# CFF 2026

# CHEMISTRY FOR THE FUTURE

*International conference*

1-3 July 2026

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# BOOK OF ABSTRACT

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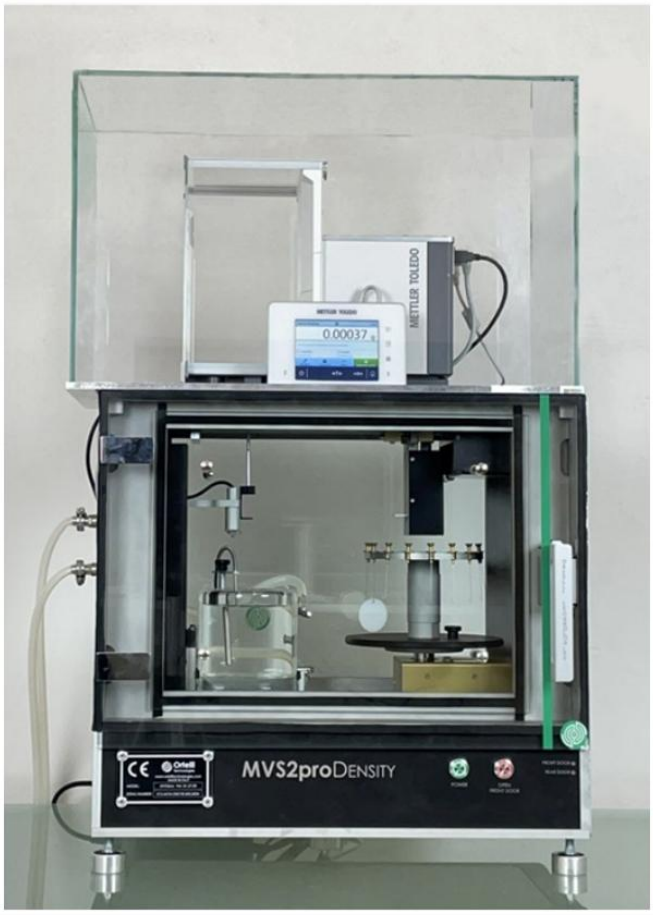


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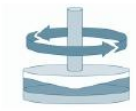

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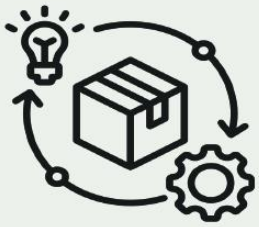

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# SCIENTIFIC PROGRAM

# Chemistry for the Future 2026

conference program

## Wednesday – 1st July

| Schedule | Speaker | Affiliation | Activity |
|---|---|---|---|
| 13:45 – 14:30 | | | ***Registration*** |
| 14:30 – 14:45 | | | ***Welcome and Opening*** |
| ***Session 1 - Chair: Samuele Botticelli, Benedetta Bertoncini*** | | | |
| 14:45 – 15:25 | **Prof. Inês C. B. Martins** | University of Copenhagen | ***Plenary lecture*** |
| | *From disorder to diversity: exploring the future and structural complexity of amorphous forms of drugs* | | |
| 15:25 – 15:50 | **Arianna Ghelardi** | DSCM - University of Pisa | ***Keynote lecture*** |
| | *Solid state characterization of a new dual drug co-crystal using MAS NMR and DNP spectroscopy* | | |
| 15:50 – 16:15 | **Amanda Arcidiacono** | DSCM - University of Pisa | ***Keynote lecture*** |
| | *Excited-state properties and dynamics of carotenoids in photoprotective protein environments* | | |
| 16:15 – 16:40 | **Luca Melega** | DSCM - University of Pisa | ***Keynote lecture*** |
| | *Cholesky decomposition implementation of molecular response properties at the Coupled Cluster level* | | |
| 16:40 – 17:10 | | | ***Coffee break*** |
| ***Session 2 - Chair: Marta Filomena, Federico Paolino*** | | | |
| 17:10 – 17:50 | **Prof. Alvise Vianello** | Aalborg University | ***Plenary lecture*** |
| | *Micro- and nanoplastic analysis at a crossroads: between scientific discovery and analytical credibility* | | |
| 17:50 – 18:15 | **Leonardo Barlucchi** | DSCM - University of Pisa | ***Keynote lecture*** |
| | *Analytical pyrolysis for the detection and quantification of microplastics in workplaces and biological matrices* | | |
| 18:15 – 19:30 | | | ***Poster session + happy hour*** |

Chemistry for the Future - 2026

# Thursday – 2nd July

| Schedule | Speaker | Affiliation | Activity |
|---|---|---|---|
| ***Session 3 - Chair: Alessia Cinci, Claudia Ghelarducci*** | | | |
| 09:00 – 09:40 | **Prof. Claude Piguet** | University of Geneva | ***Plenary lecture*** |
| | *Linear light-upconversion in molecules: a challenge* | | |
| 09:40 – 10:05 | **Chiara Zappelli** | DSCM - University of Pisa | ***Keynote lecture*** |
| | *Design and synthesis of new transition metal complexes for diagnostic and therapeutic applications* | | |
| 10:05 – 10:30 | **Andrea Volpe** | DSCM - University of Pisa | ***Keynote lecture*** |
| | *Characterization of Type II Deep Eutectic Solvents based on choline chloride and metal chloride hydrates* | | |
| 10:30 – 10:55 | | | ***Coffee break*** |
| ***Session 4 - Chair: Matteo Cei, Giuseppe Fulvetti*** | | | |
| 10:55 – 11:35 | **Prof. Reiko Oda** | CNRS – University of Bordeaux - Tohoku University | ***Plenary lecture*** |
| | *Order, disorder, and the emergence of hierarchical chirality* | | |
| 11:35 – 12:00 | **Ludovica Dei** | DSCM - University of Pisa | ***Keynote lecture*** |
| | *Design, synthesis and biological evaluation of novel chiral peptoid-based chelators* | | |
| 12:00 – 12:30 | **Alessia Cipolli, Miao Miao Dong, Elena Ducoli, Xuezhi Feng, Lorenzo Lapi, Gianmarco Papi** | | ***Flash presentations*** |
| 12:30 – 14:00 | | | ***Lunch break*** |
| ***Session 5 - Chair: Samuele Botticelli, Benedetta Bertoncini*** | | | |
| 14:00 – 14:40 | **Prof. Larisa Florea** | Trinity College Dublin | ***Plenary lecture*** |
| | *Fast and reversible stimulus-driven hydrogel micro-actuators* | | |
| 14:40 – 15:05 | **Luca Soldati** | DSCM - University of Pisa | ***Keynote lecture*** |
| | *Diarylacetonitrile (DAAN) fluorescent probes for monitoring mechanoradical formation in commodity plastics* | | |
| 15:05 – 15:30 | **Marco Diciotti** | DSCM - University of Pisa | ***Keynote lecture*** |
| | *Plasticization and compounding of vinyl chloride polymers for sustainable fire-resistant applications* | | |
| 15:30 – 15:55 | **Leonardo Arrighetti** | DSCM - University of Pisa | ***Keynote lecture*** |
| | *Cutin as functional additive for biodegradable innovative polymer materials* | | |
| 15:55 – 16:25 | | | ***Coffee break*** |
| ***Session 6 - Chair: Matteo Cei, Giuseppe Fulvetti*** | | | |

| | | | |
|---|---|---|---|
| 16:25 – 17:05 | **Prof. Luca Dell'Amico**<br>*Mechanistic investigations in light-driven synthetic chemistry from direct photochemistry to organophotoredox catalysis* | University of Padova | ***Plenary lecture*** |
| 17:05 – 17:30 | **Caterina Campinoti**<br>*Electrochemical approaches for the controlled generation and functionalization of reactive nitroso intermediates* | DSCM - University of Pisa | ***Keynote lecture*** |
| 17:30 – 17:45 | **Maurizio Ortelli**<br>*MVS2pro density measurement system: a revolution in polymer density measurement* | Ortelli Technologies | ***Sponsor*** |
| 17:45 – 19:00 | | | ***Poster session*** |
| 20:00 | *Social dinner at "La Carraia", San Piero a Grado, Pisa (Via Livornese, 766)* | | ***Social dinner*** |

# Friday – 3rd July

| *Schedule* | *Speaker* | *Affiliation* | *Activity* |
|---|---|---|---|
| | ***Session 7 - Chair: Alessia Cinci, Claudia Ghelarducci*** | | |
| 09:00 – 09:40 | **Prof. Agi Smolinska**<br>*Out of thin air: decoding volatolomics data for gastrointestinal and lung diseases* | University of Maastricth | ***Plenary lecture*** |
| 09:40 – 10:05 | **Mariano De Cristofaro**<br>*Quantitative peptidomics: a DoE-optimized UHPLC-MS/MS method with applications in translational cardiorenal research* | DSCM - University of Pisa | ***Keynote lecture*** |
| 10:05 – 10:30 | **Serena Reale**<br>*Chemical profiling of maternal body odour across pregnancy* | DSCM - University of Pisa | ***Keynote lecture*** |
| 10:30 – 10:55 | | | ***Coffee break*** |
| | ***Session 8 - Chair: Marta Filomena, Federico Paolino*** | | |
| 10:55 – 11:20 | **Lorenzo Sembranti**<br>*Electrochemical sensors for dialysis efficiency assessment* | DSCM - University of Pisa | ***Keynote lecture*** |
| 11:20 – 11:45 | **Cecilia Campi**<br>*Silk degradation and impact of cleaning strategies through mass spectrometric techniques* | DSCM - University of Pisa | ***Keynote lecture*** |
| 11:45 – 12:10 | **Elena Betti**<br>*First-principles modeling of light harvesting in plant photosystems* | DSCM - University of Pisa | ***Keynote lecture*** |
| 12:10 – 12:40 | | | ***Best Poster Awards and Closing Remarks*** |

# PLENARY LECTURE

# Mechanistic investigations in light-driven synthetic chemistry From direct photochemistry to organophotoredox catalysis

L. DELL'AMICO

Department of Chemical Sciences, University of Padova
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In this presentation, I will focus on two different topics from my research group, moving from the design of new photosensitizers to the development of powerful redox catalysts

1. Based on experimental evidence and mechanistic information, we have identified and structurally optimized a new family of photosensitiser.[1] This class of molecules is characterized by a short S1-T1 gap. We observed and increased selectivity in the strain-release functionalization of azabyclic scaffolds. This new reaction manifold grants access to highly functionalized azetidine scaffolds.

2. We have designed and developed two new classes of photoredox catalysts (PCs) capable of activating diverse types of redox inert substrates. To do so, we have used i) a catalytic proton-coupled electron-transfer (PCET) manifold;[2] and ii) an unconventional regenerative photocatalytic mechanism.[3]

**References:**
[1] Rodríguez, R. I., Corti, V., Rizzo, L., Visentini, S., Bortolus, M., Amati, A. Natali, M., Pelosi, G., Costa, P., Dell'Amico, L. *Nat. Catal.,* **2024**, *7*, 1223–1231.
[2] Bortolato, T.; Simionato, G.; Vayer, M.; Rosso, C.; Paoloni, L.; Benetti, E. M.; Sartorel, A.; Lebœuf, D.; Dell'Amico, L. *J. Am. Chem. Soc.* **2023**, *145*, 1835–1846.
[3] Rosso, C.; Barison, G.; Droghetti, F.; Michelazzo, N.; Sartorel, A.; Pelosi, G.; Bortolus, M.; Costa, P.; Natali, M.; Dell'Amico, L. *ChemRxiv Preprint*, **2024**. https://doi.org/10.26434/chemrxiv-2024-dgxlp

# Fast and reversible stimulus-driven hydrogel micro-actuators

L. FLOREA, A. SORT-MONTENEGRO, J. DELENTE, Ž. ROBLEK, Y. TSKHE, T. FARAONE, C. DELANEY
*School of Chemistry & AMBER, The SFI Research Centre for Advanced Materials and BioEngineering Research, Trinity College Dublin, Ireland*
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Stimuli-responsive hydrogels are attractive candidates for soft micro-actuation due to their ability to convert external inputs into mechanical motion; however, their widespread application has been limited by slow response times and restricted structural complexity. In this work, we address these challenges through the development of fast, reversible hydrogel micro-actuators enabled by advanced microscale fabrication via two-photon polymerisation (2PP) and polymer design strategies. By rationally tailoring both material composition and microstructure design, we establish a wide range of stimuli-responsive micro-actuators that are able to undergo coordinated, multi-step transformations that resemble responses observed in natural systems, while retaining control over the speed, direction and extent of actuation.[1-3]

Copolymer hydrogel networks, engineered to exhibit stimulus-responsive behaviour, are structured using 2PP, allowing the fabrication of complex three-dimensional architectures with sub-micron precision. This approach provides fine spatial control over material composition, crosslinking density, and mechanical properties through modulation of fabrication parameters such as laser power, writing speed, and hatching or slicing distance. As a result, local variations in stiffness and swelling behaviour can be encoded within a single structure, enabling anisotropic and programmable 4D responses.

The resulting micro-actuators exhibit rapid and reversible actuation, with response times as low as 200 ms and large deformation amplitudes, significantly outperforming traditional hydrogel actuators. Electrical stimulation provides a highly tuneable input, allowing precise control over actuation behaviour, while responsiveness to additional stimuli, including temperature and chemical gradients, enables adaptive and multifunctional performance.

Furthermore, multi-material fabrication strategies allow for the integration of independently addressable components, facilitating complex motions such as bending, twisting, and directional steering. Coupled with predictive modelling approaches, including finite element analysis, this platform enables the rational design of shape-morphing microstructures with tailored dynamics.

Overall, this work establishes a framework for bridging responsive materials and microscale engineering, opening new possibilities for fast, programmable, and bio-inspired micro-actuators in applications such as soft robotics, sensing, and biomedical devices.

**References:**

[1] J. Delente, S. Kolagatla, N. Lopez-Larrea, M. Criado-Gonzalez, M. Carlotti, B. J. Rodriguez, C. Delaney, D. Mecerreyes, V. Mattoli, L. Florea. *J. Mat. Chem. C,* 14*,* 3181-3189 (2026).
Y. Sun, X. Fan, *Anal. Bioanal. Chem.*, 399, 205-211 (2011).
[2] S. Donato, S. Nocentini, D. Martella, S. Kolagatla, D. S. Wiersma, C. Parmeggiani, C. Delaney, L. Florea, Small, 20.20, 2306802 2306802 (2023).
[3] A. Ennis, D. Nicdao, S. Kolagatla, L. Dowling, Y. Tskhe, A. J. Thompson, D. Trimble, C. Delaney, L. Florea, Adv. Funct. Mat., 33, 2213947 (2023).

# From disorder to *diversity*: Exploring the future and structural complexity of amorphous forms of drugs

I. C. B. MARTINS[1]

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Solid dosage forms remain the dominant platform for delivering small-molecule drugs. Yet, the solid state encompasses a broad spectrum of structural organization, and there is increasing interest in high-energy solids with varying degrees of disorder, ranging from stable and metastable crystalline forms to super-cooled liquid crystalline forms and fully amorphous forms.

Among these, amorphous forms are particularly attractive for enhancing the solubility and potentially the oral bioavailability of poorly water-soluble drugs. Traditionally, amorphous forms generated through different preparation methods have often been treated as representing a single "amorphous state." However, our recent work challenges this view by demonstrating that amorphous drugs can exhibit significant structural and physicochemical *diversity*. Depending on the preparation pathway, distinct amorphous forms with different molecular organizations and properties may be obtained and even interconverted in a phenomenon termed poly*A*morphism.[1–3] The recognition of such *diversity* within disorder is opening new perspectives in the design and understanding of oral drug formulations.

In this presentation, we will discuss the landscape of solid-state forms and their relevance for future drug delivery strategies. Particular emphasis will be placed on the structural complexity and *diversity* of amorphous forms, especially poly*A*morphism, and on how preparation methods influence their molecular organization and physicochemical behaviour (**Figure 1**). Together, these aspects highlight how rethinking *disorder* may open new opportunities for the future of pharmaceutical materials science.

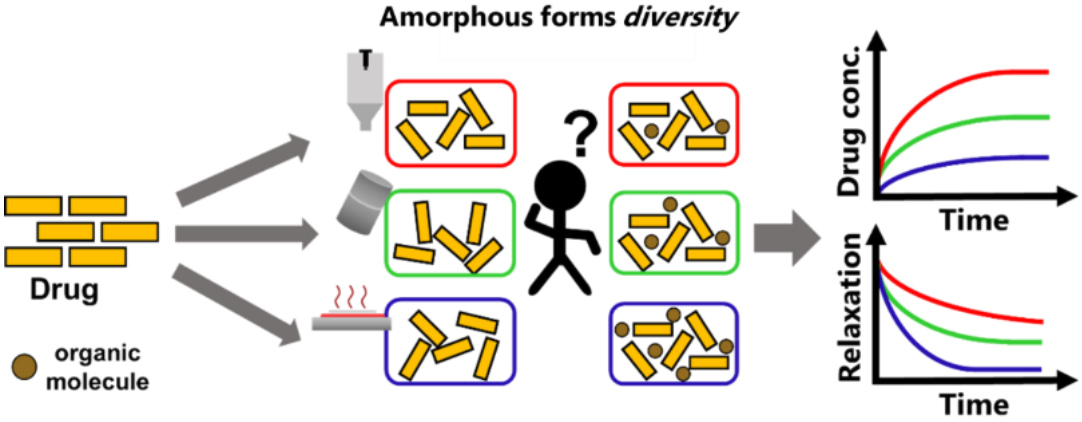


**Figure 1**. Schematic representation of the diversity within amorphous forms and its impact on structural organization and physicochemical properties

**References:**
[1] I.C.B Martins, A.S. Larsen, A.Ø. Madsen, O.A. Frederiksen, A. Correia, K.M.Ø Jensen, H.S., Jeppesen, T. Rades, *Chem. Sci.*, 14, 11447-11455 (2023).
[2] M. Wang, O.A. Frederiksen, A.Ø. Madsen, K.M.Ø Jensen, M.R.V. Jørgensen, J. Gong, T. Rades, I.C.B. Martins, *Int. J. Pharm.*, 66, 124470 (2024).
[3] D. Musumeci, J. Zhou, J.X. He, T. Rades, I.C.B. Martins, *Mol. Pharm.*, 22, 2065-2076 (2025).

# Order, Disorder, and the Emergence of Hierarchical Chirality

R. ODA[1,2]

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Why does chirality exist, and why does nature so persistently break mirror symmetry across scales[1]? How is such chirality expressed and measured[2]? Chirality is not confined to molecules. It propagates, through electromagnetic fields, spin structures, and emergent collective order[3], from the atomic scale to mesoscopic assemblies to macroscopic objects. The mechanisms of this propagation are complex, scale-dependent, and rarely reducible to a single physical principle. Hierarchical nanostructures based on molecular self-assembly play a crucial role in bridging the gap that neither top-down nor bottom-up approaches can easily reach.

Over several decades, we have developed helical nanostructures with controlled dimensions[4] (10–100 nm) and defined handedness, and used them as platforms to transmit chiral information across scales,[5] from electrons and atoms to polymers and nanoparticles, demonstrating chiral induction, amplification, crystallization, catalysis, and recognition[6]. This talk examines how order and disorder compete within hierarchical chiral systems, and how that competition determines whether chirality is expressed, amplified, or suppressed. The answer is sometimes counterintuitive: disorder can actively promote chiral order. These effects are traced through morphological, chiroptical, reactive, and recognition-based observables across organic and inorganic chiral matrices.

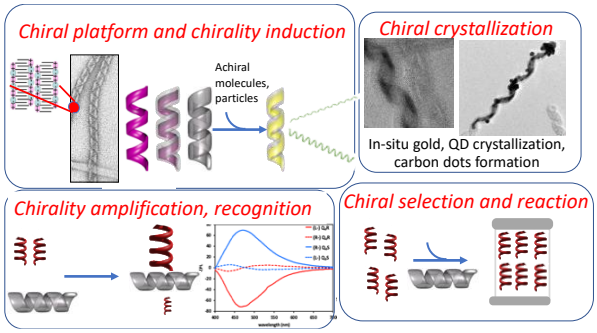


**Figure 1**. Helical chiral nanostructures as a common platform for chirality induction, crystallization, amplification/recognition, and selective reactions.

**References:**

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# Light Upconversion in Molecules: A Challenge

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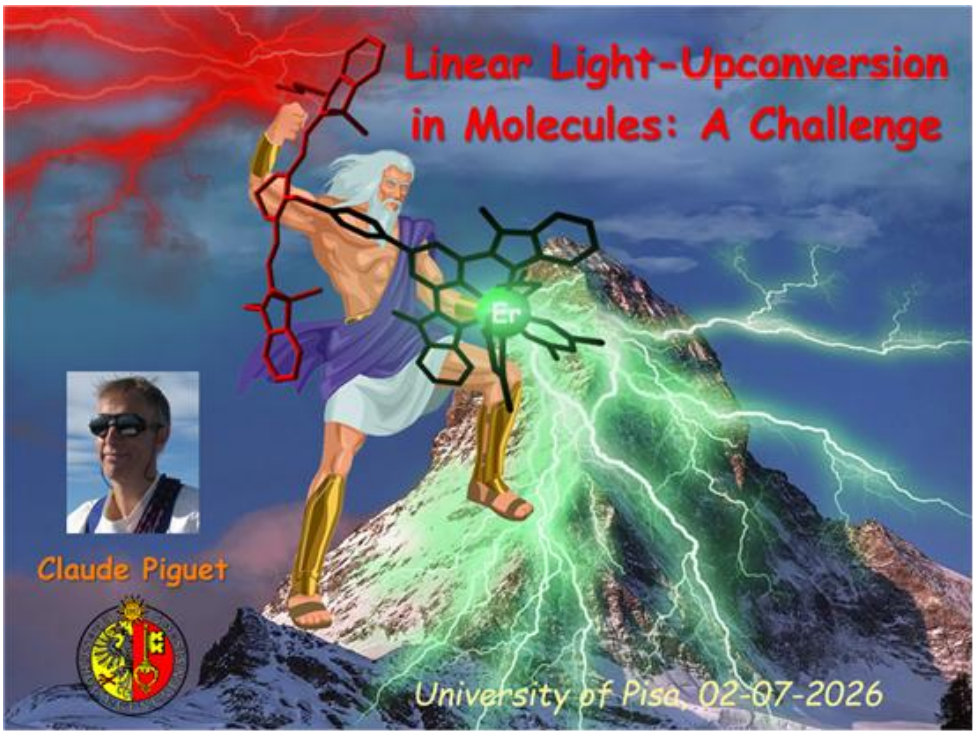
Since solar cells used for energy conversion operate only within the visible part of the electromagnetic domain, approximately 50% of the air mass solar spectrum escapes to be collected. Light downshifting, light downconversion and light upconversion may then become bankable challenges. Similarly in photobiology, which requires energies within the visible domain, the huge light scattering of the incident photons prevents tissue penetration and light conversion processes are highly wanted. Accordingly, low-phonon doped ionic solids or nanoparticles have been developed for performing these linear light conversion processes during the last two decades.

At the molecular level, the considerable thermal vibrational bath brings drastic limitations which proved to be compatible only with light-downshifting obeying the antenna effect: one high-energy photon is transformed into one low energy photon + heat. Light downconversion, also referred to as quantum cutting, where one high-energy photon is transformed into two low energy photons appears to be much more challenging, and it remains currently unknown in molecules, thus leaving this field free for the new generations. Recent pioneering efforts aim at pushing molecular-based linear light upconversion, i.e. the reverse situation where two low-energy photons provide one high energy photons, within the frame of reality. This is this recent shift from statistically doped light upconverting solid materials toward controlled and reproducible molecular light upconverting (supra)molecular assemblies that will be discussed in this lecture.



# Out of thin air: decoding volatolomics data for gastrointestinal and lung diseases

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Volatile organic compounds (VOCs) measured in exhaled breath, urine, and feces provide a promising opportunity for non-invasive disease diagnosis and monitoring. As products of ongoing metabolic processes, VOCs reflect biochemical changes associated with health and disease and therefore have considerable potential as diagnostic biomarkers. Realizing this potential requires a comprehensive approach that combines appropriate study design, reliable analytical methodologies, and robust data analysis strategies.

In this presentation, a chemometrics-based volatolomics workflow using gas chromatography–mass spectrometry (GC-MS) will be presented and illustrated through several biomedical applications. Examples from studies on asthma, colorectal cancer, irritable bowel syndrome (IBS), and inflammatory bowel disease (IBD) demonstrate how VOC profiles can be used for differential diagnosis, patient stratification, and monitoring of treatment response in both clinical and preclinical settings.

Particular attention will be given to essential data processing steps, including baseline correction, peak deconvolution, retention time alignment, normalization, and quality control, as these are critical for generating reliable and reproducible results. In addition, the application of chemometric and machine learning methods such as exploratory data analysis, supervised classification, and one-class modeling will be discussed for extracting meaningful biological and diagnostic information from complex, high-dimensional VOC datasets.

The combination of rigorous analytical workflows and advanced chemometric analysis enables the translation of VOC measurements into biologically meaningful and clinically relevant outcomes. This presentation will provide practical recommendations on study design and data analysis strategies that can improve the robustness, reproducibility, and translational value of volatolomics research.

# Micro- and Nanoplastic Analysis at a Crossroads: Between Scientific Discovery and Analytical Credibility

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Micro- and nanoplastics (MNPs) have rapidly evolved from an emerging environmental concern into a major scientific, societal, and regulatory issue. Reports describing MNPs in environmental matrices, food systems, and human tissues have increased exponentially over the last decade [1], accompanied by growing public attention, media visibility, and political pressure. At the same time, analytical techniques for the detection and characterization of these materials have undergone remarkable development. Yet, despite this progress, substantial challenges remain regarding data robustness, methodological harmonization, interstudy comparability, and the interpretation of analytical findings. Analytical capability is no longer the only challenge; analytical credibility has become equally important. The intrinsic complexity of MNPs, including their diversity in size, morphology, polymer composition, weathering state, and associated chemical signatures, together with the analytical difficulties associated with smaller microplastics and nanoplastics, complicates the generation of reliable and decision-relevant datasets [2]. Rather than focusing solely on individual analytical techniques, the broader question becomes what constitutes scientifically defensible, comparable, and stakeholder-relevant MNP data. Increasing societal visibility and media attention have intensified expectations toward the field, often placing scientific uncertainty and analytical limitations under public scrutiny [3]. Contamination control, false positives, matrix interferences, lack of reference materials, insufficient QA/QC harmonization, and the limitations of current analytical workflows for nanoplastics remain major obstacles to generating robust and comparable datasets. At the same time, different stakeholders, including regulators, toxicologists, industry, monitoring agencies, and academia, frequently require fundamentally different types of analytical information, complicating efforts toward universal standardization and reinforcing the need for fit-for-purpose analytical strategies [4].

The future of MNP analysis may not lie in the search for a single “best” method, but rather in the development of transparent, harmonized, and fit-for-purpose analytical ecosystems combining complementary methodologies, validated workflows, robust QA/QC practices, and stakeholder-oriented data interpretation. In this context, analytical rigor, uncertainty awareness, and interdisciplinary collaboration will be essential to ensure that MNP science can effectively support environmental assessment, regulatory decision-making, and public trust.

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# KEYNOTE LECTURE

# Excited-state properties and dynamics of carotenoids in photoprotective protein environments

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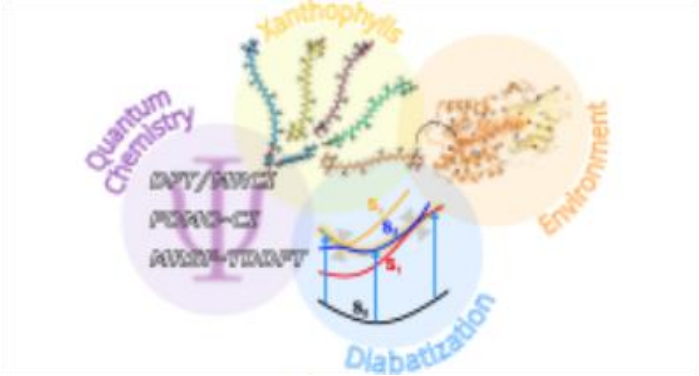
Carotenoids are a diverse family of highly conjugated pigments naturally found in photosynthetic organisms. They have been extensively studied for their role in photosynthesis, particularly for their photoprotective function [1]. Indeed, carotenoids can accept excess energy from nearby pigments and dissipate it as heat, thereby preventing photodamage through a mechanism known as non-photochemical quenching (NPQ). Their function is closely linked to their excited-state properties, which, however, remain only partially understood. Computational investigations of carotenoid excited states are especially challenging due to (i) their inherently complex electronic structure, (ii) the presence of multiple low-lying electronic states that may cross or mix along specific nuclear coordinates [2] and (iii) in biological settings, the influence of a protein environment that finely modulates their excited-state properties.

Our goal is to elucidate the behavior of carotenoid excited states in relation to their biological function, while also investigating the excited-state dynamics of these pigments in proteins. To this end, we first analyze the electronic states of carotenoids using a combination of electronic structure methods and a property-based diabatization technique [3]. We further investigate the solvatochromic behavior of carotenoids in both solvents and protein environments [4]. Subsequently, we employ nonadiabatic molecular dynamics simulations to study the photoactivation mechanism of the orange carotenoid protein, a photoreceptor that relies on a bound keto-carotenoid both for its photoactivation and its excitation quenching function [5]. Finally, we propose a machine-learning-based approach to accelerate nonadiabatic simulations in environment and explore how property-based diabatization can be leveraged to improve model accuracy.

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# Cutin as functional additive for biodegradable innovative polymer materials

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The growing demand for sustainable material solutions has intensified interest in the valorization of underexploited biomass and industrial residues within circular economy strategies. This approach demonstrates the broader opportunities offered by waste valorization, simultaneously reducing environmental burdens and creating innovative material resources. Increasing attention has been devoted to plant-based biopolymers, especially naturally abundant compounds that remain insufficiently exploited, such as cutin. Cutin is a complex structural biopolyester constituting the outer protective cuticle of higher plants and is mainly composed of $C_{16}$ and $C_{18}$ hydroxy- and epoxy-fatty acids linked through ester bonds in a highly crosslinked architecture. Recent progress in extraction techniques, including solvent-assisted processes, enzymatic treatments, and mild chemical depolymerization methods, has enabled the recovery of cutin oligomers from agro-industrial residues, particularly tomato peels [1].

Oligomers derived from cutin hydrolysis have been investigated as building blocks for aliphatic polyesters, polyurethanes, and hybrid polymeric systems, where they can improve hydrophobicity and barrier properties [2]. At the same time, the long aliphatic chains characteristic of cutin confer inherent biodegradability [3] and promote compatibility with different polymer matrices.

Nevertheless, many currently available approaches rely on long reaction times or involve the use of hazardous solvents, limiting their sustainability and industrial applicability.

From a technological standpoint, incorporating cutin-derived oligomers into thermoplastic materials represents an attractive route toward scalable processing strategies. Their application as modifiers in polymer blends can influence rheological properties and interfacial interactions, aspects that are particularly important during melt-processing operations such as extrusion and 3D-printing. Within this scenario, the present work supports the development of integrated approaches aimed at the efficient valorization of heterogeneous biomass streams and their conversion into functional materials with enhanced sustainability profiles.

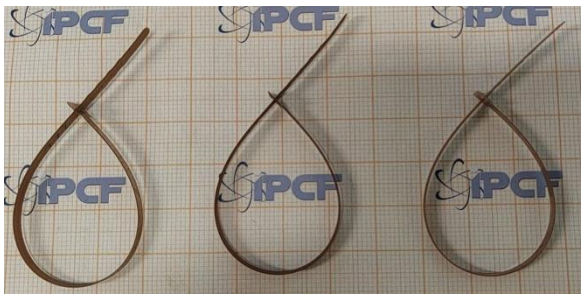


**Figure 1**. 3D-printed ties based on polymer/cutin blends

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# Analytical pyrolysis for the detection and quantification of microplastics in workplaces and biological matrices

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The widespread use of synthetic polymers has led to a significant environmental crisis caused by plastic pollution, with microplastics (MPs) being found in various environments and posing risks to human health and ecosystems. MPs in the environment undergo continuous mechanical fragmentation, leading to the formation of smaller plastic debris, more prone to being transported by atmospheric agents. The fragments dispersed in the air as particulate matter could be inhaled by humans, causing potential harm to the respiratory and other systems, posing a particular necessity to study MPs as an air pollutant [1]. It was also reported by in vivo and in vitro studies that MPs can cross the gastrointestinal barrier and cellular membranes, triggering inflammatory responses and morphological changes in cells [2]. In this research, airborne MPs were sampled and quantified in different working environments associated with plastic manufacturing and mechanical waste treatment processes, where workers may be exposed to MPs (Figure 1). Alongside environmental monitoring, recovery experiments were performed on spiked murine blood and lung samples to evaluate the digestion efficiency and analytical reliability for MPs determination in biological tissues, collected on different filters. Furthermore, preliminary investigations were carried out using Py-GC-SICRIT-HRMS, exploring the potential of coupling pyrolysis-gas chromatography with soft ionization and high-resolution mass spectrometry for the analysis of MPs in biological tissues. Initial analyses were conducted on both MPs standards and blood samples, representing an early-stage evaluation of the applicability of this emerging analytical approach for the detection and quantification of MPs in blood matrices.

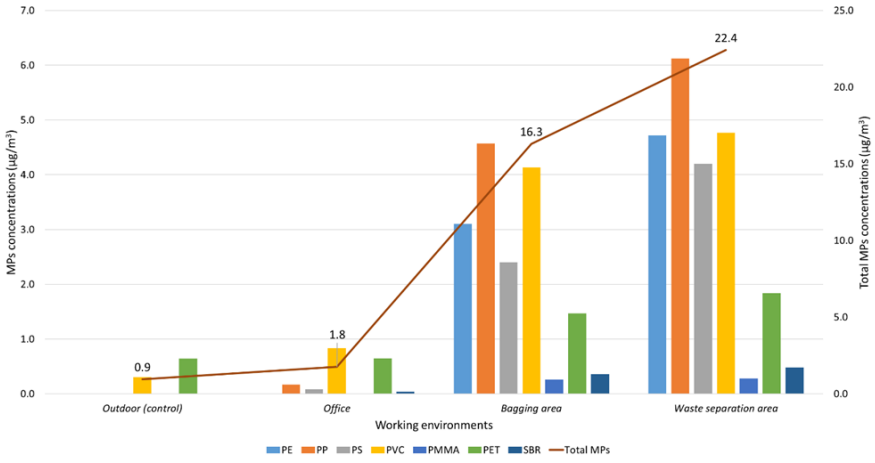


**Figure 1**. Airborne MPs quantified in different working environments of a waste treatment facility by Py-GC-MS.

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# First-principles modeling of light harvesting in plant photosystems

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Photosynthetic organisms rely on large biomolecular machines, called photosystems (PS), to convert solar energy into chemical energy [1]. In plants, PSI and PSII are formed upon aggregation of an antenna system, which harvests light, and a core complex, which hosts the catalytic reaction centers. Excitation energy transfer to the reaction centers occurs with very high efficiency. Time-resolved spectroscopies [2,3] and cryo-EM techniques [4,5] revealed a variety of optical features and supramolecular arrangements across different supercomplexes, despite the close similarity between the antenna constituents. The variety, size, and complexity of these systems prevent an immediate understanding of strategies for efficient light harvesting just from structural and spectroscopic information. Computational, structure-based models have the potential of bridging the atomistic detail and the bulk behavior, but they still represent a challenge for such complex systems. In this contribution, we show a novel strategy, which can fully characterize the energy landscape and predict photophysical properties of large photosystems from first principles. We first tackle the problem of obtaining a good representative structure for the photosystem aggregate, by resorting to forcefield-based refinements. Then, we directly calculate, on top of the refined structure, all excited-state quantities of interest using first-principles QM/MM methods, overcoming the use of fitted excitation energies common to previous models. Finally, the temporal and spatial dimensions of the excitation dynamics is extensively explored through analysis of trapping times and population fluxes across different excitation conditions. We applied our multiscale model to plant PSI [6] and PSII [7], gaining new insights on light-harvesting in the two systems and characterizing diverse strategies implemented to achieve efficient light conversion.

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# Silk degradation and impact of cleaning strategies through mass spectrometric techniques

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Silk is a proteinaceous material primarily produced by the silkworm *Bombyx mori* and has been used for producing valuable textiles for more than 5,000 years. Over time, silk is particularly sensitive to ageing, becoming yellowed, brittle, and fragile [1]. Its mechanical fragility, combined with the complex three-dimensional structure of textiles and the risk of dye fading or colour alteration, makes silk cleaning especially challenging. For this reason, traditional cleaning methods are often unsuitable for these artefacts, and innovative conservation strategies are currently being explored. Among these, the MOXY project is developing a cleaning method based on an atomic oxygen (AO). AO is a highly reactive species capable of oxidizing carbon-based contaminants into volatile compounds such as CO, $CO_2$, and $H_2O$ [2]. To validate AO as a cleaning method, its performance was compared with that of laser cleaning, an already established non-mechanical contact technique. To this aim, mock-up silk samples were dyed with carminic acid (CA), a natural and photostable mordant dye, and rhodamine B (RhB), a synthetic and photo-unstable direct dye, to evaluate the influence of dyes on ageing and cleaning of silk, and possible effects of AO on the dyes. The aim of the present study was to investigate the effects of ageing, dyeing, and cleaning treatments on silk at the molecular level using two mass spectrometry-based analytical approaches: thermoanalytical techniques (Py-GC-MS coupled with cryotrap and EGA-MS) and proteomics (LC-MS/MS). Using Py-GC-MS coupled with cryotrapping, degradation markers were identified. This knowledge was pivotal in interpreting EGA-MS analyses, exploited to further investigate the ageing process and the impact of AO treatment. The results demonstrated that silk ageing involves two main degradation phenomena: chain scission and cross-linking. AO treatment did not significantly affect the silk structure, either immediately after treatment or after seven months of natural ageing. For the proteomics investigation, two analytical protocols were developed. In the first protocol, chymotrypsin was used as the digesting enzyme in a bottom-up approach to investigate the primary structure of silk proteins. Contrary to expectations, the number of chemical modifications did not significantly increase with ageing. Instead, the number of peptide spectrum matches (PSMs) reflected the different treatments applied to silk. Ageing reduced the number of PSMs more extensively than the other treatments, indicating a higher degree of degradation. Laser cleaning showed minimal impact on the number of PSMs, whereas AO treatment caused a slight decrease in PSMs. Dyes also influenced the ageing and cleaning behaviour of silk. In particular, CA exhibited a protective effect on the fibres, resulting in higher PSM counts in all experimental conditions compared with undyed silk. The second proteomics protocol was applied exclusively to undyed samples to investigate the free peptides fractions. This method did not include an enzymatic digestion step and only the fraction with molecular weight lower than 10 kDa was analysed. Preliminary results confirmed the chain scission processes previously observed by EGA-MS. The distribution of peptide lengths was compared between unaged and aged silk samples. Unaged silk exhibited a higher abundance of longer peptides, whereas aged silk showed a Gaussian-like distribution enriched in shorter peptides. This trend suggests that silk ageing proceeds through a stochastic fragmentation process rather than through selective cleavage at specific amino acid sites.

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# Electrochemical Approaches for the Controlled Generation and Functionalization of Reactive Nitroso Intermediates

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Electrochemistry has recently emerged as a powerful platform for organic synthesis, offering a sustainable alternative to conventional redox methods by replacing stoichiometric, often toxic and wasteful reagents with electrons as *traceless* redox agents.[1,2] Beyond its sustainability advantages, electrochemistry enables a fine control over redox conditions, thus allowing for higher selectivity and access to alternative reaction pathways that might be difficult to achieve under classical conditions.[1,2] In this context, our research has focused on the use of electrochemistry for the *in-situ* generation and manipulation of reactive intermediates, which would otherwise require multi-step syntheses or harsh conditions. In particular, the *in-situ* generation of acyl-nitroso and nitroso arenes intermediates for the generation of oxazines-type scaffolds (**1-2**, Figure 1) was tackled.[3] Additionally, nitroso arene intermediates were exploited for the synthesis of azobenzene derivatives (**3**, Figure 1), a class of compounds of significant industrial interest.[4] Overall, this work highlights electrochemistry as a versatile platform for the controlled generation of reactive intermediates, enabling selective access to structurally complex molecules.

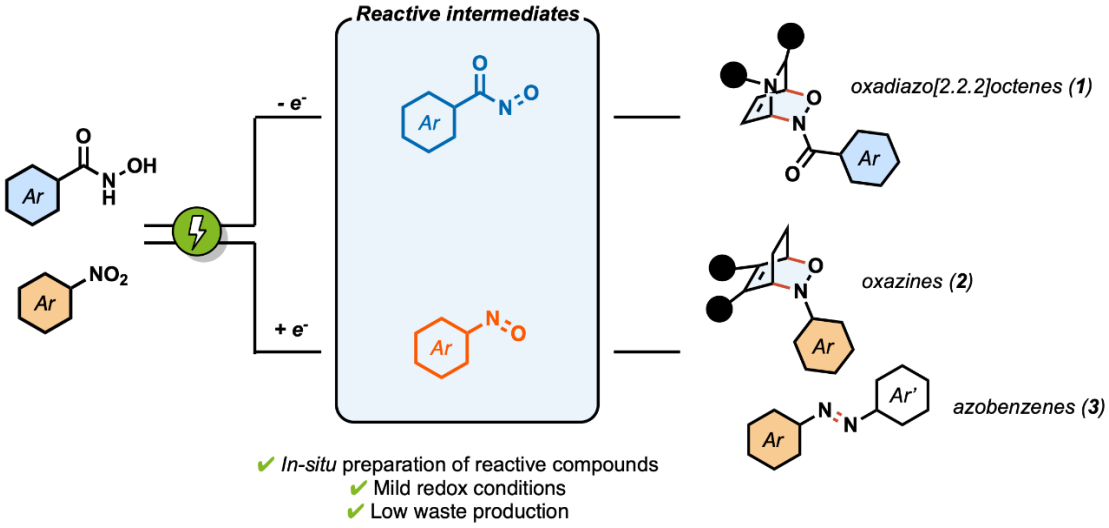


**Figure 1**. Highlights of this work

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# Quantitative peptidomics: a DoE-optimized UHPLC-MS/MS method with applications in translational cardiorenal research

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Circulating regulatory peptides play a critical role in cardiorenal homeostasis. However, routine clinical testing still relies largely on immunoassays, which are limited by cross-reactivity and single analyte readouts. Moreover, comprehensive and multiplexed quantification of intact circulating peptides in non-invasive matrices remains challenging mainly due to low concentration values (pg-ng/mL range).

This work presents a fully validated UHPLC-ESI-MS/MS workflow for the simultaneous quantification of 36 intact peptides (e.g., natriuretic peptides, endothelins, bradykinins) in human saliva, supporting clinical pilot studies to investigate cardiovascular stress and disease progression. To ensure high robustness and environmental sustainability, sample preparation employs microextraction by packed sorbent (MEPS) optimized via multivariate Design of Experiments (DoE) strategies. The effective capability of internal standard (IS) normalization was assessed through a systematic, data-driven framework based on Plackett-Burman model coefficients, ranking IS candidates by similarity in factor-response behavior. This strategy improved quantification trueness and reduced analytical variability by up to 52%. The method was validated according to IUPAC guidelines and showed low limits of detection (0.03-75 ng/mL, peptide dependent), strong linearity ($R^2$ = 0.975-0.996), and reproducible intra- and inter-day precision (≤15%), with recoveries ranging from 80 to 114%.

Application to clinical samples from chronic kidney disease patients revealed significant alterations in peptide profiles; preliminary data indicated that Fibrinopeptide B concentrations correlate strongly with blood creatinine levels ($r = 0.75$, $p < 0.05$), suggesting its potential involvement in renal dysfunction and disease progression. Furthermore, the analytical platform is currently used in a pilot study for monitoring patients with heart failure, conducted in collaboration with the Azienda Ospedaliero-Universitaria Pisana.

In parallel, complementary *in vitro* studies were performed using human cardiomyocytes to evaluate the impact of metabolic and neurohumoral stimuli on endoplasmic reticulum (ER) stress. While fatty acid treatments directly modulated ER stress, upstream peptide challenges resulted in limited cellular responsiveness, highlighting potential discrepancies in standard immortalized cell models due to receptor regulation and local proteolysis.

By discriminating bioactive peptides from degraded forms, the platform enables larger-scale clinical and mechanistic studies beyond the constraints of conventional immunoassays and *in vitro* models.

# Design, synthesis and biological evaluation of novel chiral peptoid-based chelators

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Chelating agents are therapeutics designed to bind metal ions into high-affinity complexes amenable to excretion, specifically to remove toxic metals or to reduce excess levels of essential metals in overload disorders associated with various pathologies. However, current options suffer from poor selectivity and significant side effects [1]. Peptoids are attractive peptidomimetics due to their modular synthesis, the broad availability of diverse primary amines, and their compatibility with solid-phase approaches. Several studies have already demonstrated the potential of peptoid-based metal ligands bearing aromatic moieties as effective chelators [2-4]. Yet, incorporating functionalized chiral side chains remains challenging due to protecting group requirements, resulting in higher material costs and reduced atom economy [5,6]. We developed a modular divergent strategy to access chiral oligopeptoid chelators derived from L-homoserine lactone, optimizing both the submonomer approach and conventional peptide coupling. Given the well-known cis/trans amide conformational equilibrium of peptoids, NMR analysis was employed to investigate the conformational preferences of the peptoid in its closed lactone and ring-opened forms. Metal-binding properties were assessed by NMR, UV–Vis, and ECD titrations, revealing promising chelation behaviour. Antibacterial activity was evaluated at the University of Durham by microdilution assays against antibiotic-resistant bacteria, with activity potentially arising through metal ion sequestration [7], or through their uptake facilitated by metal-chelate complex formation, the latter being further investigated by checkerboard assays with metal ions.

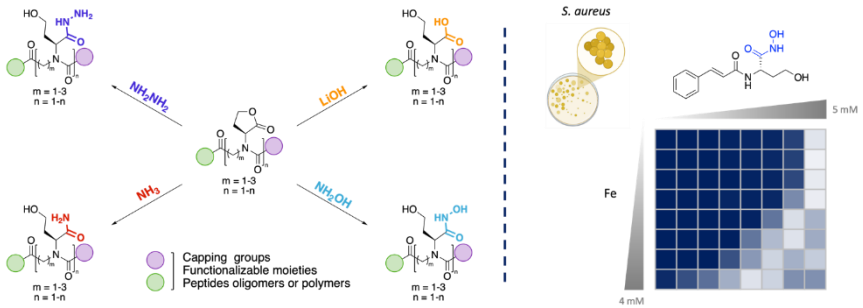


**Figure 1**. Divergent synthesis of L-HSL-based peptoids (left) and checkerboard assay of a model hydroxamic acid molecule with $Fe^{3+}$ against *S. aureus* (right).

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# Plasticization and Compounding of Vinyl Chloride Polymers for Sustainable Fire-Resistant Applications

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Poly (vinyl chloride) and vinyl chloride copolymers are widely used in cable and construction applications due to their versatility, processability and intrinsic flame resistance. Developing more durable and sustainable PVC-based formulations requires understanding PVC–additive interactions, especially with plasticizers, since they strongly influence compatibility, flexibility, ageing behavior and long-term performance [1]. This PhD project focuses on the formulation and characterization of PVC-based systems containing conventional and alternative plasticizers, with particular attention to the relationship between plasticizer chemical structure and PVC-plasticizer interactions. In this context, Fourier Transform Infrared Spectroscopy represents a valuable characterization approach. FTIR has been shown to be highly sensitive to weak interactions between PVC and plasticizers, particularly through spectral changes in the carbonyl stretching region of the plasticizer and in the C-Cl stretching region of PVC. These shifts and band broadenings can be related to dipole-dipole interactions between electrophilic groups of the plasticizer and chlorine atoms along the PVC chain, providing useful information on compatibility and plasticization efficiency [2,3]. FTIR spectra were recorded as a function of temperature for the different PVC formulations, enabling the comparison of their thermal evolution and the identification of spectral changes related to polymer–plasticizer interactions, possible plasticizer migration, and structural rearrangements of the material. This aspect is particularly relevant for flexible PVC applications, as thermally induced processes may involve dehydrochlorination, oxidation resulting in plasticizer loss and changes in physical structure and final properties [1]. Furthermore, solid-state NMR measurements can provide insights on molecular mobility and microstructural organization [4]. A variety of 13C and 1H NMR techniques were applied to three model systems: neat PVC, PVC containing 50 phr DIDP, and PVC containing 50 phr of a chlorinated ester plasticizer, also subjected to thermal ageing in an oven at 70 °C for 14 days. From solid-state NMR, information on changes in PVC and plasticizer molecular mobility and phase organization induced by plasticization and ageing have been found and discussed. Overall, this project aims to combine FTIR spectroscopy and solid-state NMR to establish structure-interaction-property relationships in plasticized PVC systems, supporting the development of safer, more stable and more sustainable formulations for technical applications requiring flexibility, flame resistance and long-term durability.

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# Solid state characterization of a new dual drug co-crystal using MAS NMR and DNP spectroscopy

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The solid-state physicochemical properties of active pharmaceutical ingredients (APIs) play a crucial role in determining key parameters such as solubility, stability, and bioavailability [1]. Among the various strategies developed to modulate these properties, multi-component solid forms, including co-crystals, have attracted considerable interest because they allow their optimization without altering the molecular structure of the API [2]. Moreover dual-drug co-crystals allow to combine the effects of the two APIs in a single formulation, with respect to the relative doses used, potentially reducing costs and the patient's discomfort associated with a combined pharmacological therapy.
In this work, the formation of a new co-crystal between levetiracetam and R-flurbiprofen, whose structure is not known [3], was investigated by means of advanced and complementary solid-state techniques. The co-crystal was successfully obtained through both solvent evaporation and liquid-assisted grinding (LAG) using a ball mill. The new solid form was characterized by solid-state NMR (ssNMR) spectroscopy, including Dynamic Nuclear Polarization (DNP)-enhanced ssNMR, in order to evaluate the number of crystallographically indipendent molecules in the unit cell, and investigate intermolecular interactions between levetiracetam and R-flurbiprofen upon co-crystal formation. Powder X-ray diffraction (PXRD) analysis confirmed the formation of a new crystalline phase, while electron diffraction (ED) enabled the determination of a preliminary crystal structure. Finally, the aqueous solubility of the co-crystal was measured and compared with those of the pure components.

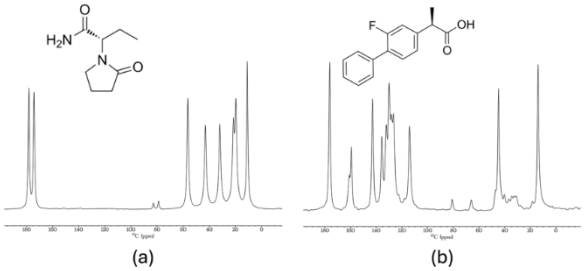


**Figure 1**. $^{13}C$ MAS ssNMR spectra of (a) levetiracetam and (b) (R)-flurbiprofen.

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# Cholesky decomposition implementation of molecular structure and properties at the Coupled Cluster level

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In recent years, rank-reducing techniques have seen a surge of interest by the quantum chemistry community, due to them being able to mitigate the intensive computational cost associated with electronic structure methods, thus extending their applicability to larger molecular systems. In that regard, we exploit the Cholesky decomposition (CD) of the electron repulsion integrals (ERI) tensor [1], reducing the impact of its manipulation on the cost of quantum chemical calculations. CD is not only able to compress the information stored within the ERI tensor, making it possible to manipulate it without recomputing or reading the integrals from disk, but also affords a strict control over the accuracy of their representation, since the approximation error is bound to be lower than the predetermined threshold used for the decomposition. Here we applied the CD of ERIs and their derivatives to the computation of analytical geometrical gradients at the Coupled Cluster (CC) level of theory [2,3]. We present an efficient and parallelized implementation of CD, using a two-step algorithm [4] that can fully exploit Abelian point-group symmetry [5] and compute not only the Cholesky vectors, but also their derivatives with respect to nuclear displacements, also fully exploiting point-group symmetry. We use the Cholesky vectors and their derivatives to achieve an efficient and parallel implementation of the CC density matrices and for the intermediates in the Z-vector equations, along with their contractions with Cholesky decomposed differentiated integrals, yielding optimized molecular structures at the CCSD level. The capabilities of our new implementation are tested on a range of systems, for which we compute the energy and molecular structures. Lastly, our implementation of CD-CCSD perturbed amplitude equations, inspired by the one developed by Gauss and Stanton [6], with the objective of computing CC second-order properties such as electric polarizabilities and NMR nuclear shieldings, will be analyzed.

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# Chemical profiling of maternal body odour across pregnancy

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Body odours are key mediators of mother-newborn chemical communication. Maternal odour is known to elicit cognitive and motor responses in newborns. Characterising the chemical nature of these active compounds may open new perspectives in maternal and neonatal health and clinical practice [1].

We applied a non-invasive analytical workflow combining thin film microextraction (TFME) with GC-HRMS and GC×GC-HRMS for comprehensive body odour profiling. Volatile organic compounds (VOCs) were passively collected from the areola and chest using PDMS/DVB (polydimethylsiloxane/divinylbenzene) and PDMS/HLB (polydimethylsiloxane/hydrophilic lipophilic balance) TFME membranes to compare their extraction performance. Internal standards were added prior to sampling to monitor sampling variability, stability, and prior to desorption to correct for instrumental variability. Single samples were analysed by GC-HRMS, while pooled samples, generated by recollection onto Tenax GR tubes, were further characterised by GC×GC-HRMS for comprehensive compound identification.

Thirty-three pregnant women were recruited at the Santa Chiara University Hospital. Samples were collected longitudinally during routine ultrasound visits across pregnancy and at delivery. To date, all volunteers completed the first sampling, 26 the second, and 14 the third. Sample collection is still ongoing.

Preliminary comparison of PDMS/DVB and PDMS/HLB membranes showed comparable extraction performance, background levels, internal standard stability, and carry-over. Approximately 400 unique VOCs were identified across samples, spanning common compound classes like ketones (21%), aromatic hydrocarbons (21%), esters (20%), aldehydes (16%), and alcohols (11%). The tentatively identified compounds covered a broad range of volatility and polarity, highlighting the chemical complexity of the matrix and the potential of this workflow for studying mother-newborn olfactory communication.

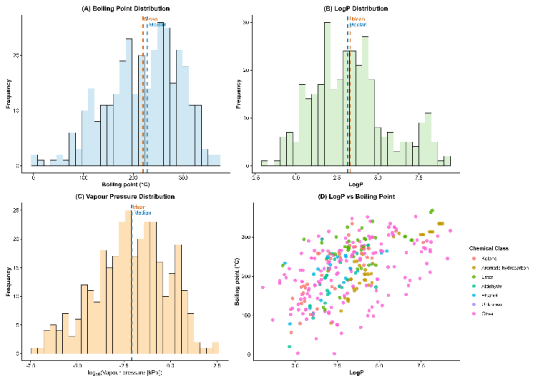


**Figure 1**. Physicochemical properties of detected compounds (A) Boiling point distribution (B) *LogP* distribution (C) Vapour pressure distribution (D) *LogP* vs boiling point

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# Electrochemical sensors for dialysis efficiency assessment

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Since the invention of dialysis, patients affected by renal diseases have experienced a significant improvement in both quality of life and life expectancy due to the progress of this therapy. In 1985 Gotch and Sargent introduced Kt/V [1], a parameter to assess the adequacy of dialysis. This parameter is correlated with pre- and post-dialysis plasma urea concentration and represents the exponential coefficient related to urea clearance. Since urea is considered a key marker for assessing the removal of small uremic solutes, monitoring its concentration in dialysate is essential for evaluating haemodialysis efficiency and optimizing treatment conditions.

In this work, different electrochemical strategies for urea monitoring in dialysate are presented, exploring two complementary approaches: enzymatic and non-enzymatic sensing.

The enzymatic approach consists of a biosensor employing urease coupled with a pH-sensitive electroactive probe. The sensing mechanism exploits the hydrolysis of urea catalysed by urease, generating local pH variations that can be measured electrochemically.

The non-enzymatic approach is based on electrocatalytic sensors employing nickel-tellurium (NiTe) and nickel-cobalt-selenium (NiCoSe) modified electrodes. These materials can promote the electrooxidation of urea in alkali environments [2], generating a measurable current response that can be correlated with urea in dialysate

While small molecules such as urea are routinely monitored through the Kt/V parameter, increasing attention is being devoted to the detection of larger and more complex uremic compounds, which are often associated with long-term complications and incomplete toxin removal during treatment [3]. For this reason, an additional VIS-based analytical device, based on Bradford assay, was developed for the quantification of total medium- and high-molecular-weight compounds in dialysate.

The combination of complementary sensing strategies, each addressing different classes of uremic toxins can thus provide versatile tools for a more comprehensive real-time evaluation of dialysis efficiency enabling a more complete assessment of the treatment and paving the way for improved personalization of the therapy.

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# Diarylacetonitrile (DAAN) Fluorescent Probes for Monitoring Mechanoradical Formation in Commodity Plastics

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The mechanical integrity of polymers is critical for many advanced applications, yet detecting molecular-level stress before macroscopic failure remains challenging. To address this issue, mechanophores covalently integrated into polymer chains have been widely explored as force-responsive molecular probes. Among the various approaches reported, mechanochromic and mechanofluorochromic systems are especially attractive because mechanical activation produces an optical signal that directly reveals stress concentration and the onset of damage [1,2]. Among the different approaches developed for polymer stress sensing, mechanophores that respond through force-induced bond scission are particularly attractive because they couple stress visualization with the generation of reactive species. Mechanical activation produces both an optical signal and mechanoradicals, providing information on local stress while creating reactive intermediates that can undergo further chemical reactions [3]. Beyond enabling stress detection, these radicals may initiate cross-linking, chain-transfer, or degradation processes, thereby affecting the material's long-term properties and performance.

In the present study, we report the synthesis and application of an unemissive para-methoxy-substituted diarylacetonitrile (DAAN) derivative as a fluorescent probe for the detection of mechanoradicals in technologically relevant polymers, including poly(vinyl acetate) (PVAc), poly(methyl methacrylate) (PMMA) and polyethylene (PE). DAAN derivatives readily trap the reactive radicals generated during mechanically induced macromolecules chain scission, leading to the formation of comparatively stable DAAN-centered radical species that display characteristic fluorescence under UV irradiation [4]. This fluorescence generated through radical trapping enables both optical detection and spatial visualization of radical formation within stressed polymer matrices, providing a valuable approach for real-time monitoring of mechanically induced damage at the molecular scale.

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# Characterization of Type II Deep Eutectic Solvents based on choline chloride and metal chloride hydrates

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Deep eutectic solvents (DESs) are a class of liquid mixtures characterized by melting points significantly lower than those of their individual precursor compounds, which are typically classified as hydrogen bond donors (HBDs) and hydrogen bond acceptors (HBAs)[1]. Depending on the identity and molar ratio of their constituent components, the physicochemical properties of DESs can potentially be tailored for specific applications[2]. However, achieving such tunability remains challenging due to the complexity of accurately describing DES systems through computational simulations[3] and the limited availability of comprehensive physicochemical datasets needed for reliable empirical predictive models[4]. The present research contributes to fill this information gap through a systematic investigation of DES physicochemical properties and their dependence on the identity of the constituent species. This work reports the characterization of Type II DESs based on choline chloride (ChCl) combined with several hydrated metal chlorides (i.e. $MCl_x \cdot nH_2O$ with M = Ba, Sr, Cu, La, Ce, Dy, Co, Ni, Al, Mn, Fe, Sn). Particular emphasis is placed on the ChCl–$CeCl_3 \cdot 7H_2O$ system, whose phase behaviour and physicochemical properties were systematically investigated. Investigation of the melting points of the mixtures by differential scanning calorimetry (DSC) enabled the construction of a preliminary phase diagram, which revealed an eutectic composition around the 11 : 9 molar ratio of ChCl and $CeCl_3 \cdot 7H_2O$ with eutectic temperature around 14°C. Visually, the cerium-based DES appears as a homogeneous, transparent and viscous liquid phase (Figure 1). Physicochemical properties such as melting point, thermal stability, electrical conductivity, viscosity, density and electrochemical window were measured across a wide range of temperatures and compositions. Electrodeposition of Ce was investigated using different experimental conditions, obtaining deposits with a maximum content of Ce of 65% (m/m).

**Figure 1:** The homogeneous liquid phase obtained after mixing and heating a mixture of ChCl and CeCl3·7H2O in a 11 : 9 molar ratio.

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# Design and Synthesis of New Transition Metal Complexes for Diagnostic and Therapeutic Applications

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The unique structural, electronic, and redox characteristics of metallodrugs make them a cornerstone of medicinal inorganic chemistry, enabling innovative therapeutic and diagnostic applications that surpass the capabilities of purely organic compounds [1]. Among them, iron-based systems represent cost-effective and low-toxicity alternatives to conventional chemotherapy. In particular, [$Fe_2Cp_2(CO)_4$ ]-derived vinyliminium complexes (**1**, Figure 1) [2] were explored as versatile scaffolds for anticancer drug design. Pyridyl-decorated vinyliminium ligands enable coordination to the iridium scaffold [IrCp*(Phpy)Cl], which itself possesses documented anticancer potential, yielding heterobimetallic iron–iridium complexes (**2**) [3]. To improve aqueous stability and modulate biological activity, redox-active thiolate or selenolate bridges were introduced between the two organometallic units, potentially enhancing intracellular redox imbalance (**3**). In parallel, dithiocarboxylate-functionalized vinyliminium complexes were developed to promote oxidative dimerization into novel tetranuclear diiron species (**4**).

Tungsten coordination complexes were also investigated as contrast agents for computed tomography (CT). Citric acid coordination affords stable, inexpensive, and low-toxicity compounds (**5**) suitable for Spectral Photon-Counting Computed Tomography (SPCCT), an emerging technique based on energy-resolved X-ray detection and K-edge imaging [4].

Structural characterization and biological evaluation highlight the promising therapeutic and diagnostic potential of these metal-based systems for biomedical applications.

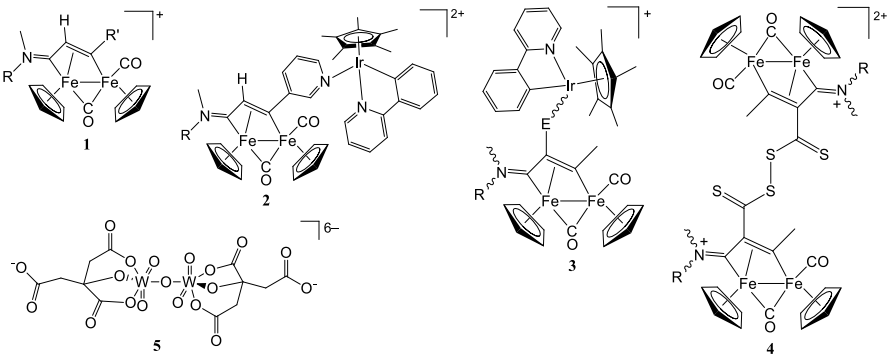

**Figure 1**. Coordination complexes synthesized. R, R': alkyl, aryl group. Counterion: $CF_3SO_3^-$ for **1**,**2**; $Cl^-/NO_3^-$ for **3**; $I^-$ for **4**; $Na^+$ for **5**.

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# SPONSOR

# MVS2pro Density Measurement System: A Revolution in Polymer Density Measurement

*Data Reproducibility, Accuracy, Validation and Full Process Automation*

M. ORTELLI

MVS2pro Research & Development Team

**Abstract**

This presentation introduces the MVS2pro Density measurement system, a fully automated instrument designed for the accurate, precise, and reproducible measurement of the density of solid non-porous polymer samples and beyond. The system is built around three core concepts: **data reproducibility, measurement accuracy and validation,** and **full process automation**. The MVS2pro employs the hydrostatic (immersion) method in full compliance with ISO 1183-1, and integrates a suite of design innovations — including a cryothermostated jacketed beaker, a high-precision infrared level sensor, an autosampler for up to 16 samples/standards, and an intelligent stabilisation algorithm — to reduce measurement uncertainty to approximately 0.01%.

The instrument is further validated through a certified reference standard whose volume is 100 times greater than conventional gradient-column spheres, thereby reducing the volumetric error by the same factor. The complete measurement and validation sequence is executed automatically, and all data are accessible in real time via the company network in an Industry 4.0 framework. Comparative analysis against gradient-column and manual immersion methods demonstrates a significant improvement in reliability, traceability, and operator independence.

***Keywords:*** *polymer density, immersion method, ISO 1183, measurement automation, data reproducibility, hydrostatic weighing, MVS2pro, Industry 4.0, metrological validation*

## Conclusions

The MVS2pro Density System represents a substantial advancement over existing polymer density measurement techniques. By combining full process automation, metrological traceability (INRIM-certified standards), intelligent data-stabilisation algorithms, and Industry 4.0 connectivity, it addresses the principal sources of measurement uncertainty inherent in both gradient-column and manual immersion methods. The system delivers reproducibility at the 0.01% level, unrestricted sample versatility, and a completely autonomous validation sequence — making it suitable for stringent quality-control environments in polymer processing, materials characterisation, and related industries.

# POSTER COMMUNICATIONS

# Bio-Based Commercial and Functionalized Flocculants for Sustainable Treatment of Marble Processing Wastewater

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Marble processing generates large volumes of wastewater rich in fine particles and chemical additives, whose treatment is typically costly and energy-intensive. In line with circular economy principles, the Marble-Up project aims to develop sustainable wastewater treatment strategies to remove these contaminants by replacing conventional flocculants, based on polyacrylamide and polyaluminum chloride (PAC), with safer bio-based alternatives, including chitosan, starch and sodium alginate [1]. The flocculation tests performed on the dirtiest wastewater stream collected in the production line showed that regarding sedimentable solids analysis chitosan and starch, both at 1 g/L, achieved significant sedimentation (4654.0 mg/L for chitosan with 25 mL and 4812.0 mg/L for starch with 18 mL), although requiring a relatively high dosage. Sodium alginate at 2 g/L provided even higher sedimentation value (5398.0 mg/L) with a lower volume (8 mL), indicating more efficient flocculant utilization. All these natural products enabled us to obtain better results than PAC in terms of sedimentable solids (2050.0 mg/L with 2 mL). In addition, turbidity analysis was performed with the best samples, confirming the same conclusions: chitosan at 1 g/L achieved 95.2% of removal and sodium alginate reached 86.0% at 2 g/L, resulting comparable with those obtained with the commercial PAC-based system (97.8%). In the second part of the research, starting from the previous commercial natural flocculants, several functionalization strategies were investigated to improve their properties. In particular, carboxymethyl chitosan, carboxymethyl chitosan quaternized with 3-chloro-2-hydroxypropyl trimethylammonium chloride (CTA), dialdehyde starch and dialdehyde chitosan were synthesized [2-3]. For these functionalized flocculants, sedimentable solids analysis and turbidity removal were also investigated, highlighting that carboxymethyl chitosan quaternized with CTA at 1 g/L showed the best performance for both parameters (1928.2 mg/L using 4 mL for sedimentable solids analysis and 90.7% for turbidity removal). Finally, different characterization tests, including charge density, the point of zero charge and FT-IR analyses, were also determined to evaluate better the flocculation mechanisms. In conclusion, sodium alginate at 2 g/L and carboxymethyl chitosan quaternized with CTA at 1 g/L emerged as the most promising bio-based commercial and functionalized alternatives respectively, enhancing environmental sustainability.

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**Acknowledgments**

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# Synthesis and Reactions of Hydrazine Trifluoroborate Salts: A Novel Class of Versatile Building Blocks

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Organotrifluoroborate salts are now established as highly valuable alternatives to boronic acids and esters not only because of their stability towards oxidation and protodeborylation but also for their wider-ranging reactivity [1]. These properties enable their combination with additional functional groups, thereby opening doors to new tailored organoboron products. In this regard, azidomethyl borate [2] and ynone trifluoroborates [3] have already been exploited for the synthesis of a series of (hetero)aromatic boronate derivatives.

We have developed a novel class of hydrazine trifluoroborate salts that can be easily prepared on gram scale as air-stable, free-flowing solids. These compounds exhibit at the *N* atoms the typical reactivity of hydrazines while maintaining the trifluoroborate for downstream chemistry, which could be further elaborated by exploiting the rich chemistry of organoboron reagents.

The highly regioselective synthesis of pyrazoles provides a regiocontrolled method for the synthesis of *N*-benzyl pyrazoles via cross-coupling reactions, whose applicability is demonstrated in the synthesis of Palovarotene analogs. The general potential of pyrazolylmethyl trifluoroborates is also demonstrated through chemoselective $S_EAr$ and Petasis Boron–Mannich reactions.

Furthermore, acylation and subsequent cross-coupling chemistry open the door to accessing functionalized hydrazines not easily obtainable via regioselective and safe procedures.

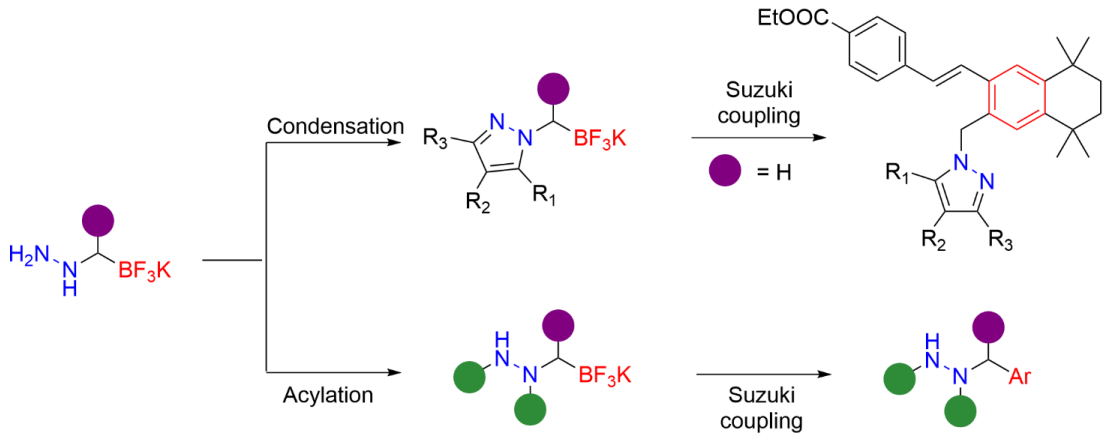


**Figure 1**. reactivity of Hydrazine Trifluoroborate Salts and downstream organoboron functionalization

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# Polymer- and aging-specific microplastic remodeling of lipid-mediator profiles in hiPSC-derived cardiomyocytes

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Microplastics (MPs) are pervasive environmental contaminants detected in human cardiovascular tissues, and growing evidence indicates that MP exposure can promote oxidative stress and inflammatory responses. However, no study has investigated how different polymer types and their environmentally aged forms influence oxylipin profiles, a class of bioactive lipid mediators involved in inflammation and its resolution, in cardiomyocytes.

Here, we combined a targeted MEPS-UHPLC-MS/MS platform with functional assays to investigate polymer- and aging-dependent effects of five common MPs, high-density polyethylene (HDPE), low-density polyethylene (LDPE), polystyrene (PS), polyethylene terephthalate (PET), and polypropylene (PP), in human induced pluripotent stem cell-derived cardiomyocytes (hiPSC-CMs) across a 7-day time course. A total of 56 lipid mediators were quantified in cell culture media and integrated with measurements of cell viability, reactive oxygen species (ROS), caspase-1 activation, and cytokine responses.

Distinct polymer-specific and aging-dependent response patterns were observed. HDPE and PS induced the strongest oxidative and pro-inflammatory oxylipin remodeling, particularly after photo-oxidative aging, whereas LDPE displayed a polymer-state-dependent profile characterized by transient responses in its virgin form and more persistent alterations after aging. PUFA precursor mobilization was strongest in virgin HDPE and aged PS, while aged LDPE remained elevated throughout exposure. Specialized pro-resolving mediators exhibited polymer-specific temporal patterns: HDPE and PS showed marked late increases, aged LDPE remained persistently elevated, and PET dis-played the most temporally stable profile. Network-based pathway analysis using Cytoscape revealed coordinated time-dependent reorganization of ω-6 and ω-3 oxylipin pathways, highlighting distinct inflammatory and pro-resolving trajectories associated with polymer chemistry and environmental aging.

Together, these findings demonstrate that polymer chemistry and environmental aging jointly shape oxidative, pro-inflammatory, PUFA precursor, and resolution-related lipid mediator remodeling in human cardiomyocytes, providing new mechanistic insight into how MPs may perturb cardiovascular homeostasis.

KEYWORDS: Microplastics; hiPSC-derived cardiomyocytes; Oxylipins; Specialized pro-resolving mediators; PUFA precursors; Photo-oxidative aging.

# Chimeric Dual-Target Agents for Precision Therapy of Aggressive Brain Tumors

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Glioblastoma (GBM) is the most aggressive brain tumor and remains largely incurable owing to extensive intratumoral heterogeneity, therapy resistance, and recurrence driven by glioblastoma stem-like cells (GSCs).[1] To address the complexity of this disease, we pursued a multitarget drug design strategy aimed at the simultaneous modulation of two enzyme systems critically involved in GBM progression and adaptation. In particular, Aldehyde Dehydrogenase 1A (ALDH1A) isoforms contribute to stemness maintenance, aldehyde detoxification, and retinoid metabolism [2], whereas Carbonic Anhydrases (CAs) regulate pH homeostasis in the tumor microenvironment. Among them, the isoforms CA IX and CA XII are upregulated under hypoxic conditions, while CA II has been associated with temozolomide therapy resistance [3].

Starting from NR6, a previously identified selective ALDH1A3 inhibitor bearing an imidazo[1,2-*a*]pyridine core, a series of chimeric compounds was rationally designed by incorporating a CA inhibitor moiety through structurally diverse linkers.[4] This approach generated multifunctional molecules capable of engaging both targets within a single chemical entity. Biological evaluation revealed that several derivatives retained significant inhibitory activity against ALDH1A3 while acquiring potent inhibition of CA II, IX, and XII. Moreover, selected compounds exhibited antiproliferative effects in U87MG glioblastoma cells.

Collectively, these findings demonstrate that the integration of complementary pharmacophores into a single chimeric architecture represents a promising strategy for the development of precision therapeutics against highly aggressive and treatment-resistant brain tumors.

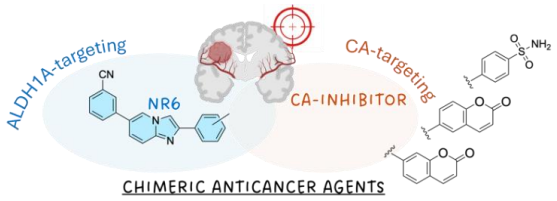


**Figure 1**. General structure of chimeric compounds containing **NR6** and the CA-inhibitor group.

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# Electrospinning of polymeric optical sensors for wound biomarker monitoring

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Polyacrylonitrile (PAN)-based electrospun meshes were developed as optical sensing platforms for the monitoring of wound-related biomarkers, such as ammonia ($NH_3$), hydrogen peroxide ($H_2O_2$) and glutathione (GSH) whose concentration variations are closely associated with oxidative stress, bacterial infection, and compromised healing processes in skin wounds [1]. The sensing approach was based on photoluminescence signal variation generated by the luminophore (KL1421), which was incorporated directly into the PAN electrospinning solution before fiber fabrication [2]. The meshes were then functionalized with rhodamine B (RhB), methyl orange (MetOr), chitosan (Chit), and graphene oxide (GO) coatings to obtain selective optical responses toward the target biomarkers. Morphological and mechanical characterization was performed to evaluate fiber structure and material properties, while the effect of GO on dye distribution and photoluminescence signal intensity was also investigated. The developed nanofibrous platforms may represent promising systems for real-time wound status monitoring through optical biomarker detection.

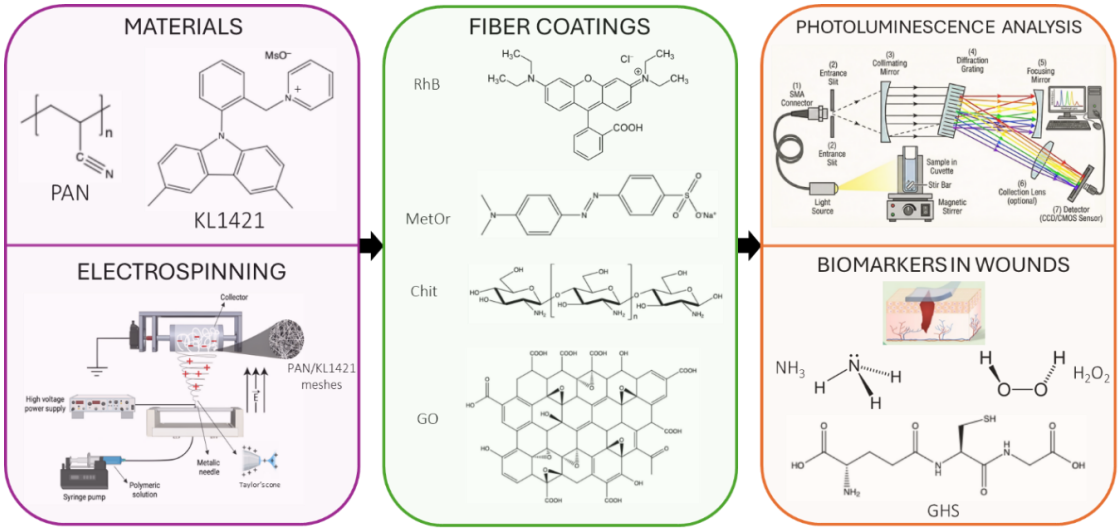


**Figure 1**. Electrospinning of PAN/KL1421 meshes, surface modification with different coatings (RhB, MetOr, Chit, and GO), and photoluminescence detection of wound biomarkers ($NH_3$, $H_2O_2$ and GSH).

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# Long vs. Short Chain Covalent Functionalization in the Preparation of Mechanochromic Polymers

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Mechanoresponsive polymers capable of translating mechanical deformation into optical outputs represent an attractive strategy for stress sensing, structural diagnostics, and early failure detection [1]. While significant progress has been achieved in the development of mechanophores, comparatively little attention has been devoted to understanding how spacer architecture influences the behavior of covalently integrated mechanochromic systems.

Herein, we report the synthesis of a perylene bisimide (PBI)-based polymeric macromechanophore incorporating flexible poly(ε-caprolactone) (PCL) spacers and terminal hydroxyl functionalities (M-PBI) [2]. The material was covalently introduced as a crosslinking unit into maleic anhydride–modified SEBS and LLDPE matrices. Its mechanochromic performance was compared with that of a structurally related short-spacer PBI crosslinker (P-PBI) as well as a non-covalently dispersed low-molecular-weight PBI derivative (S-PBI).

Under tensile strain, both M-PBI- and P-PBI-containing films exhibited deformation-triggered disaggregation phenomena accompanied by enhanced fluorescence emission, consistent with the behavior typically observed in PBI-based mechanochromic materials [3]. In particular, the ratio between monomeric and aggregated emission bands evolved systematically with strain, providing a reliable optical readout of deformation. Elastomeric SEBS samples displayed a pronounced and reversible fluorescence response over repeated loading–unloading cycles. By contrast, films prepared with physically blended S-PBI showed negligible optical variation during stretching experiments.

Importantly, incorporation of the flexible M-PBI crosslinker produced minimal changes in the mechanical properties of both SEBS and LLDPE matrices, indicating good mechanical compliance. On the other hand, the shorter and more rigid P-PBI spacer increased network stiffness, leading to reduced ductility and earlier fracture in semicrystalline LLDPE systems.

Overall, these findings highlight the critical role of spacer length and flexibility in modulating both the mechanochromic response and the mechanical performance of polymer networks, providing useful design principles for the development of durable and efficient mechanochromic materials.

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# Filament production from biodegradable polymer composites for 3D-printable enhanced efficiency fertilizers

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Sustainable agriculture requires strategies that improve nutrient use efficiency while reducing the environmental impacts of conventional fertilization. In this context, enhanced efficiency fertilizers (EEFs) based on biodegradable materials have emerged as promising alternatives aligned with the United Nations Sustainable Development Goals 2 and 12. Lignocellulosic materials (LCMs), such as lignin and cellulose, combined with starch (St) and poly(vinyl alcohol) (PVA), offer a sustainable platform for EEF development without toxic additives or compatibilizers. This study aims to optimize filament production using these components and monoammonium phosphate (MAP)/potassium nitrate ($KNO_3$) as nutrient sources. Initially, LCMs were combined with MAP via spray-drying to produce nutrient-loaded microparticles (Fig. 1a) [1]. These microparticles were incorporated into an St/PVA matrix using a thermomechanical mixer to produce composites for (I) EEFs in tablet form (Fig. 1b) and (II) filament feedstock. The filament optimization focused on the microparticle-to-nutrient ratio, the presence of cellulose in the microparticles, and the plasticizer content in the PVA matrix. The filaments were characterized for their potential use as EEFs (after pelletization, Fig. 1c) or as feedstock for additive manufacturing (Fig. 1d). Preliminary results indicate that composites containing 10 wt.% nutrient produce homogeneous filaments resistant to thermomechanical stresses during extrusion. The presence of cellulose improved filament diameter uniformity, while thermomechanical mixing enhanced morphological quality. Tensile mechanical tests and oscillatory rheology were used to select filaments for initial 3D-printing trials. Although they exhibited low elastic modulus (10-20 MPa) and high viscosity, successful printability was achieved after optimization of printing parameters. These findings highlight the potential to combine different techniques to produce sustainable EEFs with tailored nutrient release profiles and customizable geometries.

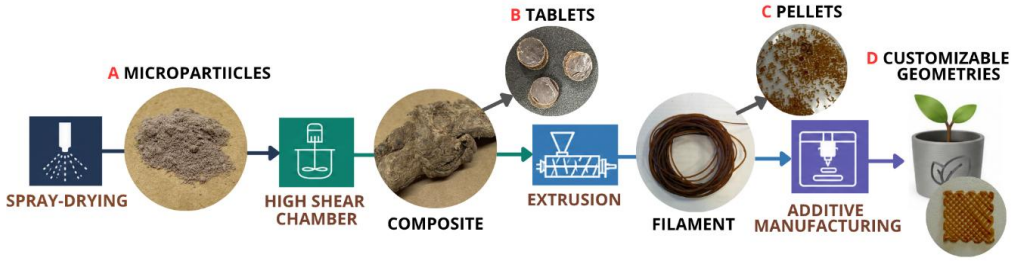


**Figure 1**. Schematic representation of the production route for EEFs in different conformations.

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# Novel palladium(II) complexes with bidentate nitrogen ligands: synthesis, characterization and anticancer activity

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Platinum complexes have been studied since the discovery of cisplatin, which is known to produce DNA damage and cell apoptosis. Due to the many similarities between Pt(II) and Pd(II), there is interest in studying Pd(II) complexes as potential anticancer drugs. Given the much faster hydrolysis of Pd(II) complexes with respect to the Pt(II) analogues, there is the need for a very strong nitrogen ligand, able to ensure the reaching of its biological target [1,2].

This work focuses on the synthesis and characterization of novel square-planar Pd(II) complexes coordinated by bidentate nitrogen ligands and chloride ions. Two classes of complexes, namely $PdCl_2L$ and $[Pd(DACH)L]^{2+}$ derivatives, were prepared using aromatic N,N-chelating ligands and (1R,2R)-1,2-diaminocyclohexane (DACH). Their physicochemical properties, including solubility, lipophilicity, and stability in DMSO and HEPES buffer, were investigated together with their interactions with DNA through melting and ethidium bromide displacement assays. Finally, the biological activity of the complexes was evaluated on selected tumor cell lines to explore their potential anticancer properties and mechanisms of action. Positively charged complexes are the best intercalators, and the complexes with 4,4'-diphenyl-1,10-phenanthroline the most cytotoxic with high cancer selectivity.

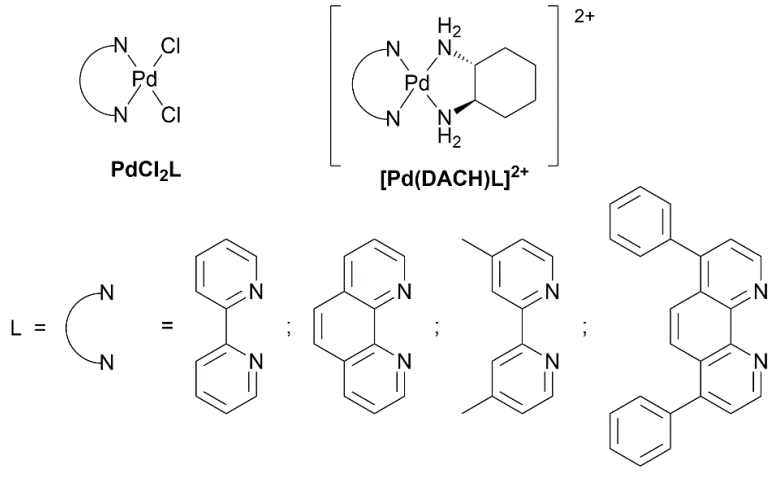


**Figure 1**. Molecular structure of investigated Pd(II) complexes

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# Insights into Curcumin Encapsulation within ZIF-8 via Solid-State NMR

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The need for controlled drug release to reduce toxicity and enhance therapeutic efficacy has driven the development of Metal-Organic Frameworks (MOFs) as drug carriers [1,2]. ZIF-8 is particularly promising due to its biocompatibility and pH-responsive nature [3,4]. A major pharmacological challenge is the delivery of Curcumin (*cur*), a natural bioactive polyphenol renowned for its antioxidant, anti-inflammatory and anticancer properties, with low aqueous solubility and poor stability [5-7]. Encapsulating *cur* within ZIF-8 offers a strategic solution to improve the stability of the molecule and its bioavailability [6-8]. Understanding how drugs interact at a molecular level with porous nanocarriers is fundamental to guide the rational design of advanced drug delivery systems. This work exploits solid-state NMR (ssNMR) as a unique atomic-level probe of structure and dynamics in *cur*@ZIF-8 systems. This technique provides definitive evidence of whether the drug is truly encapsulated, adsorbed on the surface, or present as an amorphous/crystalline bulk phase. By analyzing samples with different curcumin initial concentrations (0.5, 1, and 2 mg/mL – referring to the amount of curcumin dissolved in MeOH for the synthesis [9]), we provide detailed insights into host-drug interactions and structural modifications induced by loading, enabling the identification of stability thresholds and distinct confinement regimes within the framework. A multinuclear ($^{1}H$, $^{13}C$, $^{15}N$) high-resolution ssNMR strategy was used to investigate the structure of both the framework and the drug and, in particular, the interactions between curcumin and ZIF-8. Furthermore, spin-lattice ($T_1$) and spin-spin ($T_2$) relaxation measurements were exploited to reveal linker and guest dynamics under confinement across multiple timescales. To gain a deeper understanding of the host-guest interactions, 2D ssNMR experiments were also performed, complemented by DFT calculations to provide both structural validation and characterization of the non-covalent forces at play.

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# Old but gold? Rediscovering the use of Al-alkoxide derivatives in catalytic transfer hydrogenation reactions of furfural with ethanol

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The first examples of transfer hydrogenation of carbonyl compounds were independently reported by Meerwein, Schmidt, and Verley, who demonstrated that aldehydes could be reduced in the presence of $Al(OEt)_3$ and ethanol. Subsequently, Ponndorf showed that aluminium alkoxides derived from more readily oxidisable secondary alcohols, such as isopropanol, could efficiently reduce both aldehydes and ketones [1]. Despite these early discoveries, the study of catalystic transfer hydrogenation (CTH) mediated by aluminium alkoxides has progressively declined over recent decades due to the widespread adoption of noble-metal-based catalysts. However, although their limited activity has been attributed to aggregate formation, no in-depth study optimising their catalytic role has ever been reported. The growing pressure imposed by sustainability policies has therefore renewed interest in replacing noble-metal-based catalysts with alternatives derived from cheaper, earth-abundant elements [1].

In this context, the present study investigates the CTH of furfural (FF) to furfuryl alcohol (FA) using aluminium alkoxide derivatives. FF is one of the most important biomass-derived platform molecules, typically produced through the acid-catalysed dehydration of C5 sugars. Currently, more than 60% of the annual FF production (~300 kton) is converted to FA, a key intermediate with strategic applications in the production of biofuels, resins, pharmaceuticals, flavourings, and solvents [2]. Industrial FA production relies on molecular hydrogen and presents several drawbacks: the requirement for high-pressure $H_2$, high energy consumption, and the use of copper chromite catalysts, which raise environmental concerns due to the potential release of toxic Cr(VI) species. Moreover, commercial hydrogen is still predominantly produced from fossil resources, rendering the overall process unsustainable. CTH therefore emerges as a more sustainable alternative, offering milder reaction conditions and greener hydrogen donors such as ethanol [3].

The study initially focused on cheap, commercially available $Al(OEt)_3$, which operates via the Meerwein–Ponndorf–Verley (MPV) mechanism, achieving good FA yields (~70 mol%) at a catalyst loading of 10 mol%. To improve catalytic performance, a new library of Al-complexes bearing BINOL-derived ligands was synthesised and screened. The most active catalyst afforded good FA yields in short reaction times with very high selectivity. In summary, this work demonstrates the feasibility of CTH of FF via the MPV mechanism using ethanol as a renewable hydrogen donor and economical Al-based catalysts, contributing to a more sustainable synthesis of FA. Furthermore, a series of novel Al-BINOL complexes was successfully developed, enabling a significant enhancement in catalytic performance.

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# Modelling exciton-polaritons with an expanded Frenkel Hamiltonian framework

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Exciton-polaritons are hybrid light-matter states originating from the strong coupling between molecular excitations and confined electromagnetic modes, such as those supported by plasmonic or Fabry-Pérot cavities [1]. The formation of exciton-polaritons can induce modifications of relaxation pathways, quantum yields and decay times [1-3], offering a new approach to modulate molecular reactivity. However, simulating the excited-state dynamics of exciton-polaritons in large multichromophoric systems remains a major challenge due to the high computational cost.

Here we present a surface hopping implementation based on an extended Frenkel Exciton Model for the simulation of exciton-polaritonic states and their nonadiabatic dynamics in multichromophoric systems. The method extends the previous works of Sangiogo et al. on the excitonic Hamiltonian [4], and incorporates the photonic degree of freedom and the light-matter coupling terms [5] at the same level of the exciton coupling.

To validate the new framework, we applied it for the simulation of the polariton dispersion spectra of a self-assembled monolayer (SAM) under strong coupling conditions. We then followed the excited state dynamics of the SAM after photoexcitation.

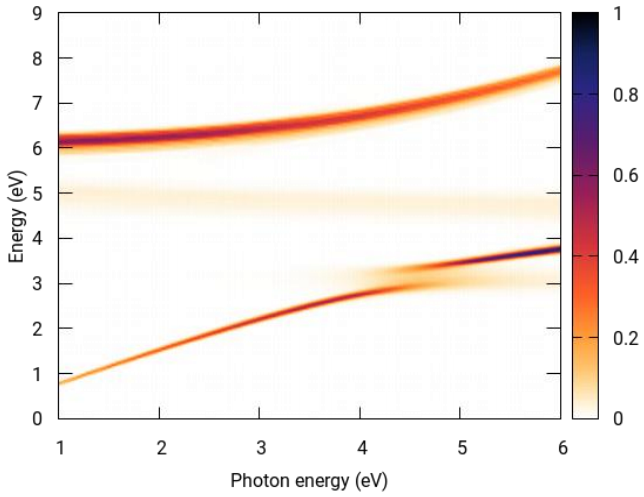


**Figure 1**. Polariton dispersion spectrum of an azobyphenyl SAM, obtained considering 10 chromophores in the QM part.

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# Electrospun bacterial polyhydroxyalkanoate mesh: A novel platform for localized Urolithin A delivery in ovarian cancer therapy

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Biodegradable meshes that release anticancer adjuvants locally may improve post-debulking ovarian cancer treatment [1-2]. Urolithin A (UA)-loaded electrospun bacterial poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) blended with poly(ε-caprolactone) (PHBV/PCL, 70/30 w/w) was investigated as surgical mesh, with PCL mesh as reference [3]. Polymeric solutions were electrospun under optimized conditions and characterized by SEM, TGA, NMR, UV-Vis spectroscopy, and *in vitro* release in PBS at 37 °C. Cytotoxicity of the released UA was assessed on A2780 ovarian cancer and Balb/3T3 clone A31 fibroblast cell lines, also with cisplatin. Both systems formed homogeneous, defect-free microfibrous meshes with randomly oriented fibres (2.1-2.5 μm), and UA loading did not significantly affect morphology or thermal behaviour. UA was efficiently encapsulated (93% in PCL; 82% in PHBV/PCL) and released with an initial burst followed by sustained delivery over 16 days (up to 63%). Free UA enhanced cisplatin activity, and UA-releasing meshes reproduced this adjuvant effect. UA-loaded (PHBV)/PCL meshes are promising biodegradable platforms for localized postoperative ovarian cancer therapy (Figure 1).

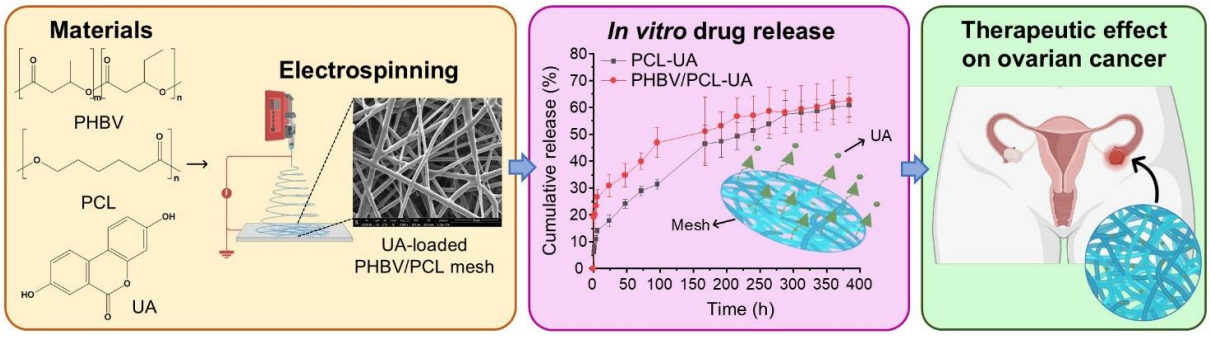


**Figure 1**. Development and therapeutic application of UA-loaded (PHBV)/PCL meshes: schematic representation of the fabrication process of PHBV/PCL meshes via electrospinning, incorporating UA, *in vitro* sustained release profile of UA from the fibrous meshes over 16 days, and their potential therapeutic effect on ovarian cancer treatment.

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# Self-Assembled ASC16 Coagels as Supramolecular Matrices: Structural Effects of Poloxamer 407 and Impact on Curcumin Solubilization and Skin Distribution

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Curcumin (CUR) is a promising anticancer agent for melanoma and non-melanoma skin cancers; however, its clinical application is limited by very low aqueous solubility, chemical instability, and poor skin permeability [1]. From a supramolecular chemistry perspective, lipid-based structured systems can enhance drug solubilization and control molecular transport through organized hydrophobic domains.

Palmitoyl ascorbate (ASC16) is an amphiphilic derivative that self-assembles into lyotropic liquid-crystalline coagel with lamellar organization, suitable for topical delivery [2]. In this work, CUR-loaded ASC16 (2% w/v) coagels were prepared and compared with a modified system in which the aqueous phase was replaced by a 15% w/w Poloxamer 407 (P407) dispersion, a thermoresponsive PEO–PPO–PEO triblock copolymer that undergoes reversible sol–gel transition near physiological temperature [3]. The study aimed to elucidate how P407 affects structure–performance relationships governing phase behavior, drug loading, rheology, release and skin distribution.

Phase transitions were investigated by differential scanning calorimetry (DSC). CUR was incorporated by heating above the critical micellar temperature (CMT), followed by hot filtration and cooling. Solubilization was quantified by fluorescence spectroscopy. Molecular interactions were analyzed by fourier-transform infrared (FTIR) spectroscopy, while viscoelastic and thermogelation properties were evaluated by rheology. *Ex vivo* permeation and distribution were assessed using porcine ear skin.

DSC showed that P407 decreased the CMT of ASC16 and induced a sol–gel transition near 37 °C while preserving lamellar ordering. The Coa-ASC16$_{P407}$ system significantly increased CUR solubilization (0.02% vs 0.80% w/v), indicating enhanced incorporation within hydrophobic microdomains. FTIR confirmed CUR incorporation and suggested intermolecular interactions within the lipid–polymer network. Both formulations permeated skin, however, permeation/penetration studies revealed distinct tissue accumulation patterns between the two formulations, indicating that P407 incorporation modifies the diffusion environment and consequently drug transport mechanisms. Overall, both ASC16-based coagels are effective cutaneous delivery systems, but differ in rheological properties and CUR solubilization and skin distribution. Indeed, P407 enhances solubilization and introduces thermoresponsive behavior, while reshaping skin transport. These findings highlight the role of supramolecular organization in rational design of lipid–polymer systems for skin cancer therapy.

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# Development of New Chiral Organic Dyes Towards Solid-State Chiroptical Characterization

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Circularly polarized luminescence (CPL) is a key phenomenon of great relevance in the development of advanced photonic and optoelectronic devices like OLEDs, security inks, sensors and detectors [1].] For this reason, in the last years, the development of new chiral materials for their application in these fields has attracted wide interest. Specifically, chiral conjugated organic molecules have emerged as powerful platforms in the field. Their primary advantages lie in the ability to fine-tune photophysical properties through precise structural modifications, and their excellent processability [2].

These compounds usually present weak CPL activity. Nevertheless, when deposited in a thin film and after post-deposition treatment, they have the capability to self-assemble in higher hierarchical/spatial structures or levels that may amplify the chirality of the molecule, and therefore, the chiroptical properties [3]. However, there are still certain limitations, including the relationship between molecular structure, supramolecular order at different levels of hierarchical organization and the chiroptical properties, so more comprehensive studies are needed [3].

In this regard, different architectures have been investigated in an attempt to find a trend that relates the structure to its final properties. So far, it has been observed that small changes in the molecular structure—such as modification of the aromatic skeleton—can produce a very different supramolecular assembly in thin films. However, there is no guiding principle that correlates these findings [4].

In this communication, we present preliminary results on the development of novel chiral conjugated organic molecules, and their chiroptical characterization in thin films, based on the employment of new scaffolds for the construction of these molecules.

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# New integrated biorefinery approaches for the production of keratin-rich hydrolysates from enzymatic conversion of bovine-hair wastes

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Traditional leather liming represents a highly impactful stage in the tanning industry, due to the widespread use of chemicals, such as $Ca(OH)_2$ and $Na_2S$. In particular this latter, despite being effective in breaking disulfide bonds to prepare raw hides, poses severe environmental and health risks, leading to hydrogen sulfide emissions. To mitigate these issues, enzymatic dehairing by proteolytic enzymes offers a sustainable alternative, by reducing both organic and sulfide loads in wastewater [1]. However, such milder treatments generate a solid by-product stream (e.g. hair), which can be valorized into high-value keratin-based products via further chemical and/or enzymatic hydrolysis [1,2].Under the framework of the ENZYCAL project, "*New processes of bovine hair removal and its valorization by means of enzymatic hydrolysis*", this study is aimed at: 1) optimizing the enzymatic dehairing proposed as a replacement for traditional liming treatments, and 2) converting this hairy-based waste stream into keratin-rich hydrolysates through enzymatic hydrolysis.Focusing on the second goal, 13 keratinases were initially screened at 35 °C, employing a fixed solid/liquid ratio of 1/20 wt/wt and an enzyme loading of 10 wt%. Screening efficiency was evaluated on the basis of the yield (wt%) in solid residue and in total nitrogen. Based on preliminary tests, the P-250 T enzyme was identified as the most suitable candidate for further optimization. Operating at pH=9 and 40°C at a reduced enzyme loading of 7.5 wt%, it has been possible to achieve the best (minimum) yield in solid residue of 55.1 wt%, and the maximum nitrogen yield of 40.1 wt%. Finally, a pre-treatment step by sodium bisulfite (sulfolysis), to be carried out prior to enzymatic hydrolysis, was investigated to break disulfide bonds of keratin texture, thereby making the subsequent hydrolysis easier [3]. Employing a solid/liquid ratio of 1/20 wt/wt and a sodium bisulfite loading of 3 wt% successfully improved the keratin solubilization. Under these optimized conditions, the lowest yield in solid residue was achieved (19.0 wt%), corresponding to the highest yield in removed nitrogen of 80.8 wt%. These remarkable results demonstrate a viable, circular economy approach for promoting the valorization of waste streams from the leather tanning sector, encouraging scale-up and process intensification.

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# New Manganese Carbonyl complexes for $CO_2$ Hydrogenation

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Various manganese compounds have been investigated for $CO_2$ hydrogenation reactions [1]. The metal centre usually bears polydentate N- or P-ligands [2], however tris(1H-pyrazolyl)methane (TPM) and its substituted analogue tris(3,5-dimethylpyrazolyl)methane (TPM*) remain overlooked in this field.

In this work, the cationic complex $[Mn(CO)_3(TPM)][Br]$ [3] was synthesized from the commercial $[Mn(CO)_5Br]$ via direct reaction with TPM in toluene under reflux.

Subsequent metathesis reaction using silver salts afforded the $BF_4^-$ and $NO_3^-$ salts in nearly quantitative yields.

Then, treatment of $[Mn(CO)_3(TPM)][NO_3]$ with $(CH_3)_3NO$ in $CH_3CN$ solution allowed for single $CO/CH_3CN$ substitution, yielding $[Mn(CO)_2(TPM)(CH_3CN)][NO_3]$.

Analogous procedures were employed to obtain $[Mn(CO)_3(TPM^*)][X]$ (X = Br, $NO_3$) and $[Mn(CO)_2(TPM^*)(CH_3CN)][Br]$.

All products were characterized by elemental analysis, IR and $^1H$ NMR spectroscopy, and by cyclic voltammetry.

Their catalytic activity in $CO_2$ hydrogenation to formic acid or methanol was then investigated.

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# Low-Cost Pyranone-Based Metallodrugs: From Albumin Transport to G-Quadruplex Recognition

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Since the discover of *cis*-platin as one of the first metallodrugs, many efforts have been put towards the development of rare metal complexes such as Pt, Au and Ag capable of interacting with biological substrates. However, these very same substances often show to be rare, expensive and possibly toxic to the organism. Hence, different metal centres have been explored to find cheaper and safer alternatives, such as iron [1], aluminium [1], copper [2] and zinc [3]. TRansforming metal Ions and Low-cost LIgands into next generation metallodrugs (TRILLI) is a nationwide initiative (PRIN 2022) that seeks to reveal important elements for the systematic design of novel metal complexes (MCs) and enhance their advancement as metallodrugs.

We examined a panel of metal complexes deriving from the coordination of four metal centres ($Cu^{2+}$, $Zn^{2+}$, $Fe^{3+}$, $Al^{3+}$) with the ligands shown in Figure 1. In particular, the interaction of these MCs with various biomolecules was analysed. The bio-substrates in question are Bovine Serum Albumin (BSA), calf thymus DNA (ctDNA) and different topologies of DNA G-quadruplexes.

Spectrofluorimetric titrations, UV-vis titrations and Fluorescent Indicator Displacement assays (FID assays) have been performed on all the above-mentioned complexes. Results show that all MCs interact and may be transported by BSA, the most abundant serum protein, without showing any specificity in the binding features. In contrast, ctDNA showed no binding with all molecules meanwhile iron and copper complexes demonstrate a promising selective interaction with specific G-quadruplex geometries. In the end, these characteristics are evaluated and examined to elucidate the binding process and determine the most advantageous MC.

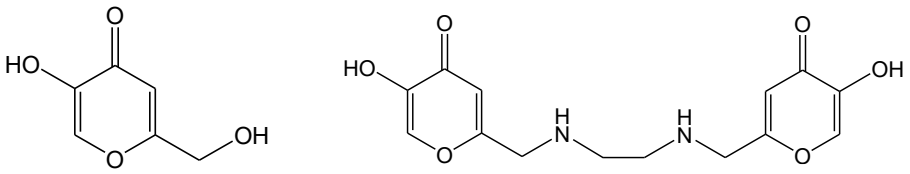


**Figure 1.** The ligands considered in this study: (a) kojic acid (KA); (b) 2,2'-[ethane-1,2-diylbis(iminomethanediyl)]bis(5-hydrohy-4H-pyran-4-one) (S2).

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# Thin Film Microextraction for Skin VOCs Sampling: A Comparison between PDMS/DVB and PDMS/HLB Sorbent Phases

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Thin Film Microextraction (TFME) is a sampling technique first introduced by Bruheim et al. In 2003 [1], based on the use of a thin carbon film coated with one or more adsorbent phases. Film dimensions are typically 40×4.85×0.04 mm (height, width, thickness), and the weight is approximately 60 mg.

These devices are robust, reusable, and flexible, and can be easily adapted to various surfaces, including the skin. The easy transport and storage makes them suitable for in-situ sampling of volatile and semi-volatile organic compounds (VOCs, SVOCs), either through direct contact, headspace sampling or immersion [2].

In this study, TFME with two different phases, namely polydimethylsiloxane/divinylbenzene (PDMS/DVB) and polydimethylsiloxane/hydrophilic-lipophilic balanced (PDMS/HLB), was used for sampling VOCs, then extracted compounds were analysed, identified, and monitored by gas chromatography-mass spectrometry (GC-MS). The two sorbent phases were compared by evaluating precision (RSD) and instrumental response (peak area) across three groups of compounds: the internal standards, a set of representative analytes covering a wide range of physicochemical properties (log*P*, boiling point, chemical class), and the compounds identified in the real samples.

No significant differences between the two phases were observed in terms of collected analytes, sensitivity, carry-over, costs, and temporal stability up to six months, supporting the use of either phase for subsequent analyses. However, PDMS/HLB fibres demonstrated a slightly higher overall extraction capacity for the detected VOCs.

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# Eu-based CPL probes for ATP detection

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Circularly polarized luminescence (CPL) is defined as the difference between left and right circularly polarized light emitted by a luminescent chiral system. The high sensitivity of this property makes CPL spectroscopy a promising technique for the study and tracking of chiral species of biological interest, *in vitro* and *in cellulo* [1,2].

Adenosine triphosphate (ATP) is the most abundant nucleotide polyphosphate in living organisms. It is the chemical energy source for most biological processes and serves as a cofactor for many enzymes [3]. For these reasons the possibility of monitoring the levels of ATP in biological media has attracted great interest in the last few years. Lanthanide complexes are suitable candidates as ATP probes, thanks to their perculiar emission features, including long luminescence lifetime. Moreover, monitoring the CPL of the ATP-Ln complex adduct could yield a selective signal, allowing one to distinguishing it from adducts with different nucleotides [4].

In this work, we propose a conjugated achiral ligand, able to sensitize the europium core of the probe. The interaction between this complex and ATP was then studied through CPL spectroscopy, lifetime measurements, time resolved CPL and two photons CPL spectroscopy (2P-CPL). The study of the interaction between the probe and possible interferents was also carried out.

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# Expanding the [FeFe]-Hydrogenase Toolbox with Cyclopentadienyl and Heterocarbyne Ligands

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Natural [FeFe]-hydrogenases (Figure 1A) have emerged as interesting models for the design of efficient electrocatalysts for $H_2$ evolution, a process of significant relevance for sustainable energy conversion and storage.[1] Over the past decades, research has mainly focused on structures based on diiron cores bearing bridging dithiolate ligands (Figure 1B).[2]

Although a broad range of ligands in classical mimics [3], as well as non-traditional mono-, di-, and trinuclear architectures,[4] have been investigated, only a limited number of studies have so far focused on systems containing additional ligands with synergistic electronic properties.

In the present work, attention has been focused on robust complexes containing cyclopentadienyl (p-donor) and heterocarbyne (p-acepptor) ligands, derived from the commercially available precursor $[Fe_2Cp_2(CO)_4]$ (Cp = $\eta^5$-$C_5H_5$) (Figure 1C). Preliminary studies will also be presented concerning structural modifications of $Fe_2$-dithiolate compounds through the incorporation of isocyanides. Results will be discussed in light of spectroelectrochemical analyses and theoretical studies.

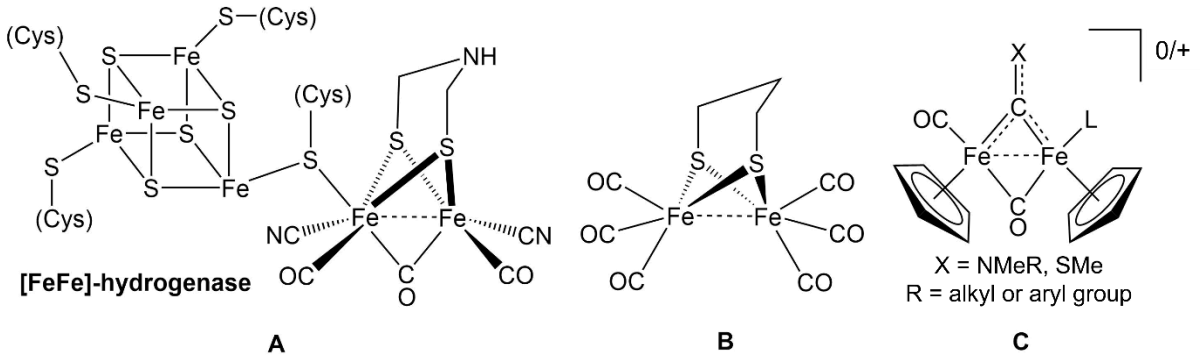


**Figure 1**. Structures of the active site of [FeFe]-hydrogenase (A), fundamental $Fe_2$-dithiolate mimic (B), heterocarbyne complexes obtained from $[Fe_2Cp_2(CO)_4]$.

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# CRISPR/Cas12a Trans-Activity as a Tool to Estimate Binding Constants Between Cas12a/gRNA Complexes and ssDNA Targets

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During the last few years, CRISPR/Cas12a-based systems have been widely used in biosensor development thanks to their endonucleasic trans-activity, which enables the generation of amplified signals following the recognition of specific nucleotide sequences [1,2]. In particular, Cas12a activation by single-stranded DNA (ssDNA) is a key component of numerous biosensor platforms and nucleic acid-based molecular circuits [3]. However, the factors governing the formation of the active ternary complex Cas12a/gRNA/ssDNA and its relative efficacy are still not fully understood [4].

In this work, an experimental approach based on Cas12a trans-activity was developed to estimate the binding constant between Cas12a/gRNA complexes and ssDNA targets, with the objective to investigate possible correlations between binding affinity, activation efficacy, and structural characteristics of the involved sequences. The proposed method relies on the correlation between Cas12a trans-cleavage activity and the formation of active ternary complexes, providing an accessible strategy for the characterization of CRISPR/Cas12a systems.

This study contributes to understanding the interaction among Cas12a, gRNA, and ssDNA and provides useful information for the optimization and rational design of CRISPR/Cas-based biosensors and nucleic acid molecular circuits.

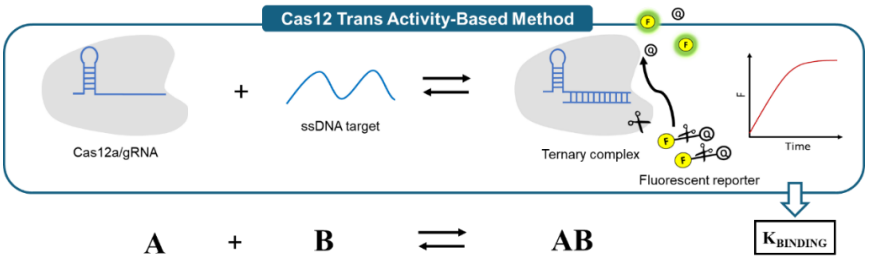


**Figure 1**. Schematic overview of the Cas12a trans-activity-based method for estimating the binding constant between Cas12a/gRNA complexes and ssDNA targets through fluorescence reporter cleavage.

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# Synthesis and Characterization of Novel Pt(II)-Gd(III) Heterobimetallic Complexes as Theranostic Agents

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Despite their efficacy as anticancer drugs, the clinical use of Pt(II)-based chemotherapeutics is limited by well-documented off-target toxicity and intrinsic or acquired chemoresistance [1]. In recent years, there has been a growing need to monitor the biodistribution and accumulation of the administered drug, as well as to evaluate the therapeutic response following treatment. To address this issue, real-time imaging techniques have been explored. In this context, conjugation to Gd(III) complexes represents a promising strategy. Although such systems may act as theranostic agents,[2] they remain scarcely investigated. The aim of this research is to develop new heterobimetallic Pt(II)-Gd(III) systems via amide bond formation between the amine group of a selected Pt(II) moiety and the carboxylic group of the Gd(III)-DOTA complex (Figure 1). Two classes of Pt(II) fragments have been synthesized. The first has the general formula $[PtX_2L]$, where X is chloride, bromide, or iodide and L is 4-(aminomethyl)benzene-1,2-diamine ligand. Based on structure–activity relationships, these complexes are designed to covalently bind DNA. The second class is an analogue in which the halides are replaced by the phenanthroline ligand, aimed at investigating DNA intercalation mechanisms [3]. All Pt(II) complexes were fully characterized by $^{1}H$ and $^{13}C$ NMR, UV-Vis spectroscopy and elemental analysis. The solution behavior of the investigated compounds will be evaluated by UV-Vis spectroscopy in DMSO, HEPES and PBS buffers to confirm their stability under physiologically relevant conditions. Their interactions, both before and after conjugation with Gd(III), will be studied by UV–Vis spectroscopy and ESI-MS to evaluate conjugation efficiency. Human serum albumin (HSA), the most abundant mammalian plasma protein [4], and the single-stranded oligonucleotide sequence ODN2 were selected as biological targets. Cytotoxicity will be evaluated on selected cancer cell lines.

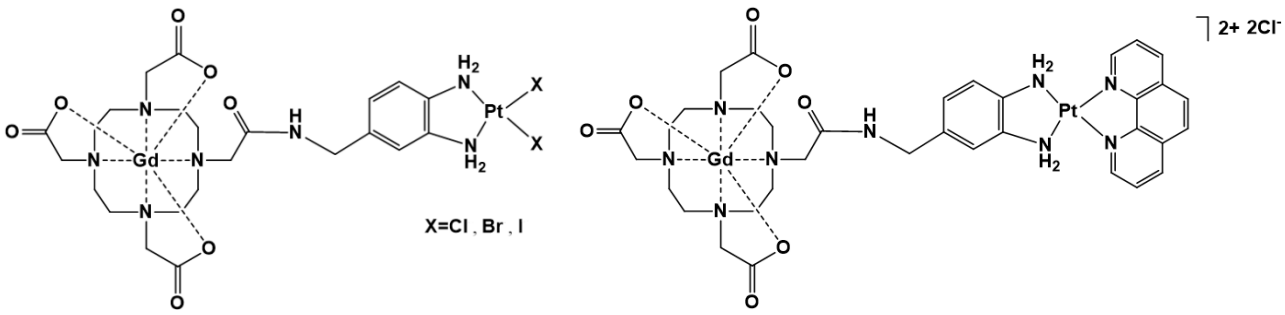


**Figure 1**. Molecular structures of the investigated Pt(II)-Gd(III) complexes

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# Novel 1,2,4-Triazole-Based ROCK Inhibitors as Potential Antifibrotic Agents for Pulmonary Fibrosis

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Pulmonary fibrosis is a chronic and life-threatening disorder characterized by progressive extracellular matrix deposition and irreversible loss of lung function. Although Nintedanib and Pirfenidone are the currently employed in clinics, they mainly slow disease progression, while lung transplantation remains the only definitive intervention for end-stage disease.[1] Thus, new antifibrotic strategies are urgently needed.

Rho-associated coiled-coil containing protein kinases ROCK1 and ROCK2 are key effectors of profibrotic signalling, also contributing to fibroblast activation. However, ROCK inhibitors currently investigated in other clinical settings generally show limited kinase selectivity and possible off-target effects, supporting the search for novel chemical entities with improved profiles. [2]

Starting from kinase inhibitors previously studied in our group for different applications, [3] we applied a rational repositioning and structural optimization approach to redirect their scaffold toward ROCK inhibition. In particular, isosteric replacement of a phenyl ring with a pyridine nucleus, together with modulation of the terminal portion of the compounds, led to a new series of 1,2,4-triazole-based derivatives bearing either a benzenesulfonamide or a phenylurea tail (Figure 1). Enzymatic assays identified promising compounds, with *in silico* studies highlighting key interactions within the ATP-binding site. Notably, selected compounds showed a preliminary antifibrotic efficacy in a cellular model of fibrosis induced by silicon dioxide nanoparticles, displaying an activity higher than that of Nintedanib under the same experimental conditions.[4]

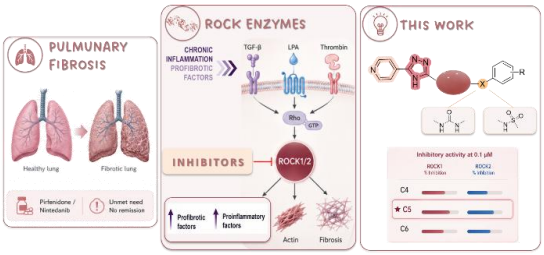


**Figure 1**. Overview of the work.

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# Dinuclear Iron Aminocarbyne Complexes as Catalysts for the Synthesis of β-Hydroxynitriles

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Readily accessible diiron(I) complexes offer a sustainable and efficient alternative for the catalytic synthesis of β-hydroxynitriles, versatile intermediates in the pharmaceutical[1] and material[2] industries that traditionally require the use of toxic cyanide sources or harsh conditions[3]. In this work, new dinuclear iron architectures of the type $[Fe_2Cp_2(CO)_2(L)(\mu\text{-}CNRR')]CF_3SO_3$ featuring tunable aminocarbyne and terminal ligands were synthesized. Synthetic procedures were optimized to obtain isocyanide derivatives, $[Fe_2Cp_2(CO)(CNR'')(L)(\mu\text{-}CNRR')]CF_3SO_3$. These complexes were evaluated as catalysts in the model aldol-type coupling between acetonitrile and p-fluorobenzaldehyde. Different reaction parameters, such as catalyst loading, temperature and base, were systematically optimized. This screening identified cesium carbonate ($Cs_2CO_3$) as the most effective Brønsted base co-catalyst, allowing the reaction to proceed under mild conditions. Experimental investigations and complementary DFT studies were combined to rationalize the factors governing catalytic performance. Specifically, the results elucidate how the introduction of terminal isocyanide ligands modulates the electronic properties and enhances catalyst robustness.

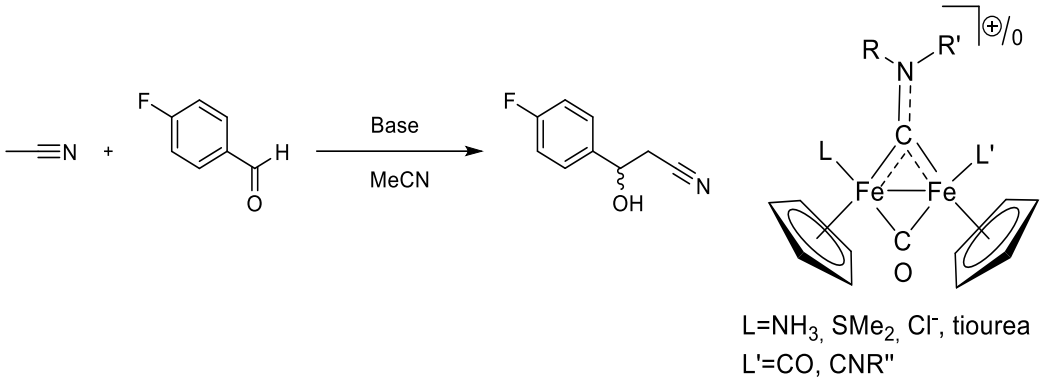


**Figure 1.** Aldol condensation reaction between acetonitrile and p-fluorobenzaldehyde, used to evaluate the catalytic activity of iron catalysts (left). Structure of the catalysts used (right).

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# Rh-catalyzed conjugated addition of arylboronic acids to unsaturated lactones: from enantioselective reactions to kinetic resolution

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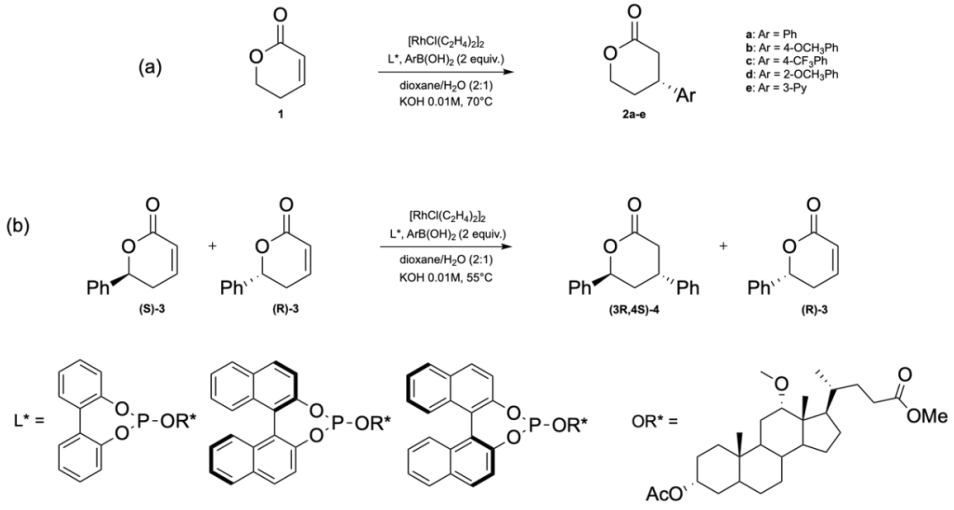
Conjugated addition of organometallic reagents to electron-poor alkenes is one of the most reliable carbon-carbon bond formation processes to afford β-substituted carbonyl compounds [1]. Although monodentate biaryl phosphites derived from deoxycolic acid have already been used extensively as chiral ligands in the Rh-catalyzed enantioselective conjugate addition of arylboronic acids to different substrates [2], no example concerning unsaturated lactones has been reported. Since substituted lactone moiety is a structural motif found in natural products and synthetic pharmaceuticals [3], we became interested in investigating this class of substrates. In this work, we screened deoxycholic acid derived *atropos* and *tropos* ligands and a variety of arylboronic acids in the addition to 5,6-dihydro-2H-pyran-2-one (**Scheme 1, a**), obtaining good conversions and high enantioselectivities. The promising results prompted us to apply these reaction conditions to the kinetic resolution of a racemic mixture of the 6-phenyl substituted lactone **3** (**Scheme 1, b**).




**Scheme 1**: Enantioselective Rh-catalyzed conjugated addition (a) and kinetic resolution (b)

The conjugated addition of phenylboronic acid to racemic **3** gave a mixture of enantioenriched lactones **4** and **3,** with ees depending on the ligand stereochemistry. The best performing ligand in both reactions was the one bearing the atropoisomeric (S)-binaphthyl moiety.

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# Microwave-assisted treatment to convert commercial polyethylene microbeads into a liquid suspension used as reference material for Py-GC-MS

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Due to its high sensitivity and selectivity, Pyrolysis-Gas Chromatography-Mass Spectrometry (Py-GC-MS) is a powerful tool for quantifying micro- and nanoplastics (MNPs) in environmental and biological samples at sub-microgram levels. Polymers can be diluted using inert solids or by dissolving them in a solvent. The latter is often unfeasible because many polymers, especially polyolefins such as polyethylene (PE), are poorly soluble in common organic solvents. For this purpose, microwave-assisted treatment (MAT) has been explored by Hermabessiere & Rochman (2021)[1] as an alternative for extracting polyolefins from environmental samples with dichloromethane (DCM) under high-pressure, high-temperature conditions. The effects of this treatment on the particles' physicochemical properties remain unexplored, as does its applicability to PE of varying characteristics. Additionally, recent studies have examined how different polymer reference materials affect the accuracy of Py-GC-MS when analyzing real samples.[2] This is especially true for PE, which encompasses polymers with very different properties (e.g., low-density PE (LDPE), high-density PE (HDPE), ultra-high-molecular-weight PE (UHMWPE)).[3] This overlooked factor can introduce additional uncertainty into MNP quantification when analyzing samples with known polymer characteristics, such as commercial materials and ecotoxicological assessments. In this ongoing work, we use the MAT strategy to produce a UHMWPE suspension in DCM from commercial microbeads. This suspension can later serve as a reference material to build calibration models for Py-GC, achieving a low limit of quantification without requiring expensive weighing equipment. The tests are performed using two commercial UHMWPE microbeads (90 and 40 µm) to assess the method's efficiency across different starting materials. All particles are characterized before and after the MAT using Fourier-Transform Infrared Spectroscopy (FTIR, for chemical composition), Scanning Electron Microscopy (SEM, for size and morphology), Py-GC-FID (for pyrolysis behaviour), and Differential Scanning Calorimetry (DSC, for thermal transitions). This array of analyses allows us to explore the impact of thermal treatment on the physical-chemical properties of the PE particles, and finally, the extent to which different PE types yield distinct pyrolysis products in Py-GC-MS. MAT strategy successfully produced a PE suspension in DCM, yielding a polydisperse suspension with an average particle size of around 30 µm and a recovery rate of 95%. Moreover, both UHMWPEs showed similar pyrolysis profiles, allowing to explore their interchangeability when building the regression models.

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# Comparative Characterization of Curing Behaviour Chinese and Japanese Urushi Lacquers

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Urushi lacquer, produced from the sap of trees belonging to the Anacardiaceae family, has been widely used in East Asia for centuries as both a protective and decorative coating on wooden and metal surfaces . In this project, we focus on urushi lacquer obtained from *Toxicodendron vernicifluum*. The lacquer sap is a water-in-oil emulsion, and its curing process is driven by enzymatic oxidation, leading to the formation of a highly resistant polymeric network, which brings gloss, toughness, and water resistance to the coated object . The curing behaviour of urushi films and their long-term ageing processes are still not fully understood because of the complexity of traditional lacquer systems. Furthermore, artists and conservators frequently report significant differences in both short- and long-term performance between Chinese and Japanese urushi lacquers, even when derived from the same botanical species. At the same time, lacquer films containing different pigments often exhibit distinct degradation pathways during ageing .

The present study focuses on the comparative characterization of the two mains commercial urushi lacquers currently available on the Chinese and Japanese markets. Six mock-up samples were prepared according to traditional methods. Two mock-ups were produced using only raw urushi Chinese and Japanese lacquer. The other mock-ups were prepared incorporating to the Chinese and Japanese lacquer two traditional natural pigments with markedly different chemical characteristics: a carbon-based black pigment, which primarily influences light absorption and an inorganic iron oxide-based pigment (Bengara), which may be associated with photochemical and oxidative degradation processes [3,4]

The evolution of the samples during curing and ageing was investigated through the combined use of Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA), following protocols developed by our research group for the study of the curing behaviour of oil paintings and oxidative lipid-based systems . These methodologies were previously applied to characterize the interaction between urushi lacquer and drying oils traditionally mixed with it .

In particular, DSC measurements were employed to investigate peroxide formation and decomposition during the oxidative curing process, while isothermal TGA experiments performed at 80 °C, according to approaches widely adopted for drying oils, allowed the evaluation of both the degree of crosslinking and the oxidation state of the material throughout curing and ageing.

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# Valorization of fish processing waste: development of new bioadhesives

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Marine fishing activities represent a fundamental source of food and nutrients, livelihoods, culture, and well-being for billions of people worldwide.

Indeed, it is well known that seafood products provide numerous health benefits, due to their high content of high-quality proteins, omega-3 fatty acids, vitamins, and essential minerals. For this reason, they are also considered a valuable source to produce effective animal-derived medicinal products [1].

However, fish processing generates a significant amount of waste, estimated at 20 million tons per year. This waste can be reused in the form of fish meal for aquaculture feed, fertilizers, and low-value fish oil [1,2]. Nevertheless, their high moisture content makes handling difficult and promotes microbial contamination. For this reason, most of this waste is usually discharged into the sea and/or disposed of in landfills, posing relevant environmental concerns. Therefore, it is essential to identify alternative ways to reuse this type of waste, which represents a highly promising source of higher value-added products.

In fact, studies reported in the literature show that marine proteins extracted from skin, fins, and scales can be used in food, nutraceutical, cosmetic, and pharmaceutical applications. However, for such purposes, the extracted protein fraction must be highly pure, and this represents a major challenge in the development of a sustainable extraction process for commercial exploitation [1]. The lipid fraction extracted from heads and viscera contains polyunsaturated fatty acids and other fat-soluble vitamins, that are exploitable to produce omega-3 capsules for the pharmaceutical industry. However, when the extracted oil does not meet the required specifications, it can be used for biodiesel production [3].

In this context, the adhesive sector represents a promising alternative to achieve a more industrially accessible valorization route while still providing a higher added value than biodiesel.

The present project fits within this framework and is part of the broader “ONE EARTH” European project, carried out in collaboration with Bolton Food Company. The objective concerns the synthesis of new wood adhesives and pressure-sensitive adhesives (PSAs) from the protein and lipid fractions of tuna waste, respectively. The production of these bio-based adhesives is under investigation, developing the polymerization of the protein and lipid fractions extracted from fish waste, and testing different types of catalysts/cross-linkers to obtain adhesives with commercially applicable properties. Indeed, adhesive performances will be carried out at the Bolton Adhesives facilities.

In conclusion, this study represents an important future challenge: the valorization of a common, abundant, and underutilized waste material.

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# Waste-derived amides for reversible $CO_2$ capture

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Plastic waste accumulation is a critical environmental challenge all over the world. At the same time, the greenhouse effect caused by excessive carbon dioxide emissions is becoming increasingly prominent. Condensation polymers, as polyethylene terephthalate (PET) and polyamide 6,6 (or nylon 66, PA66), widely employed for beverage bottles, textile fibers and food packaging, constitutes a major fraction of post consumer plastic waste. Conventional mechanical recycling is often limited by polymer degradation and quality loss [1], whereas most chemical recycling efforts focus on depolymerization to monomers [2] without generating new functional materials. In parallel, liquid $CO_2$ sorbents - especially those based on aqueous amines - suffer from high regeneration energy penalties, corrosivity, and degradation issues [3]. As a result, chemical upcycling through depolymerization offers an alternative, sustainable approach to transform waste polymers into high value-added products, such as the $CO_2$ sorbent.

Rossi et al. combined amides derived from the chemical recycling of PET plastic waste with propylene glycol to form a low transition temperature mixture (LTTM), which exhibits good reversible $CO_2$ absorption performance [4]. Based on the proof of concept, we synthesized n-(2-aminoethyl)acetamide using excess ethylenediamine and ethyl acetate. When mixed with ethylene glycol in a specific ratio, the resulting system exhibited highly efficient carbon dioxide absorption and desorption capabilities. This process boasts high feedstock utilization, mild reaction conditions, low pollution, and the ethylenediamine can be recovered.

Similarly, this research method can be applied to the depolymerization monomers of nylon 66 waste. The two expected derivative amide structures are shown in Figure 1. The liquid homogenized with the diol is also expected to serve as a $CO_2$ absorbent and maintain its absorption performance in multiple absorption-desorption cycles.

This work demonstrates that diamine and ester, or the monomers depolymerized from plastic wastes, can be converted into an efficient, stable and reversible liquid $CO_2$ sorbent, contributing to both waste valorisation and circular economy target.

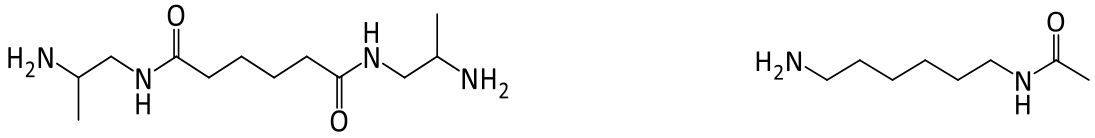

**Figure 1**. Expected derivative amide structures from nylon 66 monomers

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# Beyond fading: molecular insights into the photodegradation of azo and hydrazone pigments on cellulose-based materials

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The preservation of coloured paper-based heritage materials remains a major challenge in conservation science, as cellulose supports are intrinsically unstable and the interactions between colourants and paper during ageing are still poorly understood. Among synthetic organic colourants, azo dyes and hydrazone pigments represent some of the most widely used yellow, orange, and red dyes in both historical and modern applications, yet their light-induced degradation in solid matrices has been only rarely investigated [1]-[2].

In this work, Metanil Yellow (AY36), Orange II (AO7), and Amido Naphthol Red G (AR1) were selected as model compounds to investigate the degradation behaviour of diphenylamine, β-naphthol, and substituted β-naphthol azo dyes in paper-based systems [3]. Early synthetic dye (ESD) paper mock-ups were artificially aged and analysed through an integrated analytical approach combining colourimetry with high-performance liquid chromatography coupled to high-resolution mass spectrometry (HPLC–HRMS). Our combined analytical protocol ensures the correlation of colour variations with the molecular transformations occurring during ageing, by revealing browning for AY36, and fading for AO7 and AR1.

HRMS analyses allowed the identification of fifteen previously unreported degradation markers, revealing novel photodegradation pathways including azo bond cleavage, N-oxidation, N-dearylation, β-naphthol oxidation, phenylation, and formaldehyde addition to amino substituents. The detection of several of these degradation products in a microsample of a viscose red thread collected from an early 20th-century stage costume further validated the reliability of the developed solid-state experimental model on a cellulose matrix, similar to the paper support used in the mock-ups.

These findings provide new insights into the degradation chemistry of azo dyes on paper supports, offering valuable perspectives not only for the conservation of modern and contemporary heritage materials, but also for understanding degradation processes relevant to industrial dye applications, including wastewater treatment and quality control in food and beverages, as well as the textile, paper, and printing industries

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# Development of HA-BDDE Hydrogels and Synthesis of a Novel pH-Responsive Derivative for Smart Biomaterials

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## Introduction

Hyaluronic acid (HA) is a naturally occurring polysaccharide widely employed in the biomedical field due to its excellent biocompatibility, biodegradability, and tunable viscoelastic properties. Crosslinked HA hydrogels are currently being investigated for several applications, including regenerative medicine, wound healing, and drug delivery. Among the available crosslinking agents, 1,4-butanediol diglycidyl ether (BDDE) is commonly used to prepare stable HA-based hydrogel networks with controlled physicochemical and mechanical properties [1].
In recent years, increasing interest has been devoted to the development of “smart” biomaterials capable of responding to external stimuli associated with pathological conditions, such as pH variations occurring during inflammation and bacterial infections. In this context, chromogenic pH-responsive systems represent promising candidates for the design of multifunctional biomaterials with potential sensing capabilities.

## Results and Discussion

HA hydrogels were prepared via BDDE-mediated crosslinking under various operating conditions. The obtained HA-BDDE networks were characterised by NMR spectroscopy, allowing identification of characteristic signals associated with both the HA backbone and BDDE-derived crosslinks. Spectral analysis enabled the estimation of the degree of crosslinking, the degree of modification and the position of the linker across the different formulations [2].
In parallel, a novel pH-responsive derivative suitable for future incorporation into hydrogel matrices was synthesised, achieving isolated yields of 83% in the final step of the synthetic pathway.
Preliminary investigations demonstrated that the derivative retained its pH-responsive behaviour after chemical modification while exhibiting significantly altered chromatic properties compared with the parent compound.
Acid-base titrations and colourimetric observations revealed a transition range of pH 7.88–8.52 for the synthesised derivative, compared with pH 8.33–8.93 for the parent indicator.
These results demonstrate that the responsive behaviour of the chromogenic system can be preserved while tuning both its transition interval and visual output, features that are particularly attractive for sensing-oriented biomaterials.

## Conclusions

HA-BDDE hydrogels are emerging as a versatile platform for the development of next-generation smart responsive biomaterials. The successful synthesis of a novel pH-responsive derivative, retaining its stimulus-responsive behaviour while exhibiting modified chromatic properties and a shifted pH transition range, constitutes a significant step toward the development of multifunctional hydrogel-based systems. The forthcoming incorporation and evaluation of these functionalities under physiologically relevant conditions will be essential for validating the potential of these systems for biomedical applications.

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# Valorization of Sewage Sludge into Adsorbent Materials for Sustainable Wastewater Treatment

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Increasing concerns about water scarcity and environmental contamination are encouraging governments worldwide to introduce more stringent regulations on pollutant emissions and wastewater disposal. Consequently, technologies for sustainable water purification are attracting significant interest [1], and wastewater treatment plants generate substantial quantities of sewage sludge, a challenging residue rich in pathogens, heavy metals, and hazardous organic compounds that may negatively affect both human health and ecosystems [2]. In Italy, around 3.24 million tonnes of sewage sludge are produced annually. This waste is generally subjected to biological stabilization, dewatering, and drying treatments before being mainly incinerated for energy recovery [3]. Nevertheless, sewage sludge may represent a valuable secondary resource to produce activated carbons, suitable for removing contaminants from industrial effluents.

Within this framework, the SIRENA project, financed by the Tuscany Region, focuses on the recovery of sewage sludge generated by the municipal wastewater treatment plant of Cuoiodepur S.p.A. to prepare activated carbons for wastewater remediation, promoting a circular economy approach. Two sludge streams supplied by Cuoiodepur S.p.A. were selected as raw materials: one derived from the treatment of tannery wastewater and another collected downstream of the MBR (Membrane BioReactor) unit dedicated to civil wastewater treatment. Initially, both sludges were pyrolyzed under $N_2$ atmosphere at 400, 500, and 600 °C to investigate the influence of temperature on carbonization and the textural properties of the resulting biochars. The produced materials were analyzed by FT-IR spectroscopy, elemental analysis, and $N_2$ physisorption measurements. The results confirmed progressive carbonization during pyrolysis, although the obtained biochars still exhibited relatively low surface areas, leading to limited COD removal efficiency in the municipal wastewater treated by Cuoiodepur S.p.A. Activation treatment using $CO_2$ was subsequently explored at 800 °C, and the obtained biochar was analogously characterised and tested. Overall, this study demonstrates the potential conversion of sewage sludge into adsorbent materials that can be reused within the same industrial water treatment plant, supporting a more sustainable and circular management of waste resources.

**Acknowledgment:** The SIRENA project is funded by PROGRAMMA REGIONALE TOSCANA PR FESR 2021-2027 OP1 OS1 Azione 1.6.2 ”Ricerca e sviluppo per le imprese anche in raggruppamento con organismi di ricerca” Bando n.2 “Progetti di ricerca e sviluppo per le MPMI e Midcap”

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# Isohexide driven asymmetric activation of *tropos* biphenolic moieties by intramolecular hydrogen bonds: a combined computational-experimental approach

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The asymmetric activation [1] of flexible 2,2′-dihydroxybiphenol through the establishment of non-covalent interactions [2,3] represents one of the most recent frontiers in asymmetric synthesis.

In this work, isomannide and isosorbide were functionalized as monocarbamates [4] then linked to the *tropos* tetraphenolic unit, by EDC-DMAP mediated coupling [5]. The ability to induce a preferential torsional bias in the biphenolic core through the formation of intramolecular hydrogen bonds was investigated using a combined computational-experimental approach.

A preliminary conformational analysis was carried out on compounds **4-6,** using Conformer-Rotamer Ensamble Sampling Tool (CREST) [6], which enabled the identification of the conformations characterized by intramolecular hydrogen-bonding interactions. Moreover, this kind of approach allowed us to predict if the intramolecular hydrogen-bond formation is influenced by the *endo/exo* stereochemistry of the carbamate moiety, also enabling the identification of the minimum-energy geometries and the computational estimation of the rotational barriers through DFT [7] calculations.

The MOM-protected compounds **4, 5, 6** were subsequently characterized by $^{1}$H NMR analysis, which confirmed the *tropos* nature of these compounds, and allowed us to identify the isomannide-derived carbamate as the most promising candidate; H/D exchange studies were also performed on these compounds.

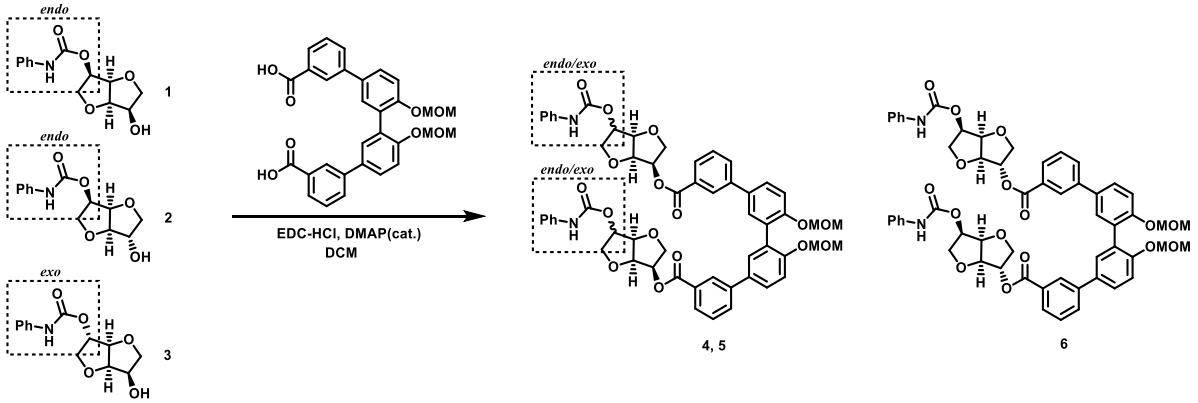


**Figure 1:** Functionalization of tetraphenolic *tropos* framework by isohexide-derived monocarbamates

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# Ligand-Mediated Biological Activity of Pd(II) Complexes: DNA Interaction and Cytotoxicity

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In recent years, palladium complexes have attracted attention as potential chemotherapeutic agents to overcome the limitations of platinum(II)-based anticancer drugs.[1] In this work, six square-planar Pd(II) complexes with the general formula $[PdAB_2]$ were synthesized, where ligand A consists of either (1R,2R)-diaminocyclohexane (DACH) or 1,10-phenanthroline (phen), while ligand B corresponds to chloride ($Cl^-$), iodide ($I^-$), or pyridine (py). All compounds were prepared following established methods[2,3] and characterized by elemental analysis and NMR spectroscopy. DNA interactions were investigated through CT-DNA melting temperature measurements and ethidium bromide displacement assays. DACH-containing complexes primarily exhibited covalent DNA binding, whereas phen-containing complexes act mainly through intercalation. Notably, compound **1** showed evidence of a dual binding mode. Cytotoxicity was assessed in ovarian cancer cell lines (A2780, A2780R, SKOV3) and in healthy human skeletal myoblasts (HSkM). Phen-based complexes demonstrated significant cytotoxic activity, with compound **3** also displaying promising selectivity. In contrast, DACH-based complexes were found to be inactive.

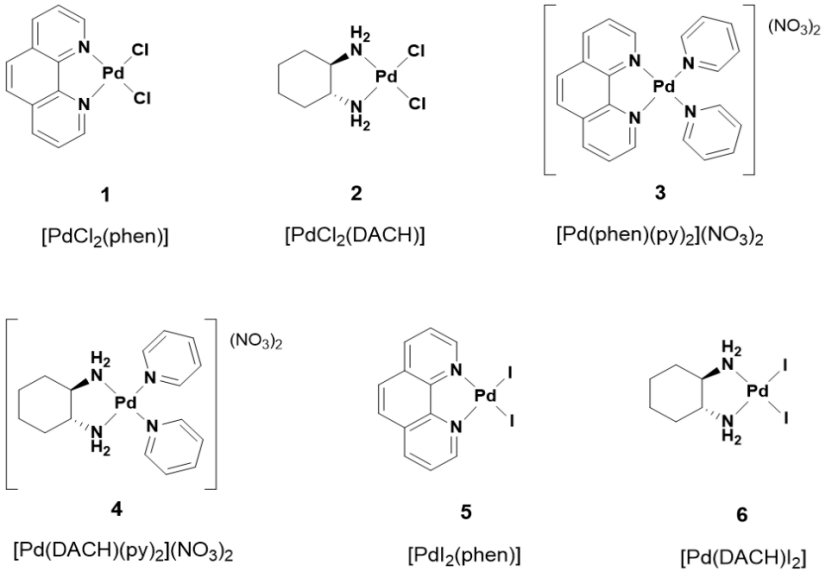


**Figure 1.** Molecular structures of the investigated Pd(II) complexes.

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# Towards Personalized Medicine with SGLT1/2 Inhibitors: Development of [$^{11}$C]Sotagliflozin

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The sodium-glucose cotransporters, SGLT1 and SGLT2, are membrane proteins primarily responsible for glucose reabsorption in the proximal tubules of the kidney. SGLT2 is a low-affinity, high-capacity transporter that reabsorbs about 90% of filtered glucose, while SGLT1, with higher affinity but lower capacity, handles the remaining 10%. These transporters are essential for maintaining glucose homeostasis. Consequently, SGLT inhibitors (SGLTis) have emerged as a therapeutic option in individuals with diabetes by preventing glucose reabsorption and promoting its excretion in the kidneys [1]. Among them, gliflozins have recently received approval for the management of type 2 diabetes (TD2). In addition, they exhibit significant cardiorenal protective effects in both diabetic and nondiabetic patients [2].
Sotagliflozin is unique among clinically used gliflozins, since it exerts dual inhibition of SGLT1 and SGLT2 and is the first FDA-approved gliflozin for the treatment of the entire spectrum of heart failure (HF) [3]. Although SGLT1 upregulation has been linked to cardiomyopathy through enhanced reactive oxygen species (ROS) generation, contributing to ventricular hypertrophy and dysfunction, nonselective inhibition may play a crucial role in improving HF outcomes. However, the mechanisms underlying sotagliflozin's benefits in HF remain poorly understood [4]. This knowledge gap highlights the need for further investigation to elucidate its actions and to identify the patient subgroups most likely to benefit, supporting a personalized medicine approach. In this respect, in the present study, a novel radiolabeled positron emission tomography (PET) tracer, [$^{11}$C]sotagliflozin, was developed, and its biodistribution and metabolite analysis were assessed.

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# Toward Dynamically Correlated Multireference Methods: An AC0-CASSCF Implementation

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Strong static correlation effects play a central role in the accurate description of molecular systems featuring near-degenerate electronic configurations, bond breaking processes, and electronically excited states. The Complete Active Space Self-Consistent Field (CASSCF) method provides a robust framework for treating static correlation, but lacks an adequate description of dynamic correlation effects, which are essential for quantitative predictions.

In this contribution, we present a preliminary implementation of the Adiabatic Connection Zero (AC0) correction [1] combined with CASSCF wavefunctions within the CFOUR quantum chemistry package. [2] Compared to widely used multireference perturbative approaches, such as CASPT2 and NEVPT2, AC-based methods provide an alternative framework for recovering dynamic-correlation effects from multireference wavefunctions while retaining favorable formal properties at a comparatively lower computational cost. The current implementation focuses on ground-state calculations and constitutes the first step toward a broader multireference response framework.

Particular attention has been devoted to the integration of the method within the existing CFOUR infrastructure and to the evaluation of computational bottlenecks affecting the present implementation. Preliminary tests on representative multireference systems demonstrate the correct behavior of the implementation and highlight the potential of the approach for future developments involving excited states and polarizable embedding methodologies. [3]

Future work will address algorithm optimization, inclusion of point-group symmetry, analytic gradients, and the extension of the AC0 formalism to excited-states for applications to photochemical and biological systems.

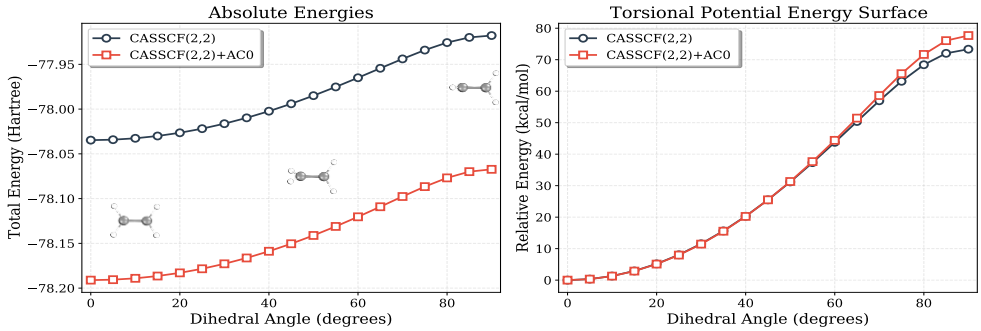


**Figure 1**. Torsional potential energy surface (PES) of ethylene along the H-C-C-H dihedral angle computed at the CASSCF(2,2)+AC0 level. On the left, absolute total energies are reported. On the right, relative energies in kcal/mol show an increased torsional barrier for the AC0-corrected PES due to dynamical correlation effects.

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# Application of Mechanochemical Synthesis and Functionalization of Oxadiazo[2.2.2]Octenes through oxidative nitroso Diels-Alder reaction and hetero-Cope Rearrangement

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A mechanochemical reaction is defined as: “a chemical reaction induced by the direct absorption of mechanical energy.” [1] To generate the required mechanical energy, the substrates are placed in jars of appropriate size and then they are loaded into an instrument called Ball Miller. Typically, spheres of suitable diameter are also placed in the jars to homogenize the system. The combined effect of high-energy collisions and friction promotes the reaction between reagents and additives, opening different regioselectivities, if compared to common batch reactions. In this context we present a synthetic protocol for the efficient mechanochemical synthesis of oxadiazo[2.2.2]octenes derivates *via* oxidative nitroso Diels-Alder (nDA) reaction. These substrates are a key intermediate for the synthesis of aza-sugars and GLP-1 receptor ligands for the treatment of diabete.[2] On the other hand, the [3+3] hetero-Cope rearrangement of these substrates provides functionalized dioxazines, a molecular scaffold included into complex molecules with pharmacological and crop activity.[3] In this work we had been able to obtain a considerable reduction of reaction time up to one minute, maintaining a good reaction outcome in terms of yield and regioselectivity of the nDA product, compared to Knaus and Streiths’ previous works in batch. [4,5] We investigated the effects of multiple parameters on both the reactions, including LAG and grinding auxiliaries’ effects, number of spheres, grinding time, frequency, stoichiometry of reagents and nature of oxidizing agent, in order to find the best optimized conditions and testing them on substate scope (Figure 1).

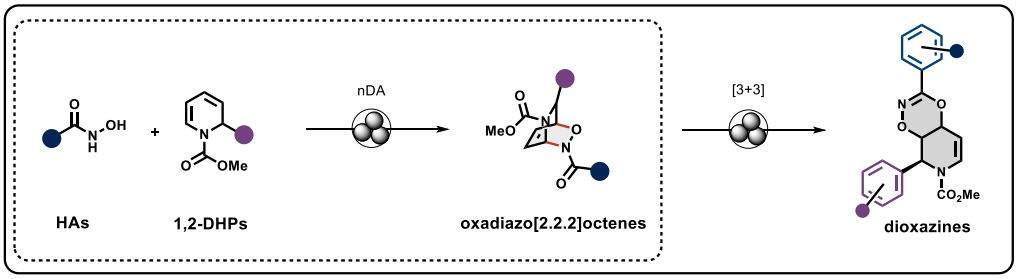


**Figure 1**. Sequential mechanochemical n-DA between hydroxamic acids (HAs) and 1,2-dihydropyridines (1,2-DHPs) and mechanochemical [3+3] hetero-Cope rearrangement.

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# Synthesis of Novel Hydroxamic Acid-Based Chelators as Potential Pharmaceuticals Agents

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Hydroxamic acids have attracted great interest in medicinal chemistry due to their ability to chelate a large variety of metal ions through their characteristic bidentate chelation mode, which varies with the nature of the target metal ion [1]. For example, hydroxamic acids can form complexes with metal ions present in the active site of metalloenzymes, resulting in inhibitory properties, as exemplified by the $Zn^{2+}$ chelator vorinostat (SAHA), an FDA-approved histone deacetylase (HDAC) inhibitor for the treatment of cutaneous T-cell lymphoma [2]. Another example is acetohydroxamic acid (AHA), a $Ni^{2+}$-chelating urease inhibitor approved for the treatment of chronic urinary tract infections [3]. Among all metal ions, hydroxamic acids display particularly high affinity for $Fe^{3+}$ and are therefore also employed to reduce iron overload in diseases such as thalassemia [4].

In this work, L-homoserine lactone (L-HSL), a natural amino acid-derived building block, was incorporated via peptide coupling. Ring-opening of the lactone with hydroxylamine as the final synthetic step afforded the target hydroxamic acid functionality (**Figure 1**). Notably, this lactone handle offers potential access to diverse chelator libraries through ring-opening with a variety of nucleophiles. By synthesizing different structural motifs, we aim to address the poor metal selectivity typical of hydroxamic acid-based chelating drugs [5]. A systematic Isothermal Titration Calorimetry (ITC) characterization of the compounds will allow a better understanding of the structure-affinity relationships through a metal ion selectivity screening and provide a rational basis for the design of new selective chelators.

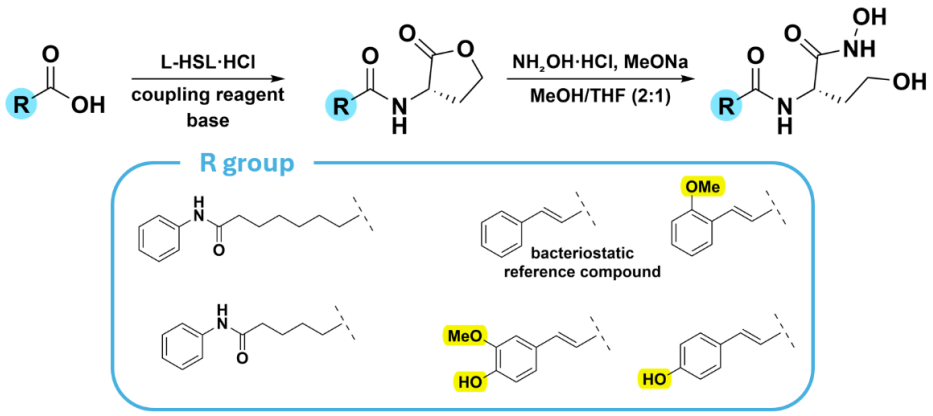


**Figure 1**. General synthetic scheme toward L-homoserine lactone-derived hydroxamic acids from diversified carboxylic acids (RCOOH). R groups include aniline-based aliphatic chains and cinnamoyl motifs inspired by natural phenylpropanoids.

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# Homogeneous TBAX/Boric Acid Catalyst for $CO_2$ Fixation into Styrene Carbonate: Medium Effects and Mechanistic Analysis

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The cycloaddition of $CO_2$ to epoxides is a useful model reaction for converting an abundant C1 feedstock into value-added cyclic carbonates [1]. In this contribution, styrene oxide (SO) was converted into styrene carbonate (SC) using homogeneous tetrabutylammonium halide/boric acid systems under solvent-free, SO-rich conditions. The work connects three levels of evidence: **physicochemical characterization of the reaction medium**, **reaction optimization** and **DFT-based mechanistic analyses**. DSC phase-behaviour studies, conductivity, viscosity and Walden analysis [2] showed that concentrated SO/TBAI/BA and SC/TBAI/BA mixtures are non-ideal associated liquids, where ion pairing, hydrogen bonding and phase boundaries influence the temperature/composition range where the mixture remains in the liquid state. In contrast, the investigated SO/TBACl/BA mixtures remained homogeneous for weeks at -25 °C, supporting their practical use as liquid catalytic media.

Catalytic screening identified TBACl/BA as the most effective practical system. Under excess $CO_2$, the optimized 13:1:0.3 SO:TBACl:BA composition gave **98.5% SC yield after 4 h at 100 °C**. Computational models with TBAX and BA indicate that the halide trend cannot be rationalized by considering only the intrinsic anion nucleophilicity: local solvation, ion pairing, BA-assisted activation and the stability/lability of ring-opened intermediates jointly determine the observed catalytic behaviour.

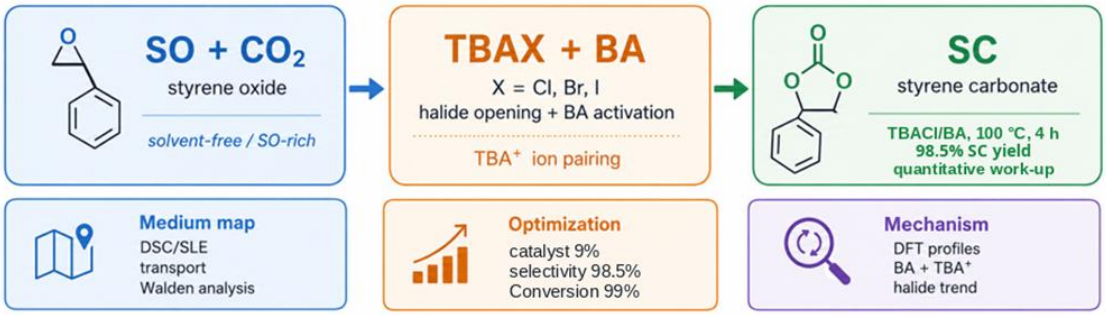


**Figure 1**. Graphical summary: TBAX/BA catalysis couples $CO_2$ fixation, reaction-medium physicochemistry, chloride-based optimization and molecular-level mechanistic interpretation.

Overall, the study shows that catalyst performance in concentrated TBAX/BA media is an emergent property of halide identity, boric-acid interactions and transport properties. TBAI/BA was the most informative benchmark for medium characterization, whereas TBACl/BA provided the best optimized catalytic performance.

**Keywords:** $CO_2$ fixation; cyclic carbonates; styrene oxide; tetrabutylammonium halides; boric acid; phase behaviour; Walden analysis; DFT.

**References:**

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# Development of an Automated Bottom-Up Proteomics Workflow and Its Application to Drug Resistance Profiling in B-cell Acute Lymphoblastic Leukemia

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Manual sample preparation is one of the most critical, laborious, and error-prone steps of a mass spectrometry-based bottom-up proteomics workflow. Automated liquid handling platforms enable high-throughput parallel processing with minimal operator intervention, while significantly reducing analytical variability. This study aims to develop and optimize an automated sample preparation workflow using an Agilent AssayMAP Bravo liquid handling platform. The optimized protocol was subsequently applied to explore the molecular mechanisms of drug resistance in B-cell acute lymphoblastic leukemia (B-ALL). To better reflect the high genetic heterogeneity of the disease, the study included four different B-ALL cell lines (HAL-01, REH, RS4;11, and KOPN8), and compared the protein content of the chemo-sensitive parental cells with clones made resistant to two chemotherapeutic agents (Doxorubicin and Vincristine). For statistical power 5 biological replicates were prepared for each cell line/condition, resulting in 60 individual samples (a number legitimately cumbersome if manually processed).

We automated the reduction, alkylation, enzymatic digestion, peptide desalting, and fractionation steps, before peptide injection on a nano-LC-MS/MS system. The automated workflow demonstrated high reproducibility and robustness, yielding average coefficient of variation (CV) values below 3%. Nano-LC-MS/MS analysis of B-ALL samples identified 9408 protein groups from a pooled sample, and which was used to build a mass spectral library. An average of 8630 protein groups were quantified from the 60 individual samples. Comparative proteomics profiling revealed significant differential expression of proteins in the resistant variants compared to their sensitive counterparts, with distinct proteomic signatures associated with Doxorubicin and Vincristine resistance across the diverse B-ALL models.

This automated high-throughput protocol provided a powerful analytical strategy for large-scale proteomics studies, reducing sample processing time while improving reproducibility, and thereby enhancing data quality. The deep biological insights provided by high-throughput, in-depth proteomics can help guide the design of novel targeted therapies, in this example to overcome drug resistance in B-ALL. Nevertheless, the platform is equally applicable to all proteomics investigations.

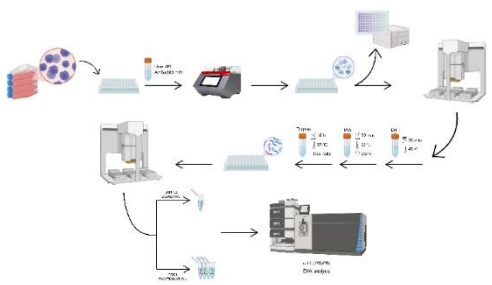

**Figure 1**. Summary of the automated bottom-up proteomics workflow

# Selective dissolution of polyolefins from complex waste

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In 2017, only 42% of plastic packaging waste was recycled in the EU, with the rest sent to energy recovery or landfilled. Particularly troublesome are multilayer flexible plastics (MFPs), composite materials made of multiple plastic layers widely employed – especially in the food industry – as they combine key properties of different polymers. However, this very heterogeneity makes them hard to recycle.[1]

In this study, a full recycling process applied to real plastic waste provided by COREPLA (Consorzio nazionale per la raccolta, il riciclo e il recupero degli imballaggi in plastica) is described. The first step is a delamination carried out in formic acid (85 °C, 4 h) to dissolve polyurethane adhesives, polyamides and dyes, while the second is a density-based separation between PET and vinyl polymers (PE, PP and extruded PS) in water. An additional alkaline hydrolysis reaction can be carried out on the polyolefinic fraction to get rid of possible PET residues. This study then focuses on the recovery of distinct polyolefinic fractions by means of a bio-based solvent able to selectively dissolve polyolefins at different temperatures: *p*-cymene solubilizes LDPE at 95 °C and PP at 120 °C at a concentration of 40 mg/mL.[2] Moreover, PS dissolves readily in *p*-cymene at room temperature, enabling an easy recovery of all three. The main challenge is to also efficiently recover an HDPE fraction, whose dissolution temperature is close to that of PP. Alternatively, other solvents are analysed, namely fatty acids and their ethyl esters, which are obtained by stoichiometric or substoichiometric saponification of waste cooking oil by using an ethanol solution of KOH at room temperature. Partially chlorinated fatty acid methyl esters manufactured by Altair Chemical, commercially available as PVC plasticizers under the name of Essebiochlor, are also investigated as solvents.

**Acknowledgements:** The authors gratefully acknowledge COREPLA (Consorzio nazionale per la raccolta, il riciclo e il recupero degli imballaggi in plastica) for providing the waste starting material and financial support.

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# Engineering the optical properties of lanthanide-doped halide nanocrystals

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The development of advanced inorganic materials with tunable optical properties has attracted considerable interest due to their potential applications in optoelectronics, sensing, and energy-related technologies [1,2]. In this work, we study the synthesis and optical properties of lanthanide-doped inorganic nanocrystals prepared by a hot colloidal injection method. Particular attention is paid to understanding the effect of lanthanide incorporation on the photoluminescent behavior of the host crystal lattice. Structural characterization techniques were employed to evaluate the crystallinity and morphology of the obtained materials, while optical spectroscopy was used to study their absorption and photoluminescence properties. The results reveal a strong relationship between the material structure and its emission behavior, highlighting the role of compositional modification in tuning the optical response. These results provide insight into the mechanisms governing the optical performance of these materials and demonstrate their potential for future applications in photonic and energy conversion technologies. The approach presented contributes to the development of efficient inorganic chromophores with controllable properties.

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# Rosemary and Eucalyptus Biomass Valorization through Mild Bleaching and Incorporation as Fillers in PCL-based Biodegradable Composite for Agricultural Applications

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It is estimated that global plastic production reached 8.3 trillion kilograms by 2017. Of the 6.3 × $10^9$ kg of plastic waste generated up to 2015, only 9% was recycled, while 12% was incinerated and 79% accumulated in the environment, representing a major environmental challenge [1].

This study aims to develop bio-based composite materials from biodegradable polymers and lignocellulosic biomass residues. Polycaprolactone (PCL) was selected as the matrix because of its high biodegradability and broad applicability, despite its petroleum-derived origin [2]. Rosemary and eucalyptus residues from essential oil extraction were valorized as reinforcing fillers after mild bleaching through a novel, mild sodium-percarbonate-based process, in which hydrogen peroxide is generated in situ. The treated fibers were incorporated into PCL at 20, 40, and 60 wt%, yielding a series of composites (Figure 1). Their structural and thermal properties were investigated by Fourier-transform infrared spectroscopy (FT-IR), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA), while micro-computed tomography (μ-CT) was used to evaluate fiber dispersion within the polymer films. Tensile and biodegradation tests were performed to assess the influence of biomass on mechanical performance and environmental degradation.

The obtained materials are being evaluated for agricultural applications, including white biodegradable mulch films and pot covers, where they may reduce weed growth and thermal stress while limiting the use of conventional non-biodegradable plastics.

**Figure 1**. Images of the prepared composites: from left to right, neat PCL, 20%, 40% and 60 wt% rosemary fibers.

**Acknowledgements**:
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# Valorization of tanned waste from leather industry

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Leather, traditionally produced from animal hides, is one of the earliest materials used by humans. Nowadays, its manufacturing process raises significant concerns, particularly regarding the management of the large amounts of solid waste generated,[1] e.g. leather scarps wastes. These are rich in valuable compounds such as collagen, a fibrillar structural protein, and in some cases also tannins, plant-derived polyphenolic compounds used in the tanning process to convert raw hides into durable leather.[2,3] In this study, we propose a sustainable strategy for valorizing leather industry waste through the production of collagen-based bio-adhesives and the recovery of tannins, starting from vegetable-tannin leather scarps from sturgeon.[4] One of the aims was to assess the effectiveness of the protocol previously optimized for tanned leather scarps from bovine source. The scraps were treated under mild conditions (1 h, 60 °C) using a Natural Deep Eutectic Solvent (NADES) composed of lactic acid and urea in a 2:1 molar ratio. The resulting bio-adhesives exhibited interesting binding performance and were characterized using Fourier Transform Infrared Spectroscopy with Attenuated Total Reflectance (ATR-FTIR) and Thermogravimetric Analysis (TGA). Significant differences compared to bovine leather were observed in both composition and macromolecular organization of hydrolyzed collagen.[5] Vegetable tannins were recovered through antisolvent extraction using pure ethanol, followed by consecutive centrifugation steps (10,000 rpm, 10 min, 40 °C). The obtained powder was analyzed using ATR-FTIR, TGA, and Ultraviolet–Visible spectroscopy (UV–Vis). The preliminary results confirm the presence of mimosa and quebracho tannins. Overall, this study demonstrates the feasibility of transforming leather waste into high-value products through an environmentally friendly process, with a particular focus on processing marine fish waste.

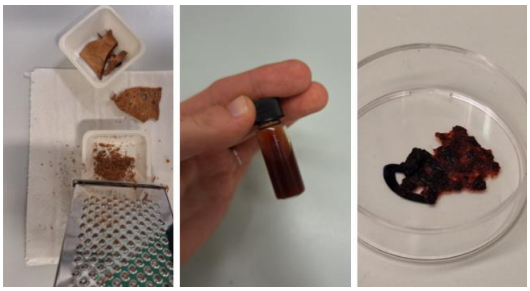

**Figure 1**. Sturgeon leather waste valorization: from tanned material to collagen-based adhesives.

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# Circularly polarized lasing cavities using cellulose nanocrystal as polarization-selective reflectors

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Optical cavities are devices designed to confine and amplify light through multiple reflections between two mirrors, and represent a key component in laser technology. Cavities capable of emitting circularly polarized light (CPL) are particularly attractive for applications in photonics, displays, and optical sensing. However, their realization remains challenging because the handedness of circularly polarized light reverses after each reflection [1].

Cellulose nanocrystals (CNCs) are rod-like nanoparticles produced through acid hydrolysis of cellulose. As renewable, biocompatible, and low-cost materials, they have attracted significant interest in materials science and biomedical applications [2]. In aqueous suspension, CNCs spontaneously self-assemble into a chiral nematic phase, forming left-handed helical structures that are typically preserved after solvent evaporation [3]. The resulting films preferentially reflect left-handed CPL at tunable wavelengths, which can be adjusted through the drying conditions. Owing to this unique optical behavior, self-standing CNC films are promising candidates as polarizing elements [4], which we propose to employ in the fabrication of CPL laser cavities.

To achieve this, a thin layer of a suitable emissive organic dye is embedded between two CNC reflective films. The assembly conditions were optimized to maximize the chiroptical response and tune the reflection wavelength to overlap with the dye emission. This approach represents a promising route towards sustainable and highly tunable CPL laser cavities based on renewable and low-cost materials.

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# Nanocomposite elastomeric film for long-lasting total uv shielding in xeroderma pigmentosum patients

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Xeroderma pigmentosum (XP) is a rare autosomal recessive genetic disorder characterized by UV hypersensitivity leading to severe skin damage and dramatically increased risk of early-onset skin cancers [1]. No effective therapy has yet been devised for XP patients, and prevention by total sunlight avoidance and/or total protection of skin, eyes, lips are the only tools available to prolong life expectancy of XP patients. The most effective sun creams show a UV-blocking action that lasts for a short period of time (1-2 hours) and can be weakened by sweat and water [2]. Therefore, XP patients are forced to wear outdoor bulky protective gear, affecting their quality of life and social interactions. To reduce the burden on XP patients and improve their daily lives, we have developed an “artificial skin” (SUN-film, Figure 1) based on new formulations for skin application, capable of generating in situ a nanocomposite elastomeric film, shielding UV-light. The elastomeric films were prepared via platinum-catalyzed hydrosilylation between a vinyl-terminated polydimethylsiloxane and a hydride-functional siloxane crosslinker. To achieve broad-spectrum UV protection, the silicone matrix was functionalized with a combination of inorganic nanoparticles and molecular UV absorbers, enabling both scattering and absorption mechanisms. The type and dispersion of the UV-filters as well as crosslinking time, mechanical properties and water vapour permeability were carefully optimized to balance optical performance and mechanical integrity as well as breathability. The obtained films (30-40 μm in thickness) were proven to show excellent UV-blocking properties, with less than 0.02% transmittance in the total UV spectrum. Moreover, they were translucent, elastic to safely adhere to the skin and easily peelable, but not tacky. Differently, from the commercial sun creams, the UV-protection efficacy of such artificial skin was waterproof and durable after prolonged contact with water.

**Figure 1.** SUN-film applied on human skin, showing waterproof behavior in when exposed to water.

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# Undoped and Sn-doped $In_2O_3$ Nanocrystals: a versatile platform for infrared plasmonic applications

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Doped metal oxide (MO) nanocrystals (NCs), such as Sn-doped indium oxide (ITO), have emerged as a highly versatile platform for infrared plasmonics.[1] They exhibit broadly tunable optoelectronic properties very useful for advanced applications such as photocatalysis,[2] light-driven energy storage,[3] redox sensing,[4] and surface-enhanced infrared spectroscopy.[1] A key advantage of these materials is their tunable free-carrier density, which supports localized surface plasmon resonances (LSPR) spanning a wide spectral range from approximately 1.5 to 10 μm.[5] Carrier density can be controlled during synthesis by adjusting the amount of aliovalent dopant introduced or by tailoring its spatial distribution (core@shell systems). Furthermore, the plasmonic response can be dynamically modulated via post-synthetic approaches, such as photo- or electrochemical-doping.[6] In this study, we synthesized multiple batches of ITO NCs, systematically varying their sizes, overall doping levels, and dopant spatial segregation. Finally, to correlate the Sn dopant content with the free electrons introduced into the semiconductor lattice, and to study the effects of photo- and electrochemical modulations, we extracted the fundamental charge carrier parameters – carrier density and mass - by applying a fitting model based on the Mie and Drude theories to the experimental optical and magneto-optical data.[7] The results achieved are expected to significantly improve the understanding of doping mechanism and LSPR tunability in conductive oxides, prompting advancement in their application in optoelectronics and tunable plasmonics.

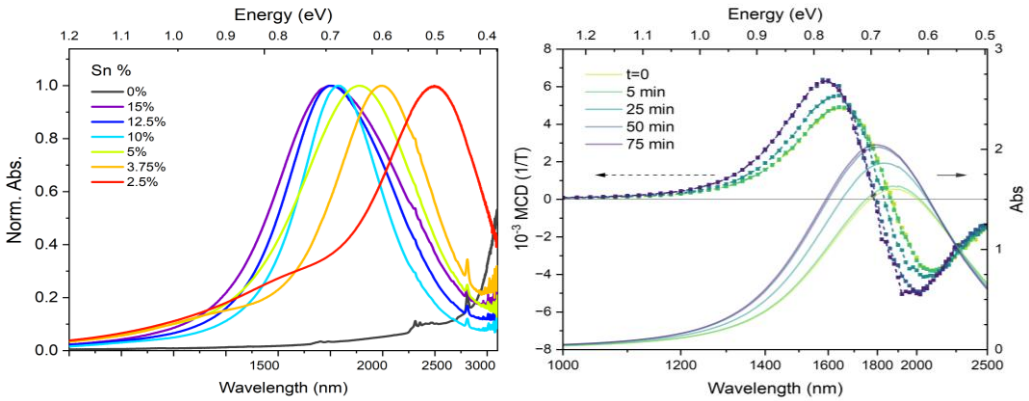


**Figure 1**. Optical response of ITO NCs with different amount of Sn (left), and effect of UV-irradiation time on the optical response (absorption and MCD) of ITO-10 (right).

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# PTP-Based Anion Exchange Membranes: Structure–Transport Relationships Tuned by Co-Monomer Design

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Anion exchange membranes (AEMs) are attracting increasing attention as enabling materials for sustainable energy technologies, including anion exchange membranes water electrolysis (AEM-WE) and fuel cells (AEM-FC) (Figure1a). Compared to other technologies, these devices do not require costly noble-metal-based systems which ultimately results in a reduction of the overall device costs [1]. Despite these advantages, their widespread implementation remains limited by relatively low hydroxide conductivity and insufficient chemical stability under strongly alkaline conditions. In recent years, ether-free aromatic polymers bearing piperidinium groups have emerged as promising candidates due to their enhanced alkaline stability and favorable ion transport properties. Among these, poly(terphenyl piperidinium) (PTP) (Figure1b) stands out as a robust platform for next-generation AEMs [2].

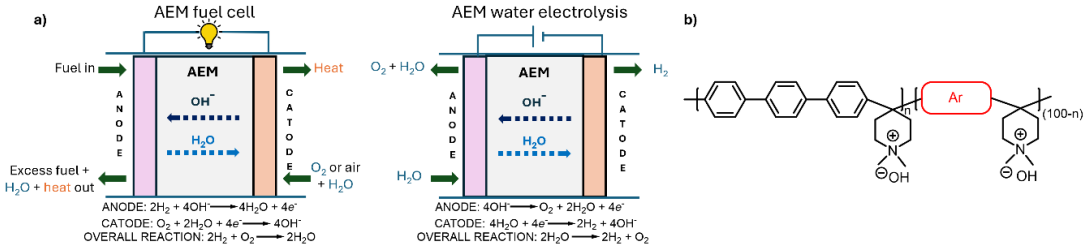


**Figure 1**. a) Schematic of AEM-WE and AEM-FC. b) Structure of poly(co-monomer methylpiperidinium).

In this work, we report the development of new PTP-based AEMs modified through the incorporation of selected co-monomers designed to induce steric and conformational effects [3]. The aim is to investigate how the chemical structure of the co-monomers influences the organization and connectivity of ionic domains. The introduction of appropriately designed units is expected to induce a more open polymer architecture, promoting the formation and connectivity of ion-conducting pathways while preserving the chemical robustness of the PTP backbone. The resulting materials are systematically characterized in terms of water uptake, ion exchange capacity, mechanical properties, alkaline stability, and ionic conductivity. This study provides new insights into structure–property relationships in PTP-based AEMs, highlighting the role of structural design in optimizing ion transport.

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# Application of Laser-Induced Graphene (LIG) as electrode material in Organic Electrosynthesis

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Over the past years, Organic Electrochemistry (OE) has been viewing a significant expansion in the field of synthesis. Avoidance of strong oxidants and reductants, relatively mild conditions, good functional groups tolerance and low waste production all stand out as attractive advantages of this technique for synthetic purposes [1,2]. The vast number of reaction variables, such as the choice of electrolyte, solvent, catalyst, current or potential, allows a modular optimization by changing selectively one of each. Amongst these parameters, the choice of *electrode material* plays a central role since the electron transfer occurs at its surface; in OE, *carbon electrodes* are usually preferred over noble metal material due to their lower cost and environmental impacts well as easier availability [3]. In this context, we present the first application of Laser-Induced Graphene (LIG), produced from Kapton® polyimide, as electrode material in organic electrosynthesis. LIG has already found applications in many fields, such as electrochemical sensing, energy storage and water splitting [4-6], but never in organic synthesis. In this work, we successfully tested different electrochemical protocols with LIG as electrode material instead of other commonly used carbon electrodes. LIG proved to be suitable in both constant and alternating current conditions, leading to comparable or better yields than the ones reported in literature. The resistance of Kapton® to a broad variety of organic solvents and the easy scalability of the production of LIG make it a promising material for applications in OE, with elevated degree of recyclability.

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# Optimization of a fast, low-cost, selective and eco-friendly synthetic route for the synthesis of new diarylmethane-based molecules

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In 2016 we reported a first series of diarylmethane-based compounds [1], among which **SG2** showed prominent *in vitro* and *in vivo* biological effects [2], [3]. The promising results provided by **SG2** led us to expand the library of diarylmethane derivatives to explore the chemical space of these compounds. With the aim of increasing the efficiency of the process, we firstly identified the rate-limiting step of the synthetic route, namely the Suzuki-Miyaura cross-coupling reaction, and we performed a study to achieve its optimization. Subsequently, we decided to specifically functionalize the two basic nitrogens of **SG2**, singularly or together. To do so, we re-design the synthetic route, replacing the classic *O*-alkylation reaction with a Mitsunobu reaction. This change allowed us to selectively obtain three intermediates that perfectly fit with our purpose (**Figure 1**). The detailed protocols and parameters used throughout this work will be presented in this poster presentation.

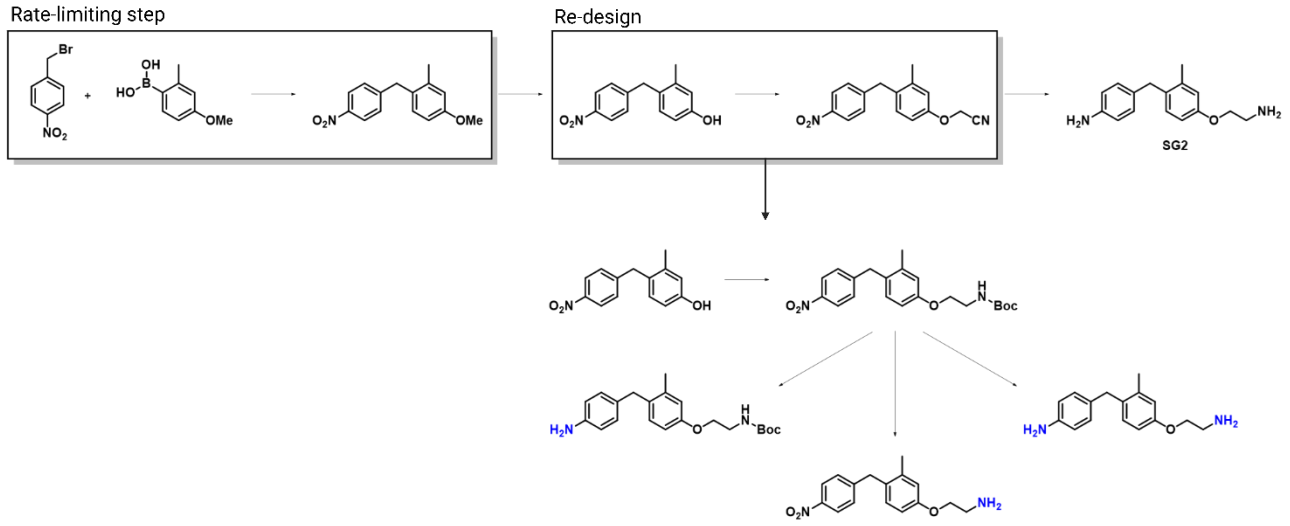


**Figure 1**. Optimization of the synthetic route for diarylmethane derivatives

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# FLEXIZYME: Purification of enzymatically-produced fatty amines by a new sustainable purification protocol

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Fatty amines (FAs) are valuable compounds widely used for the manufacturing of cosmetics, detergents, coatings, and agricultural formulations. Their industrial production still relies mainly on fossil-based chemical routes, which are anyway energy-intensive and poorly sustainable. To solve these bottlenecks, the FLEXIZYME project [1] aims to develop sustainable and cost-competitive biotechnological routes for the conversion of fat- and protein-rich industrial side streams into bio-based fatty amines through enzymatic engineering and biocatalysis, promoting bio-circularity and industrial by-product valorization. Within the project, fatty amine ($C_{12}$–$C_{18}$) production is of prevailing interest, involving a biocatalytic cascade approach with carboxylic acid reductase (CAR) and transaminase (TA), hopefully developing an efficient one-pot cascade process. Isolation of fatty amines from the reaction mixture is a difficult issue. To support the development of efficient downstream purification protocol, model reaction mixtures containing fatty acid, fatty aldehyde (intermediate), and fatty amine (product) were designed, assuming an overall acid-to-amine conversion of 80%, which represents the target value according to the scope of the FLEXIZYME project. Selective purification of the fatty amine was first investigated through direct crystallization of $C_{14}$ amine in ethanol/water/DMSO, corresponding to the solvent medium used in preliminary biocatalytic experiments. However, limited crystallization efficiency was observed, achieving the maximum amine purity of 44 % and a yield of 22 wt%.

To overcome these limitations, reactive crystallization involving the (reversible) conversion of fatty amines into ammonium carbamates, upon reaction with $CO_2$, was studied, and optimization is in progress [2]. Remarkably, the resulting carbamates selectively crystallized, enabling corresponding separation from aldehyde(s) and carboxylic acid(s). To date, this approach has been successfully applied to $C_{12}$ and $C_{14}$ model systems, enabling good recovery of the fatty amine(s) (about 80 %) and maximum purity of about 86%.

Current efforts are focused on improving the sustainability of the purification strategy, focusing on the use of green solvents, guaranteeing excellent crystallization performances. Independent evaluations will be carried out on binary mixtures of the involved components, to evaluate the feasibility of the mid-stream approach (e.g., as the intermediate purification of the aldehyde(s)-carboxylic acid(s) system).

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**Acknowledgments**

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# Plasmonic Indium Tin Oxide Nano Crystals for IR-Thermal Imaging Cameras

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Indium Tin Oxide (ITO) is a transparent conductor that, in the form of nanocrystals (NCs), exhibits localized surface plasmon resonance (LSPR) in the infrared region (IR). Its plasmonic and electrical conductivity make ITO nanocrystals (NCs) attractive for optoelectronics and IR plasmonic. Efficient thermoplasmonic effects, i.e. generation of heat upon IR irradiation, were demonstrated in ITO NCs deposits.[1] In this study, we investigate the feasibility of fabricating multi-wavelength thermal camera sensors based on pixels composed of ITO NCs with variable IR absorption, exploting their wavelength-dependent thermoplasmonic response. Aliovalent doping with Sn introduces charge carries, resulting in an LSPR response that is tunable with the Sn content. Specifically, at constant NC size, lower Sn content results in increased LSPR wavelength. Monodisperse ITO NCs with a diameter of approximately 10 nm and different Sn contents were synthesized. A bottom-up synthetic method based on the thermal decomposition of organometallic precursors was employed. In and Sn oleates and oleic acid were continuously injected at a constant and controlled rate into hot (290°C) oleyl alcohol.[2] The IR absorption spectra (Fig.1) confirm the LSPR wavelength tunability with the Sn content, ranging from 1900 nm (ITO with 10% Sn, ITO-10) to 3100 nm (2,5% Sn-doped, ITO-2.5). Thin films of NPs were prepared through spin coating on appropriate substrates and conductivity measurements were performed on the films. Oleate ligands could be removed with ligand exchange procedures to reduce inter-particle distance in the film and investigate its effect on the formation of percolative paths. Conductivity was measured with and without IR irradiation to assess the resistance variation induced by the thermoplasmonic effect and thus the applicability as IR detector. This study aims to exploit the conductivity variation of ITO associated with photo-thermal effect due to LSPR excitation and to translate exposure to different NIR wavelengths into a variation of conductivity that can be interpreted by a device such as a thermal imaging camera. Using this type of NC-based pixel would enable a system sensitive to multiple wavelengths, offering greater application flexibility and more efficient calibration. To this purpose future studies will be dedicated to deposit via injekt printing pixels containing ITO NCs with variable LSPR wavelength.

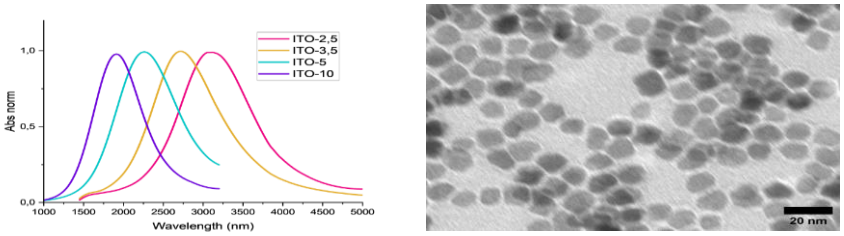


**Figure 1**. Absorption spectra of ITO with different Sn amount (left) and TEM image of ITO-3,5 (right), scale bar:20 nm.

**References:**

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# Unlocking HMF Reactivity with Tailored Sustainable DESs

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The use of eutectic mixtures such as Deep Eutectic Solvents (DES) is a subject of increasing interest in academic research [1]. The unique physico-chemical properties of DES, along with the numerous possible combinations of hydrogen-bond donors and acceptors (HBDs and HBAs, respectively) provide a robust foundation for considering DES as a valid sustainable alternative to traditional organic solvents [2]. In the presented study, divergent reaction outcomes were observed by using the same reagents upon the combination of different DES components. In particular, the versatile bio-based building block 5-hydroxymethylfurfural (HMF) reacted as a dienophile for the Diels-Alder reaction or as Oxa-Michael donor in the presence of choline chloride or L-carnitine as HBD components, respectively. For the Diels-Alder transformation, polyols used as HBDs exhibited an active role by in situ protecting the aldehyde function of HMF as a cyclic acetal. This resulted in a formal umpolung of the diene conjugated system. For the Oxa-Michael reaction, HMF promoted the addition to the double bond of maleimides when in presence of zwitterionic L-carnitine as HBA. Mechanistic studies on this divergent behaviour are currently ongoing.

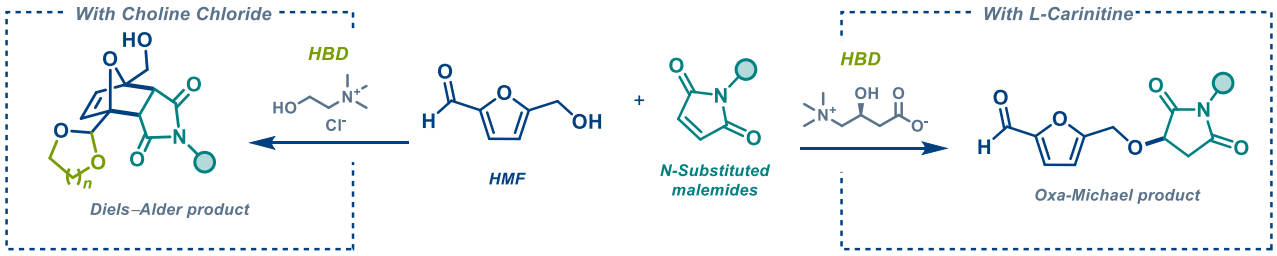


**Figure 1**. Divergent reaction outcomes by changing the DES components.

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**Acknowledgements:**
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# Synthesis of 2-Substituted 2,3-Dihydro-1*H*-Perimidines Catalyzed by Nano-$CuFe_2O_4$ and Evaluation of Their Antioxidant Activity

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Recently, perimidine derivatives have been explored as potential pharmaceutical agents due to their biological properties [1,2]. The synthesis of 2,3-dihydro-1*H*-perimidines is generally carried out through the condensation reaction between 1,8-diaminonaphthalene and aldehydes [2], catalyzed by acids, either Lewis or Brønsted–Lowry acids. Currently, the use of magnetic catalysts has also become common due to their ease of recovery and recycling [1]. On the other hand, studies concerning the antioxidant activity of 2-substituted-2,3-dihydro-1H-perimidines are still scarce in the literature. In this context, the present work proposes the synthesis of 2,3-dihydro-1*H*-perimidines using copper ferrite ($CuFe_2O_4$) as a magnetic catalyst and the evaluation of the antioxidant capacity of these molecules through the 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical scavenging methodology.

Figure 1a shows the synthesized dihydroperimidines as well as the reaction conditions employed for their preparation. It is noteworthy that the methodology used is robust and efficient, leading to the formation of dihydroperimidines 3A–D in yields 79–99%. Furthermore, the reaction leading to product 3A was applied to evaluate catalyst recyclability and, as shown in Figure 1b, the catalyst could be reused for up to six cycles while maintaining yields ranging from 99 to 80%.

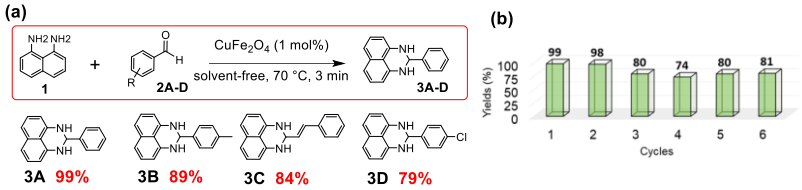


**Figure 1**. (**a**) Synthesized dihydroperimidines 3A–D, (**b**) Catalyst recycling.

The antioxidant evaluation results are presented in Table 1 as TEAC values. The synthesized 2,3-dihydro-1*H*-perimidines exhibited TEAC values close to or above 1.0, indicating antioxidant activity comparable to or greater than Trolox

| Entry | Compound | TEAC (μmolTE/μmol) |
|---|---|---|
| 1 | 3A | 1.62 |
| 2 | 3B | 1.60 |
| 3 | 3C | 1.33 |
| 4 | 3D | 1.39 |

**Table 1.** Compounds TEAC obtained values

**References:**
[1] N. Sahiba, S. Agarwal, Top. Curr. Chem., 378, 44 (2020).
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# The Inclusion of (+)-Pinoresinol from Flaxseed Extracts into β-Cyclodextrin elucidated by liquid state NMR techniques

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(+)-Pinoresinol (PIN) (Fig. 1a) is a bioactive plant lignan commonly found in flaxseed (*Linum usitatissimum*) and known for its antioxidant and potential health-promoting properties [1]. However, its direct identification by Nuclear Magnetic Resonance (NMR) spectroscopy in complex food matrices is difficult because of signal overlap and low concentration. Cyclodextrins (Fig. 1b) are cyclic oligosaccharides able to form host–guest inclusion complexes with hydrophobic molecules, improving their solubility and stability [2]. In this work, we exploit the formation of a 1:1 complex between PIN and β-cyclodextrin (β-CD) [3] to define an NMR-based strategy for the selective identification of PIN directly in a multicomponent flaxseed extract. The method combines $^{1}$H NMR spectral pattern recognition, quantitative $^{31}$P NMR analysis of phenolic hydroxyl groups, and selective spiking experiments. Structural validation was obtained by characterizing the pure PIN@β-CD inclusion complex. The complex was investigated through chemical shift variation analysis, ROESY, and DOSY, which supported a predominant 1:1 stoichiometry in solution. In parallel, the antioxidant capacity of the flaxseed-derived mixture was evaluated, providing complementary evidence of the bioactive potential of the extract and linking the NMR-based identification of PIN to its functional properties [4]. The agreement between the isolated system and the crude extract indicates supramolecular recognition of PIN within the natural matrix. Overall, this study provides an NMR-based approach for the identification of minor lignans in food-derived extracts and supports its application to complex food systems [5].

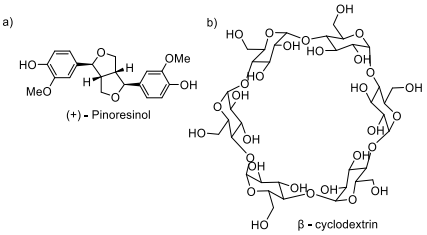


**Figure 1**: Chemical structures of (+)-pinoresinol and β-cyclodextrin.

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# Tuning magneto-optical response of copper tetraphenylporphyrin by means of supramolecular organization and of plasmon-molecule interactions

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Tuning and exploiting the modulation offered by plasmonic nanoantennas for spectroscopic applications is a frontier topic of great importance in nano-optics [1,2]. The use of magnetic fields to modulate the plasmonic response allows fast, precise and practical implementation. A first proof-of-concept already demonstrated the enhancement of the magneto-optical response for a $TbPc_2$ molecular complex [3], however an in-detail description of the influence of the different physico-chemical degrees of freedom is still lacking.

In this work, we aim to fill this gap by investigating copper tetraphenylporphyrin (CuTPP) by Magnetic Circular Dichroism (MCD) spectroscopy. In particular, we explore two possible routes: (1) studying the interaction of plasmonic nanodisks on top of which CuTPP films of different thickness are deposited by thermal evaporation; (2) studying the supramolecular ordering of CuTPP films on glass deposited by spin-coating. Copper tetraphenylporphyrin (CuTPP) is, among porphyrinoids, a simple molecular system, suitable for applications in magneto-optical spectroscopy thanks to the electronic configuration of the metal cation. In the first case, CuTPP films are deposited on gold and silver nanodisks (AuND and AgND), and subsequently characterized by absorption spectroscopy, room temperature MCD at 1 T and cryogenic temperature MCD (down to 2 K and up to 10 T of applied field). We observe an amplification of the CuTPP response together with the variation of the relative intensity of the peaks in the Q band region of the porphyrin spectrum, around 550 nm. In the second case, we assess the impact of supramolecular organization of CuTPP molecules obtained by solvent annealing, which consists in exposing molecular films on glass prepared by means of spin-coating to a saturated atmosphere of chloroform vapor. This method has shown to enable a local reorganization of the films, enhancing the magneto-optical activity [5]. The same magneto-optical spectroscopic analysis was then repeated on these films prior to and after the annealing. Thanks to this comparative study, we believe it is possible to understand the mechanisms behind the modulation of the magneto-optical activity of molecular systems.

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# Development of a novel chitosan/β-TCP scaffold functionalized with silver vanadate for bone regeneration

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The development of a scaffold that stimulates tissue regeneration and prevents infection is essential for tailored bone engineering strategies [1]. This study aimed to develop novel scaffolds made from chitosan/β-tricalcium phosphate (β-TCP), bioactive materials, and coated with antimicrobial silver vanadate (SV)-loaded gelatin methacryloyl (GelMA) for bone regeneration. To determine the optimal 3D printing ink composition, different concentrations of β-TCP (10, 20, 30, 40% w/w) suspended in chitosan solvent were tested. Dynamic light scattering was employed to measure the β-TCP particle size (1.69 μm) to avoid needle blocking, and the printing parameters were optimized. 40% β-TCP was chosen as the optimal concentration resulting in scaffolds with the highest compressive modulus (24.17 kPa). A scaffold coating made from photocrosslinked GelMA loaded with SV was optimized and confirmed by FT-IR. Ongoing cell culture investigations aim to assess the ability of the developed scaffolds to support bone regeneration *in vitro*.

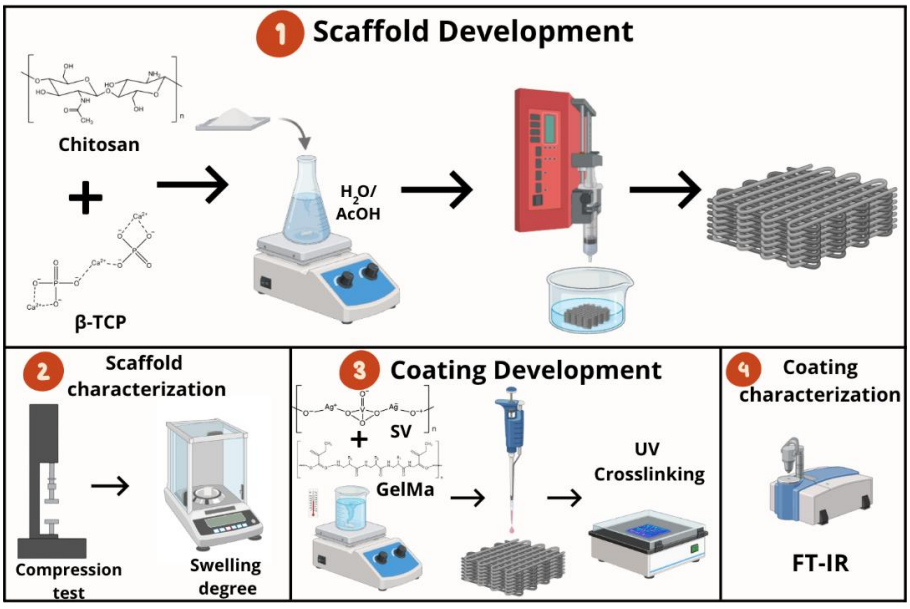


**Figure 1**. Steps in the development of a β-TCP/chitosan scaffold coated with GelMA/silver vanadate (SV).

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# Py-GC-MS analysis of MNPs in environmental samples from the Bazaruto archipelago (Mozambique)

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Microplastic and nanoplastic (MNP) contamination is an emerging concern in marine ecosystems, with potential effects on organisms and trophic dynamics. [1] In this context, the western Indian Ocean remains poorly investigated, despite being subject to significant plastic debris inputs. [2] This work is part of the environmental monitoring activities carried out by the Bazaruto Center for Scientific Studies (BCSS), a multi-platform ocean observatory studying coastal and offshore ecosystems of the Bazaruto Archipelago, Mozambique. [3]

The aim of this study is to identify and quantify MNPs in a range of environmental and biological matrices, in order to assess their distribution across trophic levels. Samples include surface seawater, corals and invertebrates, zooplankton, fish, for a total of 212 samples. Seawater samples were filtered through stainless steel filters to collect particles; the filters were then treated by sonication in ethanol to resuspend MNPs, followed by filtration to remove salts. Biological matrices were oven-dried, then subjected to microwave-assisted acid digestion and subsequent filtration. Qualitative and quantitative analysis was performed by pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS), which enables polymer identification and quantification based on characteristic pyrolysis products. [4]

In surface seawater samples, PP and PVC are the ubiquitous polymers, with concentrations ranging from 0.005 to 0.252 µg/L and 0.159 to 1.013 µg/L, respectively. PE, PS, PC, N-6, and N-66 were detected in a subset of samples, while ABS, SBR, PMMA, and PET were rarely quantifiable. Preliminary analyses of corals and fish confirm the presence of MNPs with polymer profiles consistent with those observed in water, suggesting trophic transfer.

This study provides the first quantitative MNP data from a tropical marine area of the western Indian Ocean and confirms the potential of Py-GC-MS for the determination of MNPs in complex environmental and biological matrices.

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# Synthesis and self-assembly of amphiphilic chelating polymers for radionuclide sequestration in water

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Amphiphilic random copolymers offer a powerful strategy for obtaining nano-objects (< 20 nm) via intramolecular single-chain folding in water that leads to the formation of unimer micelles [1,2]. The ability to create a confined hydrophobic environment, combined with their stability, makes them attractive nanoplatforms, while their LCST-like thermoresponsiveness enables easy recovery of the material [3,4]. Functionalizing the copolymers with selective chelating agents through covalent attachment provides highly effective systems for the efficient sequestration of metals ions with potential applications in radionuclide sequestration and recovery.

PEGMA-*co*-FA random copolymers were synthesized through RAFT and ARGET-ATRP controlled polymerization techniques. Selective metal chelators were functionalized with polymerizable moieties and covalently incorporated into the amphiphilic copolymer structure. Aqueous copolymer solutions were evaluated through turbidimetry and dynamic light scattering (DLS), while the sequestration of radionuclides was investigated through radio-TLC. DLS measurements confirmed that PEGMA-*co*-FA copolymers self-assembled in water into nanostructures with sizes between 7 and 10 nm. All solutions displayed a cloud point temperature $T_{Cp}$, tuned by varying the oxyethylenic side chain length. The unimer micelles collapsed above $T_{Cp}$ in larger aggregates (100-1000 nm), that can be removed from solution by filtration. Complexation experiments demonstrated the exceptional ability of the chelating polymers to sequester radionuclides, including $^{68}$Ga and $^{99m}$Tc.

These systems represent promising nanostructured materials for radionuclide sequestration and recovery, combining nanoscale confinement, selective complexation, and temperature-triggered separation.

**Acknowledgments**: This work was supported by the Italian MUR through the project PRIN 2022 PNRR AquaGreen, P20222ALWS, CUP I53D23005960001. Multidetector GPC/SEC were performed at CISUP (Centro per la Integrazione della Strumentazione della Università di Pisa).

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# 8-HQA Metal Complexes as Selective DNA and G-Quadruplex Binders

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8-Hydroxyquinoline-2-carboxylic acid (8-HQA, Figure 1) is a naturally occurring derivative of 8-hydroxyquinoline identified in high concentrations in several organisms [1]. As a terminal metabolite of tryptophan, 8-HQA is believed to act as a siderophore involved in microbiota regulation. In humans, 8-HQA has shown antiproliferative and antimigratory effects against colon cancer cell lines [2] and has emerged as a promising antitubercular and broad-spectrum antibacterial agent [3].

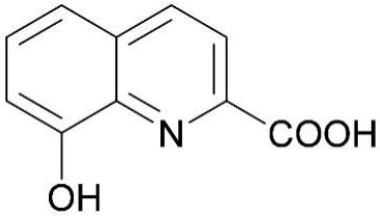


**Figure 1.** Structure of 8-hydroxyquinoline-2-carboxylic acid (8-HQA).

Owing to its strong affinity for metal ions, biocompatibility, and low cost, 8-HQA is one of the main binding species investigated within the national PRIN2022 - TRILLI project (TRansforming metal Ions and Low-cost LIgands into next-generation metallodrugs). The project aims to unveil key aspects for a rational design of new metal complexes and boost their development as metallodrugs based on simple essential metal ions and inexpensive ligands. It will, inter alia, determine the binding of several selected low-cost metal complexes (MCs) to biomolecules, and examine the relationships between the biological activity and thermodynamic stability of the MCs.

In this context, we present here the results obtained for the binding between metal complexes made from different metal centres ($Cu^{2+}$, $Zn^{2+}$, $Fe^{3+}$) and 8-HQA to bovine serum albumin (BSA), to natural DNA (calf thymus, ctDNA) and to DNA G-quadruplexes of different topologies. Spectrofluorimetric titrations are performed under different conditions for all the systems surveyed. The results indicate that all MCs may be transported by the major blood protein albumin with a not so distinctive fingerprint of the binding features. On the contrary, the binding to ctDNA and G-quadruplexes is found to be selective, with respect to metal centre and G-quadruplex geometry. These aspects are compared and discussed to contribute for a rationalization of the binding mechanism and the identification of the more promising MC.

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# Quantitative Determination of Polyethylene in Biodegradable and Compostable Shoppers with ATR-FTIR and Chemometrics

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Plastic production has increased from the 1950s to the present day, leading to a rapid accumulation of plastic waste and raising the challenge of its disposal. Bioplastics represent a valid alternative to conventional plastics, and their production is expected to increase in the near future. One of the attractive aspects of bioplastics is the possibility of end-of-life valorisation, thanks to their biodegradability and compostability. However, these processes can be affected by the presence of additives and other unsuitable substances, such as polyethylene (PE). Since the percentage of these components in bioplastic blends is regulated by European standards, including UNI EN 13432:2000, it is essential to develop analytical methods for their quantitative determination. Hyphenated techniques such as analytical pyrolysis coupled with gas chromatography–mass spectrometry (Py-GC/MS) are efficient methodologies for measuring small amounts of polymers, but they are not suitable for rapid screening analyses. Attention has therefore turned to spectroscopic techniques such as ATR-FTIR. In this study, we developed a procedure for PE quantification in bioplastics using ATR-FTIR integrated with multivariate data analysis. IR spectra of reference samples were acquired, and the data were pre-treated through baseline correction, normalization, and second-derivative calculation. Through principal component analysis (PCA), PE-specific wavenumbers were identified and then used to perform partial least squares (PLS) regression. Subsequently, bioplastic bags were analysed, and the data were processed using the developed procedure (Fig. 1) to determine the content of PE. Finally, the presence of additives in bioplastic bags was screened by (TD)GC/MS to investigate possible matrix effect on the ATR-FTIR analysis arising from the overlap between additive IR bands and those characteristic of PE. The results indicate that the developed ATR-FTIR method can be employed as a screening tool for the identification of potentially non-compliant items according to European regulations.

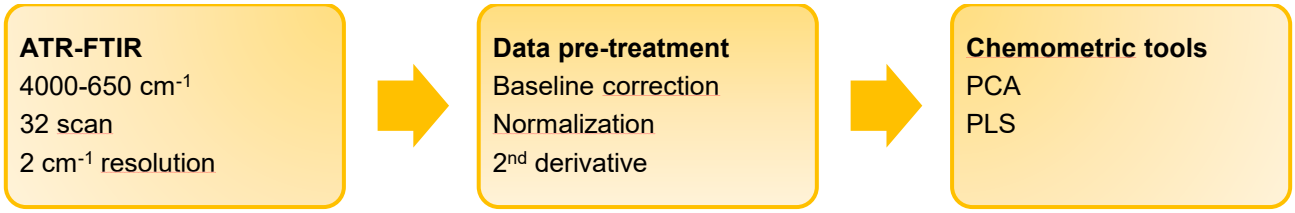


**Figure 1**. Flowchart of the developed procedure

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# Electrochemical Baeyer-Mills Reaction for the Synthesis of Non-Symmetric Azobenzenes

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Azobenzenes are organic substrates with a broad applicability in the fields of smart materials, photonics, nanotechnology, and biological chemistry, owing to their ability to undergo photoisomerization [1,2]. The synthesis of unsymmetrical azobenzenes is generally carried out using Baeyer-Mills conditions, which involve the condensation reaction between nitroso arene and anilines under acidic conditions (fig.1A) [3]. Despite their synthetic utility, the application is limited by the access to nitroso arenes, which are generally challenging to handle due to their high intrinsic reactivity. Moreover, their preparation frequently relies on harsh conditions that often lead to over-reduction and condensation byproducts. In this work, we propose an electrochemical approach for the generation of nitroso arenes from widely available nitro arenes and their *in-situ* functionalization with anilines, overcoming typical limitations associated with the Baeyer–Mills reaction (fig.1B). The reaction is performed under galvanostatic conditions using alternating current (AC), which plays a crucial role in the efficiency of the process, allowing the reaction to proceed at room temperature with good faradaic efficiency. Upon screening different substrates, the reaction was found to perform more effectively with electronically mismatched substrates, affording excellent yields and good conversions with no side polymerization of aniline.

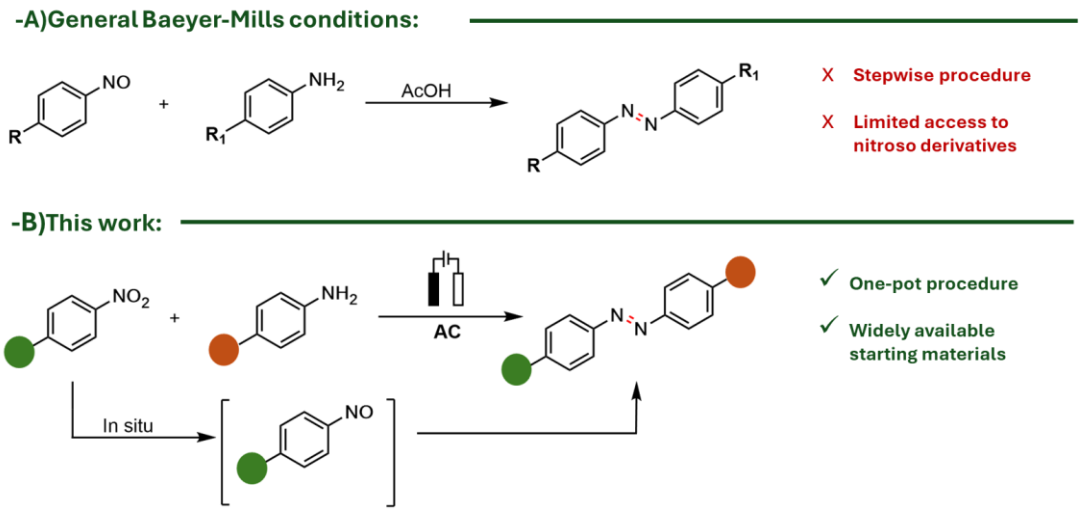


**Figure 1**. (A) Typical Baeyer–Mills reaction for the synthesis of azobenzenes; (B) This work: electro-generation of aryl-nitroso intermediate and synthesis of non-symmetric azobenzenes.

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# Biowaste-derived hard carbons from hazelnut shells for sustainable hybrid energy storage

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The development of sustainable electrode materials from biomass precursors is attracting growing interest in the field of next-generation energy storage systems. In this context, hard carbons (HCs) are emerging as promising electrode materials for hybrid capacitors, due to their favorable charge- storage mechanisms [1]. However, their practical use in hybrid capacitors is still limited by several bottlenecks, including relatively low initial Coulombic Efficiency, complex solid electrolyte interphase formation and the difficult tunability between surface physico-chemical properties and corresponding electrochemical behavior [1]. Lignin-rich precursors are particularly attractive for HCs production, as they promote disordered carbon structures with enlarged interlayer spacing and good structural stability, both beneficial aspects for promoting ion storage [2]. Among the various carbon-based precursors, hazelnut shell (HS) is a promising and abundant waste biomass , up to now unexplored for HCs synthesis [2-3].

On this basis, the present work aims to investigate the potential of HS-derived HCs as negative electrodes for lithium-ion capacitors, with particular attention to the effect of feedstock pre-treatment on the electrochemical performances in full-cell configurations. For this purpose, different mild pre-treatments, including water washing, particle size selection, acid treatment and hydrothermal carbonization, were applied to HS biomass before the last pyrolysis step. The effects of these pre-treatments on the corresponding electrochemical performances of the HC materials were systematically investigated. All synthesized HCs were first evaluated through electrochemical tests in half-cell configurations, and the best-performing materials were subsequently employed in full-cell devices. In all cases, the HCs were used as anodic materials, while an activated carbon derived from HS was employed as the cathodic one. In conclusion, the development of sustainable hybrid energy storage devices was evaluated, by integrating waste-derived bio-materials into full-cell configurations for practical electrochemical applications.

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**Acknowledgments**

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# The BIO-TEXTILE-SSbD project: safe and sustainable by design bio-based compounds for the next generation of liquid repellent textile coatings

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Materials with both hydrophobic and oleophobic qualities (also referred to as omniphobic or amphiphobic) have a range of commercial applications, including in the textile industry. Per- and poly-fluoroalkyl substances (PFAS) are the traditional choice of coating when looking to synthesise omniphobic materials, but these substances are highly persistent, bioaccumulate, and have documented negative effects on human health [1]. Many PFAS alternatives are based on polysiloxanes, but synthesis is extremely energy intensive, and recycling of these materials is not commercially mature [2]. Therefore, there is a compelling need for omniphobic coatings that are safe and sustainable by design (SSbD). In this scenario, the BIO-TEXTILE-SSbD project aims at designing and synthesising a fully bio-based omniphobic coating for textile applications while conforming to SSbD principles. Drawing from bio-based feedstocks, the project applies sustainable methodologies at all stages of materials synthesis, generating non-toxic outputs (for both humans and the environment), with a biodegradable final material. To achieve this, BIO-TEXTILE-SSbD will utilise computational techniques to design bio-based molecules suitable for omniphobic coatings, reducing waste and energy usage (Figure 1.). Sustainable synthesis routes will be prioritized, specifically those which utilise enzymes as a catalyst. The ecotoxicity and biodegradability of these new coatings will be assessed before application to textiles. Finally, infrared thermal activation (IRTA), as an efficient surface functionalisation technique with great potential for scale up [3], will be applied in the coating step.

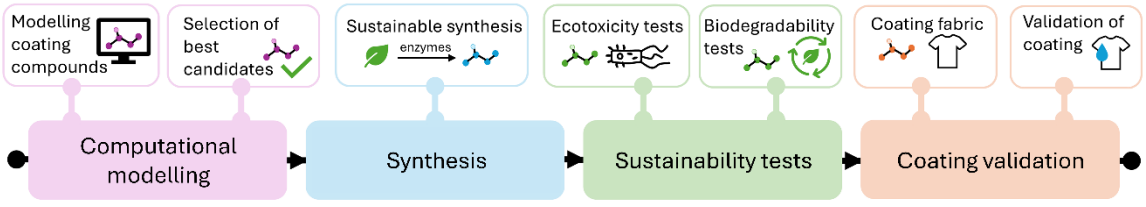


**Figure 2.** Workflow of the BIO-TEXTILE-SSbD project.

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# Sangiovese grape seeds extract as a nutraceutical candidate for the support of cardiac amyloidosis therapy

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Systemic amyloidosis comprises a group of diseases caused by the deposition of misfolded fibrillar proteins in the extracellular space. Among cardiac amyloidoses, transthyretin amyloidosis (ATTR) is of particular interest due to the accumulation of transthyretin-derived amyloid deposits in the heart [1]. Several studies have demonstrated that certain polyphenols can inhibit the self-assembly of specific peptides and proteins associated with amyloid diseases [2].

In this context, the present study focused on wine industry by-products, specifically on a phenolic extract derived from Sangiovese grape seeds, sourced from Collemassari estate in the Maremma area of Tuscany, with the aim of characterizing its chemical composition and evaluating its biological activity. Chemical characterization and quantification of the extract were carried out by High-Performance Liquid Chromatography (HPLC), complemented by colorimetric assays for the determination of total polyphenol and total flavonoid content.

Antioxidant capacity was assessed through a multi-method approach encompassing both radical scavenging assays in tube and a tissue-based oxidative stress model using rat tissue homogenate (TBARS). Metal chelating activity was additionally evaluated by UV-Vis spectroscopy.

The extract exhibited a well-defined phytochemical profile and consistent antioxidant activity across the methodologies employed. Based on these results, in vitro studies were conducted to investigate the potential interaction with TTR. The findings suggest that the bioactive compounds present in the extract bind TTR and contribute to the stabilization of its tetrameric structure, thereby preventing the misfolding process. Overall, the extract possesses a biological profile compatible with its use as an active component of nutraceutical supplements intended to support existing pharmacological approaches to ATTR management.

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