of the outcomes derived from these analyses suggests the presence of lignin in some fractions exiting the hydrothermal reactor, albeit requiring further purification before utilization.
Further investigations will be carried out, for example by solvent extraction. This will enable the repetition of FTIR, HPSEC and TGA analyses to assess the feasibility of producing lignin nanoparticles.

References

[1] Marini F, Portoghesi L, Manetti M, Salvati L, Romagnoli M. Gaps and perspectives for the improvement of the sweet chestnut forest-wood chain in Italy. Ann Silvic Res
[2] Santana-Méridas O, González-Coloma A, Sánchez-Vioque R. Agricultural residues as a source of bioactive natural products. Phytochem Rev. 2012 Dec;11(4):447–66.
[3] Abu-Omar MM, Barta K, Beckham GT, Luterbacher JS, Ralph J, Rinaldi R, et al. Guidelines for performing lignin-first biorefining. Energy Environ Sci. 2021;14(1):262–92.
[4] Bridgwater AV. Review of fast pyrolysis of biomass and product upgrading. Biomass Bioenergy. 2012 Mar;38:68–94.

BIotechnologies for SUstainable REmediation – BISURE: Development of integrated chemical-physical-biological processes for the contaminated groundwater remediation

Maria Presutti*, Giulia Simonetti, Marco Zeppilli, Marco Petrangeli Papini

Department of Chemistry, Sapienza University of Rome, Rome, Italy

**maria.presutti@uniroma1.it*

The chlorinated aliphatic hydrocarbons (CAHs) are organic compounds widely used in various sectors of the industrial field (i.e. for cleaning metals, as solvents and raw materials in the chemical-pharmaceutical industry) (1). The wide diffusion of CAHs over the past years and their incorrect disposal and storage made these substances become one of the most common contaminants of both subsoil and groundwater in the world. CAHs are persistent compounds and some of them have densities greater than water, thus can migrate towards deeper aquifers landing to a widespread soil and groundwater contamination (2). In addition to CAHs, also heavy metals (HM) are widespread toxic pollutants often found as co-contaminants in groundwater, representing a relevant concern for the quality of the natural resources. In this context, the BISURE project focus on the application of combined biological and chemical-physical remediation technologies to promote simultaneous CAHs and HM biodegradation or biotransformation. Indeed, the combination of autochthonous specialized microbes, such as *Dehalococcoides mccartyi*, with the use of sustainable biomaterials (i.e. polyhydroxyalkanoates, biochar) (3) or strategies (i.e. bioelectrochemical systems) (4) represents a significant advantage for boosting biological remediation. The BISURE project follows a transversal methodological approach involved by focusing on two main objectives. The first objective is to obtain microbial consortia able to remove simultaneously CAH and HM and evaluate the metabolic/functional of the leading key players using advanced biomolecular tools (-omics); while the second objective is the development of innovative BRT, including bioelectrochemical system PHA, biochar at laboratory scale, for the combined removal of CAH and HM.

Acknowledgements: The project BISURE (2022AXYMKY) has been funded within the framework of the PIANO NAZIONALE DI RIPRESA E RESILIENZA (PNRR) Missione 4 “Istruzione e Ricerca” – Componente C2, Investimento 1.1, “Fondo per il Programma Nazionale di Ricerca e Progetti di Rivelante interesse Nazionale (PRIN).

References

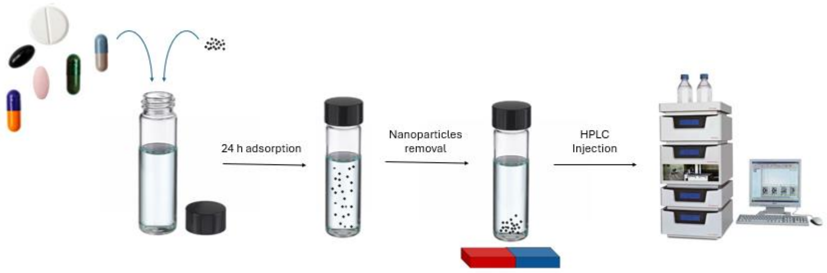
[1] Lai A. *et al.*, Chemosphere 169, 351-360, 2017.
[2] Ciampi P. *et al.*, Heliyon 8, e11402, 2022.
[3] Di Franca M. L. *et al.*, Frontiers in Microbiology, Vol. 13, art. 951911, 2022
[4] Zeppilli M. *et al*. Journal of Environmental Chemical Engineering, Vol. 9, art. 104657, 2021.

Removal of Pharmaceuticals from Water Using Polyoxazoline-Functionalized Magnetic Iron Oxide Nanoparticles

Agnese Ricci[1*], Luca Stefanuto[1], Sara Del Galdo[1], Simone Pepi[2], Valerio Graziani[1], Barbara Capone[1], Claudio Rossi[2], Gaspare Varvaro[3], Luca Tortora[1], Stefano Casciardi[4], Giancarlo Masci[5] and Tecla Gasperi[1]
[1]Department of Science, Roma Tre University, Rome, Italy
[2] Department of Chemistry, Siena University, Siena, Italy
[3]Institute of Structure of Matter ISM, CNR, Rome, Italy
[4]Department of Occupational Hygiene, INAIL, Rome, Italy
[5]Department of Chemistry, Sapienza University, Rome, Italy

**Agnese.Ricci@uniroma3.it*

Pharmaceutical pollution is an emerging environmental concern, with increasing amounts of pharmaceuticals being detected in water bodies due to human and industrial activities. These contaminants pose significant risks to aquatic ecosystems and human health, as conventional water treatment processes are often inadequate for their removal.[1] This study investigates the synthesis and application of iron oxide nanoparticles functionalized with polyoxazoline, a biocompatible polymer, for the removal of pharmaceutical contaminants from water, focusing on water remediation. Polyoxazoline was chosen due to its excellent biocompatibility, hydrophilicity, and ability to form stable coatings on nanoparticle surfaces, enhancing their adsorption properties.[2] Characterization techniques, including Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), and Thermogravimetric analysis (TGA) confirmed the successful synthesis and functionalization of the nanoparticles. Magnetization measurements using Vibrating Sample Magnetometry (VSM) demonstrated that the nanoparticles maintain their magnetic properties post-functionalization, ensuring their suitability for magnetic separation techniques. Adsorption experiments, conducted as shown in the figure, demonstrated that the polyoxazoline-coated iron oxide nanoparticles exhibit high affinity for pharmaceutical compounds in water, significantly reducing their concentrations. The results indicate that these functionalized nanoparticles can effectively remediate water contaminated with pharmaceuticals, showcasing their potential for practical applications in wastewater treatment. Future studies will aim to optimize the adsorption process, evaluate the long-term stability and reusability of the nanoparticles, and assess their performance in real environmental conditions. The promising findings of this study suggest that polyoxazoline-functionalized iron oxide nanoparticles could play a vital role in improving water quality and protecting environmental health.



References

[1] Chopra, S. et al., *Heliyon*, 2020, **6**, 6.
[2] Nemati Mahand S. et al., *European Polymer Journal*, 2022, **178**, 111484.

Lignin-based catalysts for hydrogen production

Tahreem Saleem[1,2,]*, Pietro Colucci[3], Elisabetta Borsella[2], Heiko Lange[1]

[1] Department of Earth and Environmental Sciences, University of Milano-Bicocca,
Piazza della Scienza 1, 20126 Milan, Italy
[2]Research Centre ENEA Casaccia, Via Anguillarese 301, 00123 Rome, Italy
[3] Research Centre ENEA Trisaia, SS 106 Jonica km 419+500, 75026 Rotondella, Italy

** t.saleem@campus.unimib.it*

Biochar exhibits potential as catalyst in biomass gasification for hydrogen production. Preliminary findings indicate the feasibility to retain key functional groups of lignin during a pyrolysis approach by controlling biochar formation conditions, like temperature, reaction time especially heating rate. This allows for the production of biochar with oxygen-containing functionalities, facilitating modifications toward higher value-added products [1]. The investigation of lignin-based biochar using technical kraft and organosolv lignins aims to identify those suitable for catalytic functionalization. Comparative analysis with lignosulfonate and commercial alkali lignin offers valuable insights into the selection process.

Biochars were produced from various lignins using vacuum pyrolysis with a rapid heating rate of 700°C per minute. The samples were heated to 600°C and held for 2 minutes to prevent side reactions and unwanted product formation [2]. Characterization of the biochar included specific surface area and porosity analysis, thermogravimetric analysis, elemental analysis, scanning electron microscopy, and nuclear magnetic resonance. Liquid and gaseous fractions were analyzed using GC-MS detecting phenolic compounds and/or aromatic hydrocarbons during pyrolysis, having applications in biochemical intermediates and biofuel additives.

From the preliminary results, lignosulphonate and alkaline lignins seem to be the most reluctant to react, highlighting an unsuitability for the formation of a functionalizable biochar. The high sulfur content in lignosulfonate lignin and its derived biochar makes it unsuitable for catalyst development. Differently, the technical lignins appear to be the most promising lignins in the production of functionalizable biochar. TGA analyses on pyrolytic biochars demonstrate a great thermal stability at 600 °C compared to the precursor lignins, and BET and NMR studies show biochar structures easily malleable to the insertion of catalytically active metals.

Acknowledgement:

TS, PC and EB acknowledge to Energy Technologies and Renewable Sources Department (TERIN) of ENEA for its support and contributions to this project. This research was funded by the European Union - NextGenerationEU from the Italian Ministry of Environment and Energy Security, POR H2 AdP MEES/ENEA with involvement of CNR and RSE, PNRR - Mission 2, Component 2, Investment 3.5 "Ricerca e sviluppo sull'idrogeno", CUP: I83C22001170006

References

[1] Amalina, F., et al., *Biochar production techniques utilizing biomass waste-derived materials and environmental applications–A review.* Journal of Hazardous Materials Advances, 2022. **7**: p. 100134.

[2] Ippolito, J.A., et al., *Feedstock choice, pyrolysis temperature and type influence biochar characteristics: a comprehensive meta-data analysis review.* Biochar, 2020. **2**: p. 421-438.

Novel Solutions for Enhanced Performances in Fluoride-Ion Batteries

Federico M. Scesa[a], Marco Gregorio[a], Luca Magagnin[a,b], Maurizio Sansotera[a,b]

[a]*Department of Chemistry, Materials and Chemical Engineering "G.Natta", Politecnico di Milano, via Mancinelli 7, Milano, Italy*

[b]*Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (UdR-PoliMi), via G. Giusti, 9, 50121 Firenze, Italy*

**federicomaria.scesa@polimi.it*

The rising demand for greater energy storage capacity at reduced costs necessitates a new generation of electrochemical energy storage devices. Additionally, as battery production continues to grow, there is a pressing need to develop more sustainable chemistry that avoids depleting limited resources. Recently, fluoride-ion shuttle batteries have garnered significant interest. This is due to their potential to employ a cost-effective, high-capacity conversion cathode that exploit multi-electron transfer processes and utilizes a metal anode without the dangers of dendrite formation, thereby improving safety and performance. Currently, one of the major obstacles in creating a fluoride-ion battery that can rival contemporary lithium-ion batteries is identifying a suitable electrolyte. This study explores an innovative solution in electrolyte technology aimed at ensuring ionic conductivity and high chemical and electrochemical stability, which enables cycling between metal and metal fluoride electrodes at room temperature. Herein this work, a solid-state electrolyte demonstrated its ability to cycle Pb/PbF_2 electrodes at room temperature, achieving an initial capacity of 90% of the theoretical maximum.

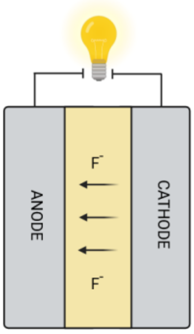


Figure 2. Working principle of Fluoride-ion battery

References

[1] Xiao, A. W.; Galatolo, G.; Pasta, M. *Joule* **2021**, *5* (11), 2823–2844.

[2] Davis, V. K.; Bates, C. M.; Omichi, K.; Savoie, B. M.; Momčilović, N.; Xu, Q.; Wolf, W. J.; Webb, M. A.; Billings, K. J.; Chou, N. H.; Alayoglu, S.; McKenney, R. K.; Darolles, I. M.; Nair, N. G.; Hightower, A.; Rosenberg, D.; Ahmed, M.; Brooks, C. J.; Miller, T. F.; Grubbs, R. H.; Jones, S. C. *Science* **2018**, *362* (6419), 1144–1148.

[3] Davis, V. K.; Munoz, S.; Kim, J.; Bates, C. M.; Momčilović, N.; Billings, K. J.; Miller, T. F.; Grubbs, R. H.; Jones, S. C. *Mater. Chem. Front.* **2019**, *3* (12), 2721–2727.

[4] Galatolo, G.; Alshangiti, O.; Di Mino, C.; Matthews, G.; Xiao, A. W.; Rees, G. J.; Schart, M.; Chart, Y. A.; Olbrich, L. F.; Pasta, M. *ACS Energy Lett.* **2024**, *9* (1), 85–92.

Hydrogen and methane production in a microbial electrolysis cell

Federico Scopetti[1*], Igino De Bellis[1], Clara Marandola[1], Marco Zeppilli[1], Roberto Ciccoli[2],
Antonella Signorini[2], Antonella Marone[2], Marianna Villano[1]

[1]Department of Chemistry, Sapienza University of Rome, Rome, Italy
[2]Casaccia Research Center, Italian National Agency for New Technologies Energy and Sustainable Economic Development (ENEA), Rome, Italy

**federico.scopetti@uniroma1.it*

Microbial Electrolysis Cells (MEC) are bioelectrochemical devices which can be employed to couple wastewaters treatment to the generation of valuable products (i.e., fuels or chemicals), by adding a small external voltage [1]. This research focused on the set up and operation of a two-compartment lab scale MEC aimed at the production of hydrogen and methane. The anode chamber of the MEC was inoculated with activated sludge (deriving from a municipal wastewater treatment plant) which, upon operation under anaerobic conditions, rapidly enriched in electrochemically active microorganisms capable of using the anode as final electron acceptor for the oxidation of organic substrates. The anode electrodic material consisted of graphite granules, which also functioned as a physical support for the growth of the electroactive biofilm. A stainless-steel plate was used in the cathode chamber as electrode material. Two successive MEC runs were performed: one aiming at hydrogen production using an abiotic cathode (Run 1) and one aiming at methane production, in which the cathode compartment was inoculated with an anaerobic microbial culture enriched into hydrogenophilic methanogens (Run 2). In the latter case, the MEC cathode was continuously flushed with a gaseous mixture containing carbon dioxide (30 % v/v, N_2 balance) simulating the composition of a biogas from an anaerobic digester. Throughout the overall experimentation, the MEC was operated by controlling the anode potential at +0.20 V vs. SHE (Standard Hydrogen Electrode). The anode compartment was fed with a synthetic solution containing sodium acetate at an applied organic loading rate of 1.14 gCOD/Ld. In both runs, a high COD (Chemical Oxygen Demand) removal efficiency was observed (equal to 87 ± 2 % and 61 ± 6 % for Run 1 and Run 2, respectively), with an average current generation of 59 ± 2 and 54 ± 2 (for Run 1 and Run 2, respectively). The resulting columbic efficiency (CE), which represents the fraction of the consumed COD diverted into current, accounted for 77 ± 8 % and 84 ± 10 % (for Run 1 and Run 2, respectively), clearly indicating the establishment of an electroactive biofilm in the anode compartment of the MEC. As expected, hydrogen (generated at a rate of up to 46 meq/d) was the main cathodic product in Run 1, whereas methane (up to 141 meq/d) was produced in Run 2. The obtained results were compared with literature data, wherein a mixed metal oxide (MMO) plate was used as the cathode material in the same reactor configuration [2]. Overall, the stainless-steel plate was revealed to be a more efficient MEC cathode material than the MMO plate for hydrogen and methane production.

Acknowledgements: This research was funded by the European Union – NextGeneration EU from the Italian Ministry of Environment and Energy Security POR H2 AdP MMES/ENEA with involvement of CNR and RSE, PNRR - Mission 2, Component 2, Investment 3.5 "Ricerca e sviluppo sull'idrogeno" CUP: I83C22001170006.

References

[1] Angelidaki I., Treu T., Tsapekos, P., Luo, G., Campanaro, S., Henrik, W., Panagiotis G. K., *Biotechnology Advances*, 2018, **36**, 452-466
[2] Cristiani, L., Zeppilli, M., Fazi, G., Marandola, C., & Villano, M. *Biochemical Engineering Journal*, 2024, **205**, 109249.

Liposomes and lipoplexes for food safety in agriculture

Beatrice Simonis[1*], Giulio Testone[2], Zeineb Aturki[2]

[1]CNR-Institute for Biological Systems (ISB), Secondary Office of Rome-Reaction Mechanisms c/o Department of Chemistry, Sapienza University, P. le A. Moro 5, Rome, 00185, Italy
[2]CNR-Insitute for Biological Systems (ISB), Rome 1 Reaserch Area, Montelibretti, 00015, Italy

**beatrice.simonis@cnr.it*

Food safety challenges have evolved with the emergence of new agricultural practices and the development of novel formulation techniques and tools. [1] In this scenario, the encapsulation of bioactive substances (essential oils, plant extracts, fungal metabolites, etc.) is a promising and sustainable tool to preserve foods from contamination and organoleptic spoilage. [2]

In this work, different formulations of liposomes and lipoplexes will be studied with the aim of developing nanosystems able to improve the organoleptic qualities of agri-food products and able to prevent food degradation. Several liposome and lipoplex formulations composed of a natural phospholipid with or without the presence of cholesterol mixed with synthetic ligands will be investigated. Different preparation methods and several encapsulation strategies of bioactive compounds and genetic materials will be explored. The developed formulations will be characterized from a physico-chemical point of view by assessing the colloidal stability over time in terms of size, polidispersity index (PDI) and ζ potential evaluated by Dynamic Light Scattering (DLS) and by electrophoretic mobility measurements.

The study of plant responses to treatments is mandatory to ensure that both crop quality and food safety are preserved. Therefore, formulations with the highest efficacy will be tested on plants or their edible products, followed by metabolomics and transcriptomics surveys targeting key (e.g. beneficial or undesired) compounds.

Acknowledgements:

This project is supported by "ON Foods-Research and innovation network on food and nutrition Sustainability, Safety and Security—Working ON Foods" NRRP Next Generation EU project (Project code PE00000003).

References

[1] Calicioglu O., Flammini A., Bracco S, Bellù, L., Sims, R., *Sustainability*, 2019, **11**, 222.
[2] Zabot GL, Schaefer Rodrigues F, Polano Ody L, Vinícius Tres M, Herrera E, Palacin H, Córdova-Ramos JS, Best I, Olivera-Montenegro L., *Polymers*, **14**, 4194.

CMC and Sodium Alginate as novel water-soluble binders for NMC cathodes

Eleonora Stornelli[1*], Arianna Tiozzo[2,3], Nello Li Pira[2], Mauro Francesco Sgroi[3], Mohammad Abdi[3], Riccardo Rocca[2], Mattia Giuliano[2]

[1]Department of Basic and Applied Sciences for Engineering, Sapienza University of Rome, Rome, Italy
[2]C.R.F. - Stellantis South Europe Technical Center, Strada Torino 50, 10043 Orbassano (TO), Italy,
3Department of Chemistry, University of Turin, 10125 Turin, Italy

**eleonora.stornelli@uniroma1.it*

In recent years the issue of carbon emissions in the atmosphere has become more and more urgent, focalizing the attention of the automotive industry on the research and development of e-mobility technologies.

Novel water-based binders for battery materials represent, in this context, an important opportunity for the e-mobility market, due to simplification in electrode preparation (simple water can be used as a solvent instead of N-Methyl-2-Pyrrolidone) and in active material re-use at the end of the battery life cycle[1].

This study aimed to evaluate the electrochemical performances and surface morphologies of NMC 811 cathodes with Sodium Alginate and Carboxymethyl Cellulose in different combinations substituting the commercially used PVdF as the electrode binder.

The obtained electrodes underwent 50 charge and discharge cycles at 0.5 C and 21 cycles at 0.1 C charge and increasing C-rate discharge to determine cycling and C-rate performances. Additionally, SEM images and Raman spectra of the electrodes before and after the cycles were acquired. Our findings showed good performances obtained from the 4% alginate + 1% CMC composition of polymers, which will be further examined in future studies (in which the active material will undergo different pre-treatments such as ball milling and doping.)

References

[1] Jianlin Li, Yingqi Lu, Tairan Yang, Dayang Ge, David L. Wood III, and Zheng Li. *iScience*, 2020, **23**, 101081.

Theme H - Chemistry and Biology

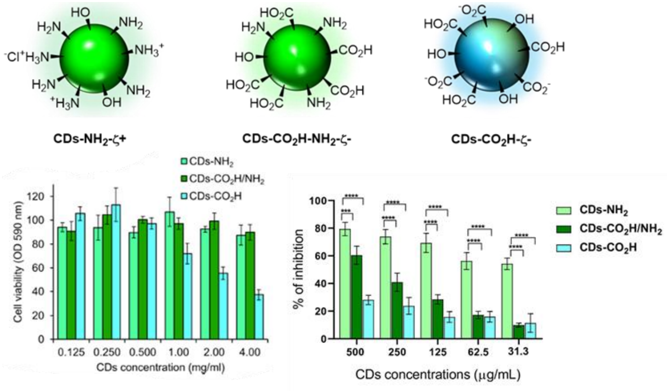
Influence of Surface Functional Groups of Carbon Dots on the Inhibition of *Candida albicans* Biofilm

Alessandro Camilli[1*], Elisa Sturabotti[2], Alessio Valletta[3], Giovanna Simonetti[3], Elena Miranda[4],
Andrea Giacomo Marrani[1], Luisa Maria Migneco[1], Fabrizio Vetica[1], Francesca Leonelli[1]

1Department of Chemistry, Sapienza University of Rome, Piazzale Aldo Moro 5, 00185 Rome, Italy
[2]Center for Cooperative Research in Biomaterials (CIC biomaGUNE), Basque Research and Technology Alliance (BRTA), Donostia-San Sebastian, Spain
[3]Department of Environmental Biology, Sapienza University of Rome, Piazzale Aldo Moro 5, 00185 Rome, Italy
[4]Department of Biology and Biotechnologies "Charles Darwin", Sapienza University of Rome, Piazzale Aldo Moro 5, 00185 Rome, Italy

**alessandro.camilli@uniroma1.it*

Carbon Dots (CDs) are an emerging class of photoluminescent, zero-dimensional and quasi-spherical carbon nanomaterials which, for their exceptional and tuneable features, have found applications in many fields, such as sensing, catalysis and biomedicine [1]. Within this context, CDs are regarded as a new means to overcome the issue of Antimicrobial Resistance, as they show water dispersibility, chemical stability and biocompatibility [2]. However, most of the attention is focused on their antibacterial properties, while their use as antifungal agents has been scarcely investigated. Therefore, in this work[3] we report a systematic study of the CDs' surface functional groups to evaluate their effects against *Candida albicans*. Three classes of different surface charged CDs have been synthesized and fully characterized. Then, a thorough *in vitro* and *in vivo* biological screening was performed to test CDs' cell viability and to evaluate their antifungal, antiadhesion and antibiofilm formation properties. Our results led us to state that positively polarized amino groups are essential for the internalization of CDs into cells. Also, positively charged CDs were able to inhibit the adhesion and biofilm formation of *C. albicans*, to interact with its cellular membrane and to increase the survival of *G. mellonella* infected larvae. Hence, CDs may represent a new strategy to overcome infections caused by *C. albicans.*



References

[1] Dordevic L., Arcudi F., Cacioppo M., Prato M., *Nature Nanotechnology*, 2022, **17**, 112-130.
[2] Ghirardello M., Ramos-Soriano J., Galan M. C., *Nanomaterials*, **2021**, 11, 1877.
[3] Sturabotti E., Camilli A., Moldoveanu V.G., Bonincontro G., Simonetti G., Valletta A., Serangeli I., Miranda E., Amato F., Marrani A. G., Migneco L.M., Sennato S., Simonis B., Vetica F., Leonelli F., *Chem. Eur. J.*, 2023, e202303631.

Mercury in benthos organisms: formalin fixation or freezing?

Fucile G.[1,2], Berducci M.T. [1], Fabrizi V. [1], Trigilio L. [1], Maggi C. [1]

[1]*ISPRA Institute for Environmental Protection and Research,, Rome, Italy*
[2]*Tor Vergata University of Rome*

**giulia.fucile@alumni.uniroma2.eu*

Formalin is commonly used to preserve and fix the tissue for the animal's recognition.
Some studies have found that formalin fixation does not alter tissue trace element concentrations, whereas other studies have found that formalin fixation significantly alters tissue trace element concentrations, either by increasing or decreasing concentrations, suggesting issues of contamination and leaching, respectively.[1]
Mercury (Hg) particularly its organic form, methylmercury (MeHg), is an acute neurotoxin that bioaccumulates in aquatic biota, reaching high concentrations in apex predator which pose a risk to human health. [1]
In this work mercury (Hg) was analysed to evaluate bioaccumulation in benthos organisms from Italian Seas. When measuring trace element concentrations in animal tissues, it is imperative that sample collection, preservation, and processing do not alter tissue trace element concentrations. Although fresh or frozen tissues are preferable for trace element analysis, formalin-fixed tissues are often the only option available. [2]
In this study frozen and formalin-fixed benthos organisms were analyzed. The frozen sample was immediately fixed in falcon and taken to the laboratory; instead, the formalin-fixed sample was put in the falcon with the solvent. In the laboratory, the organisms were separated in the main taxa groups (polychaetas, mollusks, crustaceans, and echinoderms) and then every taxon was analyzed, and Hg measured.
Mercury was determined with Direct Mercury Analyzer, DMA-80 (FKV) using SRM 2976 as a Reference Material.
The results showed some differences in Hg concentration from frozen and formalin-fixed samples. In some cases, the concentrations were lower in formalin-fixed tissues compared with them in frozen tissues, it is likely because trace elements were leached from tissues into the preservative solution. Moreover, sometimes, Hg concentrations in formalin-fixed tissues were greater than concentrations in frozen tissues, it was likely because the solvent could contain impurities of Hg. The formalin used to preserve and fix organisms showed a Hg contamination in some cases.
Our results suggest that it is possible to account for the effects of formalin following short-term and/or long-term storage but leaching and contamination must be carefully considered when using formalin-preserved tissues for trace element analysis.

References

[1] Wesley W. H., G. Dam H., Robert P. M., Zofia B. Science of the Total Environment, 2020, 738.
[2] Meaghan A. M., Brian P. J., Jessica D. Environmental Toxicology and Chemistry, 2020, 39, 6.

Seleno-glycoconjugates for the prevention of oxidative stress

Claudia González[1*], Reinier Lemos [1,2], Mauro De Nisco[3], Silvana Pedatella[1]

[1] Department of Chemical Sciences, University of Naples Federico II, Via Cintia 4, I–80126, Naples, Italy
[2] Organic Synthesis Laboratory, Faculty of Chemistry, University of Havana, Zapata, 10400, Havana, Cuba
[3]Department of Sciences, University of Basilicata, Via dell´Ateneo Lucano 10, I-85100, Potenza, Italy

**claudia.gonzalezcastro@unina.it*

Since the evaluation of Ebselen as glutathione peroxidase (GPx) mimetic,[1] organoselenium compounds are gaining interest in the medicinal chemistry community due to their promising biological activities for a wide range of clinical applications.[2] Several Se-bearing molecules were indeed reported as anticancer, anti-inflammatory, antidepressant and antibacterial.[3] Even if organoselenium compounds do showcase important biological properties, their actual clinical exploitability could be hampered by the low aqueous solubility which precludes them from reaching therapeutically relevant doses in blood.[3] A possible strategy to overcome this barrier is to combine the important pharmacological properties of selenium with the physicochemical properties of sugars, leading to the class of selenosugars and their derivatives.[3]

Moreover, polyphenols are molecules with antioxidant[4] capacity due to their structure: they have a broad conjugate system and hydroxyl function capable of deactivating or inhibiting radical precursors or free radicals. In this contest, the design of new molecules that consider synergistic interactions among the different antioxidants, could be useful to develop possible therapeutic agents.

This work is part of a project aimed to the preparation of glycoderivates with antioxidant functions useful for the prevention of oxidative stress: namely, seleno-glycoconjugates. They can express, by combining the antioxidant properties of Se with the chelating and antioxidant properties of a polyphenolic unit, a synergistic antioxidant activity greater than the individual components.[5] Based on remarkable results[6] obtained with previous generation of compounds, using D-ribose, in this work we started from the commercially available D-mannose, which was then used as donor for the preparation of glycoconjugates using different polyphenols.

References

[1] Sies, H. et al. In Advances in Pharmacology; Sies, H., Ed.; Academic Press, 1996; Vol. 38, 229–246.
[2] Lenardão, E. J. et al. New Frontiers in Organoselenium Compounds; Springer International Publishing: Cham, 2018.
[3] Mangiavacchi, F. et al. Pharmaceuticals 2020, 13(9), 211.
[4] Tapiero, H. et al. Biomed. Pharmacother. 2002, 56(4), 200–207.
[5] Vertuani, S. et al. Curr. Pharm. Des. 2004, 10(14), 1677–1694.
[6] Serpico, L. et al. Molecules 2021, 26(9), 2541.

Metagenomics of a column reactor promoting reductive biological dechlorination by coupling TCE biodegradation and adsorption with bio-based materials

Bruna Matturro[1*], Simona Rossetti [1] , Laura Lorini [2] , Marco Petrangeli Papini [2]

[1] Water Research Institute of the National Research Council, IRSA-CNR, Rome, Italy
[2] Chemistry Department, Sapienza University, Rome, Italy

**bruna.matturro@irsa.cnr.it*

The development of new biotechnologies for the remediation of chlorinated solvents contaminated sites attracts research activities, in particular when the use of bio-based materials is proposed. Bio-based materials are capable of stimulating and supporting the reductive dechlorination (RD) with valuable implications for the development of novel bioremediation treatments in the circular economy. Some studies have demonstrated the effectiveness of the polyhydroxybutyrate (PHB), a bio-synthesized polyester completely biodegradable in the environment, as a slow-release electron donor suggesting that PHB can successfully sustain the RD also for in situ application in bioengineering systems. Also, organic waste-derived biochar (BC) has received attention as it can accelerate the electron transfer in several bioprocesses. BC is a carbon-rich bio-material BC, produced by the pyrolysis of diverse biomass species and commonly used for contaminants' adsorption and recently emerged as a good candidate for mediating electron transfer in contaminants biotransformation processes.

Recently, bioreactors that employ PHB or biochar for remediation applications have been tested at laboratory scale. However, the composition and functions of the microbial communities established when PHB or biochar are used in a biological reactor for RD has been poorly investigated.

In this study we describe the composition and metabolic features of the microbial community established in a column bioreactor that couples PHB and biochar as bio-based materials to prompt the RD of TCE-contaminated groundwater. The PHB and BC reactive zones were described via metagenomics sequencing to investigate the central biological pathways occurring in the biofilm growing on the biomaterials used for the system.

.

Acknowledgements: This study has been conducted within the project BISURE (2022AXYMKY). BISURE has been funded within the framework of the PIANO NAZIONALE DI RIPRESA E RESILIENZA (PNRR) Missione 4 “Istruzione e Ricerca” - Componente C2, Investimento 1.1, “Fondo per il Programma Nazionale di Ricerca e Progetti di Rilevante Interesse Nazionale (PRIN).

Screening of synthetic molecules active towards Bacillus cereus group

Elena Passarini[1*], Angela Cirigliano[2], Claudia Marconi[3], Iolanda Francolini[3], Anita Scipioni[3], Giancarlo Masci[3], Luciano Galantini[3], Teresa Rinaldi[1].

[1]Department of Biology and Biotechnology, Sapienza University of Rome, Rome, Italy.
[2]Institute of Molecular Biology and Pathology, CNR, Department of Chemistry,
Sapienza University of Rome, Rome, Italy.
[3]Department of Chemistry, Sapienza University of Rome, Rome, Italy.

**elena.passarini@uniroma1.it*

Bacillus spp. are gram-positive bacteria able to produce and release spores, more resistant to adverse environmental conditions than the vegetative form. Spore decontamination of the *Bacillus cereus* group is a critical issue in industrial and medical fields. For instance, *Bacillus cereus* is responsible for toxin-related food intoxications and is of pivotal concern for the food industry [1]. *Bacillus anthracis* strains can cause lethal gastrointestinal, cutaneous, and systemic infections and it is a health concern because it has been used as bioweapon in bio-terroristic attacks [2]. To inactivate spores, chemical and physical methods, or a combination of them, are currently applied but, unfortunately, they are not always effective or suitable, in fact, food perishability and safety are limiting factors for the use of some chemical methods. Hence, the importance to find an effective and safe decontamination method. In this context, our aim is to test and screen the sporicidal activity of synthetic molecules, which could be safe for the operators and *green* for the environment [3]. The antimicrobial activity of selected molecules active towards *Bacillus* spores has also been tested with other bacterial species, considering that the emergence of antimicrobial resistance is becoming critical [4,5]. Currently, we are testing the effect of a set of molecules towards some bacterial species and this screening highlighted a promising activity of the compounds as antimicrobics.

References

[1] Tuipulotu DE., Mathur A., Ngo C., Ming Man S. *Trends in microbiology,* 2021, **29**, 458.
[2] Koehler TM., *Molecular aspects of medicine,* 2009, **30**, 386.
[3] Ebbensgaard A., Mordhorst H., Toft Overgaard M., Gyrup Nielsen C., Møller Aarestrup F., Bech Hansen E. *Plos One*, 2015, **10**, e0144611.
[4] Jurado-Martìn I., Sainz-Mejìas M., McClean S. *International journal of molecular sciences,* 2015, **22**, 3128.
[5] Nikolic P., Mudgi P. *Microorganisms*, 2023, **11**, 259.

Pisum sativum L. ‘Eso’: Metabolic profiling of yellow seeds to define the optimal harvest time.

Adriano Patriarca[1*], Fabio Sciubba[2,3], Alberta Tomassini[4], Ottavia Giampaoli[2,3], Michele de Rosa[1], Federico Marini[1,3], Walter Aureli[4], Alfredo Miccheli[3], Elisa Brasili[2,3]

[1] Department of Chemistry, University of Rome Sapienza, Piazzale Aldo Moro 5, 00185 Rome, Italy;
[2] Department of Environmental Biology, University of Rome Sapienza, Piazzale Aldo Moro 5, 00185 Rome, Italy;
[3] NMR-based Metabolomics Laboratory, University of Rome Sapienza, Piazzale Aldo Moro 5, 00185 Rome, Italy;
[4] R&D Azienda Agricola Aureli Mario, Via Mario Aureli, n.7, 67050 Ortucchio AQ

** adriano.patriarca@uniroma1.it*

Yellow pea (*Pisum sativum* L. ‘Eso’, sin. *Lathyrus oleracaeus* Lam. (YP)) is an annual herbaceous plant that belongs to the Fabaceae family. Peas, along with other legumes, are an excellent source of proteins and essential amino acids; the yellow variety is known for maintaining a good protein profile even if subjected to industrial processing [1]. However, the presence of antinutrients, such as phytates and oligosaccharides, limits its consumption as a fresh legume addressing its use as a source of isolated proteins or for animal feed [2]. The aim of the study is to evaluate the changes in the entire phytochemical profile of YP seeds as a function of the harvest time. YPs harvested at about 40, 50, 60 and 70 days from sowing were examined by high-resolution NMR spectroscopy employing ^{1}H-NMR, ^{1}H-^{1}H TOCSY and ^{1}H-^{13}C HSQC [3]. Multivariate data analysis was carried out by combining multivariate data with the design experiment using ANOVA-simultaneous component analysis (ASCA) [4]. 40 molecular species have been identified and quantified; it was observed that there is a monotonous decrease in amino acids, carbohydrates, and secondary metabolites as a function of time. Antinutrients levels increased, but only in later sampling times. This study identified the optimal harvest time for yellow peas “Eso” in fortieth day from sowing adding new information about the best nutritional outcome for humans.

References

[1] Nosworthy, M.G.; Franczyk, A.J.; Medina, G.; Neufeld, J.; Appah, P.; Utioh, A.; Frohlich, P.; House, J.D. Effect of Processing on the in Vitro and in Vivo Protein Quality of Yellow and Green Split Peas (Pisum Sativum). *J Agric Food Chem* 2017, **65**, 7790–7796, doi:10.1021/acs.jafc.7b03597.

[2] Deshpande, S. S. *Handbook of food toxicology, Toxicants and Antinutrients in Plant Foods,* 2002, Chapter 10, pp. 321–386, Boca Raton, FL, CRC press.

[3] Giampaoli, O.; Sciubba, F.; Conta, G.; Capuani, G.; Tomassini, A.; Giorgi, G.; Brasili, E.; Aureli, W.; Miccheli, A. *Red Beetroot’s NMR-Based Metabolomics: Phytochemical Profile Related to Development Time and Production Year*. Foods 2021, **10**, 1887, doi:10.3390/foods10081887.

[4] Rust, A., Marini, F., Allsopp, M., Williams, P. J. & Manley, M. *Application of ANOVA-simultaneous component analysis to quantify and characterise effects of age, temperature, syrup adulteration and irradiation on near-infrared (NIR) spectral data of honey*. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 2021, **253**, 119546.

Fabrication of intracellular releasing induced prodrug nanoparticles by hydrogen peroxide reaction

Aki Shibata[1*], Yoshitaka Koseki[1], Keita Tanita[1], Showa Kitajima[1], Kouki Oka[1],
Kiyotaka Maruoka[1], Ryuju Suzuki[2], Anh Thi Ngoc Dao[3], Hitoshi Kasai[1]

[1]Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, Sendai, Japan, 2National Institute of Technology, Sendai College, Natori, Japan, 3Graduated School of Integrated Science and Technology, Nagasaki University, Nagasaki, Japan

**shibata.aki.p3@dc.tohoku.ac.jp*

To reduce the side effects of anticancer drugs, prodrug nanoparticles-based drug delivery has been proposed. In particular, we have developed carrier-free prodrug nanoparticles termed nano-prodrugs (**NPDs**), which are composed solely of prodrug molecules fabricated using the reprecipitation method [1]. These **NPDs** have been reported to exhibit pharmacological effects following uptake and dissolution within cancer cells as intact particles [2]. Based on this background, if **NPDs** can be designed to release drugs only in response to tumor-specific triggers after intracellular uptake and subsequent dissolution, the side effects could be significantly minimized.

In this study, we aimed to design a prodrug that release drugs exclusively in response to hydrogen peroxide (H_2O_2), a compound presents at high concentrations (100 µM) in cancer cells compared to normal cells [3]. We synthesized a prodrug (**CPT-TML**), which consists of a trimethyl lock (**TML**) group containing H_2O_2-responsive aryl boronic acid and camptothecin (**CPT**), an anticancer drug. The **CPT-TML NPDs** were successfully fabricated with particles sizes within 100 nm. The drug release kinetics of **CPT-TML** was evaluated by HPLC-MS/MS analysis, both in the form of **NPDs** dispersion in water and upon dissolution in dimethyl sulfoxide (DMSO), by reacting with 100 µM H_2O_2 solution. As a result, the **NPDs** dispersion in water did not release **CPT** when reacted with H_2O_2 solution, whereas upon dissolution in DMSO, it released approximately 80% of **CPT** after 48 h (Figure 1A). Thus, we demonstrated that the combination of H_2O_2-responsive prodrugs and solubility-controlled nanoparticles can improve cancer-selective drug release properties (Figure 1B).

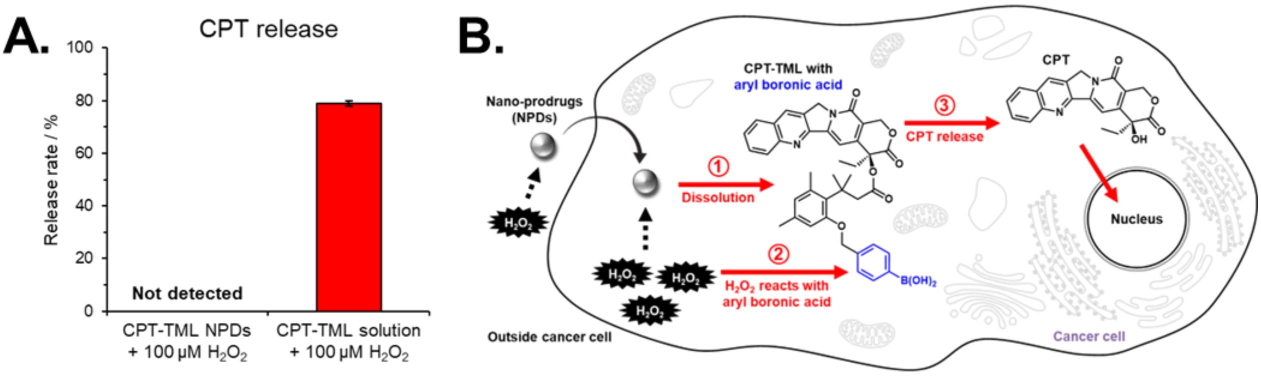


Figure 1. (A) **CPT** release rate of **CPT-TML NPDs** in water and **CPT-TML** in DMSO incubated with 100 µM H_2O_2 solution for 48 h. (B) Schematic representation of proposed intracellular selective **CPT** release mechanism from **CPT-TML NPDs** by H_2O_2 in cancer cells, red arrow: main **CPT** release route.

References

[1] H. Kasai *et al.*, ***Jpn. J. Appl. Phys.***, 31, L1132–L1134, 1992.
[2] F. Taemaitree *et al.*, ***Nanoscale***, 12, 16710–16715, 2020.
[3] M. Kita *et al.*, ***Tetrahedron Lett.***, 56, 4228–4231, 2015.

Theme I - Functional Materials

Synthesis of Dual-Emitting Nonaromatic Fluorescent Polymers through Thermal Processing of L-Glutamic Acid and L-Lysine

Cadeddu M.[1,2]*, Carboni D.[2], Stagi L.[2], Malfatti L.[2], Casula M.F.[3], Caboi F.[4], Innocenzi P.[2]

[1]Dipartimento di Chimica, Biologia, Biotecnologie, Università di Perugia, Perugia, Italia
[2]Laboratorio di Scienza dei Materiali e
Nanotecnologie (LMNT), CR-INSTM, Dipartimento di
Science Biomediche, Università di Sassari, 07100 Sassari, Italy
[3]Dipartimento di Ingegneria Meccanica,
Chimica e dei Materiali, Università di Cagliari, 09123
Cagliari, Italy
[4]Laboratorio NMR e Tecnologie Bioanalitiche, Sardegna Ricerche, Parco Scientifico e tecnologico della
Sardegna. 09010 Pula, CA, Italy

**marta.cadeddu@dottorandi.unipg.it*

Introduction

The study of absorption-emission features of non-aromatic amino acids is an emerging field that has attracted attention. UV-Vis absorption and emission in proteins is a well-known phenomenon that is generally attributed to the presence of aromatic or, more generally, conjugated groups. Recent experimental and computational studies have shown absorption and emission in the visible range for proteins lacking conjugated groups and from polymers obtained by thermally-treated glycine and lysine. In this work, optical properties of such systems have been explored by thermally treating another non-aromatic amino acid as glutamic acid.

Material and Methods

Glutamic acid has been homopolymerized in a furnace at 240C for 5h and copolymerized with lysine in the same condition with different molar ratios. The brown-black solids thus obtained have been purified by dialysis.

Results and discussion

The polypeptide-like branched polymeric structures have been synthesized via the thermal treatment of L-lysine and L-glutamic acid. The copolymers exhibit two-color centers with emissions peaking at around 380 and 450 nm. The relative homopolymers, polyglutamic acid and polylysine, exhibit only one emission at 450 nm. The second emission is observed only when the two amino acids are copolymerized. The polymerization kinetics and, thus, the incorporation and abundance of the precursors into the final polymers affect their spatial conformation, which is starkly correlated to the relative molar ratios of the two precursors. The structural characterization has shown that the increase of fluorescence is strictly correlated with the mutual spatial proximity of oppositely charged moieties, which favors charge transfer between the side chains.The fluorescent emission is related to charge transfer and recombination processes that involve acceptor and donor groups, and occasionally intermediates groups. The single emission of the homopolymers and the second emission center of the copolymers peaking at 450 follow a similar charge transfer/recombination route while the first emission center peaking at 390 of the copolymers can be explained by a different mechanism involving charge transfer as well.

References

M. Cadeddu, D. Carboni, L. Stagi, L. Malfatti, M. F. Casula, F. Caboi, and P. Innocenzi, Design of Dual-Emitting Nonaromatic Fluorescent Polymers through Thermal Processing of L-Glutamic Acid and L-Lysine. *Macromolecules*, 2024, 57(2), 514–527.
https://doi.org/10.1021/acs.macromol.3c01825

Direct conjugation of TiO_2 nanoparticles with carotenoids extracted from tomato peels

Matteo Chimento[1*], *Giorgia Perfili*[1*], Farid Hajareh Haghighi[1], Angela Marchetti[1], Marianna Villano[1], Cleofe Palocci[1,2], Laura Chronopoulou[1,2]

[1]*Department of Chemistry, Sapienza University of Rome, Rome, Itlay*
[2]*Research Center for Applied Sciences to the Safeguard of Environment and Cultural Heritage (CIABC), Sapienza University of Rome, Rome, Italy*

**perfili.1893606@studenti.uniroma1.it, chimento.1910883@studenti.uniroma1.it*

Currently, food bioactives have a paramount importance in supporting the immune system, especially in the era of the COVID-19 pandemic [1]. However, the food industry generates a massive volume of by-products, that may be considered a rich source of bioactive compounds, antioxidants and dietary fibers. The global tomato processing market size reached 46.9 million tons in 2023 and is expected to grow to an approximate value of 60 million tons by 2032. Lycopene is considered as the main bioactive compound in tomato, which constitutes 80–90% of the total carotenoids. Other carotenoids present in tomatoes include *β*-carotene, phytoene, phytofluene, neurosporene and lutein [1]. Such valuable compounds may be extracted with conventional methods using organic solvents or even with green technologies such supercritical fluid extraction (SFE). To improve the pharmaceutical efficacy of bioactive molecules, considerable efforts have been devoted to the use of inorganic-based nanodelivery systems, that offer many advantages in terms of improved pharmacokinetics and pharmacodynamics. The low toxicity, chemical inertness, and biocompatibility of photodynamic TiO_2 nanoparticles make them suitable candidates for conjugating bioactive molecules, including carotenoids. In this study, we are developing TiO_2 nanoparticles conjugated with carotenoids extracted from industrial wastes, to develop composite systems with antibacterial properties.

References

[1] Nagarajan J. Pui Kay H. Krishnamurthy N.P. Ramakrishnan N.R. Aldawoud T.M.S. Galanakis C.M. Wei, O.C. *Biomolecules* 2020, **10**, 1019.

Investigating the electrochemical behavior of graphene oxide and its derivatives

Sara Colecchia[1*], Leonardo Giaccari[1], Francesco Amato[1], Alessandro Motta[1], Andrea Giacomo Marrani[1]

[1] *Department of Chemistry, Sapienza University of Rome, Piazzale Aldo Moro, 5, 00185, Rome*

**colecchia.1858114@studenti.uniroma1.it*

Graphene has attracted interest in various fields due to its unique properties, such as mechanical, thermal, optical, and electrical, and its characteristic structure. Despite the premises, its low dispersibility in polar solvents and its low functionalizability make it poorly valid in many applications[1]. To overcome these drawbacks, the focus has shifted to one of its derivatives, graphene oxide (GO). Compared to pristine graphene, indeed, GO has distinguishing chemical characteristics, due to the wide variety of oxygen functional groups (OFGs), which include hydroxyls and epoxides on the basal plane, and carbonyl, phenol, and the less abundant carboxylic groups on the edges[2]. In fact, GO can undergo numerous chemical functionalizations which allow it to find a role in many different areas (biomedical, catalytic, and electrochemical). In addition to the latter, it can be reduced, chemically or electrochemically, leading to the formation of reduced graphene oxide (RGO). Its reduction is an effective way to partially restore the unique features of pristine graphene[3].

In this work, the electrochemical reduction of GO and GO-based nanomaterials are investigated via cyclic voltammetry (CV), a fast and reproducible way to understand the electrochemical behavior of each oxygen functional group. In this technique, indeed, the electrodic potential scanning towards negative values allows the reduction of the OFGs. These studies, also conducted on aminated GO (GO-NH_2) and carboxyl-rich GO (GO-COOH), are confirmed and supported by XPS, Raman, and UV-Vis spectroscopy.

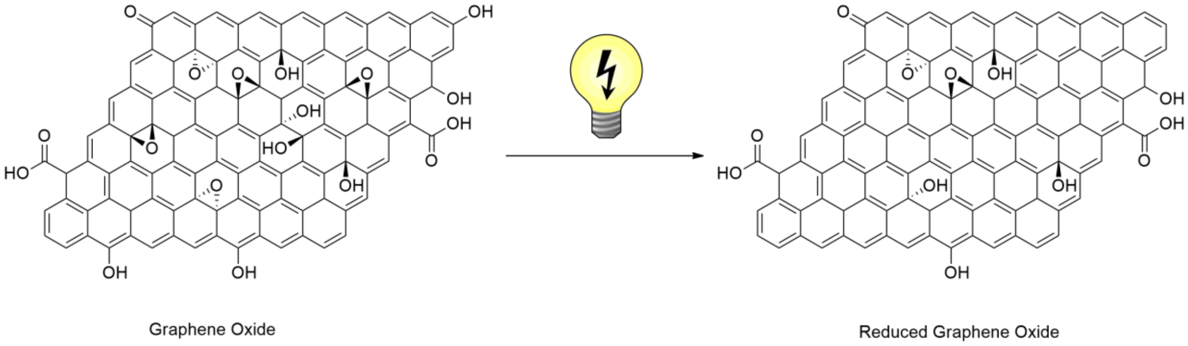


Figure 19: Schematic representation of electrochemical reduction of GO

References

[1] Guo S., Garaj S., Bianco A., Ménard-Moyon C. *Nat. Rev. Phys*., 2022, **4**, 247-262.

[2] Ambrosi A., Kiang Chua C., Naziah M. L., Huiling Loo A., Hong An Wong C., Sheng Eng A. Y., Bonanni A., Pumera M. *Chem. Soc. Rev*., 2016, **45**, 2458.

[3] Ferrari I., Motta A., Zanoni R., Scaramuzzo F. A., Amato F., Dalchiele E. A., Marrani A. G. *Carbon*, 2023, **203**, 29-38.

A multi-step synthesis of thiolated graphene oxide

Alessio Conti[1*], Leonardo Giaccari[1], Francesco Amato[1] Alessandro Motta[1], Andrea Giacomo Marrani[1]

[1] *Department of Chemistry, Sapienza University of Rome, Rome, Italy*

**conti.1852600@studenti.uniroma1.it*

Over the past decade, graphene-based materials have been extensively applied in numerous fields due to their remarkable properties. Graphene is a 2D nanomaterial composed of solely sp^2-hybridized carbon atoms with unique properties and potential applications[1]. Despite these premises, its poor water-dispersibility and scalable-production make it not suitable for a variety of applications. Hence, to overcome these drawbacks, chemically modified graphenes have been prepared[2]. To date, graphene oxide (GO), the oxidized form of graphene, is among the most studied derivatives due to its high dispersibility in polar solvents and the high presence of oxygen functional groups (OFGs) which permit a wide range of chemical derivatizations[1,2]. Indeed, the surface of graphene oxide is constituted of OFGs distributed on both sides of the basal plane and the edges. In particular, epoxyde and hydroxyl-groups are located in the basal plane while carboxyl, carbonyl, and hydroxyl-groups are mainly localized at the edges of the layer.[1]

This work aims to functionalize and characterize GO and GO-based materials, starting from the chemical oxidation of graphite using the modified Hummers-Offeman method. Then, a multi-step functionalization reaction is performed to obtain a thiolated graphene oxide (GO-SH)[3]. Each step is fully characterized with spectroscopic techniques, e.g. Raman, UV-Vis, and XPS spectroscopy. Then, the obtained material, offers a set of remarkable chemical and physical properties including the possible anchoring of gold nanoparticles that pave the way in the field of catalysis, electrochemical, and biomedical[2].

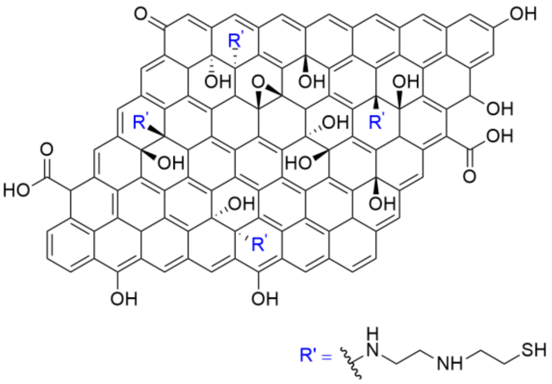


Figure 20: Schematic representation of the GO-SH

References

[1] Marrani A. G., Zanoni R., Schrebler R., and Dalchiele E. A. *J. Phys. Chem.* C 2017, **121**, 5675-5683.

[2] Thomas H. R., Marsden A. Y., Walker M., Wilson N. R., and Rourke J.P. *Angew. Chem. Int. Ed.*, 2014, **53**, 7631-7618.

[3] Guo S., Garaj S., Bianco A. and Ménard-Moyon C. *Nat. Rev. Phys.*, 2022, **4**, 247-262.

Bromine substitution in chloride hybrid perovskites

L. Costantini[1,2*], F. Toschi[2], G. Ammirati[2], A. Paladini[2], S. Turchini[2], P. O'Keeffe[2], L. Bianchi[3], E. Tamburri[4], V. Guglielmotti[4], A. Cartoni[1], D. Catone[2].

[1]*Dept. of Chemistry, Sapienza University of Rome, Rome, Italy*
[2]*Istituto di Struttura della Materia-CNR (ISM-CNR), EFSL, Rome, Italy.*
[3]*Dipartimento di Fisica, Università di Roma "Tor Vergata", Roma, Italy*
[4]*Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma "Tor Vergata", Roma, Italy.*

**costantini.1454722@studenti.uniroma1.it*

Halide hybrid perovskites are materials characterized by a structure that consists of an inorganic framework in which lead cations coordinate halide anions. The interstitial space that occurs in the framework is occupied by a molecular cation. Thanks to their photoactivity and other properties such as high absorption cross-section, high carrier mobility and low rates of non-radiative recombination of electron-hole pairs, perovskites are pivotal for the development of solar cells with high efficiency[1]. In our work, we focused our attention on the effects of the substitution of the halide anion on the perovskite's lattice[2]. The starting point was the synthesis of $MAPbCl_3$ via liquid deposition of the substrates – $PbCl_3$ and MACl - on glass and ITO glass supports. The anion exchange was then obtained from dipping the glass and the ITO supports in an isopropanol (IPA) solution of MABr. The dipping was carried out choosing different times of exposure at the IPA/MABr solution in order to acquire more information about the degree of substitution in the crystal structure.

The XRD data and the UV-VIS spectra show that the substitution occurs almost immediately at short exposure times such as 30 seconds. In particular, we can infer from the shift of the peaks shown in the XRD spectra that the lattice parameters are changing during the substitution process.

We also observed with SEM imaging that the structures obtained with this synthesis are nanocubes, whose dimensions increase after the chlorine-bromine substitution. Further investigations were carried out via photoluminescence and transient absorption spectroscopy pointing out the effect of the bromide substitution on the optical properties of the material.

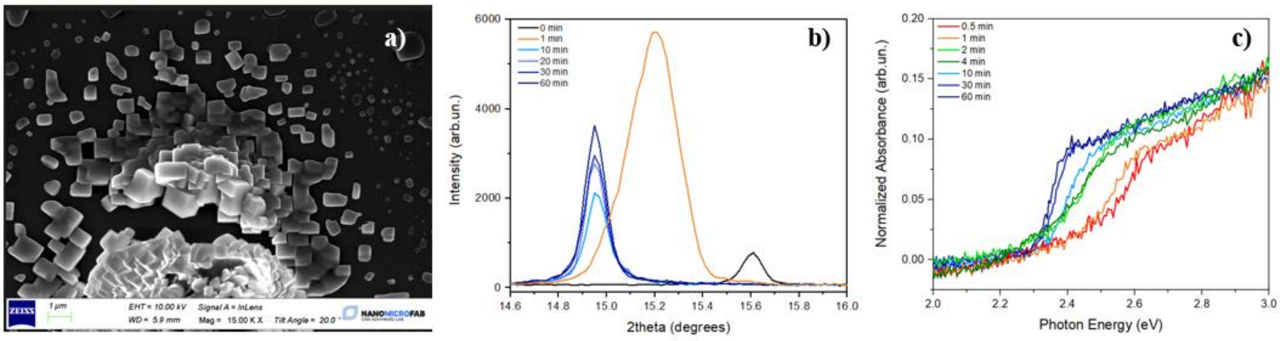


Figure 1. a) SEM image of perovskite's cubic nanostructures after substitution (1 minute); b) XRD spectra at (1 0 0) reflection and c) normalized absorbance spectra of nanostructures obtained at selected exposure times.

References.

[1] Ajay Kumar Jena, Ashish Kulkarni, Tsutomu Miyasaka, *Chem. Rev.*, 2019, 3036-3103.
[2] Andrey A. Petrov, Norman Pellet, Ji-Youn Seo, Nikolai A. Belich, Dmitriy Yu. Kovalev, Andrei V Shevelkov, Eugene A. Goodlin, Shaik M. Zakeeruddin, Alexey B. Tarasov, Michael Graetzel, *Chem. Mater.*,2017, 29, 587-594.

Functionalization of PEEK for membrane preparation

Melania Lettieri[1,2], Francesco Galiano[2], Raffaella Mancuso[1], Alberto Figoli[2], Luigi Leva[3], Alessandro Angelini[3], Wilfredo Yave[3], Bartolo Gabriele[1].

[1]*Laboratory of Industrial and Synthetic Organic Chemistry (LISOC), Department of Chemistry and Chemical Technologies, University of Calabria, Via Pietro Bucci 12/C, 87036 Arcavacata di Rende (CS), Italy*
[2]*Institute on Membrane Technology, ITM-CNR, c/o University of Calabria, Via P. Bucci 17/C, 87030 Rende, CS, Italy*
[3]*DeltaMem AG, Rothausstrasse 61, 4132 Muttenz, Basel-Land, Switzerland*

**Melania.lettieri@unical.it*

Pervaporation is a competitive and alternative technology to traditional separation techniques such as distillation for the purification and dehydration of solvents. Using dense membranes, pervaporation can separate liquid mixtures at their azeotropic point, which is not possible by standard distillation columns. This separation technique depends on the unique solubility and diffusion properties of the substances within the polymer membrane material.[1] In this process, the driving force for material transport is a chemical gradient established across the membrane, which is represented by the partial pressure difference. This gradient is stablished between the two sides of the membrane and can be created and kept by using a vacuum pump or gas flow at the permeate side of membrane.[2]

In the present work, the functionalization of polyether-ether-ketone (PEEK) such as PEEK-WC is investigated to improve processability of the polymer for the membrane preparation. PEEK is a semi-crystalline polymer known for its excellent chemical and thermal stability, which makes it suitable for applications requiring high temperatures.[3] Functionalization of PEEK has been also reported by other authors [4], where the ketone group was replaced by an acetal group, making the polymer soluble in conventional solvents, and facilitating the processability. Therefore, polymer solutions processable at room temperature allow obtaining dense membranes, which can be used for different applications like pervaporation to separate various azeotropic mixtures and separation of gases.

References

[1] Liu and Jin, *Journal of Membrane Science,* 2021, **636**, 119557.
[2] J.G. Wijmans, R. W. Baker, *Journal of Membrane Science*, 1995, **107**, 1-21.
[3] Dan Li, Dingqin Shi, Kai Feng, Xianfeng Li, Huamin Zhang, *Journal of Membrane Science,* 2017, **530,** 125-131.
[4] Sandra L. Aristiz´abal, Lakshmeesha Upadhyaya, Gheorghe Falca , Abaynesh Yihdego Gebreyohannes, Mohammed Omer Aijaz, Mohammad Rezaul Karim, Suzana P. Nunes, *Journal of Membrane Science,* 2022, **660**, 120798.

Effect of reaction conditions in PIM-1 synthesis

Fabrizio Olivito[1*], Giorgio Gatti[2], Giovanni Golemme[1]

[1]Department of Environmental Engineering, University of Calabria, Cosenza, Italy
[2]Department of Sustainable Development and Energy Transition, University of Eastern Piedmont, Vercelli, Italy

**fabrizio.olivito@unical.it*

PIM-1 (Scheme 1) is the archetypal Polymer of Intrinsic Microporosity [1], characterized by a rigid and contorted structure causing a high free volume, a continuous microporous network, a large surface area (600-900 m^2 g^{-1}), very high gas permeability and large gas selectivity. PIM-1 is amorphous and soluble in common organic solvents, therefore it lends itself to the preparation of gas separation membranes. PIM-1 is one of the polymers used in the COM3 project, aimed at improving the compatibility between polymers and fillers in Mixed Matrix Membranes [2,3].

PIM-1 is obtained through nucleophilic aromatic substitution (Scheme 1). The synthesis of PIM-1 is strongly influenced by the reaction conditions. The purity of solvents and reagents, reaction times and temperatures not only affect the yield PIM-1, but also the formation of cross-linked and insoluble products together with soluble by-products (oligomers and cyclic polymers), the molecular weight and the surface area of the polymer. Anhydrous DMF, purified reagents, a reaction time of 20 hours and a reaction temperature of 55° C, yield 81% PIM-1 with suitable M_w and 694 m^2 g^{-1}. The details for the optimization of the synthesis parameters of PIM-1 will be discussed.

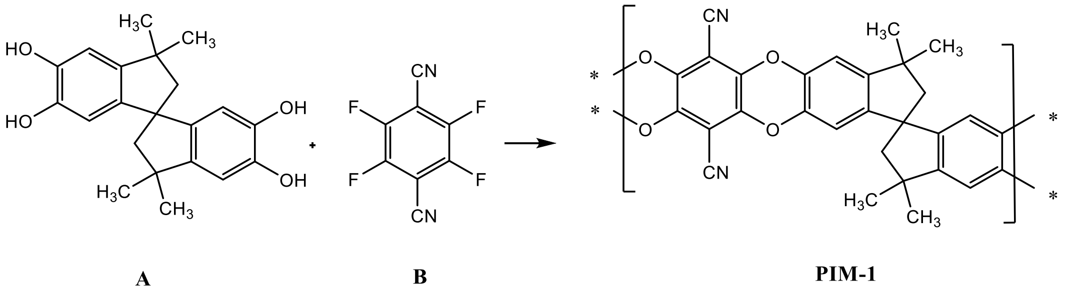


Figure 1. Reaction scheme for the base-catalyzed (K_2CO_3) synthesis of PIM-1.

Acknowledgements: Acknowledgments: We thank the Italian Ministry of University and Research, program PRIN 2022 funded by Next Generation EU - Italian PNRR - NRRP, Mission 4, Component 2, Investment 1.1, Project COM3 “Polymer-Nanofiller Compatibilization in Mixed Matrix Membranes for Advanced Gas Separation ”, Grant no. 2022SFM89K, CUP: H53D23001900006

References

[1] McKeown, M.B., *Polymer*, 2020, **202**, 122736.
[2] Mason, C.R., Buonomenna, M.G., Golemme, G., Budd P.M., Galiano F., Figoli A., Friess, K., Hynek, V., *Polymer*, 2013, **54**, 2222.
[3] Santaniello, A., Golemme, G. *Macromol. Rapid Comm.*, 2022, **43**, 2200226.

Enhancement and Analysis of Polyethylene Terephthalate Sulfonation: Technological Filtering Device

Geraldo Augusto Pereira[1*], Kátia Christina Leandro[1], André Luís Mazzei Albert[1]

[1] *Department of Chemistry, Fundação Oswaldo Cruz, Rio de Janeiro, Brazil*
**gaugusto@aluno.fiocruz.br*

Due to the significant population growth, plastics are constantly being used, reused, and discarded, often in ways considered incorrect. Currently, there is a strong demand for more efficient management and prevention of these wastes, given their extensive use, short lifespan, and long degradation time. Among the various polymers found in the environment and biota, Polyethylene Terephthalate (PET) stands out as one of the most relevant and widely used plastics today. In response to environmental pressures, PET waste management began in 1977, and recycling proves to be an excellent way to reduce waste, which can be done chemically or mechanically, potentially adding commercial value to post-consumer plastic waste[1]. For example, the sulfonation reaction, known and used for some time, commonly occurs through electrophilic substitutions, and can be employed in developing new systems for separation, purification, and recovery of metals, due to the ion-exchange nature of the sulfonic group inserted. Resins and ion exchange systems are of great interest due to their high ion-loading capacity, mechanical stability, and high ion exchange rate, being stable in different solvents, making the process economical, easy to handle, and renew. Therefore, the development of ion exchange resins from polymers capable of selectively binding to metal ions at low concentrations in solution proves beneficial for the removal of heavy metals and decontamination of waters from various sources[2]. In this context, the present work aims to produce a technological filtering device loaded with cationic resins synthesized from sulfonated PET (Figure 1), aiming at environmental decontamination by heavy metals.

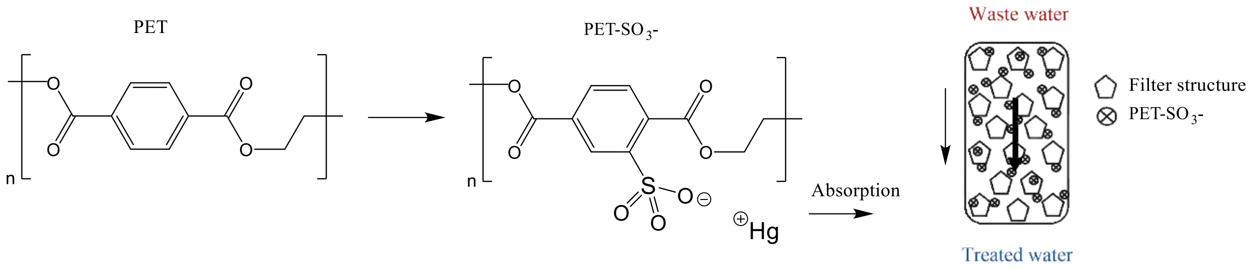


Figure 1 - Sulfonation and absorption schemes

The resulting product will be characterized qualitatively and quantitatively for its inserted sulfonic groups, as well as evaluated for its ion exchange capacity, thermal, and morphological properties. After the synthesis of sulfonated PET, which was employed in homogeneous method, an acid-base titration was carried out to assess the degree of sulfonation, showing good results of GS (percentage of sulfonic groups). It is worth noting that the study is currently ongoing.

Acknowledgements: Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES); Fundação Oswaldo Cruz (FIOCRUZ).

References

[1] Bhanderi, K.K., Joshi, J.R. and Patel, J.V., 2023. Recycling of polyethylene terephthalate (PET or PETE) plastics–an alternative to obtain value added products: a review. *Journal of the Indian Chemical Society*, 2023, **100**(1), p.100843.

[2] Escamilla-Lara, K.A., Lopez-Tellez, J. and Rodriguez, J.A., 2023. Adsorbents obtained from recycled polymeric materials for retention of different pollutants: A review. *Chemosphere*, 2023, p.**139159**.

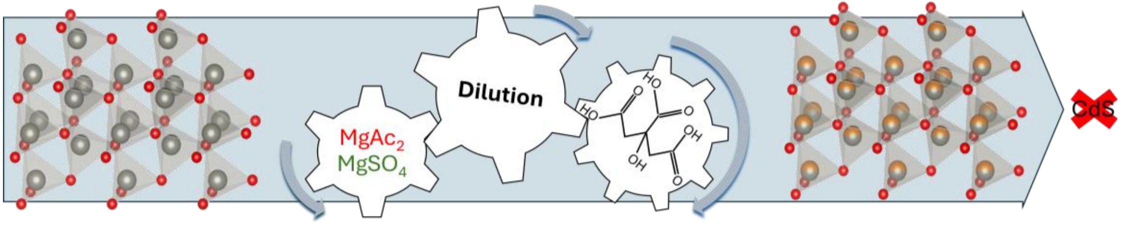
Citrate mediated chemical bath deposition of ZnMgO for $Cu(In,Ga)Se_2$ solar cells

Christian Rossi[1*], Diego A. Garzon[2], Francesco Soggia[1], Marco Grotti[1], Sascha Sadewasser[2], Diego Colombara[1]

[1]*Department of Chemistry and Industrial Chemistry, Università degli Studi di Genova, Genova, Italy*
[2]*International Iberian Nanotechnology Laboratory, Braga, Portugal*

**christian.rossi@edu.unige.it*

Climate change has been quickly worsening in recent years[1]; thus, novel green energy sources e.g. photovoltaics (PV) are crucial for the energy transition. Among them, $Cu(In,Ga)Se_2$ is one of the most promising technologies, as confirmed by the recent 23.6 % power conversion efficiency[2]. Nevertheless, this technology exploits a toxic CdS buffer layer that should be replaced. Such a layer is generally prepared through chemical bath deposition (CBD) which traditionally provides higher efficiency than other deposition techniques. In this study, we propose a chemical bath deposited $Zn_{(1-x)}Mg_xO$ buffer layer since, despite the efforts of several authors, a reliable CBD procedure able to incorporate a large amount of Mg is still missing[3], in fact the Mg concentration into our samples is much lower than the one in the reaction vessel (nominal concentration). Hence, we focused on the deposition chemistry to maximize the Mg content. Citric acid favours the inclusion of Mg into the films, and such an effect is substantially magnified when $MgSO_4$ is employed in place of $MgAc_2 \cdot 4H_2O$ (Ac=acetate). In addition, $MgAc_2 \cdot 4H_2O$ impedes strongly the deposition process already when the nominal MMZ ([Mg]/([Mg]+[Zn])) is ~25%, limiting this degree of freedom. The aforementioned findings corroborated by potentiometric titrations, suggest that acetate anions strongly bind Mg and most probably also Zn, limiting the amount of Mg free to precipitate and, ultimately, the whole film deposition. Further, the surface of the film presents a significantly higher MMZ than the whole sample, revealing interesting insights about the deposition mechanism. Citrate strongly affects also the film thickness and deposition kinetics, in fact, above a critical concentration of citric acid, the precipitation is too slow for practical applications or stops altogether.



Schematic depiction of wurtzite ZnO before (left) and after Mg incorporation (right) mediated by Mg source, dilution and citric acid.

Acknowledgements: We acknowledge the Italian Ministry of University and Research through the LEGACY national project (healing wide-gap chalcopyrite, grant No. 20223ZP4WP, PRIN 2022).

References

[1] https://ourworldindata.org/grapher/temperature-anomaly Met Office Hadley Centre (HadCRUT5)
[2] Jan Keller, Klara Kiselman, Olivier Donzel-Gargand, Natalia M. Martin, Melike Babucci, Olle Lundberg, Erik Wallin, Lars Stolt, Marika Edoff. Nature energy, 2024, 9, 467-478
[3] Nina Winkler, Stefan Edinger, Wolfgang Kautek, Theodoros Dimopoulos. Journal of Material Science, 2018, 53, 5159-5171

Theme L - Chemistry and Society

LIFE SIRIUS project: A System for Integrated EnviRonmental Information in Urban areas

Donatella Occhiuto*, Maria Agostina Frezzini, Laura Bennati, Arianna Marinelli, Simona Lucci, Alessandro Di Giosa

ARPA Lazio, Regional Environmental Protection Agency, Via Boncompagni 101, Rome 00187, Italy

* *donatella.occhiuto@arpalazio.it*

The LIFE SIRIUS project aims to enhance governance in air quality planning and management in urban settings by adopting a holistic environmental approach. Through advancing the knowledge and skills of authorities involved in air quality management and control, the project offers a concrete pathway to promote solutions aimed at solving air quality problems, with a focus on human health impacts.

Involving 7 excellent partners from 3 EU member states (Greece, Cyprus, Italy), with complementary cross-cutting expertise and many years of experience in European projects, LIFE SIRIUS aims to enhance air quality planning in 3 EU metropolitan areas (Thessaloniki in Greece, Rome in Italy, and Nicosia in Cyprus) by improving Air Quality Plans (AQPs) and considering current (2019) and future (2030) climate and environmental conditions.

Project activities mainly concern the verification and updating of AQPs, the development of air quality assessment and prediction models, and the development of a system for monitoring the effectiveness of AQPs. ARPA Lazio is involved in the implementation of air quality assessment and prediction models and in monitoring the effectiveness of remediation actions for the city of Rome.
LIFE SIRIUS aims to improve the quality of the actions of the public authorities of the three involved areas, focusing on the mitigation and adaptation actions foreseen in the respective AQPs. Expected results include enhancing the capacity, effectiveness and efficiency of the public administration of the three regions involved in the project, assessing current and future air quality, creating an integrated environmental modelling system for each urban area under study, and setting up an operational health warning system for each area involved, as well as developing an Environmental Management System to support decision-making processes to improve the elaboration of the AQPs.

Through preparatory, mitigation, and adaptation actions, the LIFE SIRIUS project aims to increase administrative capacities, assess present and future air quality, and implement effective health warning and environmental management systems to address air pollution challenges, providing a framework for increasing awareness of environmental problems associated with poor air quality.

PVA Chemical hydrogels. A sustainable tool for Cultural Heritage Conservation.

Martina Redi[1*], Gaio Paradossi[1] Fabio Domenici[1]
[1] *Dipartimento di scienze e Tecnologie Chimiche di Tor Vergata, Roma, Italia*
**E-mail: martina.redi@uniroma2.it*

Hydrogels and colloidal systems are nowadays considered important tools to perform wet cleaning treatments on sensitive historical artifacts.[1] They represent a more effective alternative to traditional methods that use volatile solvents, thus representing an advantage for the operator safety and can also help to overcome practical issues possibly linked to the work on restoration sites.[2] It has recently been proven that poly-vinyl alcohol (PVA) based systems can be appropriate allies in the field of Cultural Heritage Preservation as versatile, biocompatible, sustainable (i.e. stable and re-usable) materials. [3,4]

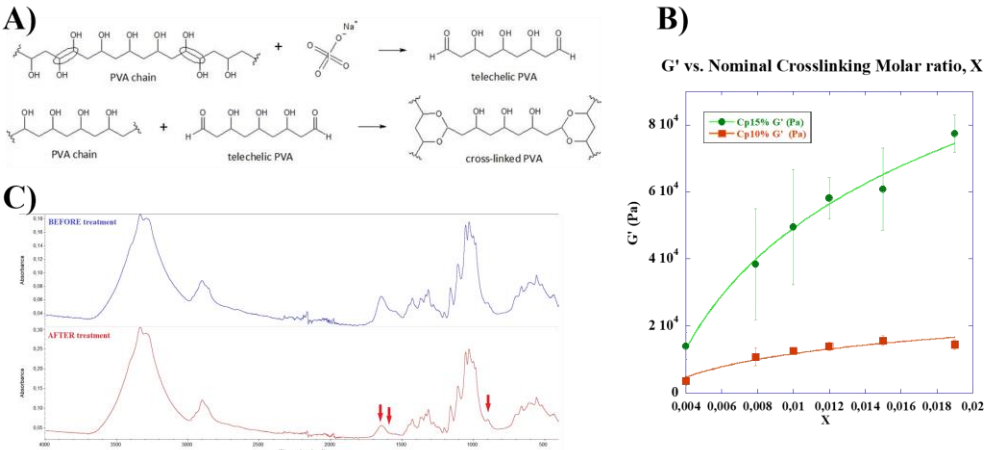
By means of an innovative method (see Fig. A) we have performed the synthesis and characterization of PVA hydrogels prepared at different polymer and crosslinker concentrations.

The objective of this work is in first place to highlight the most appropriate PVA hydrogels to be applied in paper preservation treatments, and in second instance to show some of applications of such hydrogels on paper artifacts, to prove their efficacy and their compatibility with the historical objects.

The PVA hydrogels viscoelastic properties studied (see Fig. B) have been correlated to the swelling properties, thus also confirming the significant water retaining capacity and the good elasticity and flexibility of the materials. [5,6] Homogeneity of the hydrogels pore size has been assessed by studying the diffusion coefficients of fluorescent probes inside the gels structure.

The compatibility of such systems has been tested and the efficacy of the hydrogels based wet cleaning treatments has been demonstrated through pH and FTIR-ATR analysis (see Fig. C), performed before and after treatments on XVI century paper original artifacts.

The systematic study of PVA chemical hydrogels and the overall chemical and structural properties investigated allowed us to build a deeper understanding on why such materials represent an effective tool for the application on paper conservation treatments, both to be performed in traditional laboratories and workshops, but also "on site". Further studies could allow to develop specific treatments on different surfaces and artifacts.



A) Formation of *telechelic* PVA via oxidation by $NaIO_4$ and subsequent crosslinking via acetylation reaction B) Storage modulus plot of PVA hydrogels synthetized at different polymer concentration. C) FTIR-ATR spectra of XVI century paper, before and after hydrogel treatment.

Acknowledgements: To Prof. Carola Gottscher, book and paper conservator who has given us the possibility to work on relevant historical artifacts. To Prof. Claudia Mazzuca for the FTIR measurements.

References

[1] Severini L, D'Andrea A. *et al*., Gels, 2023, 9, 509
[2] Al-Emam E., Motawea A. *et al*., Herit. Sci., 2019, 7, 22
[3] Mazzuca C., Severini L., *et al*, Colloids and Surfaces B: Biointerfaces, 2020, 188,110777
[4] D'Andrea A., Severini L., Domenici F., *et al.*, ACS Appl. Mater. Interfaces., 2021, 13, 24207
[5] Paradossi G., Finelli I. *et al*., (2009) Molecules 14, 3662–3675

Use of (LDH) Layered Double Hydroxide, for the development of catalytic sensors or biosensors and to increase the response of catalytic Fuel Cells.

Mauro Tomassetti[1], Luigi Campanella[1], Mauro Castrucci[1], Riccardo Pezzilli[2*]

[1]*Department of Chemistry, University of Rome, La Sapienza, Rome, Italy.*
[2]*Department of Industrial Engineering, University of Rome "Tor Vergata", Rome, Italy.*

**riccardopezzilli@gmail.com*

The first objective of this research, consisted in the realization of new electrochemical enzymatic biosensor and electrochemical catalytic sensor, both based LDH, i.e., Layered Double Hydroxide. New first biosensors of this type, which has been developed, was an amperometric biosensor: Glassy Carbon (GC)-coated LDH, with immobilized catalase enzyme; that is, a Catalase biosensor, fabricated to determine hydrogen peroxide. In this biosensor the enzyme was cross-linked with the LDH, using glutaraldehyde, while LDH was glued on a glassy carbon (GC) electrode. This research has proved useful a method of enzymatic immobilization in new types of materials, so-called LDHs (two dimensional Layered Double Hydroxides), also known as hydrotalcite-like compounds, or anionic clays. They are an important class of lamellar materials described by the general formula $[M^{II}_{1-x}M^{III}_{x}\,(OH)_2]^{x+}[A^{m-}]_{x/m}{*}n\,H_2O$, where M^{II} and M^{III} represent metallic cations and A^{m-} the interlayer anion. The LDH is assembled by periodically stacking $(M^{II}\,M^{III})\,(OH)_2$ octahedral layers, whose positive charge is balanced by the negative one of intercalated anions embedded between the positively charged octahedral layers. A certain number of H_2O molecules are also contained in these interlayers, so that the entire structure can swollen like gel, increasing the content of water molecules.

In this research it was investigated the real possibilities of using $[Zn^{II}\,Al^{III}\,(OH)_2]^{+}\,NO_3^{-}$ (LDH), to build both an electrochemical biosensor and a catalytic sensor, for the determination of hydroperoxides, such as hydrogen hydroperoxide. The proposed experimental routes were systematically validated by a thorough analysis of the cyclic voltammetries of the fabricated devices. To overcome the high sensitivity to possible interferences, has then also built a different type of catalase biosensor, which still makes use of adsorbed and cross-linked catalase enzyme on LDH, but based on a Clark-type electrode transducer, i.e., with a gaseous permeable membrane. This configuration permitted to avoid all redox interferences. To complete this kind of research, a voltammetric catalytic electrode, was also developed, with LDH glued on (GC), but without the immobilized Catalase enzyme. It later turned out that the response of the catalytic non enzymatic voltammetric sensor of the type: glassy carbon-modified by LDH, glued on the GC by means of silver paste, could be significantly improved by the presence of L-proline in solution. Indeed, it was studied thoroughly, this sensor, also applying it to the determination of hydrogen peroxide in real matrices. Afterwards, the voltametric sensor vas also employed for the analysis of proline, which, was used for the determination of proline in different samples of red and white wines. In another section of the research, it was also investigated the feasibility of using a small direct catalytic 'fuel cell' (DCMFC), originally constructed for the purpose of obtaining energy from methanol or ethanol, but adapted for analytical purposes, i.e., for quantitative analysis of ethanol, or methanol; but it was realized that, the use of the fuel cell, coupled by chemometric methods, also allows the qualitative analysis of different substances, having at least one alcoholic, or partially alcoholic -OH group. Finally, it has been demonstrated how, the presence of LDH, placed in the anodic section of the fuel cell, can improve the performance of a simple direct catalytic ethanol fuel cell, since it helps to increase the speed of the oxidation reaction of the alcoholic fuel. In this way, using immobilized catalase on LDH, it was possible to use the fuel cell, thus modified, for the determination of ethanol in human saliva.