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BOOK OF ABSTRACTS

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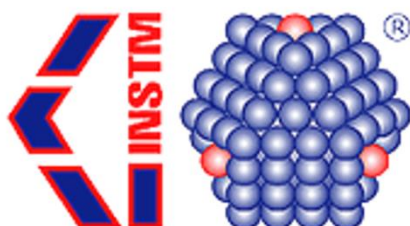
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Plenary Lectures

Programmable Nanohybrid Heterostructures: Chemical Design Principles for Optoelectronic, Biosensing and Biomimetic Applications

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Optimising the design of nanoscale hybrid materials enables the development of novel architectures for a broad range of technological applications. Critical to this effort is the ability to control the interface between the individual components—from their spatial separation to their interfacial chemistry—to enhance synergistic coupling.

I will present strategies for the assembly, (bio)functional and optoelectronic tunability of zero-dimensional (0D, QDs), one-dimensional (1D, carbon nanotubes) and two-dimensional (2D, MoS₂ and graphene) nanomaterials as well as their hybrids, with nanoscale spatial control and single-molecule resolution. We constructed mixed-dimensional heterostructures for single-molecule optoelectronic studies^[1] and for a range of applications, including photo-responsive devices^[2], phototriggered dynamic scaffolds^[3], and nanoscale biosensing chips.^[4] In particular, I will discuss how we employed DNA as a functional linking and templating moiety to assemble static and stimuli-responsive nanohybrids and devices, with tailored biosensing and optoelectronic responses.

Finally, I will present strategies for the fabrication of DNA nanostructures arrays that enable the multivalent investigation of ligand-receptor molecule interactions relevant to cancer, with nanoscale spatial resolution and single-molecule control.^[5]

References

- [1] *Journal of the American Chemical Society*, 2016, **138**, 2905-2908; *Small*, 2017 **13**, 1603042; *Journal of the American Chemical Society* 2017, **139**, 17834-17840; *Advanced Science* 2018, **5**, 1800596; *Small*, 2025, **21**, e05186.
- [2] *Advanced Functional Materials*, 2021, **31**, 2105719; *Advanced Functional Materials*, 2025, **35**, 2502140.
- [3] *Advanced Functional Materials*, 2025, e19712.
- [4] *Nano Letters* 2018, **18**, 4130-4135; *Angewandte Chemie International Edition*, 2021, **6**, 60, 20184-10189; *Nature Communications*, 2024, **15**, 7482.
- [5] *ACS Nano*, 2019, **13**, 728-73; *ACS Nano*, 2025, **19**, 35, 31467–31480.

Innovation as a driver for sustainability in Analytical Chemistry

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The pursuit of green and sustainable practices has become a cornerstone of modern analytical chemistry, urging the scientific community to fundamentally rethink the design, implementation, and assessment of analytical workflows. This presentation first highlights our recent advancements in green, circular and sustainable analytical chemistry [1–3], including the introduction of the green sample preparation concept, the development of AGREEprep, and a new solvent selection guide that integrates environmental, health, safety, and life cycle considerations. Building on this foundation, sustainability will be framed through its three interdependent pillars (environmental, societal, and economic) while critiquing reductionist approaches and advocating for systems thinking to avoid the unintended transfer of burdens across life cycle stages.

Moving from theory to transformative action, this talk then demonstrates how technological innovation can actively drive sustainability. Our disruptive work on vacuum-assisted headspace microextraction will be presented [4]. From Vac-HS-SPME to high-capacity phases such as single-drop microextraction, Twister™, SPME Arrow, and HiSorb, vacuum sampling consistently accelerates volatilization and analyte uptake, yielding high extraction efficiencies and excellent sensitivities within short times and at low temperatures. Recognizing the potential of this approach, we adopted a structured innovation strategy to translate theory into practice. In 2023, this led to the successful commercialization of a series of new products and methods through our spin-off, ExtraTECH. The path from initial concept to market launch will be discussed and translated to show how catalyzing innovation in sample preparation is interconnected with sustainable analytical chemistry.

Ultimately, this presentation calls for a paradigm shift: by revealing practical pathways for impactful change, we can foster a transformative dialogue in analytical chemistry, one that moves the sector away from being a conservative, traditional discipline to a forward-looking, impact-driven discipline that no longer sees sustainability as an external constraint but as an internal compass.

References

- [1] López-Lorente Á.I., Pena-Pereira F., Pedersen-Bjergaard S., Zuin V.G., Ozkan S.A., Psillakis E. *TrAC Trends in Analytical Chemistry*, 2022, **148**, 116530.
- [2] Psillakis E., Pena-Pereira F. *TrAC Trends in Analytical Chemistry*, 2024, **175**, 117686.
- [3] Psillakis E. *TrAC Trends in Analytical Chemistry*, **2025**, 191, 11837.
- [4] Psillakis E. *Analytica Chimica Acta*, 2017, **986**, 12.

Photoinduced Organometallic Catalysis

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Over the last decade, we have been involved in the development of more sustainable radical chemistry and have explored diverse methodologies including plasma[1] and mechano chemistry.[2] We have also introduced silicates as versatile sources of alkyl radicals upon photocatalysis. Using metallic or organic photocatalysts, alkyl radicals, including non stabilized ones, can be engaged in intermolecular reactions. This process can be merged with Ni-catalyzed C-C cross-coupling reactions.[3,4] In parallel, and following our interest in gold catalysis,[5] our recent efforts in photoredox/gold dual catalysis will also be presented. We have notably devised the first examples of photosensitized oxidation additive to an organogold(I) complex leading to C-C cross-couplings.[6,7] And we have evidenced that plasmon-mediated energy transfer enables direct activation of catalytically relevant gold complexes.[8] This lecture will also unveil the crucial use of organosilicon derivatives as another thread running through our research in different contexts.[9]

References

- [1] Bruel, F., Morand, G., Ognier, S., Dedieu, P., Favre-Réguillon, A., Ollivier, C., Fensterbank, L., Tatouliau, M. *Green Chem.* 2025, **27**, 11857.
- [2] Lakhal, A., Villeneuve, M., Haberkorn, L., Fourquez, J.-M., Forte, J., Gontard, G., Fensterbank, L., Ollivier, C. *Org. Chem. Front.*, 2024, **13**, 16207.
- [3] Cartier, A., Levernier, E., Corcé, V., Fukuyama, T., Dhimane, A.-L., Ollivier, C., Ryu, I., Fensterbank, L. *Angew. Chem. Int. Ed.* 2019, **58**, 1789.
- [4] Abdellaoui, M., Deis, T., Wiethoff, M.-A., Bahri, C., Lemièrre, G., Ollivier, C., Fensterbank, L. *Adv. Synth. Catal.* 2023, **365**, 884.
- [5] Enders, L., Mobili, R., Fensterbank, L., Helaja, J., Mouriès-Mansuy, V. *Chem. Eur. J.* 2025, **31**, e202501259.
- [6] Xia, Z., Corcé, V., Zhao, F., Przybylski, C., Espagne, A., Jullien, L., Le Saux, T., Gimbert, Y., Dossmann, H., Mouriès-Mansuy, V., Ollivier, C., Fensterbank, L. *Nat. Chem.* 2019, **11**, 797.
- [7] Lakhal, A., Gimbert, Y., Mouriès-Mansuy, V., Ollivier, C., Fensterbank, L. *JACS Au* 2025, **5**, 448.
- [8] Andreis, A., Herrera, J., Mouriès-Mansuy, V., Ollivier, C., Ba Sowid, S., Ribot, F., Fensterbank, L., Sá, J. *Communication Materials* 2026, **7**, 68.
- [9] Mutalliev, L., Beudy, E., Ballarín-Marión, M., Delattre, V., Troufflard, C., Mouriès-Mansuy, V., Gimbert, Y., Fensterbank, L. *Angew. Chem. Int. Ed.* 2026, **65**, e18534.

Photochemical permutations for aromatic rearrangement

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Aromatic compounds are among the most important structural motifs in high-value materials, including pharmaceuticals, agrochemicals, and functional materials. Their synthesis traditionally relies on the stepwise installation of substituents onto an aromatic core, following well-established reactivity rules that dictate regioselectivity and functional group compatibility. While powerful, this approach inherently constrains access to diverse substitution patterns and often requires lengthy synthetic sequences.

In this presentation, I will introduce a fundamentally different strategy based on the concept of aromatic permutation. Rather than constructing substitution patterns through sequential functionalization, I will demonstrate how a fully formed aromatic compound can be directly transformed into another fully functionalised positional isomer. This approach enables the reorganization of substituents on the aromatic framework without de novo synthesis, providing rapid access to substitution patterns that are otherwise difficult to obtain.

I will present the underlying principles of this transformation, key reaction developments, and representative examples that highlight the scope and potential of this strategy. Aromatic permutation offers a complementary paradigm to traditional methods, opening new opportunities for the efficient exploration of chemical space.

Acknowledgements: European Research Council

References

- [1] B. Roure, M. Alonso, G. Lonardi, D. Berna Yildiz, C. S. Buettner, T. dos Santos, Y. Xu, M. Bossart, V. Derdau, M. Méndez, J. Llaveria, A. Ruffoni* and D. Leonori* *Nature* **2025**, 637, 860–8670
- [2] T. dos Santos, C. S. Buettner, D. Berna Yildiz, M. Mamone, A. Ruffoni and D. Leonori* *Angew. Chem. Int. Ed.* **2025**, 64, e202423804
- [3] M. Alonso, G. Lonardi, E. M. Arpa, B. Roure, A. Ruffoni,* and D. Leonori* *Nat. Commun.* **2025**, 16, 7502.
- [4] Y. Xu, L. Poletti, E. M. Arpa, B. Roure*, A. Ruffoni,* and D. Leonori* *Nat. Commun.* **2026**, 17, 2141.

Beaming into the Future: Mechanistic Insights and Bio-Inspired Solutions in Electron Beam-Cured Coatings

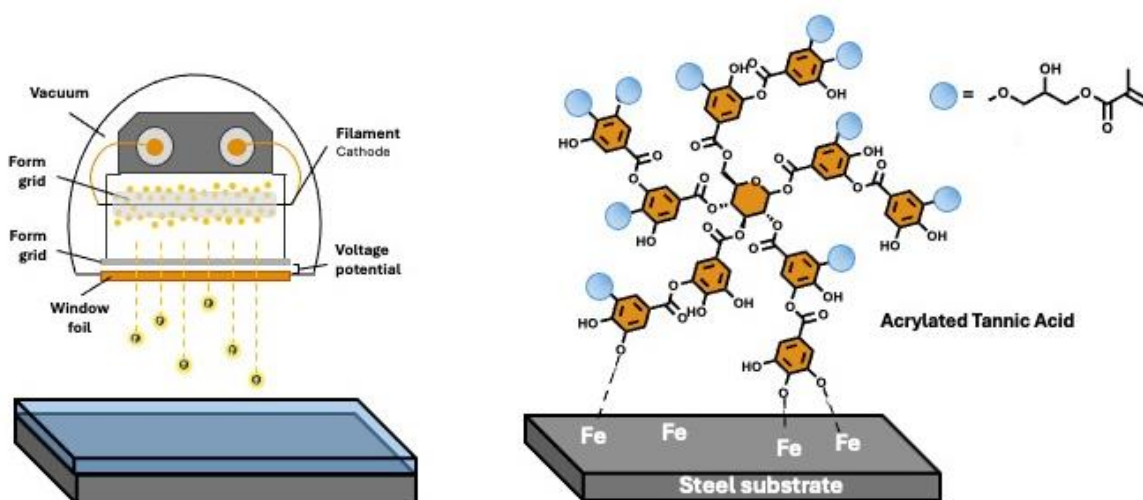
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Radiation curing technologies have gained increasing attention as a sustainable alternative to conventional thermal processing in the coatings industry. Among these technologies, electron beam (EB) curing is notable for its ability to initiate free radical polymerization using high-energy electrons without the need for photoinitiators or solvents. This eliminates potential migration issues and reduces volatile organic compound (VOC) emissions, enabling fast, energy-efficient processing. These features are of critical importance in a wide range of applications, including food-contact metal packaging, aerospace composites and highly chemical-resistant coatings.

This talk provides an overview of EB curing technology and its advantages over competing radiation-curing methods. It discusses the influence of process parameters, such as dose and dose rate, on network formation, cross-link density and viscoelastic properties of acrylic thermoset films, highlighting the complex interplay of radical and ionic reactions triggered by high-energy irradiation [1]. Based on these mechanistic insights, the development of partially acrylated tannic acid derivatives (TA-GMx) as bio-based adhesion promoters for EB-curable acrylic coatings on metallic substrates is presented [2]. Incorporating these green additives at optimised loadings significantly enhances adhesion, flexibility, and corrosion resistance, achieving performance levels comparable to those of conventional solvent-based benchmarks. Overall, these results emphasise the potential of EB curing as a sustainable platform for the next generation of high-performance coatings.



References

- [1] Frison T., Seegers W.J.M., Totev D., Esteves C. *Macromolecules*, 2024, **57**, 1291.
- [2] Bisio F., Sparnacci K., Mirone G., Pasquin S., Nicorelli A. *J. Coat. Technol. Res.*, 2026, DOI: [org/10.1007/s11998-026-01306-9](https://doi.org/10.1007/s11998-026-01306-9).

Keynote Communications

Giving PAHs a charge: challenges and opportunities with cationic polyaromatic systems

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The synthesis of positively charged polyaromatic (PAH) and nanographene systems is a hot topic in organic chemistry. The main reason for this interest is related to the great variety of potential applications for these materials, from photocatalysis to gas separation, sensing and responsive systems. However, the preparation of charged nanographenes and PAHs is often far from trivial, due to complex syntheses and high reactivity of the resulting target compounds. Recently, in our group, we developed synthetic protocols to generate phenazine dications, which proved to be quite stable ($t_{1/2}$ in $\text{CH}_2\text{Cl}_2 > 12\text{h}$) due to an interplay of Clar aromaticity and π -extension.^[1,2] This result, led to the successful application of these scaffolds as building blocks in redox responsive gas separation systems presenting an enhanced CO_2 selectivity in their oxidized form.^[3] The same design principles were then exploited in the design of photocatalytic systems, in which the formation of mono-cationic derivatives led to enhanced stability coupled with a high excited state potential in the oxidized form.^[4] Building on these exciting results we then proceeded to study and develop new synthetic protocols capable of generating more extended systems also presenting different heteroatomic dopants, resulting in an improved control over optoelectronic properties and photocatalytic performance of the materials. This led to the development of planar extended pyrazinium and phenothiazinium cations, with the latter successfully exploited in the photocatalytic oxidation of aromatics to generate C-N bonds triggered by red light (640 nm).

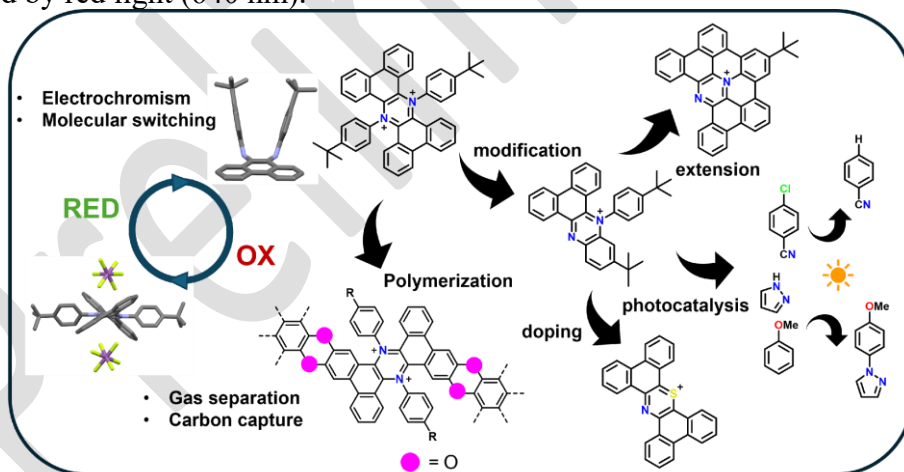


Figure 1. Synthetic approach and applications of π -extended phenazine based cationic systems.

References

- [1] J. Dosso, B. Bartolomei, N. Demitri, F. P. Cossío, M. Prato, *J. Am. Chem. Soc.* **2022**, *144*, 7295–7301.
- [2] J. Dosso, M. Prato, *Chem. Eur. J.* **2023**, *29*, e202203637.
- [3] G. C. Bezzu, B. Bartolomei, Y. Wu, M. Vaccaro, M. Longo, P. De Santo, A. Fuoco, M. Prato, M. Carta, J. Dosso, *J. Mater. Chem. A* **2025**, *13*, 21683–21691.
- [4] M. Prato, J. Dosso, *Chem. Commun.* **2025**, *61*, 2584–2587.

Electroactive Covalent Organic Frameworks in Organic Synthesis

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Covalent organic frameworks (COFs) are organic porous materials with high surface areas and modular architectures which enable the precise incorporation of functional sites within ordered networks.¹ Although their structural tunability and robustness revealed them as attractive platforms for heterogeneous catalysis, an emerging opportunity lies in exploiting COFs as precursors for electrochemically generated reactive species relevant to organic synthesis. In particular, COFs embedding redox-active functionalities such as azolium cations provide a scaffold in which cathodic reduction can directly generate N-heterocyclic carbenes (NHCs), organocatalysts widely employed in key organic transformations.² The traditional conversion of azolium salts to carbenes is carried out by means of deprotonation with bases, thereby generating varying amounts of associated byproducts as chemical waste. As a more sustainable alternative, electrochemical access to NHCs (which is well established in room-temperature ionic liquids)³ enables their formation in situ under mild conditions. By using COFs with such integrated redox-active units as electrode surface modifiers, we integrate the characteristic electrochemical behavior of azolium cations with the operational advantages of COF-based heterogeneous systems. Thus, this approach opens new possibilities for the cathodic generation of useful catalytic species on-demand and for the development of more sustainable methodologies in electro-organic synthesis.

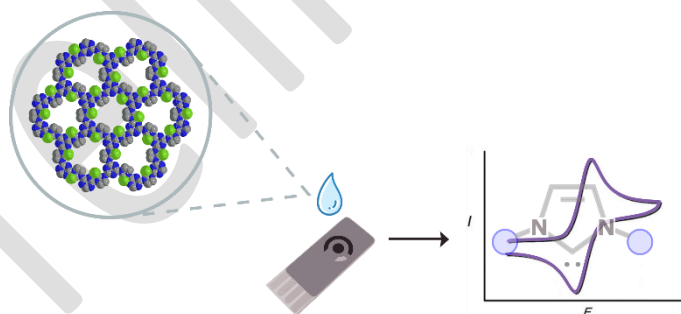


Figure 1. Electrochemical activation of azolium-based COFs as organocatalysts precursors.

Acknowledgements: Financial support from PRIN2022 “Hybrid Porous Materials for Eco-Sustainable Catalytic Organic Processes” (CUP B53C24005960006) is acknowledged.

References

- [1] N. Huang, P. Wang, D. Jiang *Nat. Rev. Mater.* **2016**, 1, 16068.
- [2] J.-M. Ju, C. H. Lee, J. H. Park, J.-H. Lee, H. Lee, J.-H. Shin, S.-Y. Kwak, S. U. Lee, J.-H. Kim *ACS Appl. Mater. Interfaces* **2022**, 14, 24404 – 24414.
- [3] C. Schotten, R. A. Bourne, N. Kapur, B. N. Nguyen, C. E. Willans *Adv. Synth. Catal.* **2021**, 363, 3189 – 3200.

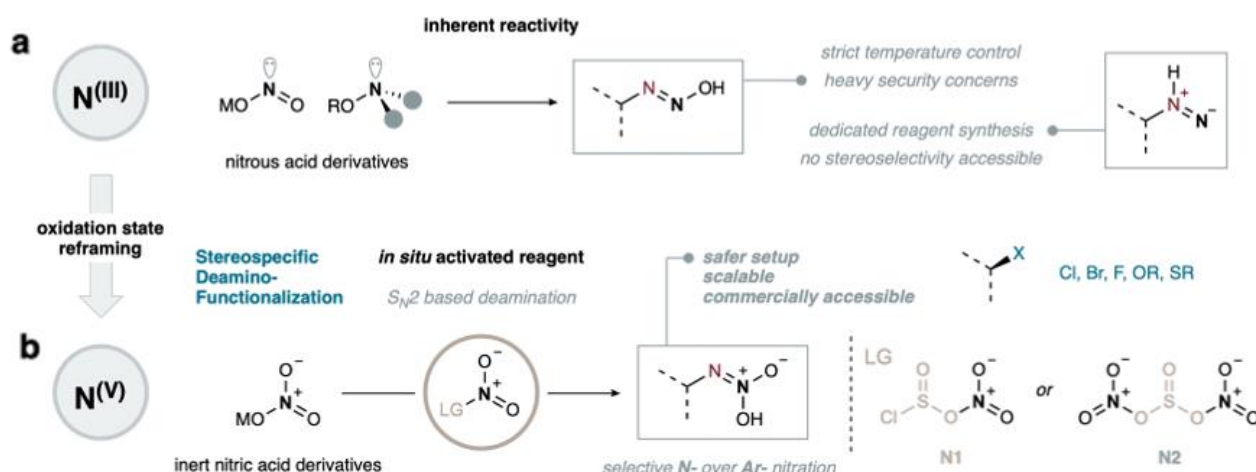
Direct Deaminative Functionalization of Primary Amines through N(V) Activation

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Aliphatic amines are among the most abundant and valuable functional groups in organic synthesis, medicinal chemistry, and chemical biology.^{1,2} Their direct conversion into alternative C(sp³)-X bonds represents an attractive strategy to repurpose readily available amine feedstocks as alkyl synthons.³ However, despite recent advances in direct deaminative functionalization,⁴ the selective replacement of unactivated C(sp³)-N bonds remains challenging, particularly when stereochemical information embedded in chiral primary amines must be preserved. Current strategies often rely on radical pathways or classical nitrosation chemistry,^{5,6} which can limit stereospecificity, functional-group tolerance, or operational generality (Scheme 1a). Herein, we present a conceptually distinct platform for the direct deaminative functionalization of unactivated primary amines based on N(V) activation. In this approach, simple nitrate sources are converted in situ into competent nitrating reagents, enabling the transient formation of N-nitroamine intermediates (Scheme 1b). These species provide access to substitution-competent electrophiles that can be intercepted by external nucleophiles under a polar, stereospecific manifold. The method offers a practical opportunity to access various alkyl derivatives from abundant primary amines, including amino-acid-derived motifs and complex amine-containing scaffolds. More broadly, this work highlights the potential of controlled N-nitration as a general activation logic for C(sp³)-N bond functionalization.



Scheme 1 a) N^{III} approach for deamination reactions b) our approach: activation of N^v with unusual nitrating reagent for selective deamination of alkyl amines.

Acknowledgements: The authors are grateful to have received generous funding from the Italian Ministry of the University and Research (MUR) under the FIS2 funding scheme (XAT2.0, FIS-2023-01733; L.C., M.L., A.C., V.M.).

References

- [1] Ertl, P.; Altmann, E.; McKenna, J. M. *J. Med. Chem.* 2020, **63**, 8408–8418.
- [2] Berger, K. J.; Levin, M. D. *Org. Biomol. Chem.* 2021, **19**, 11–36.
- [3] Dherange, B. D.; Yuan, M.; Kelly, C. B.; Reiher, C. A.; Grosanu, C.; Berger, K. J.; Gutierrez, O.; Levin, M. D. *J. Am. Chem. Soc.* 2022, **145**, 17–24.
- [4] Durka, J.; Zielińska, B.; Gryko, D. *Angew. Chem. Int. Ed.* 2024, **64**, e202419450.
- [5] Brewster, P.; Hiron, F.; Hughes, E. D.; Ingold, C. K.; Rao, P. A. D. S. *Nature* 1950, **166**, 179–180.

Structure-Function Relationships in Lipid Nanocarriers for siRNA delivery: Impact of Lipid Composition and Targeted Functionalization

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Gene therapy based on RNA interference is rapidly developing as a personalized approach for cancer treatment, exploiting the ability of small interfering RNAs (siRNAs) to silence disease-associated genes. However, the success of siRNA-based therapies critically depends on delivery systems capable of protecting the cargo, promoting cellular internalization, and enabling efficient gene silencing in target cells [1]. In this study, different Lipid Nanocarriers (LNCs) were developed to elucidate the role of lipid composition in determining LNCs size, bilayer organization, and biological performances. Cationic and Ionizable LNCs (CLNCs and ILNCs) were designed using POPC for biocompatibility, cholesterol for bilayer stability, and DOTAP or DODMA for siRNA complexation, with DODMA also conferring pH-responsive behavior. To reduce immune recognition and enable surface functionalization, DOPE-PEG2000-Maleimide was included, allowing covalent conjugation of the CGSG-T7 peptide (CGSG-HAIYPRH), targeting the human Transferrin Receptor (hTfR) [2]. A comprehensive physico-chemical characterization was performed using complementary techniques. Dynamic Light Scattering assessed size distribution and colloidal stability, while Small Angle Neutron Scattering enabled the investigation of bilayer organization and thickness before and after peptide functionalization. Electron paramagnetic resonance (EPR) further provided insight into the bilayer microstructure, and ζ -potential measurements evaluated the surface charge and pH responsiveness. Fluorescence spectroscopy was then employed to assess siRNA encapsulation efficiency, complemented by fluorescence anisotropy to probe changes in the local microenvironment and mobility of the fluorescent probe associated with encapsulation. In parallel, biological assays demonstrated that LNCs internalization and therapeutic efficacy depend on lipid composition and CGSG-T7 functionalization, with cellular uptake in hTfR-overexpressing cells and silencing efficiency both significantly affected, enabling identification of the most promising formulation. Overall, the combined physico-chemical and biological approach established clear structure–function relationships, demonstrating that lipid composition and surface functionalization critically determine LNCs performance and identifying an effective platform for siRNA delivery.

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References

- [1] El Moukhtari S.H., Garbayoa E., Amundarain A., Pascual-Gila S., Carrasco-Leon S., Prosper F., Agirreb X., Blanco-Prieto M.J. *J. Control. Release*, 2023, **361**, 130.
- [2] Han E.L., Tang S., Kim D., Murray A.M., Swingle K.S., Hamilton A.G., Mrksich K., Padilla M.S., Palanki R., Li J.J., Mitchell M.J. *Nano Lett.*, 2025, **25**, 800.

Chemical and Mechanical Characterization of Complex Materials through Brillouin–Raman Micro-Spectroscopy, FTIR, and Machine Learning

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It is an established fact that complex materials, ranging from biological systems to cultural heritage artefacts, are frequently distinguished by pronounced structural and compositional heterogeneity. Consequently, their investigation is enhanced by a multi-technical approach, whereby complementary analytical techniques facilitate access to diverse physical and chemical properties. In this context, vibrational spectroscopies, such as FTIR and Raman micro-spectroscopy, probe the vibrational modes of molecular bonds, enabling label-free identification of chemical composition and molecular structure through their characteristic spectral fingerprints. Concurrently, Brillouin spectroscopy probes the interaction between light and thermally excited acoustic phonons in the material, thereby providing information on viscoelastic and mechanical properties at the microscale. The combination of these techniques thus facilitates a thorough characterisation of complex materials by correlating their chemical composition with their mechanical behaviour¹⁻³.

In both biomedical and cultural heritage contexts, the intrinsic value of the samples and the limited availability of material, make sensitive, non-invasive, and label-free analytical approaches particularly desirable. At the same time, the integration of information obtained from these complementary techniques, together with the large volume and high dimensionality of the datasets, increasingly requires the use of artificial intelligence and machine learning approaches. These methods enable advanced data mining, multivariate analysis, and multimodal data fusion, facilitating the extraction of meaningful patterns and correlations from complex spectroscopic datasets. In particular, machine learning algorithms can assist in dimensionality reduction, classification, and predictive modeling, thereby improving the interpretation of multimodal measurements and supporting the development of robust diagnostic strategies.

Driven by these research aims, this work presents several applications of Brillouin and Raman micro-spectroscopy, combined with FTIR spectroscopy, to the study of complex materials. The presented case studies span biomedical and diagnostic applications as well as investigations relevant to cultural heritage science, demonstrating the versatility of these spectroscopic approaches in probing both chemical composition and mechanical properties. In parallel, new developments in machine learning and data fusion methodologies are introduced to facilitate the integration, analysis, and interpretation of the multimodal datasets generated by these techniques, with the ultimate goal of enhancing their diagnostic capabilities.

References

- [1] Kareem Elsayad, Francesca Palombo, Thomas Dehoux, and Daniele Fioretto, Biomed. Opt. Express 10, 2670-2673 (2019);
- [2] Francesca Palombo, Daniele Fioretto, Chem. Rev. 119 (13) 7833 – 7847 (2019);
- [3] Martina Alunni Cardinali et al. .Sci. Adv.8, eabo4221(2022);

Identifying New Potential Interstellar Molecules: The C₃H₆O₂ Isomer Family

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The interstellar medium (ISM), despite its harsh physical conditions, is known to contain more than 340 molecular species (to date), with new detections being reported on a monthly basis.¹ Most of the detected molecules have been identified thanks to radioastronomical signals, which in turn require accurate rotational spectroscopic data for interpretation. One strategy for detecting new interstellar species is to focus on a particular family of isomers, exploiting the connection between the relative stabilities of the isomers and their detectability in the ISM (Minimum Energy Principle, MEP).² In the present study,³ a computational protocol based on the MEP has been applied to the C₃H₆O₂ isomer family, providing accurate energetic hierarchies and spectroscopic parameters relevant to astrochemistry. Propanoic acid is predicted as the most stable isomer, followed by methyl acetate, ethyl formate, 1-hydroxyacetone, 2- and 3-hydroxypropanal. All these species have been experimentally studied and offer the opportunity to benchmark the computed rotational spectroscopic parameters obtained from the protocol. This benchmark has been further extended by including glycidol, a high-energy C₃H₆O₂ isomer, for which new high-frequency rotational spectroscopic measurements have been carried out. This benchmarking strategy establishes reliable uncertainties for the rotational spectroscopic parameters of the species not yet characterized in the laboratory, while the computational protocol indicates that high-energy conformers of propanoic acid should be the focus of future laboratory studies. Finally, the improved set of spectroscopic parameters for glycidol provides data for its radioastronomical search.

References

- [1] <https://cdms.astro.uni-koeln.de/classic/molecules> (CDMS database: Müller H. S. P; Schlöder F.; Stutzki J.; Winnewisser G. *Journal of Molecular Structure*, 2005, **742**, 215-227).
- [2] Lattalais M.; Pauzat F.; Ellinger Y.; Ceccarelli C. *The Astrophysical Journal*, 2009, **696**, L133-L136.
- [3] Savarese A., Alessandrini S., Melosso M., Panizzi G., Nonne M., Bizzocchi L., Puzzarini, C. *ACS Earth and Space Chemistry*, 2026, **10**, 198-209.

Determination of the Chemical Oxygen Demand Using a Cu-Au Anisotropic Nanoalloy-Modified Screen-Printed Electrode: A Sustainable and Sensitive Solution

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The increasing demand for safe and high-quality water, together with stricter environmental regulations, highlights the need for cost-effective and sensitive monitoring tools. Sensors enabling early in situ detection of contaminants are essential to ensure efficient water quality control and reduce exposure risks [1]. Among key indicators, chemical oxygen demand (COD) is widely used to assess the organic pollutant load by measuring the oxygen required for chemical oxidation of organic matter [2]. Elevated COD values indicate potential risks for aquatic ecosystems and human health. However, conventional COD methods rely on toxic reagents, require time-consuming procedures, and are unsuitable for on-site analysis, also suffering from chloride interference in saline matrices. Nanomaterial-based electrochemical sensors have emerged as promising alternatives due to their high sensitivity, rapid response, and miniaturization. In particular, non-enzymatic sensors using metallic nanocatalysts enable direct oxidation of organic compounds, avoiding harsh reagents and simplifying analysis [3], although existing materials often face limitations such as high cost or poor stability. Herein, we report a novel non-enzymatic electrochemical sensor based on gold–copper nanobrambles (Au-CuONBs) for rapid COD detection. The Au–Cu combination provides enhanced catalytic activity and resistance to chloride interference [4], with gold exhibiting enzyme-mimicking properties further boosted by copper. The nanobramble morphology was optimized via a green co-reduction and seed-mediated growth approach, followed by thiol functionalization to improve stability. Among tested conditions, 3-mercaptopropionic acid-functionalized Au-CuONBs showed optimal performance. The sensor demonstrated high sensitivity, a wide linear range (0.1–10.3 mM glucose, equivalent to 19–1978 mg L⁻¹ COD), and a low detection limit of 11 μM (2 mg L⁻¹ COD), along with good reproducibility (RSD 2–9%) and strong chloride tolerance. Validation with real wastewater samples showed excellent agreement with standard methods. Notably, the platform requires minimal sample preparation and provides results within ~5 min, significantly faster than conventional techniques (~2 h).

References

- [1] Jayaraman P., Nagarajan K. K., Partheeban P., Krishnamurthy V., *Int. J. Inf. Manage.*, 2024, **4**, 100210.
- [2] Willner M.R., Vikesland P.J., *J Nanobiotechnol.*, 2018, **16**, 1.
- [3] Gutiérrez-Capitán M., Baldi A., Gómez R., Jiménez-Jorquera C., Fernández-Sánchez C., *Anal. Chem.*, 2015, **87**, 2152.
- [4] Wang C., Wu J., Wang P., Ao Y., Hou J., Qian J., *Anal. Chim. Acta*, 2013, **767**, 141.

Quantifying Without Separation: Second-Order Fluorescence HPLC for PAHs

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Polycyclic aromatic hydrocarbons (PAHs) are priority contaminants in water monitoring[1], requiring sensitive and selective analytical methods capable of handling structurally similar compounds. In conventional HPLC with fluorescence detection (HPLC–FLD), reliable quantification is typically achieved through extensive chromatographic separation, which results in long analysis times and high solvent consumption. In this study, we present an alternative strategy based on second-order analytical data and multivariate calibration to relax this constraint.

A rapid HPLC–FLD method was developed in which fluorescence emission spectra are continuously recorded during chromatographic elution, generating second-order data matrices[2] (elution time × emission wavelength) for each sample. These data were processed using Alternating Trilinear Decomposition (ATLD), which enables the mathematical separation and quantification of overlapping analyte signals by exploiting their distinct spectral and temporal profiles. The approach does not require baseline chromatographic resolution of all target compounds.

The method was applied to the determination of 15 PAHs in water, with a total analysis time of approximately 8 minutes. Despite extensive chromatographic coelution between several PAHs, ATLD allowed their individual quantification. Limits of quantification were on the order of 0.2 $\mu\text{g}\cdot\text{L}^{-1}$ for all target analytes, consistent with regulatory monitoring needs. Linearity, precision, and trueness were evaluated using calibration and spiked samples, confirming the quantitative reliability of the approach.

These results demonstrate that second-order calibration can be effectively combined with fluorescence-based liquid chromatography to achieve fast, low-level PAH analysis. By transferring part of the selectivity requirement from the chromatographic domain to data analysis, ATLD provides a practical route to reduce analysis time while preserving analytical performance in routine environmental applications.

References

- [1] B.-H. Chen, B. S. Inbaraj, and K.-C. Hsu, “Recent advances in the analysis of polycyclic aromatic hydrocarbons in food and water,” *J. Food Drug Anal.*, vol. 30, no. 4, pp. 494–522, doi: 10.38212/2224-6614.3429.
- [2] H.-L. Wu, Y. Li, and R.-Q. Yu, “Recent developments of chemical multiway calibration methodologies with second-order or higher-order advantages,” *J. Chemom.*, vol. 28, no. 5, pp. 476–489, 2014, doi: 10.1002/cem.2570.

Comparative analysis of lipid oxidative stress biomarkers in plasma and oral fluid by UHPLC–MS/MS

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Oxidative stress is a pathological condition resulting from an imbalance between the excessive production of reactive oxygen species (ROS) and reactive nitrogen species (RNS) and the antioxidant defense systems of the organism. This condition has been implicated in the development of numerous diseases, including cardiovascular and neurodegenerative disorders. ROS and RNS induce molecular damage to lipids, proteins, and nucleic acids, promoting deleterious processes such as lipid peroxidation [1]. In this context, isoprostanes (IsoPs) are recognized as reliable biomarkers of lipid peroxidation and oxidative stress in vivo, also due to their greater chemical stability compared to other markers of oxidative damage to DNA and proteins. IsoPs are generated in situ through the ROS-mediated oxidation of arachidonic acid within cellular membranes. Due to their presence at very low concentrations in biological fluids, the development of highly sensitive analytical methods for their detection is essential. This study focused on the development of an innovative UHPLC–MS/MS analytical workflow, using QTRAP instrument, for the analysis of the total IsoPs, obtained after an alkaline hydrolysis step. In particular, a comparison was carried out between plasma, the conventional biological matrix, and oral fluid, proposed as a non-invasive alternative diagnostic matrix. To minimize the use of organic solvents during the extraction step, a miniaturized extraction, parallel artificial liquid membrane extraction (PALME), was employed for sample pretreatment. In this approach, analytes are transferred across a three-phase system driven by a pH gradient, which promotes the migration of neutral species from the sample matrix into an aqueous acceptor phase through a small volume of organic solvent (3 µL) immobilised within a membrane. This strategy enables significant analyte enrichment without an increase of matrix effect. Finally, the analytical protocol was applied to real samples collected in parallel from healthy subjects, demonstrating that an alternative matrix such as oral fluid can also represent a useful tool in the clinical setting for assessing baseline levels of oxidative stress biomarkers.

References

- [1] Valko M., Rhodes C.J., Moncol J., Izakovic M., Mazur M., Free radicals, metals and antioxidants in oxidative stress-induced cancer, *Chem. Biol. Interact.* 160 (2006) 1–40. <https://doi.org/10.1016/j.cbi.2005.12.009>

Mechanochromophores for polymer mechanochemistry

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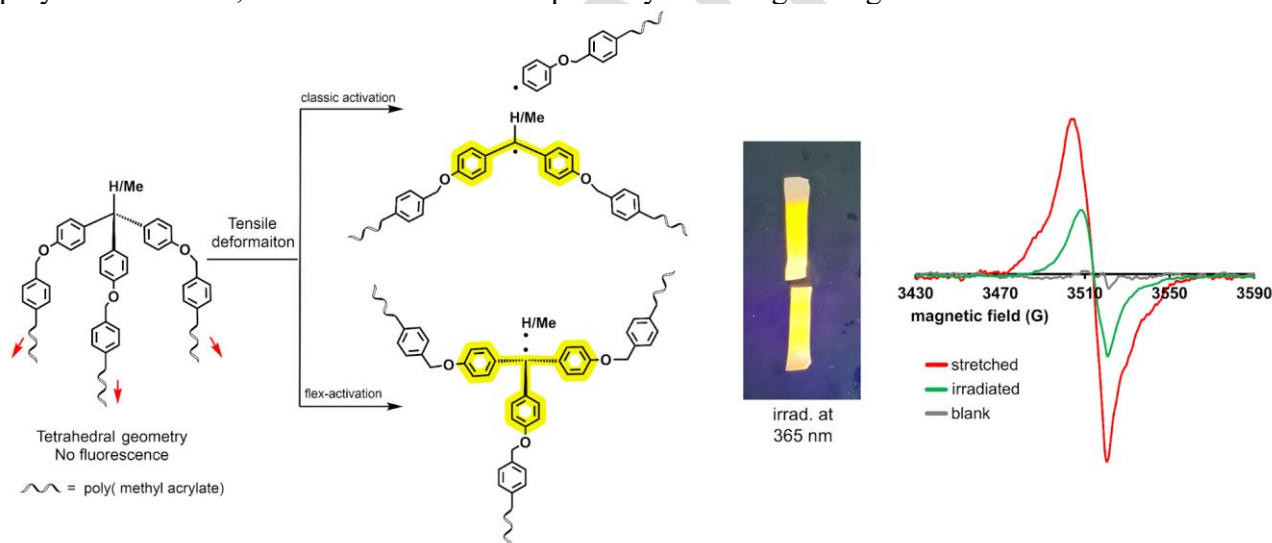
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Covalent polymer mechanochemistry explores how mechanical force can be exploited to direct chemical reactivity in polymers by selectively activating specific covalent bonds. By embedding force-responsive molecular units, known as mechanochromophores, into polymer chains, mechanical stress can be converted into optical signals such as changes in absorption or emission, enabling real-time visualization of stress, damage, and molecular-scale events in soft materials, and offering powerful strategies for self-reporting and adaptive polymer systems.¹

In recent works, the successful integration of triarylmethane mechanophores into poly(methyl acrylate-*co*-2-hydroxyethyl acrylate) or poly(*N,N*-dimethylacrylamide) matrices has demonstrated efficient force transduction accompanied by a visual color change due to the formation of highly stable and colored triarylmethane carbocations.^{2,3}

Here, we report on the capability of triarylmethanes to undergo mechanochemical activation to form highly fluorescent and relatively stable radical species, which is unprecedented for these scaffolds. Mechanistic investigations are ongoing to shed light on the homolytic cleavage underlying this transformation, which may proceed either through classical scission induced by elongation along the polymer backbone, or via a flex-activation pathway⁴ resulting from geometrical distortion.



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References

- [1] Xu D., Cheng X., Liu W., Sun Y., Niu Y., Wang M., Qian H. *Chem. Rev.* 2026, **126**, 3125.
- [2] Hemmer J. R., Rader C., Wilts B. D., Weder C., Berrocal J. A. *J. Am. Chem. Soc.*, 2021, **143**, 18859.
- [3] Hemmer J. R., Bauernfeind V., Rader C., Petroselli M., Weder C., Berrocal J. A. *Macromolecules*, 2023, **56**, 8614.
- [4] Larsen M. B., Boydston A. J. *J. Am. Chem. Soc.* 2013, **135**, 8189.

SYNChrotron Insights into Alkaline-Induced Structural Evolution of Ce-, Zr-, and Mixed Ce/Zr-MOF-808

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A combined X-ray Absorption Spectroscopy (XAS) and X-Ray Diffraction (XRD) *in-situ* approach is here presented to evaluate Metal-Organic Frameworks (MOFs) stability under harsh alkaline pH and follow real-time structural modifications in cerium coordination environment within the MOF architecture [1]. Measurements at Ce K-edge for CeMOF-808 and CeZrMOF-808 and at the Zr K-edge for CeZrMOF-808 and ZrMOF-808 were performed at beamline ID24 at the ESRF.

Unlike ZrMOF808, which remains largely intact under alkaline treatment [2], CeMOF-808 exhibits a dynamic reorganization of its structure at pH 13, culminating in the formation of a CeO₂-like phase. Fourier-Transformed EXAFS spectra (**Figure 1a**) reveal a transient loss of second-shell Ce–Ce, followed by its reappearance after roughly two hours. On the other hand, XRD patterns (**Figure 1b**) disclose a gradual loss of MOF peak intensity along with broad reflections characteristic of fluorite-type CeO₂, indicating framework degradation and the formation of nanostructured CeO₂ domains rather than bulk ceria. CeZrMOF808, meanwhile, retains remarkable structural integrity, with both Ce and Zr nodes showing only minimal perturbations.

This integrated XAS and XRD method provides a versatile tool to probe the evolution of metal coordination in MOF structures under operating conditions.

Figure 1. a) Ce K-edge FT-EXAFS spectra of CeMOF808 and b) XRD patterns of CeMOF808 recorded during the *in situ* experiment at pH 13.

Acknowledgements:

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References

- [1] M. Zhang, X. Luo, Y. Hu et al., *Chem & Bio Engineering*, 2024, **1**, 606.
- [2] P. Chang, C. Chen et al., *Journal of Colloid and Interface Science*, 2022, **623**, 627

Targeting glioblastoma with adamantane-conjugated copper complexes: structural features, activity, and mechanism of action

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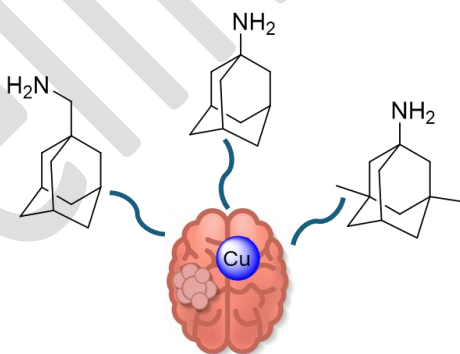
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The significant toxicity and limited selectivity of platinum-based anticancer drugs have driven the search for alternative therapeutic strategies, with copper emerging as a particularly attractive candidate due to its biological relevance and versatile coordination chemistry. In this study, we designed and synthesized a series of novel Cu(I) and Cu(II) complexes based on bis(pyrazolyl)acetate ligands functionalized with the bioactive molecules amantadine^[1], memantine^[2] and 1-adamantanemethylamine^[3], with the aim of enhancing anticancer activity through synergistic metal-ligand interactions. The resulting complexes were thoroughly characterized by spectroscopic techniques, X-ray absorption methods, DFT calculations, and single-crystal X-ray diffraction. Their biological activity was evaluated against glioblastoma cell lines (U87, T98, U251), and several compounds displayed strong antiproliferative effects, with IC₅₀ values significantly lower than cisplatin and reduced toxicity toward non-tumoral cells. Mechanistic investigations revealed that copper plays a key role, as supported by chelation experiments. The most active complexes induce reactive oxygen species production, mitochondrial dysfunction and DNA damage, ultimately leading to cell death. Notably, their ability to enhance the efficacy of temozolomide, highlighting their potential use in combination therapies. Overall, these results underscore the promise of copper-based complexes as a new generation of anticancer agents capable of improving selectivity and overcoming drug resistance.



References

- [1] Morelli M. B., Caviglia M., Santini C., Del Gobbo J., Zeppa L., Del Bello F., Giorgioni G., Piergentili A., Quaglia W., Battocchio C., Bertelà F., Amatori S., Menighini C., Iucci G., Venditti I., Dolmella A., Di Palma M., Pellei M. *J. Med. Chem.*, 2024, **67** (11), 9662.
- [2] Caviglia M., Del Bello F., Santini C., Migani S., Quaglia W., Del Gobbo J., Matteucci F., Morelli M. B., Zeppa L., Aguzzi C., Bozzuto G., Stringaro A., Battocchio C., Iucci G., Venditti I., Menighini C., Amatori S., Dolmella A., Pellei M. *J. Inorg. Biochem.*, 2025, **273**, 113035.
- [3] Caviglia M. et al. *Unpublished results*.

Producing Ethylene with Light

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Ethylene is a key platform chemical used in 50–60% of global plastics production. Industrial ethylene streams obtained from steam cracking inevitably contain trace amounts of acetylene (~1 vol.%), a highly detrimental impurity for downstream polymerization catalysts. Current acetylene removal relies on thermocatalytic hydrogenation processes that demand high energy input, external hydrogen supplies, and noble-metal catalysts, leading to safety concerns, limited selectivity, and poor sustainability metrics. Developing alternative purification strategies that are energy-efficient, selective, and based on earth-abundant materials remains a critical challenge.^[1]

In this talk, three sustainable, light-driven photocatalytic platforms for the selective semi-hydrogenation of acetylene to ethylene are presented. The proposed systems operate under mild conditions and rely exclusively on single-sites earth-abundant metals embedded within heterogeneous architectures, maximizing atom efficiency while enabling precise control over catalytic activity and selectivity. Three complementary photocatalytic materials are described, illustrating the evolution of catalyst design: (i) a metal-organic framework incorporating a cobaloxime linker (ZrCo-MOF),^[2] (ii) cobalt single-atoms on carbon nitride (Co-CN),^[3] and (iii) a pyrene-based hydrogen-bonded organic framework with embedded Cu atoms (Cu@HOF).^[4] The ZrCo-MOF system, operating in tandem with a ruthenium-based photosensitizer, achieves quantitative conversion of acetylene to ethylene within 4 hours under an ethylene-rich gas stream, with high selectivity (>99.9%). In a separate system, cobalt single atoms anchored on carbon nitride (Co-CN) function as an all-in-one photocatalyst in aqueous media, eliminating the need for external sensitizers. This system exhibits outstanding operational stability (continuous operation for over 40 days) and >99.9% selectivity, while simultaneously enabling selective oxidation of organic substrates to value-added products, further enhancing overall process sustainability. Similarly, the photocatalytic system based on Cu@HOF integrates light harvesting and high catalytic performance within a single, water-stable heterogeneous architecture enabling the selective removal of acetylene impurities within 75 minutes under ethylene-rich feed, with straightforward recovery and reuse. Overall, these results highlight the potential of noble-metal-free, light-driven catalytic systems for selective acetylene purification under mild conditions, offering sustainable alternatives to conventional hydrogenation technologies.

References

- [1] F. Arcudi, L. Đorđević, N. Schweitzer, S. I. Stupp, and E. A. Weiss, *Nat. Chem.*, 2022, **14**, 1007–1012
- [2] A. E.B.S. Stone, A. Fortunato, X. Wang, E. Saggioro, R. Q. Snurr, J. T. Hupp, F. Arcudi, L. Đorđević, *Adv. Mater.*, 2025, **37**, 2408658
- [3] A. Fortunato, D. Perilli, A. Dron, V. Celorrio, G. Dražić, L. Đorđević, L. Calvillo, C. Di Valentin, F. Arcudi, *Small Methods*, 2025, **10**, 2500527
- [4] B. Adranno, A. Fortunato, S. Silloni, M. Barbieri, S. Agnoli, L. Đorđević, and F. Arcudi, *J. Mater. Chem. A*, 2026, DOI: 10.1039/D6TA00654J

Rethinking Lithium-Ion Battery Recycling: Beyond Conventional Hydrometallurgical Pathways

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The sustainable recovery of transition metals from end-of-life lithium-ion batteries remains a central challenge for circular energy technologies. Notably, the biggest limitation of hydrometallurgical routes is the use of stoichiometric amounts of mineral acids and inorganic bases, as well as solvent extraction.^[1] In sharp contrast, mineral carbonation has emerged as a promising alternative separation and recovery route, leveraging the thermodynamic stability of metal carbonates and the availability of CO₂ as a benign reagent.^[2]

Building on this evidence, we report an entirely revisited metal recovery and separation strategy, based on the synergistic role of ethylenediamine as CO₂ absorber and transition metal binder (Figure 1).^[3] Specifically, the combination of amine-assisted mineral carbonation with electromediated stripping and regeneration (EMR), enables the selective recovery of nickel while avoiding acid-base steps. The process relies on the contrasted coordination thermodynamics and kinetic lability of ethylenediamine complexes. Simultaneously, the use of copper as a reversible redox mediator induces selective nickel decomplexation in the presence of kinetically inert cobalt complexes. Integration of this technological brick into a multi-step recycling flowsheet starting from NMC 811 blackmass highlights 50–65% reduction in total saline waste compared to solvent extraction-based processes. This work establishes a mechanistically grounded framework for replacing stoichiometric acid–base operations by redox-mediated control, opening new perspectives for greener hydrometallurgical separations.

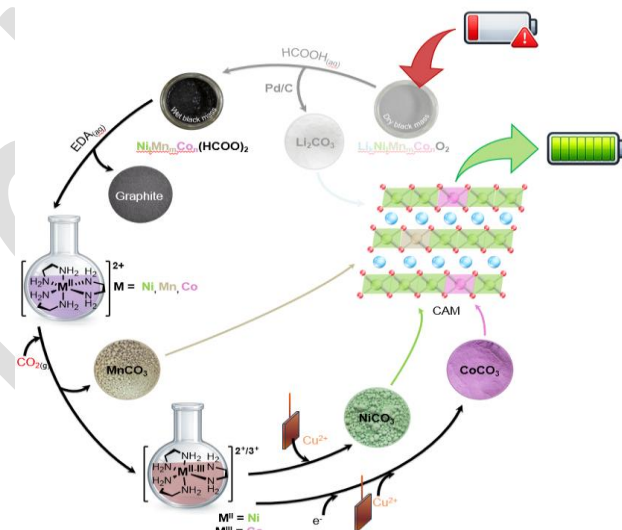


Figure 1. Schematic representation of the selective metal recovery tackled in this work.

References

- [1] G. Gonzales-Calienes, M. Kannangara and F. Bensebaa, *Batteries*, 2023, **9**, 375.
- [2] Litvinova, T., *Materials*, 2023, **16**, 3140.
- [3] J. Leclaire, T.A. Hatton, K.-J. Tan, A. Forot, D. Romito, M. Ducreux, EP24305764.3, 2024.

Topology-Gated CRISPR–Cas12a Platform for Monitoring Topoisomerase Activity and Drug Evaluation

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DNA topology is dynamically altered during essential cellular processes, leading to the accumulation of torsional stress that can compromise genome stability if not properly resolved. Topoisomerases counteract this stress by transiently cleaving and rejoining DNA strands, thereby maintaining proper DNA function. Dysregulation of these enzymes is frequently associated with human cancers, highlighting their importance as therapeutic targets.^[1] However, real-time monitoring of topoisomerase activity remains a significant challenge.

We present a CRISPR–Cas12a-based platform^[2,3] in which DNA supercoiling functions as a molecular switch to convert topoisomerase activity into a CRISPR-based signal transduction (Figure 1). Positive supercoiled DNA constructs are designed so that topoisomerase-mediated relaxation triggers CRISPR–Cas12a activation, producing an amplified fluorescent readout via collateral cleavage of the reporter molecules. This mechanism converts subtle changes in DNA topology into a direct, real-time signal. By testing inhibitors of both human and bacterial topoisomerases, we demonstrate that the platform reliably detects drug-induced modulation of enzyme activity, validating its potential for evaluating diverse classes of therapeutics.

Overall, this system establishes DNA topology as a readable molecular signal and provides a versatile tool for studying topoisomerase function, real-time enzymatic monitoring, and anticancer and antibacterial drug discovery.

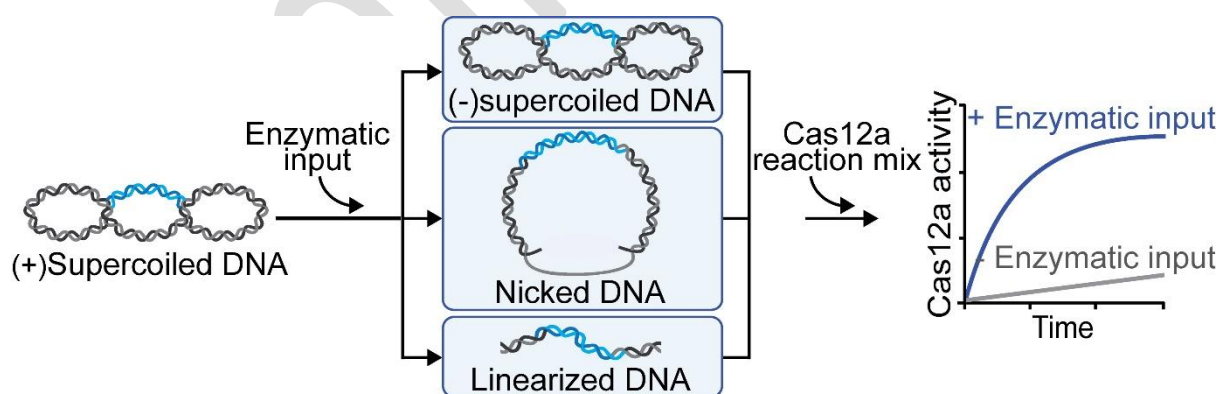


Figure 1. Enzyme-driven reconfiguration of DNA topology. Positively supercoiled plasmid DNA is converted to relaxed or linearized forms by topoisomerases resulting in restoration of Cas12a activity and signal generation.

References

- [1] Yakkala P. A., Penumallu N. A., Shafi S., Kamal A. *Pharmaceuticals*, 2013, **16**, 1456.
- [2] Del Giovane S., Bagheri N., Di Pede A. C., Chamorro A., Ranallo S., Migliorelli D., Burr L., Paoletti S., Altug H., Porchetta A. *TrAC, Trends Anal. Chem.*, 2024, **172**, 117594.
- [3] Bagheri N., Bertucci A., Merlo R., Porchetta A. *ACS Sens.*, 2026, **11**, 1634–1644.

Oral Communications

Preliminary

Theme A - Advances in Organic Chemistry

Preliminary

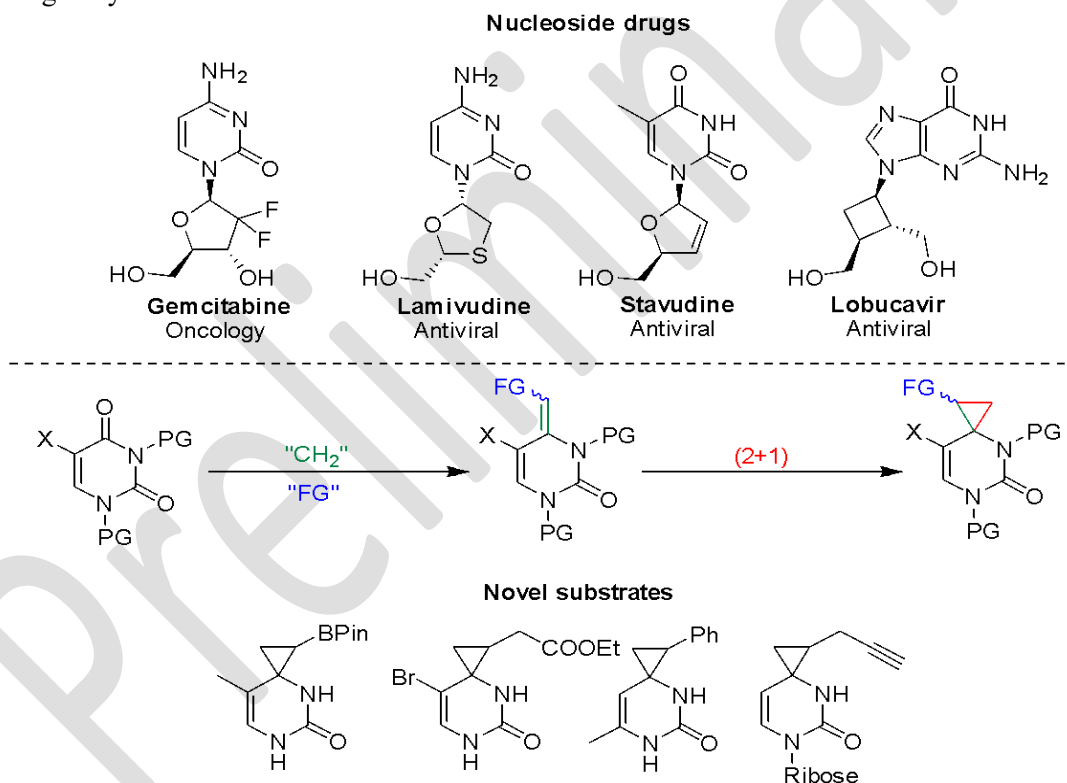
Dearomative spirocyclopropanations of pyrimidine nucleobases

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Nucleosides are the well-known building blocks of RNA and DNA present in every organism. Synthetically enhanced nucleosides represent a valuable class of antiviral and oncological pharmaceuticals since the 1950s. Medicinal chemists have chemically modified the ribose ring of nucleosides extensively over the years in the search for novel and improved activity, leading to the natural ribose motive being less and less recognizable in state-of-the-art drugs. [1]. Despite promising results this successful strategy has not been widely applied to the nucleobase ring, due to challenging synthetic routes owing to the aromatic nature of these motives [2]. Filling this gap in chemical space via introducing a spirocycle on the nucleobase would greatly increase its sp^3 richness and provide well-defined vectors for further derivatization, both key parameters in modern drug design. We present herein a straightforward strategy used to dearomatize pyrimidines in an elegant three step synthesis route. Organometallic olefination introduces a reactive handle, which can be further diversified in the following step, followed by a modified Simmons-Smith reaction to yield the spirocyclic nucleobase in moderate to good yields and diastereoselectivities.



References

- [1] E. De Clercq, *Acta Pharmaceutica Sinica B*, 2012, **2**, 535–548.
- [2] K. L. Seley-Radtke and M. K. Yates, *Antiviral Research*, 2018, **154**, 66–86.

Electrochemical generation of NHC-boryl radicals for carbon-centered radical formation

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Ligated boryl radicals[1], emerged as versatile open-shell intermediates for bond construction. Nevertheless, their deployment in electrosynthetic manifolds remains underdeveloped relative to thermal peroxide-initiated and photoredox-enabled methods[2]. Herein, we report the anodic generation of NHC-ligated boryl radicals using inexpensive graphite electrodes and demonstrate their utility across multiple radical manifolds, including radical decyanation, decyanative alkylation, and a Giese-type reductive radical hydroalkylation[3]. The nature of borane-electrode interaction has been elucidated through in-depth cyclic voltammetry analysis. The methodology reliability is demonstrated by its smooth scalability across various continuous-flow reactor systems, including a parallel-plate reactor and a Spinning Cylinder Electrochemical Reactor.

E-chemical generation of LBR via anodic oxidation

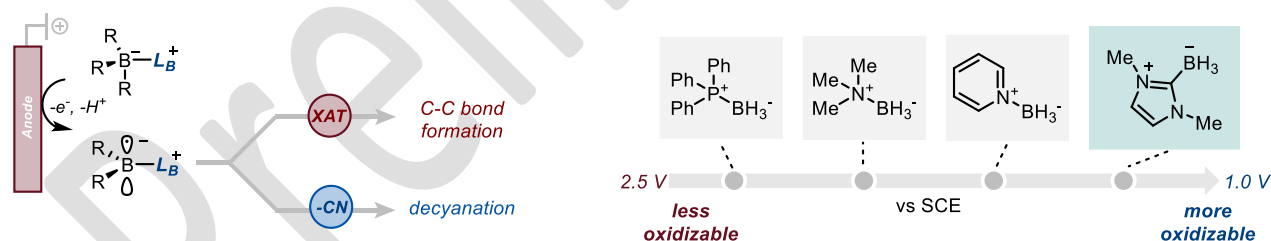


Figure 1: Anodic oxidation unleashes LBRs reactivity under electrochemical conditions.

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References

- [1] Capaldo L., Noël T., Ravelli D. *Chem Catalysis*, 2022, **2**, 957.
- [2] Tripathy, A. R.; Bisoyi, A.; Poolamanna, R.; Panuganti, A.; Yatham, V. R. *Adv. Synth. Catal.* 2025, **367**, e70094.
- [3] Morlacci V., Venturi E., Gallorini G., Scaringi S., Merli D., Cerveri A., Laudadio G., Ronchi P., Capaldo L. *ChemRxiv* DOI: <https://doi.org/10.26434/chemrxiv.15001053/v>

Divergent synthesis of novel highly functionalized indole-type compounds via the addition of (di)iodomethyl lithium to 3-iminoisatins

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The direct transfer of a reactive nucleophilic CH₂X or CHX₂ unit into an existing linkage enables the formal introduction of the moiety with the precisely defined degree of functionalization. Upon the fine tuning of the reaction conditions governing the transformation, the initial homologation event can serve as the manifold for triggering unusual rearrangement sequences leading to complex architectures through a unique synthetic operation.

Herein, we report the controlled manipulation of the iminoisatin moiety via lithium carbenoid mediated insertion of a C1 unit and consequent scaffold reassembly. By properly selecting the carbenoid employed in the protocol, a divergent synthesis of different highly functionalized indole-type compounds is accomplished. While the addition of LiCH₂I furnishes a straightforward access to 3-arylamino-2-formylindoles via chemoselective attack to the lactam-type carbonyl and Meinwald-type epoxide-aldehyde isomerization, the use LiCHI₂ enables the assembly of the (Z)-3-((phenylamino)methylene)indolin-2-one core through an unprecedented insertion of a C1 unit into a C-N double bond.

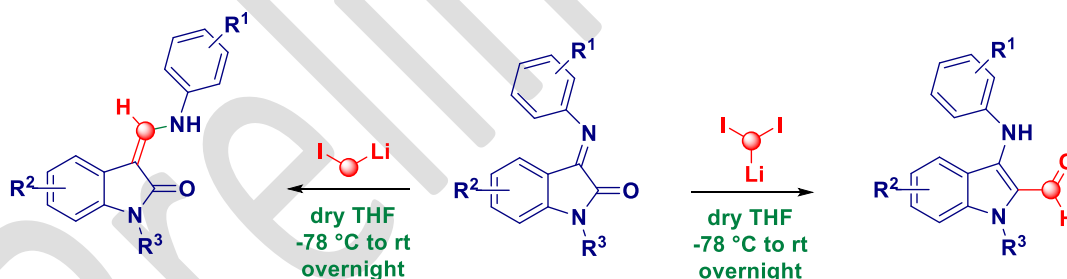


Figure 1: Lithium carbenoid mediated divergent synthesis of indole-type compounds

References

- [1] (a) L. Castoldi, S. Monticelli, R. Senatore, L. Ielo, V. Pace, *Chem. Commun.* 2018, 54, 6692-6704. (b) R. Senatore, L. Castoldi, L. Ielo, W. Holzer, V. Pace, *V. Org. Lett.* 2018, 20, 2685-2688.
- [2] (a) V. Pace, L. Castoldi, E. Mazzeo, M. Rui, T. Langer, W. Holzer, *Angew. Chem. Int. Ed.* 2017, 56, 12677-12682. (b) R. Senatore, M. Malik, T. Langer, W. Holzer, V. Pace, *Angew. Chem. Int. Ed.* 2021, 60, 24854-24858.

Development of C2-Homologation Events

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Organic synthesis is essentially the craft of constructing complex molecular frameworks by following well-planned, logical sequences, starting from simple units (known as synthons) [1]. This concept is perfectly expressed by *homologation reactions* which consist of a consecutive insertion of a constant unit [usually the methylene (CH₂) group] into a preformed chain, in order to obtain (*n*+1) carbon arrays, where *n* express the number of preformed homologations. This approach represents a valuable strategy for the construction of complex molecular architectures and it is widely employed to fine-tune the physicochemical properties of molecules, key aspect in pharmaceutical research. In this context, the aim of our research is introducing C₂ fluorine-containing fragments by exploiting the generation of lithium carbenoids and their reactivity with suitable electrophiles. For this reason, it is essential suppressing any degradative β-elimination effect triggered by the externally added promoting agent. Indeed, the carbenoid was generated at low temperature (-78 °C) for increasing their stability and in Barbier conditions, where the electrophile is present during the generation of the carbenoid [2]. The study was carried out on carbonyl compounds, thus leading to the formation of secondary and tertiary alcohols. Subsequently, the procedure was extended to isocyanates to afford N-substituted amides (Figure 1). This transformation enables the formation of previously unreported amides in a unique synthetic operation.

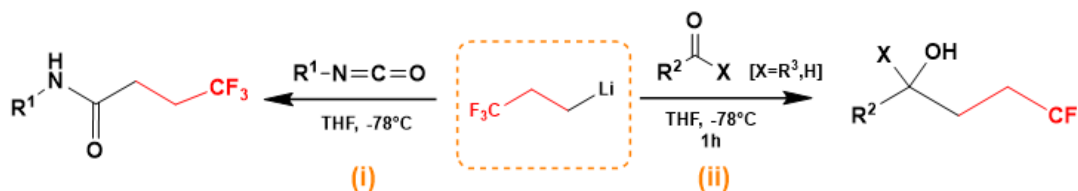


Figure 1 Strategy for the introduction of the -CH₂CH₂CF₃ motif into diverse electrophiles via lithium carbenoid reactivity.

References

1. Li, J. J., Name reactions for homologations. Wiley Online Library: 2009
2. Pace, V., Ed.; *Homologation Reactions. Reagents, Applications and Mechanisms. Vol. 1 and 2*; 2022

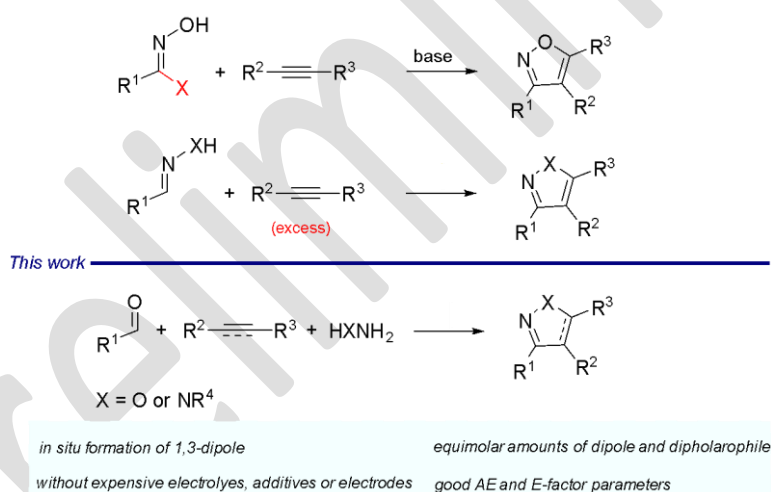
Sustainable electrochemical access to five-membered heterocycles

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Synthetic routes to isoxazole and pyrazole derivatives are an important topic in organic chemistry, due to the biological interest of these heterocycles, and their use as synthetic intermediates.¹ Among them, [3+2] cycloadditions have played a leading role, despite the preparation of nitrile oxide and nitrilimine involves the use toxic and environmentally hazardous intermediates such as oximoyl or hydrazonoyl halides. Over the years, the access to these 1,3-dipoles has been optimized thanks to the direct oxidation of oximes and hydrazones under electrochemical conditions, which avoided some synthetic steps. However, this approach also has drawbacks, mainly related to the excess of the dipolarophile required.² With this work, we further improved the sustainability of the electrochemical process through the development of a three-component domino protocol involving the *in-situ* formation of the 1,3-dipole. The electrochemical step occurs with cheap electrodes, avoids hazardous additives or electrolytes, and benefits from the use of equimolar amounts of aldehyde and alkene (or alkyne) with improvements in the atom economy and E-factor parameters with respect to previous approaches (Scheme 1).



Scheme 1. Access to isoxazole and pyrazole derivatives through cycloaddition approach

References

- [1] a) D. D. Vilela, R. R. de Rosa, P. H. Schenider, I. H. Bechtold, J. Eccher, A. A. Merlo, *Tetrahedron Lett.*, 2011, **52**, 6569. b) K. Karrouchi, S. Radi, Y. Ramli, J. Taoufik, Y. N. Mabkhot, F. A. Al-aizari, M. Ansar, *Molecules*, 2018, **23**, 134.
- [2] a) Y. Nakamura, M. Linden, J. Winter, S. Hofmann, N. Shida, M. Atobe and S. R. Waldvogel, *ACS Sustain. Chem. Eng.*, 2024, **12**, 11369. b) S. D. L. Holman, A. G. Wills, N. J. Fazakerley, D. L. Poole, D. M. Coe, L. A. Berlouis and M. Reid, *Chem. Eur. J.*, 2020, **28**, e202103728. c) M. Linden, S. Hofmann, A. Herman, N. Ehler, R. M. Bär, S. R. Waldvogel, *Angew. Chem. Int. Ed.*, 2023, **62**, e202214820.

Fe-promoted Amination with Hydroxylamine-Derived reactants: from free radical to metal-based reactivity

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The relevance of amine functions in biologically active compounds calls for the design of amination reactions with improved efficiency, selectivity, and sustainability. Fe-mediated amination with hydroxylamine-derived reactants has gained significant attention in recent years^[1], as it relies on non-toxic, cheap, and abundant iron salts or complexes and bench-stable reactants. This reaction enables NH₂ insertion on arenes in a single step, making this chemistry remarkably attractive. Over the years, different types of hydroxylammonium-derived reactants featuring electron-withdrawing O-substituents have been designed.

Two distinct aminating species, either radical cation NH₃^{•+} or an iron-coordinated aminyl radical can be involved. We investigated how the structure of the hydroxylammonium reactant controls the operating mechanism, i.e. which aminating species is formed.^[2] O-sulfonyl hydroxylammonium (MsONH₃⁺) are associated with a free radical pathway, competent for effective yet poorly selective amination of arenes as well as organic materials like graphene^[3]. In contrast, O-acyl hydroxylammonium salts are connected to a metal-based mechanism, that produces an iron-aminy radical^[4] competent for selective and controllable amination of arenes.

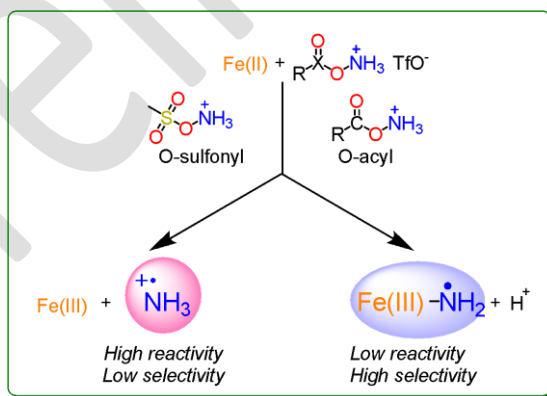


Figure 1: Radical vs metal-based pathways in Fe-promoted amination with hydroxylammonium reactants

References

- [1] (a) Gasser, V.C.M.; Makai, S.; Morandi, B.; *Chem. Commun.* **2022**, 58, 9991-10003. (b) Possenti, D.; Olivo, G.; *ChemCatChem* **2024**, 16, e202400353.
- [2] Marino, R.; Daino, M.; D'Orazio, M.; Possenti, D.; Amato, F.; Marrani, A. G.; Motta, A.; Olivo, G.; *manuscript in preparation*
- [3] Amato, F.; Possenti, D.; Daino, M.; Giaccari, L.; Marino, R.; Lucianatelli, M.; Motta, A.; Olivo, G.; Marrani, A. G.; *Carbon* **2026** 253, 121447
- [4] S. Debeer, F. Nessim, B. Morandi, et al *J. Am. Chem. Soc.* **2022** 144, 2637–265

Merging Electrochemistry and Aminocatalysis: A Reliable Platform for Enantioselective SOMO Transformations

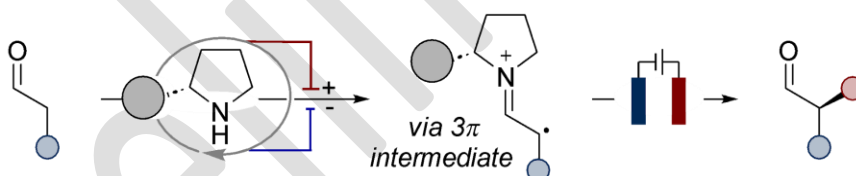
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The development of new strategies for enantioselective synthesis remains a central goal in organic chemistry. Among these, aminocatalysis has proven to be an effective approach for accessing enantioenriched compounds under mild conditions.¹ In recent years, its combination with other activation modes² has significantly expanded its synthetic potential. However, despite the rapid growth of electrochemical methods,³ their integration with aminocatalysis is still in its early stages. Our research group has demonstrated how their merger can efficiently promote asymmetric SOMO-type processes.⁴ This strategy relies on the electrochemical anodic oxidation of *in situ* formed enamines to generate reactive radical intermediates, which are later involved in stereoselective processes. Herein, we report an expansion of this approach for the synthesis of pyrrolidines and α -substituted aldehydes via α -alkylation, α -vinylation and Friedel-Craft reactions.⁵ Importantly, a crucial redox additive prevents catalyst degradation, giving the desired products in good yields and with high enantioselectivity. This study further corroborates how electrochemical activation can be smoothly combined with aminocatalysis to allow asymmetric radical transformations.



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References

- [1] Melchiorre P., Marigo M., Carlone A., Bartoli G., *Angew. Chem. Int. Ed.*, 2008, **47**, 6138.
- [2] Del Vecchio A., Sinibaldi A., Nori V., Giorgianni G., Di Carmine G., Pesciaioli F., *Chem. Eur. J.*, 2022, **28**, e202200818.
- [3] Yan M., Kawamata Y., Baran P. S., *Chem. Rev.*, 2017, **117**, 13230.
- [4] Mazzarella D., Qi C., Vanzella M., Sartorel A., Pelosi G., Dell'Amico L., *Angew. Chem. Int. Ed.*, 2024, **63**, e202401361.
- [5] Latini L., Laktsevich-Iskryk M., Mallick R. K., Ošek M., Mazzarella D., *Manuscript in preparation*.

Toward the Total Synthesis of Gnetin C: an innovative approach

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Gnetin C is a Resveratrol dimer, with a *trans* 2,3-diaryl-2,3-dihydrobenzofurane core structure. It is abundantly found in melinjo (*Gnetum gnemon*) seeds and it has shown interesting and promising properties, such as the induction of apoptotic pathways in certain cancers cell lines [1]. To date, Gnetin C has been isolated only from plant extracts, and no direct total synthesis is currently available. As described in the retrosynthetic pathway (Fig. 1), our aim was to develop an efficient synthetic strategy from *trans* 2,3-diaryloxyrane **3** as key intermediate, which requires a regio- and stereoselective nucleophilic arylation and subsequent deprotection/Mitsunobu cyclodehydration to afford the key 2,3-diaryl-2,3-dihydrobenzofurane intermediate **6**. In particular, we prepared the aldehyde **1** (Fig. 2) in five steps and 55% overall yield from the commercial 3,5-dihydroxy-4-methylbenzoic acid. Then, by Corey-Chaykovsky epoxidation with *in situ* pre-formed sulfur ylide **2**, we obtained *trans* 2,3-diaryloxyrane **3**, which was regio- and stereoselectively arylated to afford the *syn* triaryl alcohol **4** [2,3]. After deprotection of acetal moiety and stereospecific cyclodehydration *trans* 2,3-diaryl-2,3-dihydrobenzofurane **6** was obtained in good yield. Starting from compound **5**, *syn* arylated alcohol, in a few steps, we obtain the **5**. Simple elaboration of ester moiety (reduction, oxidation to aldehyde and Wittig reaction) and final de-tosylation allowed us to obtain tetramethylated Gnetin C **7**. By this synthetic approach different 2,3-diaryl-2,3-dihydrobenzofuranes were obtained, simply changing aryl boronic acid **4** (3,5-dibromo; 3,5-difluoro; 3-fluoro) and aryl substituent on ylide **2** (*p*-bromo, *p*-methoxy, *p*-tosyl), in order to investigate biological activities of the intermediates. Using chiral enantiopure sulfur ylide in the Corey-Chaykovsky epoxidation, enantiopure intermediates and final products can be achieved as well.

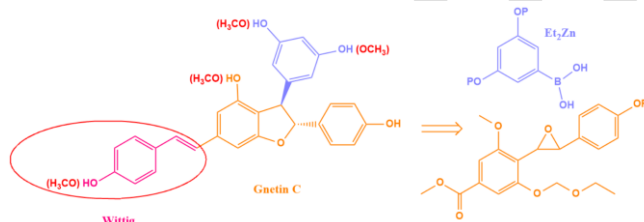


Figure 1: Retrosynthetic pathway

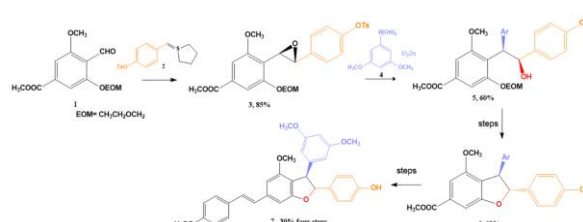


Figure 2: Synthetic Route

[1]. Campanelli, G., et al., Cancers, 2024, vol. 16, p. 1334

[2]. Laurita, T., P. Lupattelli, et al., Er. J. Org. Chem., 2019, vol. 27, pp. 4397-4403

[3]. T. Laurita, P. Lupattelli, L. Chiummiento et al., Bioorganic & Medicinal Chemistry Letters, 2021, vol. 49, p. 128264

Desymmetrization of Cyclopropane Derivatives via Non-directed Enantioselective C(sp³)-H Bond Oxidation

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The functionalization of nonactivated C(sp³)-H bonds represent a very powerful reaction, since such processes open to the possibility of converting these relatively inert bonds into functional groups suitable for further chemical transformations¹. In this context, among the available strategies for selective C(sp³)-H bond functionalization, methodologies based on hydrogen atom transfer (HAT) have proven to be successful. Factors governing HAT reactivity and site-selectivity have been discussed in detail.^{2,3} Control over enantioselectivity remains however a challenging goal. Here, we describe a catalytic enantioselective oxidation with H₂O₂ and a chiral manganese catalyst of methylenic C(sp³) H bonds in spiro[2.5]octane derivatives bearing different functional groups (FGs) at position 6. The reaction proceeds through a mechanism that involves the formation of a high-valent Mn-oxo species that engages in HAT from a substrate C-H bond, followed by a fast and stereoretentive hydroxyl transfer (O-H *rebound*) to the intermediate carbon radical⁴.

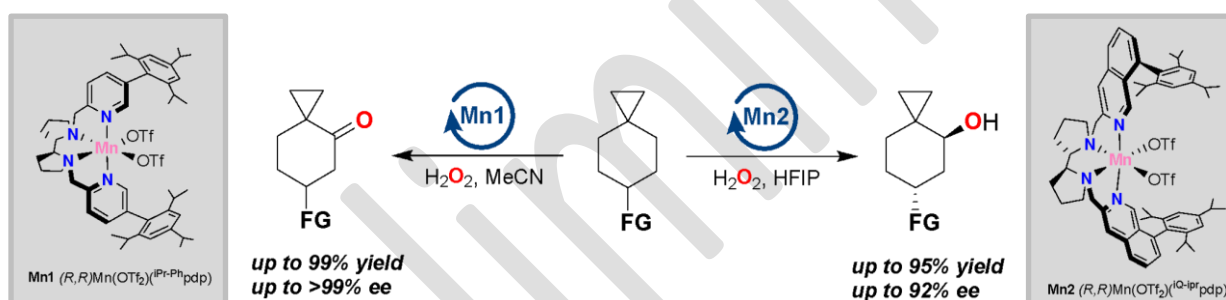


Figure 1. Manganese catalyzed methylenic C-H bond oxidation with hydrogen peroxide

Reaction optimization, carried out in MeCN and in the strong hydrogen bond donor solvent HFIP, identified Mn1 and Mn2 (Figure 1) as the best performing catalysts. In keeping with the hyperconjugative activation of the C-H bonds α - to the cyclopropane ring, highly site-selective oxygenation products (alcohols and ketones) at this site are achieved in excellent yield and enantioselectivity under mild conditions. Product chemo and diastereoselective hydroxylation is obtained when changing the solvent from MeCN to HFIP. The synthetic versatility of these newly installed groups, together with the possibility to promote cyclopropane ring-opening, enable straightforward elaboration of the obtained chiral products. These follow-up transformations provide access to new structural motifs while simultaneously preserving the chiral information acquired in the oxidation step.

Acknowledgements: European Research Council (AdvG 883922 to M.C.)

References

- [1] White, M. C.; Zhao, J. *J. Am. Chem. Soc.* **2018**, *140*, 13988–14009.
- [2] Milan, M.; Salamone, M.; Costas, M.; Bietti, M. *Acc. Chem. Res.* **2018**, *51*, 1984–1995.
- [3] Bietti, M. *Angew. Chem. Int. Ed.* **2018**, *57*, 16618–16637.
- [4] Vicens, L.; Olivo, G.; Costas, M. *ACS Catal.* **2020**, *10*, 15, 8611–8631.

Carbon Nanodots: a new photocatalytic platform for radical alkylation reactions

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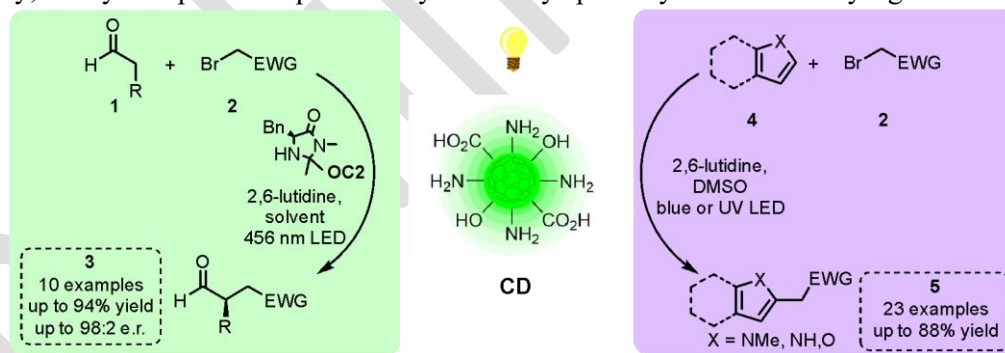
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Carbon nanodots are a new class of carbon-based nanoparticles that are currently finding numerous applications in sensing, bio-imaging and heterogeneous catalysis, thanks to their easily tunable optical properties and superficial moieties.¹ These versatile metal-free nanoparticles have been successfully employed in photocatalytic transformations as green and convenient replacements for the toxic, environmentally unsustainable and expensive transition metal complexes.^{2,3} However, their application in asymmetrical photocatalysis has not been explored yet.

Herein, we report our studies regarding the use of carbon dots as a nano-photocatalytic system in radical alkylation reactions. In our first work, we developed a synergistic approach towards the stereoselective α -alkylation of aldehydes by combining the photocatalytic activity of carbon dots with the chiral information provided by the organocatalyst. Through this method, we were able to activate different bromo-alkylating agents and obtain α -alkylated aldehydes with excellent yields (up to 94%) and enantioselectivities (up to 98:2 e.r.).⁴ In our following work, we employed the same photocatalytic system to access 2-alkylated indoles, furanes and pyrroles with high yields (up to 88%). Photochemical and mechanistic studies consisting of Stern-Volmer analyses, fluorescence lifetimes, quantum yield and light-dark experiments were undertaken to gain additional insights on the reaction pathway. Furthermore, recyclability experiments proved the promising potential of these carbon nanodots as heterogenous and sustainable photocatalysts. Owing to their high photostability, this system presented photocatalytic activity up to 5 cycles without any significant loss in yield.⁵



Scheme 1. Carbon dots as nano-photocatalyst system

References

- [1] M. Bortolami, I. I. Bogles, C. Bombelli, F. Pandolfi, M. Feroci, F. Vetica, *Molecules* **2022**, 27, 5150.
- [2] M. Sbacchi, M. Mamone, L. Morbiato, P. Gobbo, G. Filippini, M. Prato, *ChemCatChem* **2023**, 15, e202300667.
- [3] M. Mamone, G. Gentile, M. Prato, G. Filippini, *ChemSusChem* **2025**, 2500521.
- [4] A. Di Sabato, M. Santoni, V. G. Moldoveanu, A. Camilli, M. Feroci, G. Olivo, B. Simonis, E. Sturabotti, F. Leonelli, F. Vetica, *Adv. Synth. Catal.* **2025**, 367, e202500354.
- [5] J. Sargueil*, M. Santoni*, S. Cichella, A. Di Sabato, V. G. Moldoveanu, E. Sturabotti, B. Simonis, M. Giustini, L. M. Migneco, F. Leonelli and F. Vetica, *Chem. Eur. J.* **2025**, 31, e02043.

Atom-Efficient Synthesis of Trifluoromethylated Molecules via Stereoselective Allylic Alkylation

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Asymmetric allylic alkylation (AAA) represents one of the most powerful catalytic strategies for the stereoselective construction of C–C bonds. However, conventional protocols typically suffer from poor atom economy because the leaving group is generally discarded as waste. To address this limitation, this work introduces an innovative fluoride-transfer asymmetric allylic alkylation (AAA) platform where every atom from the starting materials is incorporated into the final products. The methodology facilitates a cross-electrophile coupling between allyl fluorides and gem-difluoroalkenes, achieving high efficiency by utilizing the departing fluoride ion to generate a trifluoromethyl (CF₃) motif.^{1,2} A defining feature of this catalytic system is its regioselectivity, which is governed by the specific activation of the electrophilic partners. When a chiral Lewis base is employed, the reaction follows a γ -selective pathway, yielding homoallylic trifluoromethylated compounds with two adjacent stereocenters in excellent enantiomeric ratios (up to 99:1 e.r.).³ Conversely, activation with tetrabutylammonium fluoride (TBAF) shifts the regioselectivity toward the α -position, producing racemic trisubstituted trifluoromethylated olefins. Supported by kinetic studies and DFT calculations, this atom-efficient protocol provides a versatile and regiocontrollable access to complex fluorinated molecules, which are of significant interest in medicinal and materials chemistry.

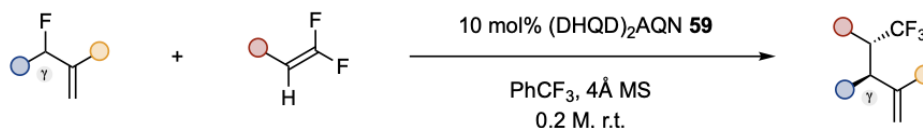


Figure 1 - Asymmetric Allylic Alkylation for the synthesis of new trifluoromethylated scaffolds.³

References

- [1] T. P. Loh, X. Feng et al., *Nature Communications*, 2017, **8**, 14040.
- [2] N. Shibata et al, *Angew. Chem. Int. Ed.*, 2007, **46**, 5435-5439.
- [3] J. Duran, X. et al., *Angew. Chem. Int. Ed.*, 2026, **65**, e20513.

Selective C-H Functionalization directed by Dynamic Covalent Chemistry

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The functionalization of non-activated C-H bonds represents a significant challenge due to their low intrinsic reactivity that makes control of selectivity particularly difficult. Classical methodologies rely on intermolecular reactions that occur on the most reactive substrate site or intramolecular radical processes that are typically limited to δ position of the chain.^[1] However, in both cases, C-H bonds remote from functional groups remain largely indistinguishable and cannot be selectively functionalized. Moreover, the reaction site is often difficult to predict, especially when there are minimal differences in the electronic and steric properties of the substrate C-H bonds.

Seeking to overcome these limitations, we designed a C-H functionalization catalyst equipped with a boronic acid receptor capable of reversibly interacting with alcohols and diols through dynamic covalent chemistry (Figure 1).^[2] Such binding places remote, non-intrinsically activated positions of the substrate in the range of the catalytic site, thus enabling a geometrical control of the reaction selectivity.^[3] By exploiting proximity, we aim to use radical processes such as HAT or others to introduce different functional groups at well-defined positions on the substrate, predictable based on their distance from the binding group. Herein, we will report the application of this strategy to the selective functionalization of alcohols using radical and/or radical-like reactants.

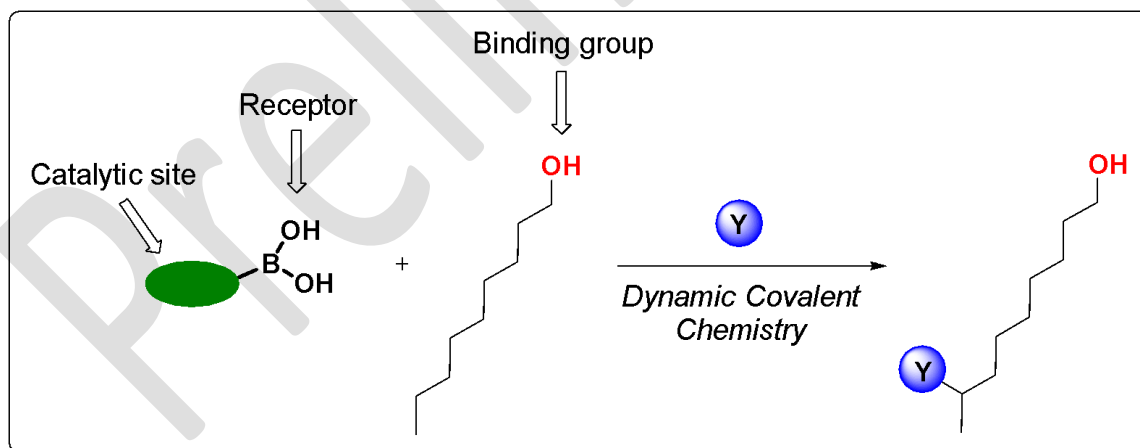


Figure 1. Functionalization of remote C-H bonds using dynamic covalent chemistry.

Acknowledgements

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References

- [1] Davies, H. M. L.; Morton, D. *J. Org. Chem.* 2016, **81**, 343-350.
- [2] James, T. D. et al. *Acc. Chem. Res.* 2013, **46**, 312-326.
- [3] Olivo, G. et al. *Angew. Chem. Int. Ed.* 2017, **56**, 16347-16351.

Site-Selective Deuteration via Aliphatic Sulfonium Platforms

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The selective replacement of hydrogen atoms with deuterium (deuteration) is establishing itself as a cornerstone transformation in the synthetic chemist's toolbox. Deuteration of pharmaceutically active compounds can improve their metabolic profile, safety, and efficacy, as exemplified by the FDA approval of deutetrabenazine (2017) and deucravacitinib (2022).¹ In addition, deuterated organic compounds find widespread applications across diverse fields: they serve as mechanistic probes in chemical and biological processes, and as internal standards for quantitative LC-MS analysis. Furthermore, these compounds are essential in forensic sciences for detecting substances of abuse, in material sciences, notably for enhancing OLEDs and optical fibers, and as non-radioactive probes for metabolic imaging diagnostics.²

Methodologies for deuterium incorporation that have recently appeared in literature mainly rely on photochemical (PC) and electrochemical (EC) activation, or transition metal (TM) catalysis.^{3, 4} The former pose scalability (PC) or reproducibility (EC) issues; on the other hand, the precious metals used in TM catalysis cause concern about their residual traces in pharmaceutical products. Hydrogen-deuterium exchange (HDE), which can directly introduce deuterium, is the most efficient method for deuterium incorporation.⁵ Nonetheless, traditional HDE methods are frequently hampered by a limited substrate scope and a lack of operational simplicity, which are crucial for *real-world* applications.

Herein we present versatile platforms based on aliphatic sulfonium salts that enable site-selective deuteration at benzylic and aliphatic sites. These platforms promote D-enrichment of building blocks and complex drug molecules at significantly reduced cost and with minimal waste (excellent E-factor). Indeed, they undergo nucleophilic displacement *in/on*-(heavy)water via one-pot tandem processes, exhibiting a wide substrate scope and high functional group tolerance. Selected examples include the trideuteromethylation of biologically active compounds, the synthesis of *d*₂- α -aminoacids and the preparation of D-labelled thioethers. Furthermore, this approach can be exploited to generate deuterated phosphonium reagents via sulfonium- to phosphonium- salts metathesis, useful for deuterio-Wittig reactions. Beyond HDE, aliphatic sulfonium salts are amenable to 1) radical chemistry such as in photoredox-catalyzed C(*sp*²)-C(*sp*³) bond formation, 2) ylide chemistry, as in deuterio-Corey-Chaykovsky reactions, and 3) Ugi multicomponent processes. Overall, these platforms provide reliable, selective, and sustainable access to deuterium-enriched compounds.

References

- [1] Di Martino R. M. C., Maxwell B. D., Pirali T. *Nat. Rev. Drug Discov.*, **2023**, 22, 562
- [2] De Feyter H. M., Behar K. L., Corbin Z. A., Fulbright R. K., Brown P. B., McIntyre S., de Graaf R. A. *Sci. Adv.*, **2018**, 4, eaat7314.
- [3] Li N., Li Y., Wu X., Zhu C., Xie J. *Chem. Soc. Rev.*, **2022**, 51, 6291.
- [4] Kang Q. K., Li Y., Chen K., Zhu H., Wu W. Q., Lin Y., Shi H. *Angew. Chem. Int. Ed.*, **2022**, 61, e202117381.
- [5] Qiu F., Yang L., Wang Y., Gao Y., Chen Y., Lei A., Li W. *Nat. Synth.*, **2025**, 4, 1141

Beyond the Surface: Probing the Internal Structure of Carbon Dots

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Carbon dots (CDs) are among the most extensively studied nanoparticles in materials science, owing to their versatile physicochemical properties. Since their serendipitous discovery in 2004,¹ CDs have found widespread application in catalysis, biotechnology, and sensing; yet their internal structure has received comparatively little attention. They are generally depicted as spherical nanoparticles bearing a hydrophilic, functional-group-rich surface and an aromatic core assumed to be inaccessible. A previous study by our group challenged this view, demonstrating through calorimetry and X-ray scattering that a specific class of polyamide CDs possesses a framework permeable to water.² Building on these findings, the present work extends the structural investigation to broader classes of CDs. Following an initial screening of reagents and reaction conditions, three classes were synthesised via microwave-assisted solvothermal synthesis: polyamide CDs from β -alanine reacted with ethylenediamine (EDA) and/or pentaethylenhexamine (PEHA); polyester CDs from glucose and sodium polyacrylate; and CDs from citric acid reacted with urea or ethylenediamine, selected for their prominence in the literature and thus their structural relevance. Given the structural focus of the work, rigorous purification was a prerequisite, and its outcome was systematically monitored by combining NMR-DOSY and HPLC. Notably, citric acid-based syntheses yielded CDs only as a minor fraction, with molecular fluorescent byproducts dominating the crude mixture. Calorimetric and X-ray analyses were then performed to assess water permeability. Our results show that the amorphous framework of polyamide CDs hosts water more effectively than the other classes. CDs derived from citric acid, by contrast, exhibited a hybrid amorphous-graphitic structure, further confirmed by HRTEM. Moreover, the comprehensive characterisation of polyamide CDs revealed structural correlations within this class, identifying early-stage parameters for the rational tuning of their architecture. Overall, this study provides new insights into the internal structure of CDs, an aspect that, to date, has remained largely unexplored.

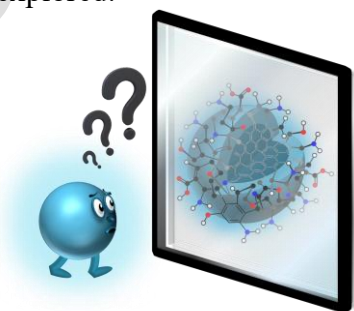


Figure 1. Conceptual illustration of a carbon dot probing its own architecture.

References

- [1] Xu X.; Ray R.; Gu Y.; Ploehn H. J.; Gearheart L.; Raker K.; Scrivens W. A. *J. Am. Chem. Soc.* 2004, *126*, 12736–12737.
- [2] Sturabotti E., Di Lisio V., Cardo L., Camilli A., Moretón Alfonsín E., Cangialosi D., Iturrospe Ibarra A., Arbe A., Prato M. *Advanced Materials*, 2025, e10992.

Impeding β -eliminative degradation for the design of unprecedented C2 homologating synthons

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Despite the tremendous advancements achieved in Organic Synthesis within the last decades, the development of efficient and straightforward tactics remains a formidable challenge, far-to-be fully addressed. In this sense, the progressive introduction within a carbon system of CH₂ units constitutes a conceptually simple approach towards chemical synthesis, being the origin of the inserted C1 fragments crucial for the effectiveness of the tactic.¹ Herein, we report the even more challenging introduction of two sequential carbon atoms – tunable under both radical or nucleophilic regimes. Crucial for the productivity of the logic is hampering the degradative β -elimination: to this end, through the in-depth electronic study of the competent metal-carbon bond, we individuated a series of metals fulfilling these characteristics, thus making them suitable to be engaged in C2-homologative sequences.²

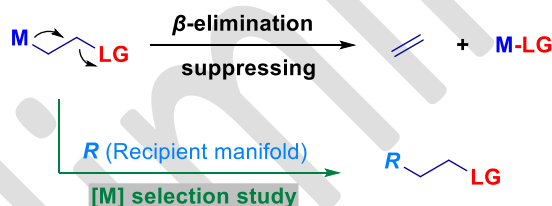


Figure 1: Common degradative sequence in C-2 reagents.

References

- [1] (a) Homologation Reactions. Reagents, Applications and Mechanisms. Vol. 1 and 2; Pace, V., Ed.; Wiley-VCH: Weinheim, 2023. (b) Pace, V.; Castoldi, L.; Mazzeo, E.; Rui, M.; Langer, T.; Holzer, W. *Angew. Chem. Int. Ed.* **2017**, *56*, 12677-12682.
- [2] (a) Ielo, L.; Castoldi, L.; Touqeer, S.; Lombino, J.; Roller, A.; Prandi, C.; Holzer, W.; Pace, V. *Angew. Chem. Int. Ed.* **2020**, *59*, 20852-20857. (b) Ielo, L.; Touqeer, S.; Roller, A.; Langer, T.; Holzer, W.; Pace, V. *Angew. Chem. Int. Ed.* **2019**, *58*, 2479-2484.

Entanglement-driven enhancement of basicity in phenantroline-based [2]catenanes

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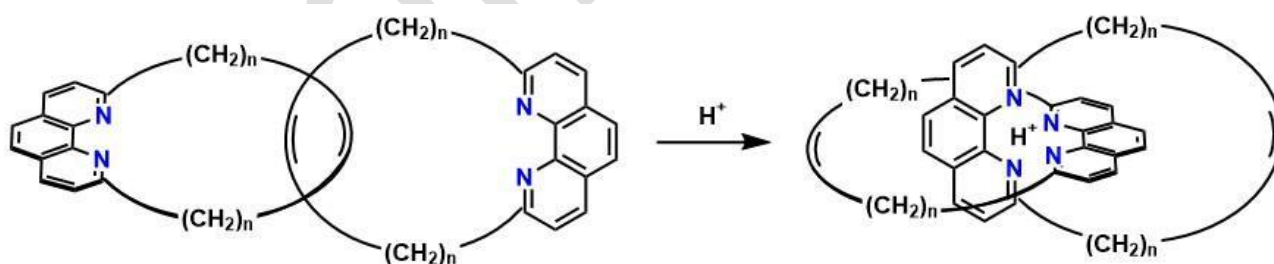
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The mechanical bond in interlocked molecules often generates physicochemical properties that fundamentally differ from those of their non-entangled components. An example of the possible results of mechanical entanglement is the topological enhancement of basicity, due to the forced proximity of multiple basic sites within an interlocked cavity, which significantly increases proton affinity by allowing the sharing of the proton among multiple sites. [1]

This phenomenon was first observed by Sauvage in 1986, who reported a 2500-fold increase in the basicity of a phenantroline-based [2]catenane relative to its acyclic analogue, a result of the proton being shared among the four nitrogen atoms. [2]

More recently, Di Stefano and coworkers have further highlighted the potential of these systems, demonstrating that another Sauvage-type catenanes can exhibit basicities approximately five orders of magnitude higher than conventional aliphatic amines like dibutylamine. [3] Building on these findings, we report the synthesis and characterization of a series of Sauvage-type phenantroline-based [2]catenanes with macrocycles of varying carbon chain lengths. We systematically investigated the basicity of these compounds, with the aim of determining their pK_aH values to study the correlation between macrocycle dimensions and the magnitude of the topological basicity enhancement.



General scheme for the protonation of a phenantroline-based catenane. The value of “n” varies between 11 and 13.

References

- [1] Capocasa, G. et al., Commun. Chem. 2024, **7** (1), 116
- [2] Cesario, M. et al., J. Am. Chem. Soc. 1986, **108** (20), 6250–6254
- [3] Berrocal, J. A. et al., Angew. Chem. Int. Ed Engl. 2016, **55** (24), 6997–7001

Radical *para*-Selective C-X (X=C, N, S) Functionalisation of Nitrobenzene

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Achieving selective C-H activation and bond formation in aromatic molecules remains a central task in organic chemistry. Conventional strategies rely on metal-catalysts, pre-functionalized reagents, or harsh conditions, increasing synthetic complexity and waste. Radical-based approaches offer a compelling alternative thanks to their unique reactivity patterns, enabling transformations under comparatively mild conditions. Here, by leveraging a single electron transfer (SET) process between Lewis pairs, we report a general radical-based mechanism that affords the one-pot regioselective C-X (X=C, N, and S) functionalisation of bare nitrobenzene.¹ Detailed NMR, EPR and XRD spectroscopies coupled to DFT studies show that after SET, the resulting pair of radicals engages in a cross-coupling reaction, which, after hydride abstraction, leads to the formation of *para*-functionalised product under mild conditions. These findings demonstrate that SET to nitrobenzene is far more accessible than previously appreciated,² with a wide variety of carbanions, amides, alkoxides, organophosphides, and thiolates as compatible partners, positioning the broader class of nitroaromatics as versatile platforms for harnessing radical-pair reactivity in synthesis and expanding the scope of metal-free functionalisation strategies. More broadly, they highlight that nitro groups cannot always be regarded as innocent functionalities in the presence of anionic species, with important implications for reaction design and mechanistic interpretation.

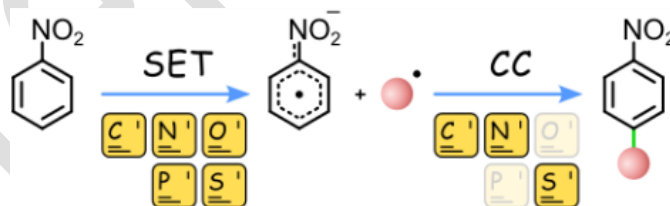


Figure 1: SET-mediated radical ion-pair formation and *para*-selective functionalization of nitrobenzene.

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References

- [1] Balahoju, S. A.; Bhattacharjee, N.; Lezama, L.; Lopez, X.; Salcedo-Abraira, P.; Rodríguez-Diéguez, A.; Reta, D. *ACS Omega* **2025**, *10* (22), 23798–23807.
- [2] Zhao, Y.; Zhu, H.; Sung, S.; Wink, D. J.; Zadrozny, J. M.; Driver, T. G. *Angew. Chem. Int. Ed.* **2021**, *60* (35), 19207–19213.

Harnessing acidic deep eutectic solvents for sustainable benzofuran synthesis

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Deep eutectic solvents (DESs) have emerged as promising green sustainable media, due to their low toxicity, low vapor pressure, minimal flammability, high recyclability, biodegradability, ease of preparation, and applicability, since they can act as both solvents and catalysts. [1]

Benzofurans are oxygen containing heterocycles widely present in natural products, pharmaceuticals, and materials, with different biological activities, from antimicrobial to anticancer effects. A possible approach to benzofuran nucleus is the base- or metal-promoted cyclization of *o*-alkynylphenols and *o*-alkynylanisoles, but these approaches often rely on hazardous reagents or transition-metal catalysts. [2]

In recent years, our research group has developed a growing interest in sustainable chemistry, using acidic deep eutectic solvents (DESs) as active and recyclable media, often in combination with microwave irradiation, for the synthesis of heterocycles. [3] A serendipitous observation during the study of DES-promoted alkyne hydration [3c] revealed the formation of benzofurans from *o*-alkynylanisoles in acidic DESs. Herein, we report the results of our investigation into a selective and sustainable strategy for benzofuran synthesis in DESs. We developed a simple microwave-assisted protocol in which the DES acts as both solvent and catalyst, promoting the cyclization of *o*-alkynylanisoles to afford 2-substituted benzofurans.

The scope and functional group tolerance of the method were evaluated, leading to the synthesis of 17 compounds in yields of up to 90%. The recyclability of the reaction medium and the scalability of the process were also investigated to assess the overall sustainability of the methodology. In addition, a plausible reaction mechanism is proposed. [4]

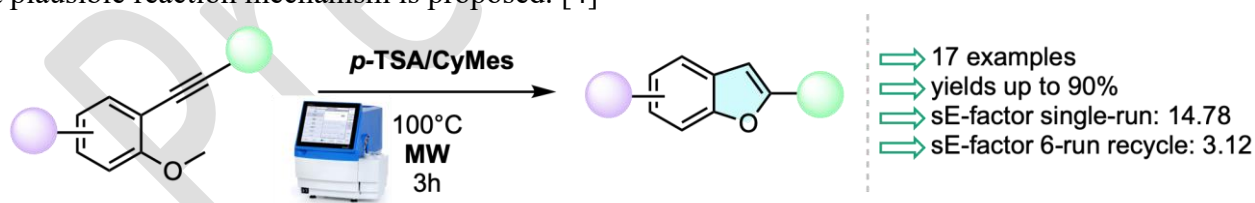


Figure 1: DESs-based MW-enhanced benzofuran synthesis

References

- [1] E. L. Smith, A. P. Abbott, and K. S. Ryder, *Chem. Rev.*, 2014, **114**, 11060
- [2] D. Dwarakanath, S. L. Gaonkar, *Asian J. Org. Chem.*, 2022, **11**, e202200282.
- [3] a) E. Brambilla, A. Bortolla, V. Pirovano, A. Caselli, M. Tiecco, G. Abbiati, *App. Organomet. Chem.*, 2022, **36**, e6669. b) E. Brambilla, A. Gritti, V. Pirovano, A. Arcadi, R. Germani, M. Tiecco, G. Abbiati, *Eur. J. Org. Chem.*, 2023, **26**, e202300204. c) A. Gritti, V. Pirovano, A. Caselli, A. Torregrosa-Chinillach, M. Tiecco, G. Abbiati, *Chem. Sus. Chem.*, 2025, **19**, e202501421.
- [4] A. Gritti, A. Sita, M. Goudarzi, S. Fedeli, E. Lepore, D. Nava, M. Tiecco, A. Caselli, V. Pirovano, G. Abbiati, *Eur. J. Org. Chem.*, 2026, e70463.

Theme B - Advances in Physical and Colloids Chemistry

Humic Acid-Derived Carbon Nanodots as Sustainable Fluorescent Probes for Metal Ion Detection

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Sustainable nanomaterials are essential for environmentally responsible sensing technologies. Here, we report a green hydrothermal synthesis of fluorescent colloidal carbon nanodots (CNDs) using humic acids as abundant, renewable precursors. The eco-designed process avoids toxic reagents and energy-intensive conditions, aligning with green chemistry principles.

The resulting CNDs exhibit stable photoluminescence, negative surface charge, and excellent colloidal stability in water. Spectroscopic and structural analyses reveal that oxygen-rich surface functionalities inherited from the precursor govern emission behaviour and metal-binding capability.

Fluorescence quenching studies demonstrate selective responses toward environmentally relevant metal ions, with Cu²⁺, Fe²⁺, and Pb²⁺ producing the strongest effects. Stern–Volmer analysis and lifetime measurements indicate predominantly static quenching at low concentrations due to complex formation with surface groups. Detection limits in the nanomolar range highlight the potential of these nanodots for trace-level monitoring.

This work demonstrates the valorisation of natural organic matter into sustainable fluorescent nanoprobes for environmental sensing applications.

Unraveling Structure–Property Relationships in Carbon Nanodots: a Computational Challenge

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Carbon nanodots (CNDs) are sub-nanometric carbon-based nanoparticles exhibiting intense and tunable photoluminescence, low toxicity, and high chemical versatility, which have paved the way for applications in biomedicine, sensing, catalysis, and optoelectronics [1,2]. Since their discovery in 2004, extensive experimental efforts have been devoted to understanding the origin of their optical properties. However, a comprehensive atomic-level description of carbon nanodots and their structure-property relationships remains elusive due to their intrinsic structural complexity [3,4].

CNDs are commonly described as quasi-spherical nanoparticles composed of a partially amorphous carbonaceous core, in which sp^2 -ordered domains coexist with disordered sp^3 regions, surrounded by a heterogeneous and chemically rich surface functionalization. Their final structure depends heavily on synthesis conditions, precursor chemistry, and degree of carbonization, resulting in significant differences in size, morphology, and optical response. Therefore, any realistic theoretical model must capture the complex interplay of these factors, which poses a significant challenge for the computational modeling of CNDs [4].

Early theoretical approaches often relied on small aromatic molecules or polycyclic aromatic hydrocarbons (PAHs) as simplified models, or on polymer-like and random-network representations of the amorphous carbon core [5,6]. While these strategies have provided valuable insights, they only partially capture the intrinsic disorder and structural diversity of experimentally synthesized CNDs.

In this contribution, we present a multiscale computational strategy, schematically summarized in Figure 1, that employs progressively larger carbon clusters (CCs) as effective structural motifs to model the unsaturated and amorphous regions of the carbon nanodot core. This approach combines the GOAT-EXPLORE algorithm, for the sampling of low-energy isomers of CCs, with TD-DFT calculations for the determination of their optical properties [7]. In parallel, we are exploring the extension of the model through Monte Carlo-based approaches to broaden the accessible configurational space and move toward more statistically representative descriptions.

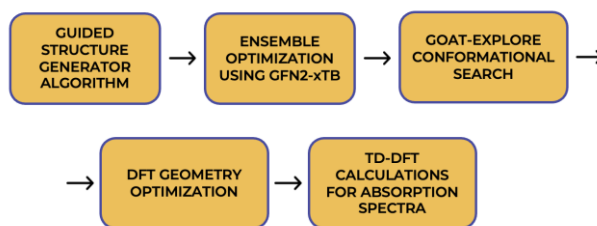


Figure 1 Scheme of the computational protocol applied.

References

- [1] Li H., Kang Z., Liu Y., Lee S.-T., *Journal of Materials Chemistry*, 2012, **22**, 24230.
- [2] Arcudi F., Đorđević L., Prato M., *Accounts of Chemical Research*, 2019, **52**, 2070.
- [3] Mintz K. J. et al., *Carbon*, 2021, **173**, 433.
- [4] Mocci F. et al., *Chemical Reviews*, 2022, **122**, 13709.
- [5] Margraf J. T., Strauss V., Guldi D. M., Clark T., *Journal of Physical Chemistry B*, 2015, **119**, 7258.
- [6] Sinitsa A. S., Lebedeva I. V., Popov A. M., Knizhnik A. A., *Journal of Physical Chemistry C*, 2017, **121**, 13396.
- [7] de Souza B., *Angewandte Chemie International Edition*, 2025, **64**, e202500393.

Exploring new thiophosphates solid state electrolytes through deep learning

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All-solid state batteries (ASSBs), have been proved to be an excellent alternative to liquid Li-ion technology. In comparison, ASSBs have several advantages [1-3], such as greater stability, better safety, and higher energy density. But they also have an intrinsic, still unsolved, problem caused by their solid nature, the lower ion mobility. Glassy-ceramic Lithium thiophosphates, LPS ($x\text{Li}_2\text{S}-(1-x)\text{P}_2\text{S}_5$) and LPSO, LPS oxygen doped, are among the most promising electrolytes materials, and by tuning their composition is possible to optimize their performance and achieve high ion conductivities, at least 10^{-3} S/cm to be competitive with liquid electrolytes. This is an extremely difficult task because the complicated anionic environment greatly affects the electrochemical properties, and we not yet know deeply why. As result the optimization of the composition process, to get the best electrolyte, requires laborious trial-and-error laboratory procedures. We can help make this process much quicker by using molecular modelling. Typically, computational approaches to electrochemistry involve ab-initio molecular dynamics (AIMD) methods, which despite their accuracy, are very slow and computationally intensive, compared to classical molecular dynamics (MD), which instead relies on parametric force fields (FF). Classical MD calculations on LPS and LPSO are, at the moment, difficult to perform because they require the development of a suitable FF whose analytical form is complicated because of the different states of chemical coordination that Li^+ assumes in the amorphous solid. Nevertheless, it is important for the electrochemical community to have access to a quick and efficient way to model electrolytes such as LPS and LPSO.

To leverage the advantages of both methods we used deep learning molecular dynamics [2-5] and generated a new deep learning force field (DLFF). The deep neural network has been trained using our ab-initio data, this way the DLFF has the high accuracy [6-8] of the ab-initio level chosen for the training set and, being parametric, a high efficiency (classical MD level). Using this DLFF, we have performed fast and accurate simulations on model systems beyond the actual limits of AIMD in size and time scales. This way we determined the electrochemical properties of different compositions of LPS and LPSO in a quick and accurate way, which was rarely achieved before. This approach is in order to make this technology competitive in a large-scale industrial environment.

References

- [1] Sun, Y.-K., ACS Energy Lett. 2020, 5, 3221–3223.
- [2] Zhang, Z. et al., Energy Environ. Sci. 2018, 11, 1945–1976
- [3] Grady, Z. A. et al., Front. Energy Res. 2020, 8.
- [4] Unke, O. T. et al., Chem. Rev. 2021, 12, 10142–10186.
- [5] Mo, Y. et al., Chem. Mater. 2012, 24, 15–17.
- [6] He, X. et al., npj Comput Mater 2018, 4, 1–9.
- [7] Wang, H. et al., Comp Phys. Comm. 2018, 228, 178–184.
- [8] Zhang, L. et al., Phys. Rev. Lett. 2018, 120, 143001.

Tailoring Lignin Particle Architecture via Levulinic Acid-Based Green Solvent Shifting

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The development of functional lignin particles (LPs) represents a fundamental challenge in the valorization of industrial byproducts through the lens of colloid science. In this study, the formation of LPs is controlled via a solvent-shifting process utilizing levulinic acid (LA) and its derivatives—specifically its ethyl ester (EL) and the ketal (K) obtained from EL and glycerol—as sustainable solvent media. The physicochemical driving forces governing the nucleation and growth of these colloids are systematically investigated to establish a correlation between solvent nature and the resulting supramolecular architecture.

It is demonstrated that the choice of solvent fundamentally modulates the internal organization of lignin macromolecules, specifically influencing the degree of π - π stacking between aromatic moieties. This molecular-level control translates into distinct morphological transitions: LA promotes the formation of irregular particle clusters (Figure 1a), whereas EL induces the assembly of compact well-defined spheres (Figure 1b), and the ketal derivative leads to the generation of planar fragments (Figure 1c). Such structural diversity is linked to the varying solubility parameters and the specific interactions between the lignin backbone and the solvent molecules during the anti-solvent addition. The characterization of these LPs reveals that the composite structure and high surface area achieved through LA-mediated synthesis result in enhanced functional properties, such as antioxidant capacity. Furthermore, the understanding of these assembly mechanisms is essential for governing the interfacial behaviour of lignin in multiphase systems. These tailored LPs could be employed as stabilizers for high-performance Pickering emulsions, platforms for the encapsulation of bioactive compounds, and as reinforcing agents in functional composite hydrogels based on polysaccharides such as alginate and chitosan. This work provides a robust framework for the design of bio-based soft materials with tunable properties for advanced interfacial applications.

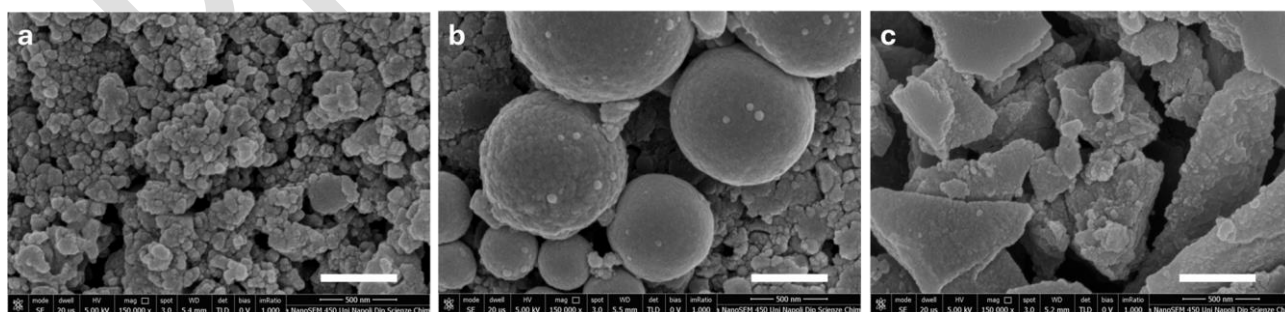


Figure 1. SEM micrographs at room temperature of the samples LA-LP (a); EL-LP (b); K-LP (c). The bottom part of each panel shows the operative parameters with scalebar (white line in the bottom right of the micrographs) fixed at 500 nm.

Ambient-Temperature 3D Printing of Crosslinked PS and PMMA-based Polymers

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Polystyrene (PS) and polymethyl methacrylate (PMMA) are widely used in structural and functional applications, yet their additive manufacturing remains highly constrained. Conventional Fused Deposition Modeling (FDM) relies on the extrusion of pre-polymerized thermoplastic filaments at elevated temperatures, which limits design freedom, energy efficiency, and the fabrication of crosslinked architectures. The objective of this work is to develop a versatile ambient-temperature extrusion approach for the 3D printing of crosslinked PS and methacrylate-based polymers with tunable mechanical properties.

High internal phase emulsions (HIPEs) possess the non-Newtonian rheological properties required for extrusion-based 3D printing techniques¹, properties that liquid monomers such as styrene and methylmethacrylate do not exhibit on their own. For this reason we employed oil-in-water HIPE inks composed of styrene and divinylbenzene, or methacrylate monomers, dispersed in an aqueous solution of dextran methacrylate (DexMA). During ink deposition, UV irradiation triggers the instantaneous curing of the continuous phase, forming a crosslinked hydrogel that ensures structural integrity. Subsequent thermal curing converts the oil phase into crosslinked polymers. This dual-curing strategy decouples shape retention from polymerization kinetics, enabling the printing of complex constructs at room temperature.

Compression tests revealed mechanical performance comparable, and in some cases superior, to benchmark FDM polymers such as ABS and PETG², demonstrating robust interlayer cohesion achieved through in-situ crosslinking. Additionally, multi-layered constructs based on methacrylate polymers were fabricated and investigated, showing that their mechanical response can be tuned by varying the relative softness and rigidity of the methacrylic layers. This approach opens new possibilities for energy-efficient and scalable additive manufacturing of advanced polymer architectures, offering broad control over material performance and structural complexity

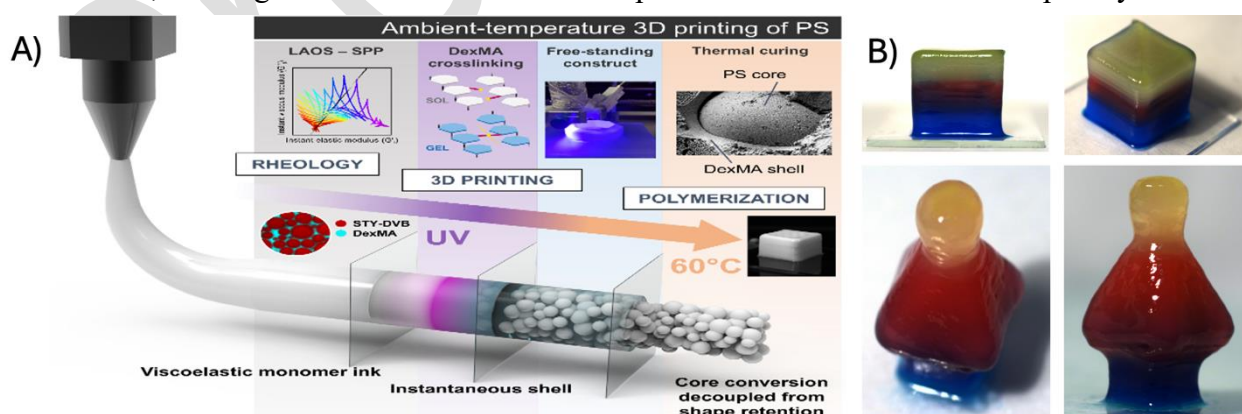


Figure 1. A) Overview of the printing strategy B) Three-layer multi materials constructs

References

- [1] Rosciardi V. et al. *Journal of Colloid And Interface Science*, 2026, **706**, 139571.
- [2] Kholil A. et al., *Journal of Physics: Conference Series*, 2022, 2377. 012008

Ultrafast Fluorescence of a Photo-Crosslinking Model, Interpreted by an Innovative Computational Approach

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Isolation of transient nucleoprotein complexes in their biological conformation is a challenging task: a promising technique is to induce in vivo crosslinking between the nucleic acid and the protein, by UV light. The photo-cyclization of 5-benzyluracil (5BU) to 1,2-indaneuracil has been proposed as a model reaction to study the mechanism of photo-crosslinking.¹ In competition with the reactive path, 5BU also exhibits an ultrafast radiative decay - probed by Fluorescence Up-Conversion (FIUC) – whose fastest component is debated to be due either to a decay from the upper excited states to S₁, or to a vibrational relaxation of the first excited state.² In this context, we present a theoretical study of the ultrafast photo-activated dynamics of 5BU in methanol, exploiting the framework of the DFT and TD-DFT. At the same time, we propose a new protocol to simulate FIUC spectra, making easier the comparison between simulation and experiment. From our previous work⁷ (which characterized the ground-state thermal equilibrium and the photophysics, via an ADMP⁴ ab-initio molecular dynamics exploiting the ONIOM⁵ QM/MM partition scheme and non-periodic boundary conditions⁶), we are aware of the presence of two conformers in equilibrium at room temperature and multiple excited states responsible for the absorption propaedeutic to the photocyclization, whose brightness depends by the conformation and microsolvation of 5BU. Starting from this knowledge, to give a molecular interpretation of the fluorescence signal, we conducted a non-adiabatic mixed quantum/classical molecular dynamic of 5BU in implicit (C-PCM) methanol, by adopting the Fewest-Switches Surface Hopping approach. The initial conditions were generated by sampling a quantum Wigner distribution for each of the two conformers and for each involved transition. The simulated time-resolved spectrum and the FIUC experiment have different time scales, since the first starts from the absorption regime and the latter, having an IRF of 300 fs,² starts from an already advanced point of the excited-state evolution of the system: our new protocol, based on the fit of the simulated spectral peaks, gave us a clear and direct comparison with the experimental data. We were thus able to simulate the transient emission spectrum; we then performed a vibrational analysis through an innovative protocol, based on the wavelet transform of time resolved generalized modes extracted from the trajectories. We thus detailed the molecular mechanisms underlying the formation of the high-energy emission band, the red shift of the low-energy band and the ultrafast component of the decay of both bands.

References

- [1] L. Zhang et al., *Biochem. Biophys. Res. Commun.*, 2004, **322**, 705.;
- [2] G. Sun et al., *Org. Lett.*, 2006, **8**, 681.
- [3] M. Valadan et al., *Phys. Chem. Chem. Phys.*, 2019, **21**, 26301.
- [4] S.S. Iyengar, *J. Chem. Phys.*, 2001, **115**, 10291.; H. B. Schlegel, *J. Chem. Phys.*, 2002, **117**, 8694;
- [5] T. Vreven et al., *J. Chem. Theory Comp.*, 2006, **2**, 815; N. Rega et al., *J. Phys. Chem. B*, 2004, **108**, 4210.
- [6] N. Rega et al., *Chem. Phys. Lett.*, 2006, **422**, 367.
- [7] G. Iuzzolino et al., *Phys. Chem. Chem. Phys.*, 2024, **26**, 11755.

Infrared-Activated Dynamic Crystals: Remote Motion in a Metal-Organic Framework

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Dynamic crystals are smart materials that respond to external stimuli with structural transformations that translate into shape and size changes, producing motion at the micrometer scale. They are promising candidates for soft microrobotics and memory devices and can be built from organic, biological or inorganic components. [1,2]. Metal-Organic Frameworks (MOFs) are porous crystalline materials that have demonstrated structural and morphological flexibility. [3-6]

Here we demonstrate the actuation of MOFs triggered by low-energy infrared (IR) radiation from a low-power laser (~100 mW) (Figure). The stimulus is user-tunable, spatially addressable, and potentially tissue-penetrating compared with commonly employed triggers. IR absorption arises from lanthanide ions forming the coordination nodes, producing a temperature increase that drives the phase transition. Notably, the introduction of additional lanthanide dopants enables upconversion energy transfer that activates non-radiative relaxation pathways, generating further localized heating and allowing the phase transition to occur at lower IR power densities.

The phase transitions induce microscopic motions, including crystal contraction, morphology changes, and jumping. These responses are reversible and repeatable over multiple cycles. The structural transformations underlying the dynamics were elucidated using complementary spectroscopic techniques, including in situ single-crystal X-ray diffraction under irradiation.

This strategy can be integrated into several MOF architectures, opening new opportunities for remotely controlled, low-energy crystal actuators.

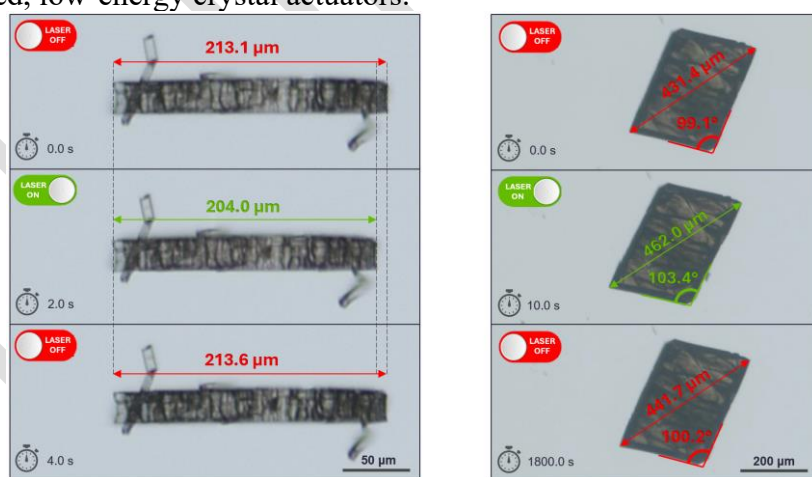


Figure. Optical microscopy images of lanthanide-based Metal-Organic Frameworks with and without IR laser irradiation.

References

- [1] P. Naumov et al, *J. Am. Chem. Soc.* 2020, 142, 31, 13256-13272
- [2] M. Irie et al, *Nature* 2007, 446, 778-781
- [3] S. Kitagawa et al, *Nat. Chem.* 2009, 1, 695-704
- [4] O. Yaghi et al, *ACS Cent. Sci.* 2020, 6, 8, 1255-1273
- [5] R. Robson et al, *J. Am. Chem. Soc.* 1989, 111, 15, 5962-5964
- [6] M. C. di Gregorio et al, *Nat. Commun.* 2020, 11, 380

Chalcogenide perovskites: synthesis, characterization and study of stability of novel materials for photovoltaic applications

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Chalcogenide perovskites such as BaZrS₃ have emerged in recent years as a promising alternative to metal halide hybrid perovskites for next generation photovoltaic cells, thanks to their superior thermal and chemical stability, combined with high absorption coefficients in the visible range and band gap values especially suited for application in tandem solar cells. However, the large majority of the studies reported on chalcogenide perovskites are performed by means of computational methods, due to the harsh conditions typically used for their synthesis, so there is a remarkable lack of experimentally determined physicochemical properties for this class of materials.

In this connection, we describe herein a recently developed strategies for the synthesis of BaZrS₃ and BaHfS₃, making use of milder conditions than those of previously reported methods, namely a temperature as low as 500 °C and the absence of hazardous reagents such as H₂S or CS₂, which has been also applied successfully to the preparation of solid solutions of the two materials, synthesized for the first time [1]. BaZrS₃ and BaHfS₃ were found to be miscible in the entire compositional range, and the structural and optoelectronic properties of their solid solutions were studied both experimentally and computationally [2].

Moreover, thermal stability and decomposition at high temperature of BaZrS₃ were investigated through thermal analysis and Knudsen effusion mass spectrometry, and the heat capacities at low temperatures of BaZrS₃ and BaHfS₃ were measured for the first time, thus allowing the determination of absolute entropies. These, in turn, were used to make predictions regarding the intrinsic and extrinsic thermodynamic stability of these materials [3].

Finally, motivated by computational studies suggesting a lowering of the band gap value of sulfide perovskites such as BaZrS₃ upon doping with selenium [4], and by the almost total lack of experimental reports in this sense, we synthesized several BaZrS_{3-x}Se_x solid solutions, and performed a preliminary characterization through powder XRD, SEM-EDX, UV-visible and Raman spectroscopy. We found the retention of the perovskite structure up to a selenium concentration of 21.4%, while for higher concentrations other phases, different from the perovskite one, are formed. Furthermore, a linear decreasing trend of the band gap with increasing selenium concentration was observed, thus confirming theoretical predictions and revealing selenium doping as a useful strategy for band gap tuning.

This contribution is therefore aimed at providing an overview of the potential of chalcogenide perovskites and a summary of the recent advancements in this field achieved by our group.

References

- [1] Romagnoli, L.; Ciccioli, A.; Dale, P. J.; Yetkin, H. A.; Panetta, R.; Latini, A. *J. Am. Ceram. Soc.* 2024, **107**, 698–703..
- [2] Romagnoli, L.; Motta, A.; Latini, A. *ChemPhysChem* 2025, **26**, e202500466.
- [3] Gibson, A.; Ciccioli, A.; Parkinson, N.; Testa, R.; Di Conzo, C.; Rossi, M.; Latini, A.; Vecchio Cipriotti, S.; Yetkin, H. A.; Dale, P. J.; Woodfield, B.; Romagnoli, L. *J. Phys. Chem. C*, accepted.
- [4] Odeh, Y.M.; Azar, S.M.; Al-Reyahi, A.Y.; Mousa, A.A.; Jaradat, E.K.; Al Aqtash, N. *AIP Adv.* 2023, **13**, 075118

Synergistic electrostatic and π - π stacking interactions triggering Doxorubicin-Alginate supramolecular gels

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Doxorubicin hydrochloride (DX) is one of the most widely used drugs in anticancer therapies, though its clinical use is limited by serious side effects, mainly cardiotoxicity and bone marrow suppression. One strategy to reduce its systemic toxicity is through the encapsulation in polymeric or lipid matrices to achieve targeted delivery into tumour tissues. DX has a distinctive chemical structure, with a planar anthraquinone unit and a unique spatial organization of hydrogen bond donor/acceptor groups, which gives fluorescent properties and Circular Dichroism (CD) activity. One of its peculiarities is its capability to self-associate into dimers. Moreover, at high drug concentrations (> 10 mM) and ionic strength, DX can undergo a supramolecular polymeric self-assembly process leading to the formation of a characteristic gel phase, DX_{GEL}, not observed for other anthracycline molecules [1,2]. The unique gelling properties of DX derive from the particular spatial arrangement of its hydrogen-bond groups [2,3]. However, DX_{GEL} is easily disrupted by dilution, necessary to reach DX therapeutic concentration. As shown with polystyrene sulfonate (PSS), an anionic polymer can promote stable DX self-assembly [4]. We have also demonstrated that pH can be used to control the interaction between the drug and other components, by modulating their charge and solubility [5]. Interestingly, in a recent study [6], sodium alginate (ALG) was shown to interact with a cyanidin dye, leading to a marked enhancement of the system's CD properties due to supramolecular induced chirality; in that case as well, pH was identified as a fundamental parameter influencing the interaction. Based on this observation, ALG – a biocompatible and pH-sensitive polymer – is proposed as an alternative template for the formation of supramolecular nanogels complexed with doxorubicin hydrochloride, using the pH as a trigger to control the interactions, stability, and morphology of the nanogels in physiological and tumour-like environments.

References

- [1] M. Giomini, *Biophys. Chem.* 45 (1992) 31–40
- [2] E. Tasca, *Chem. Eur. J.* 24 (2018) 8195-8204
- [3] E. Tasca, *Colloids and Surfaces A* 577 (2019) 517–522
- [4] C.G. Chen, *Phys. Chem. Chem. Phys.* 24 (2022) 12027-12035
- [5] L. Desiderio, *J. Colloid Interface Sci.* 664 (2024) 972-979
- [6] N. Chotechuang, *Carbohydrate Polym.* 315 (2023) 120957

Design of eugenol-conjugated amphiphilic polymers for bioactive self-assembled nanoparticles

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Amphiphilic polymers are promising platforms for nanoscale drug delivery due to their ability to self-assemble in aqueous media and encapsulate hydrophobic molecules. In this work, eugenol (4-allyl-2-methoxyphenol), a naturally derived compound with antioxidant, antimicrobial, and anti-inflammatory properties¹, was conjugated to polymers synthesized via RAFT polymerization², namely poly(2-hydroxyethyl methacrylate) (PHEMA) and the cationic block copolymer PDMAPMA₁₁₆-b-PHEMA₇₆. The functionalization was designed to impart intrinsic bioactivity and modulate amphiphilicity, promoting self-assembly in aqueous solution. The resulting nanostructures were used to encapsulate Coumarin-6 (Cou), widely used as a model hydrophobic compound³ during the self-assembly process. The presence of the cationic PDMAPMA block significantly affected both encapsulation and antioxidant properties. In particular, the cationic copolymer showed lower encapsulation efficiency, likely due to the solvated charged groups promoting a more extended conformation and limiting the formation of compact hydrophobic domains. Conversely, this structure enhances the accessibility of eugenol moieties to DPPH radicals, resulting in higher antioxidant activity compared to PHEMA. Overall, this approach enables the development of multifunctional nanoplateforms with self-assembly capability, colloidal stability, and intrinsic bioactivity for potential biomedical applications.

References

- [1] M. Di Consiglio, E. Sturabotti, B. Brugnoli, A. Piozzi, L. M. Migneco, I. Francolini. *Polymer Chemistry*, 2023, 14, 3, 432-442.
- [2] A. Gregory, M. H. Stenzel. *Progress in Polymer Science*, 2012, 37, 1, 38-105.
- [3] P. L. Jacob, B. Brugnoli, A. Del Giudice, H. Phan, V. M. Chauhan, L. Beckett, R. B. Gillis, C. Moloney, R. J. Cavanagh, E. Krumins, M. Reynolds-Green, J. C. Lentz, C. Conte, V. Cuzzucoli Crucitti, B. Couturaud, L. Galantini, I. Francolini, S. M. Howdle, V. Taresco. *Journal of Colloid and Interface Science*, 2023, 641, 1043-1056.

Investigating the structural properties of a novel inorganic Low-Transition Temperature Mixture

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The search for new liquid media capable of meeting the requirements for efficiency, cost-effectiveness, sustainability, and low toxicity is a critical area of current chemistry research.

In this context, Low-Transition Temperature Mixtures (LTTMs) - a broad class that includes important examples such as ionic liquids [1] and DES (Deep Eutectic Solvents) [2] - have emerged as promising solvents. Among their applications, their use as Phase Change Materials (PCMs) for thermal energy storage is particularly relevant [3]. In particular, inorganic salt hydrates show interesting characteristics such as higher thermal conductivity and higher volumetric storage density compared to organic PCMs. They are often studied as mixtures, with the aim of reducing their transition temperature [3,4]. Studying the structural properties of inorganic salt hydrate mixtures can help to elucidate their macroscopic behaviour and to understand the underlying interactions that lead to the formation of the liquid mixture.

In this work we introduce a new inorganic LTTM, formulated from a combination of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. By employing spectroscopic and computational analyses, it was possible to characterize the structural properties of the system. As is widely known in the literature, physicochemical properties of LTTMs can be tailored by using cosolvents, often offering significant advantages in terms of cost and efficiency. For this reason, the effects of adding excess water at different concentrations were also investigated.

The metal speciation has been probed with X-ray Absorption Fine Structure (XAFS) experiments performed with synchrotron light, providing insights also into Zn^{2+} , an ion not easily detectable by conventional techniques [5]. Principal Component Analysis (PCA) was used to determine the number and concentration of the Zn^{2+} complexes in the $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}:\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}:\text{water}$ mixtures with different 1:1:water molar ratios. Subsequently, the calculation of theoretical signals and the fitting of the experimental data were performed for the extracted PCs.

The XAFS results were then combined with conventional UV-Vis spectroscopy, confirming the previous findings about Co^{2+} speciation. The medium and long-range structures of the system were investigated with X-ray scattering, again obtained with synchrotron light. Experimental results were compared with and validated by classical molecular dynamics simulations of the liquid phase, showing a good agreement between experiment and theory in the description of a highly structured liquid. The multi-perspective approach used in this research provides a detailed and comprehensive understanding of the system, offering valuable insights into its potential technological applications.

References

- [1] Lei Z., Chen B., Koo Y.M. and MacFarlane, *Chem. Rev.*, **2017**, 117(10), 6633-6635.
- [2] Smith E. L., Abbott A. P. and Ryder K. S., *Chem. Rev.*, **2014**, 114(21), 11060-11082
- [3] Pielichowska K., Pielichowski K., *Prog. Mater. Sci.*, **2014**, 65, 67-123.
- [4] Xie, N. et al. *Appl. Sci.*, **2017**, 7 (12), 1317.
- [5] Fratello F. et al., *J. Phys. Chem. Lett.*, **2022**, 13(24), 5522-5529.

Amphiphilic Polymers as Platforms for Antimicrobial Peptide Delivery: Co-Assembly and Nanostructure Formation

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Antimicrobial peptides (AMPs) are naturally occurring cationic amphiphilic molecules that have attracted increasing attention as potential alternatives to conventional antibiotics due to their broad-spectrum antimicrobial activity and their ability to disrupt microbial membranes through electrostatic and amphiphilic interactions.[1] Because they act at the membrane level, bacteria have a limited ability to develop resistance against them. However, their biomedical application is often limited by susceptibility to enzymatic degradation, possible cytotoxicity, and poor stability under physiological conditions. To overcome these limitations, significant efforts have focused on engineering AMP-derived systems and incorporating them into polymeric carriers to enhance stability and improve therapeutic performance.

Effective bacterial membrane disruption requires a balance between cationic and hydrophobic domains. While positively charged residues promote electrostatic interactions with negatively charged bacterial envelopes, hydrophobic segments facilitate insertion into lipid bilayers.

In this work, amphiphilic polymers were investigated as transport platforms for antimicrobial peptides. The strategy of polymer-peptide co-assembly in aqueous media was explored by appropriately tuning the amphiphilicity of the assembling components. The hybrid nanostructures were obtained via nanoprecipitation and characterized by dynamic light scattering under different conditions, including pH and presence of cosolvents. Poly(glycerol adipates) (PGA) and amphiphilic polydiacetylenes (PDA) will be explored as tunable amphiphilic systems. PGA is a degradable and bio-based polymer widely used for drug delivery.[2] Amphiphilic PDAs have stimuli-responsive optical properties and ability to form vesicles or micelles thanks to the presence of a polar head and hydrophobic alkyl chains.[3] Results showed how this strategy represents a promising approach for generating hybrid materials with potential applications in antimicrobial systems and biomaterials.

References

- [1] Zhao H., Sun J., Cheng Y., Nie S., Li W. *J. Mater. Chem. B*, 2025, **13**, 1518.
- [2] Jacob P. L., Brugnoli B., Del Giudice A., Phan H., Chauhan V. M., Beckett L., Gillis R. B., Moloney C., Cavanagh R. J., Krumins E., Reynolds-Green M., Lentz J. C., Conte C., Cuzzucoli Crucitti V., Couturaud B., Galantini L., Francolini I., Howdle S. M., Taresco V. *J. Colloid Interface Sci.*, 2023, **641**, 1043.
- [3] Brugnoli B., Axioti E., Jacob P. L., Berfi N. A., Lei L., Couturaud B., Chauhan V. M., Cavanagh R. J., Galantini L., Francolini I., Taresco V. *Macromol. Chem. Phys.*, 2025, **24**, e00259.

Computational approaches provide a reliable atomic-level view of full-length LZTR1 and its functional partnerships

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Recent studies have identified the proteins KCTD17 (Potassium channel tetramerization domain-containing protein 17) and LZTR1 (Leucine zipper-like transcription regulator 1) as important modulators of MAPK signaling and RAS protein stability. Both proteins function as substrate adaptors within Cullin3-based E3 ubiquitin ligase complexes. KCTD17 promotes cellular proliferation and migration by inducing the polyubiquitination and degradation of LZTR1. In turn, LZTR1 facilitates the polyubiquitination and subsequent proteasomal degradation of RAS proteins. The dysregulation of the KCTD17-LZTR1 interaction has been associated with tumour cell growth, as KCTD17 overexpression is linked to enhanced RAS stabilisation via LZTR1 degradation^[1-5]. Despite the biological importance of LZTR1 and its partnerships within Cullin3-based E3 ubiquitin ligase complexes, the structural basis of LZTR1 interactions with KCTD17 and Cul3 remains poorly understood, and high-resolution structural data are currently lacking.

In this context, this study aims to characterize the structural and dynamic properties of LZTR1 structure and partnership, combining predictive approaches, such as AlphaFold predictions, with extensive molecular dynamics (MD) simulations.

Predictions of the LZTR1-Cul3 complex have shown that LZTR1 can bind Cul3 via one of its two BTB domains, while the Kelch domain is deputed to substrate binding (RAS proteins) for ubiquitination. On the other hand, a significant interaction between KCTD17 and LZTR1 has also been predicted. The overall and individual stability of these models and the specific interactions at the binding interfaces have been extensively evaluated. In particular, key inter-molecular contacts were characterized to define the structural determinants of complex formation and stability. Preliminary MD data indicate that these complexes maintain an overall stability in the simulated timescale. Altogether, this approach provides mechanistic insights into their functional organization and suggests potential strategies to modulate RAS signaling.

References

- [1] Bigenzahn J. W. et al. *Science*, 2018, **362**, 1171-1177.
- [2] Steklov M. et al. *Science*, 2018, **362**, 1177-1182.
- [3] Jung Y. H. et al. *Clinical and Molecular Hepatology*, 2024, **30**, 895-913.
- [4] Esposito L., Balasco N. et al. *Biomolecules*, 2021, **11**, 1862.
- [5] Balasco N. et al. *Int. J. Mol. Sci.*, 2024, **25**, 1881.

Computational modeling of tryptophan fluorescence in proteins

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Tryptophan fluorescence is a very useful probe of protein conformational changes and ligand binding, thanks to the large transition dipole associated with its electronic transitions and its strong sensitivity to the surrounding environment. However, the prediction of fluorescence spectra remains challenging, especially because of the difficulty of evaluating excitation energies of the relevant excited states in realistic environments. In this study, we adopt a theoretical-computational method to predict fluorescence spectra and maximum emission wavelengths of tryptophan in proteins.

Our goal is to develop a useful tool to assist the assignment of spectral signals in protein fluorescence emission spectra, as well as to improve the understanding of the interactions underlying these different Stokes shifts.

The theoretical framework adopted is the Molecular Dynamics-Perturbed Matrix Method (MD-PMM)¹, which efficiently combines molecular dynamics simulations of the whole protein in water with high-level quantum-mechanical calculations on a small subsystem, the quantum center (QC). This allows extensive sampling of the electronic properties of the QC in a realistic protein and water environment. This approach has already proven suitable for the prediction of both fluorescence spectrum and fluorescent decay of indole in water². Accordingly, we employed indole as the QC within the protein environment.

The method was tested on 18 single-tryptophan proteins, for which experimental studies were available. While predicted λ_{max} values were slightly blue-shifted relative to experiment, they successfully reproduced the expected red shift from apolar to polar environments around tryptophan. Ongoing work is focused on improving the sampling of the selected proteins and analyzing the environment properties responsible for the differential stabilization of the bright excited state of indole.

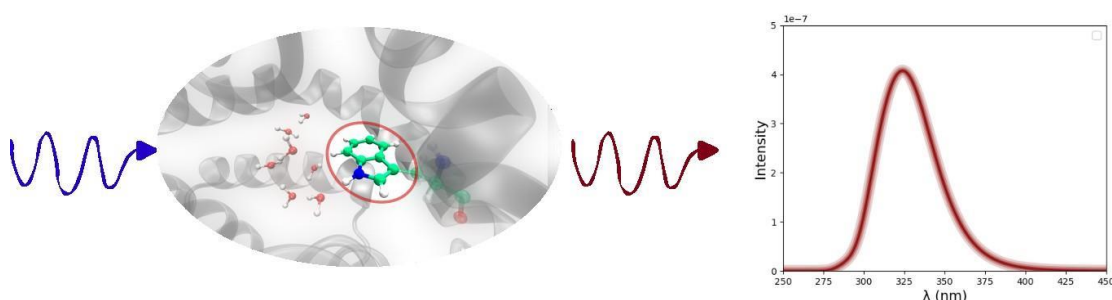


Fig 1: Representation of the indole QC inside the protein/water environment and typical predicted emission spectrum.

References

- [1] Amadei, A., and Aschi, M. *RSC Adv.*, 2018, 8(49), 27900-27918.
- [2] Chen, G.C.; Giustini, M.; D'Abramo, M.; Amadei, A. *J. Chem. Theory Comput.* 2023, **19**(13), 4114–4124.

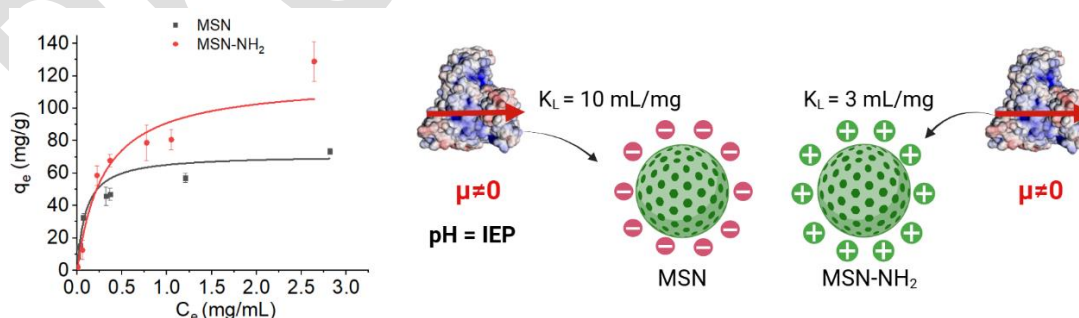
Unveiling protein adsorption: bovine serum albumin (BSA) interactions with silica nanoparticles (MSN) at the isoelectric point

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Understanding the interactions between serum proteins, such as bovine serum albumin (BSA), and drug carriers, including mesoporous silica nanoparticles (MSN), is essential for elucidating the protein corona effect. The formation of a protein corona critically influences the biological fate of nanocarriers, depending on the nature of the adsorbed proteins (opsonins versus dysopsonins) [1]. Protein adsorption is commonly investigated at physiological pH (7.4), where both BSA (isoelectric point 4.7-4.9) and silica nanoparticles are charged [2]. Under these conditions, according to DLVO theory, adsorption is governed by a complex interplay between electrostatic interactions, arising from electric double layer (EDL) overlap, and dispersion (van der Waals interactions) forces. In this work, we investigate BSA adsorption onto bare mesoporous silica nanoparticles (MSN) and amino-functionalized nanoparticles (MSN-NH₂) at the protein isoelectric point (pH $\approx$ 4.8), a condition that minimizes net protein charge and allows non-electrostatic interactions to be more clearly probed. Adsorption isotherms were obtained using UV-Visible spectroscopy and Quartz Crystal Microbalance with dissipation monitoring (QCM-D). In the concentration range 0.03 – 3 mg mL⁻¹, BSA adsorption follows a Langmuir model. UV-Vis measurements yield affinity constants (K_L) of 10 ± 2 mL mg⁻¹ for MSN and 3 ± 1 mL mg⁻¹ for MSN-NH₂, with maximum adsorption capacities ($q_{\max}$) of 71 ± 4 mg g⁻¹ and 117 ± 15 mg g⁻¹, respectively. QCM-D measurements corroborate these findings, revealing higher adsorbed amounts on MSN-NH₂ compared to MSN (725 versus 678 ng cm⁻²). To rationalize the observed differences in adsorption behavior, a theoretical framework based on the BSA dipole moment is proposed, integrating computational modelling (Visual Molecular Dynamics -VMD and pdb2pqr) with experimental ζ -potential measurements. The results suggest that, in addition to dispersion forces, protein dipolar interactions play a key role by influencing BSA orientation during the adsorption, ultimately governing protein-nanoparticle affinity at the isoelectric point.



References

- [1] Xiao, Q.; Zoulikha, M.; Qiu, M.; Teng, C.; Lin, C.; Li, X.; Sallam, M. A.; Xu, Q.; He, W. *Adv. Drug Delivery Rev.* **2022**, *186*, 114356.
- [2] Ballicu, A.; Meloni, G. M.; Farci, M.; Tocco, D.; Piludu, M.; Parsons, D. F.; Carucci, C.; Jachimska, B.; Salis, A. *Langmuir* **2026**, *42* (13), 9170–9182.

Multiscale approach to the calculation of kinetic rates of elementary reactions in condensed phases

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Predicting macroscopic kinetic constants from molecular parameters in condensed phases requires accounting for electronic properties, environment effects and transport dynamics. Such a complex problem covering different spatial scales can be approached with a multiscale computational approach able to treat the different aspects mentioned at proper approximated levels of accuracy and account for their coupled influence on the reaction kinetics. It is especially important to handle cases when diffusion and reactivity operate on comparable timescales, condition which is found, for example, in enzymatic catalysis. The objective of this work is to develop and validate such a multiscale framework in which hybrid quantum/classical molecular dynamics simulations are employed to access the rates to overcome free energy barriers along the reaction coordinate(s), and a stochastic diffusion-reaction equation couples quantum mechanical and transport properties. Here, firstly a simple benchmark model for S_N2 reactions is used to provide the basic framework and its applicability. Secondly, the extension to the molecular interpretation of Michaelis-Menten enzyme kinetics is discussed.

Methods. To treat the bimolecular S_N2 kinetics, inspired by the approach of Severin and Moro [1], we build a reaction-diffusion model in which the reactive species are point particles and the stochastic variable describing mass transport is the mutual distance between the two reactants. In the diffusion-reaction equation, the diffusive term is governed by a diffusion coefficient calculated via hydrodynamic modeling, and a mean-field interaction potential obtained via steered molecular dynamics [2]. The reactive term is a master equation parameterized with microscopic quantum rate constants [3,4]. As a benchmark, we study the S_N2 nucleophilic substitution $\text{Cl}^- + \text{CH}_3\text{Br} \rightleftharpoons \text{Br}^- + \text{CH}_3\text{Cl}$. The model can be solved exactly by calculating the eigenvalues of the time evolution operator. We also show that equivalent results can be obtained from Brownian dynamics (BD) trajectories with random jumps between the reactants and products states occurring with probabilities related to the quantum rate constants. The solution strategy based on BD trajectories is then extended to enzymatic systems by incorporating orientational and conformational degrees of freedom. The enzyme is treated as a rigid rotor with interaction sites distributed on a spherical surface, while the substrate is a non-rigid sphere described by translation, rotation, and one internal coordinate.

Results. For the S_N2 system, the model accurately reproduces macroscopic kinetic constants with the proper units naturally arising from the treatment [5]. The usage of BD trajectories is validated across a wide dynamic range of transport/reaction time scales. The extension to enzyme kinetics demonstrates the scalability of the approach and the ability to interpret at atomistic level the Michaelis-Menten mechanism, opening to the molecular design of enzymes.

References

- [1] G. Moro et al. J. Chem. Phys. 114 (2001) 4565.
- [2] D. Case et al. J. Chem. Inf. Model. 63 (2023) 6183.
- [3] M. Bortoli et al. Phys. Chem. Chem. Phys. 24 (2022) 7474.
- [4] J. Campeggio et al. Phys. Chem. Chem. Phys. 22 (2020) 3455.
- [5] L. Moriconi et al J. Chem. Phys. 163, (2025) 034104

Asymmetric Surfactants for the Synthesis of Chiral Gold Nanorods

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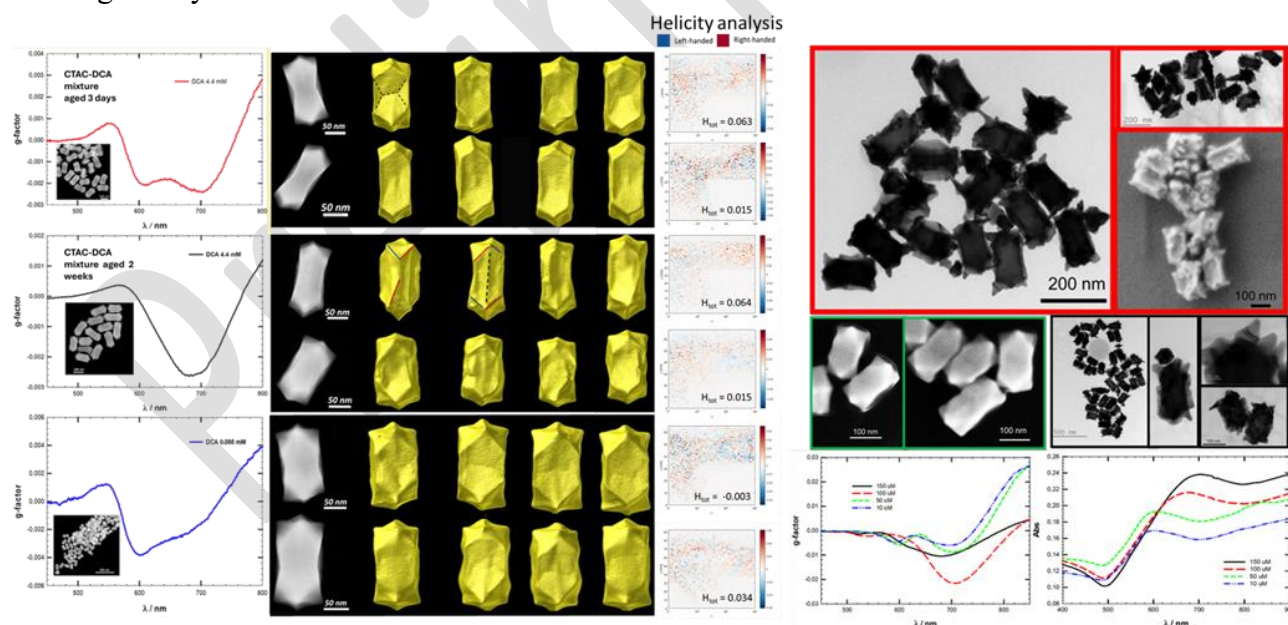
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Colloidal synthesis of chiral gold nanostructures is largely based on the use of chiral molecules that can induce asymmetric patterning to growing nanocrystals either by specifically binding to their surface [1] or by promoting the formation of helically structured micellar semi-hard templates [2]. Generally, chiral agents formed by molecules with local specific asymmetric centers are used (like amino acids with one or two asymmetric carbons) or compounds with conformational (or axial) chirality like binole or binamine. We report here synthesis of chiral gold nanorods exploiting molecules with a complex extensive chirality. Extensive chirality allows these molecules to direct the synthesis to asymmetric particles having different morphologies, ranging from a pasteur like facial chirality, to chiral spyky gold nanorods depending on the conditions used. Along with different morphologies different chiroptical responses are obtained. The hybrid inorganic-organic systems are investigated using small-angle x-ray scattering (SAXS), UV-vis absorption and circular dichroism (CD). The obtained inorganic nanoparticles are structurally characterized by transmission electron microscopy 2D imaging and tomography. Optical properties of the inorganic nanoparticles are investigated by circular dichroism measurements.



References

- [1] B. Ni et al., Adv. Mater. 2023, 35, 2208299.
- [2] González-Rubio et al., Science 368,1472 (2020)

Theme C - Analytical Chemistry

Preliminary

Dichloromethane as an Effective Alternative for Microplastics Sample Pre-Treatment in Complex Airborne Matrices

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In recent years, growing evidence of the widespread presence of microplastics and their potential impacts on human health has driven increasing scientific interest in their analysis across different matrices. While early research primarily focused on natural environments, attention has more recently expanded to indoor settings, particularly occupational environments. In many workplaces—such as those involving the production or processing of plastic materials, or high-abrasion mechanical activities—airborne polymer particles can be generated. In these complex and highly heterogeneous scenarios, risk assessment requires specific attention to the inhalable fraction, which represents the main route of worker exposure and is still affected by significant methodological and analytical challenges.

Sample pre-treatment represents a critical step in the analytical workflow, as it must ensure the selective removal of interfering substances without compromising the physical and chemical integrity of microplastics. To this end, optimized protocols combining density separation, controlled chemical digestion, and contamination prevention strategies were developed. Particular attention was devoted to minimizing secondary contamination through the adoption of rigorous precautionary measures, including the use of thoroughly cleaned glassware, dedicated sampling materials, procedural blanks, and appropriate laboratory clothing, thereby ensuring the reliability and quality control of the analytical data.

In this context, the present work aimed to optimize the use of dichloromethane as an alternative to conventional flotation and digestion approaches, both for cleaning real matrices from organic components and for extracting additives contained within microplastics. The extracted additives were identified and characterized by GC-MS, and the reliability of the optimized procedure was evaluated through recovery tests to assess its efficiency and accuracy. To verify that dichloromethane does not exert an aggressive effect on polymer particles, but rather selectively removes organic interferences, specific tests were carried out using μ -FTIR and particle size analysis. The results demonstrated that the treatment does not alter either the chemical composition or the dimensional characteristics of the microplastics, confirming the suitability of the solvent for analytical applications on real matrices.

References

- [1] Zhang X, Yu C, Wang P, Yang C. Microplastics and human health: unraveling the toxicological pathways and implications for public health. *Front Public Health*. 2025;13:1567200. Published 2025 Jun 18.
- [2] Gomiero A, Skogerbø G. From waste to workplace: Airborne microplastics and endotoxins in an indoor industrial environment. *Int J Hyg Environ Health*. Published online March 21, 2026.

A novel analytical approach for the pre-treatment and identification of airborne microplastics

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Microplastics (MPs) are solid plastic particles composed of mixtures of polymers and functional additives, ranging in size from 1 μm to 5 mm, and have been detected in a wide range of environmental and biological matrices. While extensive research has focused on MPs in natural ecosystems, the atmospheric compartment remains comparatively underexplored, particularly indoors, where individuals spend up to 90% of their time and are directly exposed to airborne MPs via inhalation [1]. Although MPs are widely recognized as emerging contaminants, growing scientific concern has highlighted several key knowledge gaps. In particular, no standardized operational protocols (SOPs) currently exist for their sampling, pretreatment, and analysis, which hampers comparability across studies. Moreover, the identification and attribution of emission sources remain a challenge, yet it is essential for developing effective mitigation strategies to reduce their impact on both human health and the environment [1].

In this context, the aim of this study is to develop an integrated multi-analytical and correlative approach for the characterization of airborne MPs in occupational environments. The selected workplace is a water bottling plant, where airborne particulate matter was collected on polytetrafluoroethylene (PTFE) and polycarbonate (PC) filters at different work sites. To isolate MPs from the PTFE filters and minimize environmental interferences, a pretreatment method based on oil-extraction was developed, exploiting the oleophilic properties of MPs [2]. This represents a faster, more versatile, and environmentally friendly alternative to conventional density separation techniques. For comprehensive characterization, a multi-technique analytical strategy was employed, combining field emission scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (FE-SEM-EDS) for morphological analysis with spectroscopic techniques (micro-FTIR and micro-Raman) for chemical identification. This strategy is further strengthened by a correlative spectroscopic approach applied to the same particles, enhancing result reliability and providing complementary information on polymer composition and associated plastic additives (e.g., pigments). The developed pretreatment method also addressed some of the limitations typically associated with spectroscopic techniques, such as particle size constraints and fluorescence effects, improving signal resolution and interpretability. The correlative spectroscopic approach enabled the identification of several polymers, including polyethylene terephthalate (PET), cellophane, and textile fibers, as well as pigments such as diarylide yellow (PY83) and indigo dye (NB1). In addition, FE-SEM-EDS analysis revealed typical MP morphologies, including fibers, films, fragments, and flakes. Overall, the proposed multi-analytical and correlative protocol demonstrates high effectiveness for the characterization of airborne MPs and may contribute to the development of standardized analytical procedures in this emerging field.

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References:

- [1] Campanale C., et al.; *Building and Environment*, 2026, 297:114567
- [2] Rosso B., et al.; *Environmental Pollution*, 2023, 328:120889

Rapid Evaluation of Particulate Matter Oxidative Activity via Electrochemically Accessible Capacity: A Bioelectrochemical Approach

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Particulate matter (PM) contains redox-active components capable of inducing oxidative stress through multiple mechanisms, including antioxidant depletion, reactive oxygen species (ROS) generation, and redox cycling. Conventional acellular assays such as dithiothreitol (DTT), ascorbic acid (AA), and dichlorofluorescein (DCFH) probe specific aspects of PM oxidative activity, but are typically limited by probe-specific chemistry, lack of temporal resolution, and partial mechanistic coverage.

Here, we present a bioelectrochemical platform based on a cytochrome c–modified electrode that enables real-time quantification of electron transfer between a reducing electrode and oxidizing species in PM extracts. The resulting signal is expressed as electrochemically accessible capacity (EAC), quantifying the intrinsic electron-accepting capability of PM. EAC is not a direct measure of biological effect; rather, it captures a fundamental physicochemical property that is biologically relevant, as it reflects the ability of PM to compete with endogenous redox systems such as Glutathione and NADPH, potentially driving redox imbalance.

In parallel, H₂O₂ additions provide a ROS-equivalent response describing matrix-dependent catalytic behaviour rather than direct ROS production. Compared with DTT, AA, and DCFH assays, EAC captures a broader pool of redox-active species, operating upstream of specific biochemical pathways. The combined metrics enable discrimination between electron-accepting capacity, antioxidant depletion, and ROS-generating processes, providing a rapid and mechanistically informative framework for PM oxidative activity.

References

- [1] S. Duangthaijornsuk, E.J. Farrell, A.C. Alba-Rubio, P. Zelenay, D.S. Kim, *Biosensors*. **11** (2021).
- [2] K.E. Berg, K.M. Clark, X. Li, E.M. Carter, J. Volckens, C.S. Henry, *Atmos. Environ.* **222** (2020) 117132.
- [3] M.P. Romano, M.G. Lionetto, A. Mangone, A.R. De Bartolomeo, M.E. Giordano, D. Contini, M.R. Guascito, *Anal. Chim. Acta*. **1206** (2022) 339556.
- [4] C.M. Silveira, R. Zumpano, M. Moreira, M.P. de Almeida, M.J. Oliveira, M. Bento, C. Montez, I. Paixão, R. Franco, E. Pereira, M.G. Almeida, *ChemElectroChem*. **6** (2019) 4696–4703.
- [5] E. Vaccarella, L. Massimi, S. Canepari *Science of the Total Environment* **965** (2025) 178651

Characterization of Particulate Matter Emissions from Fuels Used in Beekeeping Smoking Practices

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Biomass combustion is a major source of particulate matter (PM) [1]. While emissions from residential and industrial biomass burning have been widely studied, limited attention has been given to smoking applications used in beekeeping, where smoke is routinely generated to calm bees during hive management. These emissions may represent a relevant but underexplored source of exposure for beekeepers. The aim of this study is to compare particulate emissions from different fuels commonly used in beekeeping smokers and to assess their emission characteristics and potential health implications.

Representative fuels, including wood pellets, compressed fuels, jute, paper, and cardboard, were investigated under controlled laboratory conditions. The elemental composition of both raw materials and emitted particulate matter was determined by inductively coupled plasma mass spectrometry (ICP-MS) following collection using electric smoker and personal air-sampling pumps equipped with mixed cellulose ester (MCE) filters. Real-time particulate matter monitoring and high-resolution field emission scanning electron microscopy (HR-FESEM) were used to characterize PM fractions (PM₁, PM_{2.5}, PM₁₀) and particle morphology.

Marked differences in particulate emissions were observed across fuel types. Pellet fuels showed higher PM₁/PM_{2.5} ratios, indicating a predominance of fine particles, whereas processed cellulosic materials exhibited broader size distributions, highlighting the influence of fuel structure on particle formation mechanisms.

Elemental analysis revealed the presence of several potentially toxic elements in both fuels and emitted particulate matter, including Cd, Cr, Cs, Cu, Mn, Pb, and Zn. Significant variability in elemental concentrations was observed across fuel types, indicating fuel composition as a key driver of exposure risk. In occupational context, repeated inhalation of contaminated smoke may pose health risks, particularly due to elements such as Cd and Pb, which are associated with chronic toxicity. The environmental dispersion of these emissions also raises concerns regarding pollinator health and the potential transfer of contaminants to honey and other hive products.

Acknowledgements:

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References

[1] Chen J., Li C., Ristovski Z., Milic A., Gu Y., Islam M. S., Dumka U. C. *Science of the Total Environment*, 2017, **579**, 1000-1034.

Multifunctional Eugenol-Derived Nanogels: A Single-Motif Design for Bioactive Drug Delivery and Intrinsic Fluorescence

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Developing multifunctional polymeric nanomaterials that integrate therapeutic bioactivity with diagnostic capabilities remains a challenge in nanomedicine.

This work presents the development of amphiphilic nanogels synthesized via the dispersion copolymerization of a eugenol-based methacrylate monomer (EUMA)¹ and hydroxyethyl methacrylate (HEMA). By preserving the phenolic moiety of the plant-derived eugenol, we achieved a single-motif design where intrinsic antioxidant and antimicrobial properties are embedded directly into the polymer backbone.

Physicochemical characterization *via* DLS, Cryo-TEM, and SAXS revealed spherical nanogels with diameters ranging from 80 to 210 nm, where increased EUMA content led to more compact structures and pearl-like aggregation patterns. These systems demonstrated exceptional colloidal stability in water and albumin for up to nine months. Notably, the nanogels exhibited emergent visible fluorescence (420 nm) is attributed to the partial oxidative coupling of eugenol units. This pH-dependent emission provides a self-reporting mechanism for tracking the nanocarriers without external fluorophores.

The therapeutic potential was evaluated by encapsulating Usnic Acid (UA), a hydrophobic antimicrobial compound. The pHEMA:EUMA architecture significantly enhanced the water solubility of UA and reduced its *in vitro* cytotoxicity while maintaining potent activity against Gram-positive bacteria. Combining high drug-loading capacity with inherent phytochemical bioactivity, these nanogels offer a streamlined, biobased platform for the next generation of multifunctional, self-reporting nanotherapeutics.

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References

- [1] M. Di Consiglio, E. Sturabotti, B. Brugnoli, A. Piozzi, L. M. Migneco and I. Francolini, *Polym. Chem.*, 2023,**14**, 432–442,

Towards rapid monitoring of disinfection by-products in water: A MicroNIR/Chemometrics platform for trihalomethanes detection

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Disinfection by-products (DBPs) are compounds formed during water disinfection processes aimed at reducing microbial risks, with around 1000 diverse species identified to date [1]. DBPs occur across multiple aquatic matrices, including drinking, surface (e.g., seawater) and recreational waters (e.g., swimming pools). Many DBPs are associated with adverse human health effects, including carcinogenicity, and may also pose risks to aquatic ecosystems due to their ecotoxicological potential [2]. Despite their relevance, current regulations address only a limited subset of DBPs in drinking water [3] and a restricted group, mainly trihalomethanes (THMs) in recreational waters [2,4]. Monitoring is largely based on conventional chromatographic techniques [1], which are accurate and sensitive but require sample handling, are solvent- and time-consuming, and are not suitable for real-time assessment. This highlights the need for faster and more sustainable analytical approaches.

This study explores the potential of miniaturized near-infrared spectroscopy (MicroNIR) combined with Chemometrics as a rapid, non-destructive, and reagent-free platform for THMs detection in water. Although successfully applied to aqueous matrices [5,6], MicroNIR/Chemometrics application to DBPs remains unexplored. Chloroform (CHCl₃) and bromoform (CHBr₃), representative THMs typically associated with freshwater and saline environments, respectively, were selected as target analytes. Experiments were performed on spiked pure water samples at environmentally relevant concentrations (1-200 µg/L), considering both individual compounds and their co-presence. Different measurement configurations were evaluated, including Onsite-W (reflectance, vials) and PAT-L (transmittance, static and flow setups). Chemometric models (PCA, PLS-DA, PLSR) were developed for exploratory analysis, classification, and quantification.

Preliminary results indicate that PCA discriminates between blanks and spiked samples and captures concentration-related variations. PLS-DA achieves near 100% specificity and non-error rate, with low prediction root mean square errors. Among the tested configurations, PAT-L setup in flow mode demonstrated the most promising performance, with PLSR models providing accurate quantification and limits of detection for CHCl₃ around 1 µg/L. Overall, the results demonstrate the feasibility of MicroNIR/Chemometrics platform for DBPs monitoring in water, paving the way for rapid, green, and potentially real-time screening tools. This approach aligns with Green Analytical Chemistry principles, supports a One Health perspective, and may contribute to the achievement of Sustainable Development Goals related to water quality, environmental protection, and public health.

References

- [1] Li J., Richardson S.D. *TrAC*, 2026, **198**, 118668.
- [2] Pobat T., Frasca C., Bruno A., Valeriani F. *Water*, 2026, **18(9)**, 1050.
- [3] Directive (EU) 2020/2184 on the quality of water intended for human consumption. *OJL435*, 2020.
- [4] Pobat T., Mandilara G.D., Nigro Di Gregorio F., et al. *Water*, 2025, **17(17)**, 2544.
- [5] Gullifa G., Barone L., Papa E., et al. *Front. Chem.* 2023, **11**, 1214825.
- [6] Risoluti R., Gullifa G., Materazi S. *Front. Chem.* 2020, **8**, 614718.

MicroNIR/Chemometrics: an Advanced Analytical Technology for Quality Assessment of Plasma-Derived Medicinal Products

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Plasma-derived medicinal products are life-saving drugs industrially produced from human blood or plasma, that are considered essential by the World Health Organization [1,2]. Ensuring their quality, safety, and efficacy throughout their entire lifecycle, from production to post-marketing, is crucial and regulatory authorities promote the integration of new scientific developments into quality control [3]. In this study, an innovative analytical strategy based on Near-Infrared (NIR) spectroscopy and multivariate statistical analysis techniques was proposed for the quality assessment of two classes of plasma-derived medicinal products. Factor VIII concentrates (FVIII) and Factor VIII/ von Willebrand Factor concentrates (FVIII/vWF) were analyzed, using the MicroNIR instrument, a miniaturized spectrophotometer, which allows rapid acquisition of spectral profiles of no-treated samples. Spectral data were processed using chemometric techniques such as the Principal Component Analysis (PCA) and the Partial Least Squares Discriminant Analysis (PLS-DA), to investigate variability in the spectral fingerprints. The MicroNIR instrument demonstrated to be a prompt, non-destructive tool for defining new quality indices of these products and chemometrics allowed to extrapolate the meaningful chemical information in the analytical measurements, providing reliable analytical technology. Exploratory data analysis based on PCA showed a clear separation between products under investigation, and the PLS-DA model enabled classification of samples based on their spectral profiles with high accuracy and specificity, also successfully differentiate the same products but at different active ingredient concentrations.

Results proved the efficiency of the NIR/Chemometric approach, highlighting its potential for quality monitoring of FVIII and vWF/FVIII concentrates.

References

- [1] Strengers P.F.W. Challenges for Plasma-Derived Medicinal Products. *Transfusion Medicine and Hemotherapy*, 2023, 50, 116-122.
- [2] World Health Organization. *World Health Organization Model list of Essential Medicines: 21st list*. 2019, 34-35.
- [3] European Directorate for the Quality of Medicines & HealthCare (EDQM), Need for Studies to Apply New Technologies in the Control of Medicinal Products, 2022, EDQM, Council of Europe, Strasbourg, France.

Theme D - Advances in Inorganic Chemistry and Functional Materials

From bulk to flow: microfluidic synthesis of hydrophilic thiol-functionalized gold nanoparticles

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The controlled synthesis of functionalized gold nanoparticles (AuNPs) is essential in different field of applications, where surface chemistry plays a crucial role in defining the colloidal stability, interfacial interactions and/or molecular recognition. Conventional bottom-up batch syntheses tend to be fairly reproducible, with relatively controlled size distributions [1,2]. Microfluidic reactors offer a promising alternative to improve reproducibility by enabling rapid mixing, precise dosing, and well-defined reaction environments, yet their potential for the direct synthesis of thiol-stabilized AuNPs remains underexplored [1,3]. In this work, a microfluidic approach, using a commercially available chip, was used for the synthesis of AuNPs capped with the positively charged 2-diethylaminoethanethiol hydrochloride (DEA) thiol as a hydrophilic functionalizing ligand, at room temperature. In the microfluidic approach, flow rate ratios and HAuCl₄/thiol/reducing agent molar ratios were optimized allowing to successfully synthesize water-dispersible, pH-responsive AuNPs-DEA with diameters below 5 nm and polydispersity (PDI) indexes in the 0.200–0.250 range. Implementation of continuous dialysis procedure allowed a straightforward purification of colloidal AuNPs-DEA. Characterizations were carried out *via* UV-Vis spectroscopy, dynamic light scattering (DLS), transmission electron microscopy (TEM), and ζ -potential. The comparison with conventional wet chemical reduction synthesis allowed to establish a narrower size distribution, higher operator-independent reproducibility, faster purification, and scale-up potential of the microfluidic approach (**Figure 1**). The obtained results demonstrate that microfluidic synthesis provides a robust and tunable route to hydrophilic thiol-functionalized AuNPs, offering enhanced control over particle morphology and surface chemistry compared with traditional bulk methods to obtain nanomaterials for advanced applications.

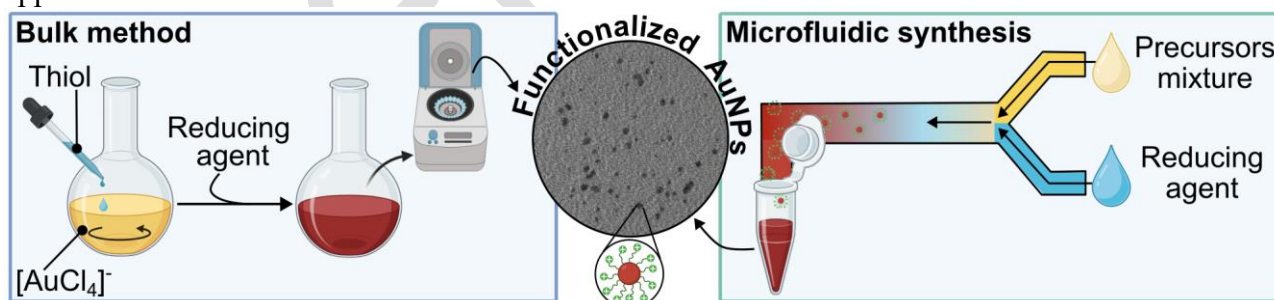


Figure 1. Positively charged thiol-functionalized gold nanoparticles synthesis: conventional batch synthesis vs microfluidic approach.

References

- [1] Saeed M.M., Carthy E., Dunne N., Kinahan D. *Lab Chip*, 2025, **25**, 3060–3093.
- [2] Venditti I., Testa G., Sciubba F., Carlini L., Porcaro F., Meneghini C., Mobilio S., Battocchio C., Fratoddi I. *J. Phys. Chem. C*, 2017, **121**, 8002–8013.
- [3] Kumar S., Santhanam V. *Chem. Eng. Res. Des.*, 2025, **220**, 329–334.

Towards chiral graphene oxide layers: a facile route based on covalent functionalization with amino-acids

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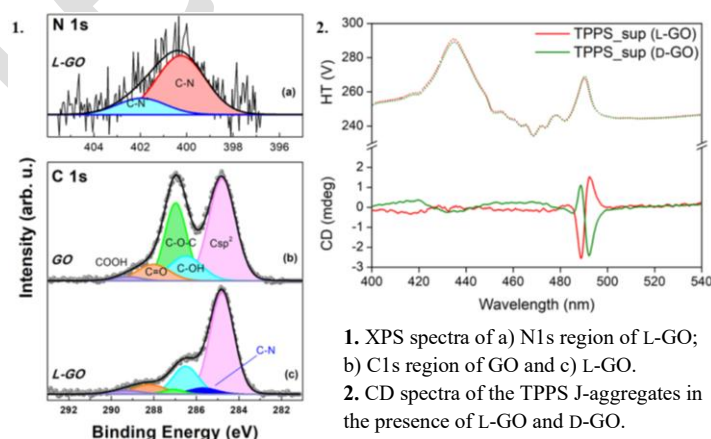
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Graphene Oxide (GO) is a two-dimensional non-stoichiometric nanomaterial, consisting of a graphitic carbon sheet, decorated with abundant Oxygenated Functional Groups (OFGs), such as epoxy, hydroxyl, carbonyl and carboxyl moieties¹. These groups open many functionalization routes in GO, paving the way for its application in numerous different fields, from biomedicine to optoelectronics, from energy to environment². Nevertheless, as the OFGs are randomly distributed across its plane, GO has an ill-defined and non-reproducible stereochemistry, limiting its use in applications where chiral recognition is crucial, like asymmetric catalysis or chiral separations³.

In this context, a promising strategy is based on the covalent attachment of an optically pure chiral compound, and the consequent transfer of the asymmetric information to GO layers. In this work, we developed a one-pot reaction between GO and the Lysine amino-acid, in both its L- and D-enantiomeric forms, through a nucleophilic substitution on the epoxy rings located on the basal plane of GO, as supported by DFT calculations. After extensive purification, the reaction products (namely L-GO and D-GO) were spectroscopically and electrochemically characterized, confirming the successful covalent grafting. In particular, X-ray Photoelectron Spectroscopy (XPS) measurements allowed to estimate the nitrogen content and functionalization degree.

The chirality of L-GO and D-GO was evaluated by their supramolecular interaction with the 5,10,15,20-meso-tetra(4-sulphonatophenyl)-porphyrin (TPPS), a water-soluble porphyrin known to form rod-like, chiral J-type aggregates when exposed to an asymmetric inducer. The obtained Circular Dichroism (CD) spectra unambiguously confirmed the opposite chirality induced by the templating functionalized GO layers, indirectly revealing their chiral properties. The ability to engineer enantiomeric GO through controlled covalent chemistry lays the groundwork for the integration of carbon-based nanomaterials into the most various chirality-based applications.



References

- [1] Amato, F. et al., *Nanoscale Adv.* **5**, 893-906 (2023).
- [2] Jiříčková, A. et al., *Materials* **15**, 920 (2022).
- [3] Guo, S. et al., *Nat. Rev. Phys.* **4**, 247–262 (2022).

Tuning Optoelectronic in Polymer–Nanoparticle Blends Using Thiol-Functionalized AuNPs

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Gold nanoparticles (AuNPs) exhibit unique physicochemical properties dependent on their size and shape; moreover, they display localized surface plasmon resonance (LSPR), characterized by strong extinction band in the visible region¹. The choice of surface ligands is crucial for determining the stability of colloidal dispersions as well as their functional properties. Poly(3-hexylthiophene-2,5-diyl) (P3HT) is a widely used p-type semiconducting polymer in organic solar cells and organic field-effect transistors (OFETs) due to its charge transport properties, which strongly depend on the structural ordering of polymer chains in the solid state²⁻³. The incorporation of AuNPs covalently functionalized with hydrophobic ligands into conjugated polymer matrices has been shown to improve electronic and optical properties⁴.

In this work, AuNPs were synthesized *via* a bottom-up approach and functionalized with two thiol ligands: the synthetic 2-(2-methyl-2-(acetylthio)ethyl)-4,5-(ethylenedioxy)thiophene (ProDOT) and the commercial 1-dodecanethiol (DDT). After optimization of the synthesis parameters, hydrophobic AuNPs with size less than 10 nm were obtained. The AuNPs were then mixed at different weight ratios with P3HT to form nanocomposite blends. Spin coated thin films of the resulting blends exhibited a significant enhancement in electrical conductivity compared to the pristine polymer. Electrical measurements carried out on interdigitated electrodes showed an increase up to 10 times in the 1% wt AuNPs blend, at room temperature (**Figure 1**). Furthermore, spectroscopic and morpho-structural characterizations were carried out on the synthesized materials

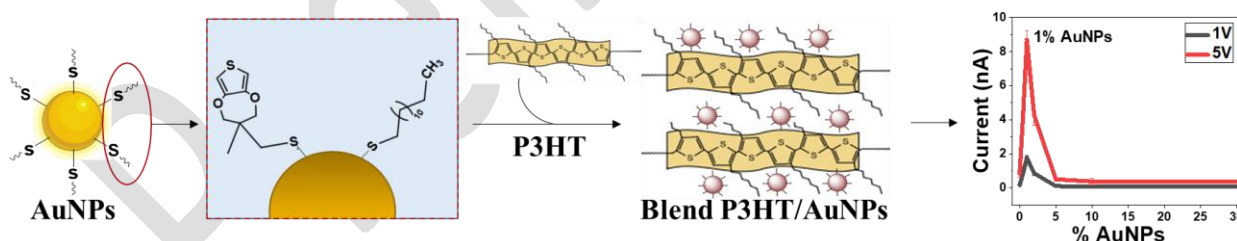


Figure 1: Electrical measurements on thin films made with functionalized AuNPs and P3HT.

References

- [1] Kang, H., Buchman, J. T., Rodriguez, R. S., Ring, H. L., He, J., Bantz, K. C., Haynes, C. L. *Chem. Rev.* 2019, **119**, 664-699.
- [2] Mauer, R., Kastler, M. and Laquai, F. *Adv. Funct. Mater.* 2010, **20**, 2085-2092.
- [3] Tremel, K., Ludwigs, S. *Advances In Polymer Science*, 2014, 2, 39-82, Springer, Berlin, Germany.
- [4] Grigorian, S., Fontana, L., Cerra, S., Pietsch, U., Scaramuzzo, F. A., Fratoddi, I. *Synth. Met.* 2022, **283**, 116973

Understanding the role of coordination chemistry in nanomaterials synthesis and microfabrication

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Coordination chemistry is often overlooked in nanomaterials synthesis and microfabrication, being treated as a black box to improve or enable these chemical processes. Actually, the mechanism of reaction of coordination compounds is pivotal for future improvements in such fields. Here, we present our investigations on a wide range of applications: from energy storage and conversion to micropatterned devices. Electrochemical and optical spectroscopy techniques allowed us to design coordination chemistry-based processes for the synthesis of two-dimensional layered double hydroxides,[1,2] magnetic nanoparticles, alloys[2] and formulations for conformal copper films.[3]

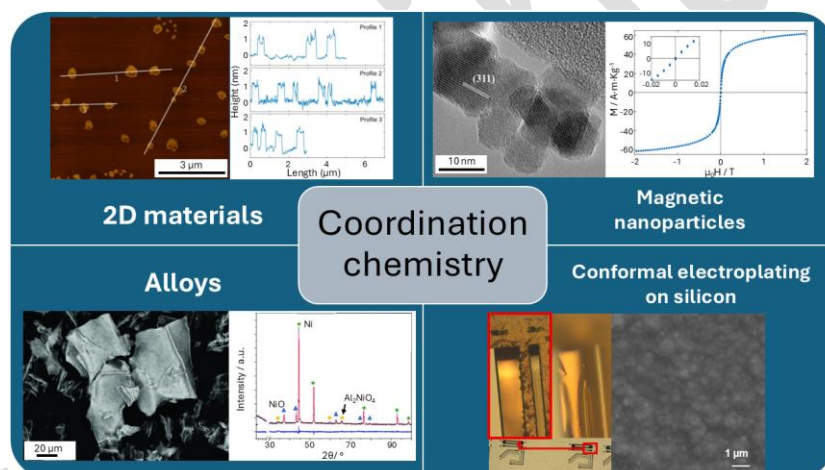


Figure 1. Adapted with permission from *Inorg. Chem.* 2022, 61, 11, 4598–4608. Copyright 2022 American Chemical Society; *J Therm Anal Calorim* 2025, 150, 6677–6684. Copyright 2024 Springer Nature.

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References

- [1] M. Piccinni, S. Bellani, G. Bianca, F. Bonaccorso *Inorg. Chem.*, 2022, 61, **11**, 4598–4608.
- [2] M. Piccinni, C. Rossi, D. Colombara, F. Bonaccorso *Inorg. Chem. Front.*, 2025, **12**, 1257–1272.
- [3] M. Fortunato, M. Piccinni, A. Pastorino, A.M. Cardinale *J. Therm. Anal. Calorim.*, 2025, **150**, 6677–6684.
- [4] M. Piccinni, D. Carrea, M. Casale, D. Colombara *Electrochem. Commun.*, 2025, **175**, 107909.

Investigation of doping strategies in chalcopyrite semiconductors

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CuGaSe₂ (CGS) is a chalcopyrite semiconductor with significant potential as top junction absorber in tandem photovoltaic applications due to its direct band gap and favourable optoelectronic properties [1]. Alkali metal doping is an effective strategy to improve charge transport, and crystal quality in Cu (In,Ga)Se₂ according to various complex mechanisms [2, 3]. In this study, alkali metal selenides (Ak₂Se) are used as stable and controllable doping sources to grow CGS single crystals by chemical vapor transport (CVT) with iodine as transporting agent. The initial part of this project involves optimizing growth conditions, with thermochemical evaluations based on thermochemical parameters [4]. Single crystals of CGS are synthesized using the CVT method in a TransTemp tube furnace. Alkali metal doping is introduced by adding Ak₂Se to the precursors at the beginning of the reaction, potentially enabling its introduction into the crystal lattice during the growth process. Ak₂Se is synthesized separately using the flux method. After synthesis of the chalcopyrite single crystals, the as-grown samples are subjected to a comprehensive set of characterization techniques to evaluate their structural, chemical, and optical properties. Structural and compositional analyses are performed to confirm phase purity, crystallinity, and successful incorporation of dopants within the crystal lattice. These studies provide detailed insight into the overall structural quality of the grown crystals. Subsequently, optical characterization techniques are employed to investigate the optoelectronic properties of the material, including its photoluminescence emission behaviour and defect-related features. Together, these complementary analyses allow for a thorough understanding of the relationship between growth conditions, structural quality, and optical performance of the single crystals.

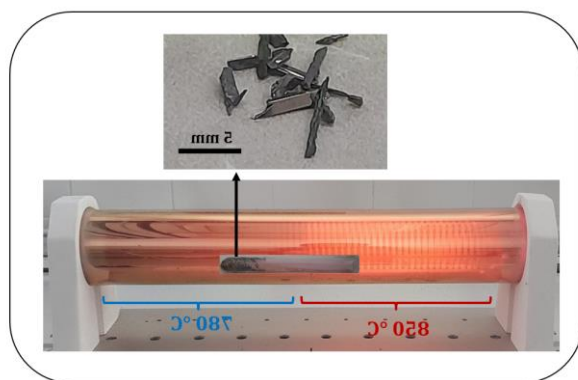


Figura 1. Schematic of CGS single-crystal growth via CVT in a TransTemp tube furnace.

References

- [1] F. Larsson *et al.*, "Record 1.0 V open-circuit voltage in wide band gap chalcopyrite solar cells," *Progress in Photovoltaics: Research and Applications*, vol. 25, no. 9, pp. 755-763, 2017.
- [2] D. Colombara, K. Conley, M. Malitckaya, H.-P. Komsa, and M. J. Puskas, "The fox and the hound: in-depth and in-grain Na doping and Ga grading in Cu (In, Ga) Se₂ solar cells," *Journal of Materials Chemistry A*, vol. 8, no. 14, pp. 6471-6479, 2020.
- [3] D. Colombara, B. J. Stanbery, and G. Sozzi, "Revani diffusion model in Cu (In, Ga) Se₂," *Journal of Materials Chemistry A*, vol. 11, no. 48, pp. 26426-26434, 2023.
- [4] O. Knacke, O. Kubaschewski, and K. Hesselmann, "Thermochemical properties of inorganic substances," (*No Title*), 1991.

Enhancing Colloidal Stability of Anisotropic Magnetic Nanodiscs through Mesoporous Silica and P(NIPAM/MAA) Copolymer Coatings

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Magnetic fields minimally invasive neuromodulation has been recognised in a handful of breakthrough studies using magnetically responsive materials for neuronal cells stimulation.¹ If the magnetically responsive materials showcase an anisotropic morphology, they could be exploited to produce mechanical stimulation, aside from heat production that could potentially be used in conjunction with piezoelectric or thermally responsive polymers. that could transfer mechanical actuation on electrical stimulation and fine tune heat transport, respectively.^{2,3} Both these phenomena can be exploited in neurostimulation when thermosensitive and mechanosensitive channels are targeted.^{2,3}

In this work, we attempt to solve the issue of colloidal stability for hexagonal-shaped magnetic nanodiscs (MNDs). Despite near-zero net magnetization, in large concentrations interparticle forces become dominant leading to aggregation, which prevents their utilisation in biomedical applications. We present the synthesis optimisation of MNDs via the wet reduction of hematite nanodiscs (HNDs) and investigate the use of oleic acid as a dispersant during the reduction. The freshly synthesised inorganic materials were characterised through various techniques, both before and after the reduction step. Further stabilisation of the MNDs was accomplished by growing a thin mesoporous silica coating on the HNDs,⁴ effectively diminishing aggregation in water while allowing conversion to MNDs during reduction. Since the silica layer facilitates subsequent silane chemistry,⁵ the grafting of poly(N-isopropylacrylamide-co-methacrylic acid) P(NIPAM/MMA) coatings with 80:20 and 50:50 ratios, yielding highly stable aqueous suspensions of MNDs both in aqueous and cell culture media. These findings establish a versatile pathway toward colloiddally stable MNDs, thereby broadening their applicability in biomedical research.

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References

- [1] T. Potrč, S. Kralj, S. Nemec, P. Kocbek and M. E. Kreft, *Nanoscale*, 2023, *15*, 8611–8618.
- [2] S. A. Heschem, P. H. Chiang, D. Gregurec, J. Moon, M. G. Christiansen, A. Jahanshahi, H. Liu, D. Rosenfeld, A. Pralle, P. Anikeeva and Y. Temel, *Nat. Commun.*, 2021, *12*, 1–10.
- [3] D. Gregurec et al., *ACS Nano*, 2020, *14*, 8036–8045.
- [4] C. Gao, F. Lyu and Y. Yin, *Chem. Rev.*, 2021, *121*, 834–881
- [5] M. A. Macchione, C. Biglione and M. Strumia, *Polym.* 2018, Vol. 10, Page 527, 2018, *10*, 527.

Unlocking Direct Amination of Graphene-Based Materials via Iron-Mediated Radical Chemistry

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Graphene-based nanomaterials are widely investigated due to their outstanding physicochemical properties; however, their facile covalent functionalization remains challenging, particularly when aiming to achieve a high degree of functionalization without disrupting the extended π -conjugation. Herein, we report a mild and efficient protocol for the direct amination of graphene nanoplatelets (Figure 1), graphene oxide, and reduced graphene oxide using hydroxylamine-derived reagents under iron-mediated conditions [1].

This method enables a one-pot introduction of amine groups both at the edges and on the basal plane of graphene-based materials, achieving nitrogen atomic contents up to ~10% while largely preserving the structural integrity of the π -system, as confirmed by Raman spectroscopy [2]. The functionalized materials were thoroughly characterized by XPS, UV-Vis, and electron microscopy, and the reaction mechanism was investigated through DFT calculations, supporting a radical-mediated pathway. Notably, the introduction of amine functionalities significantly enhances the dispersibility of graphene-based materials in polar media (Figure 1) without compromising their electrical properties. These findings provide a versatile and scalable approach for the chemical modification of graphene, enabling the development of advanced carbon-based nanoassemblies through covalent functionalization.

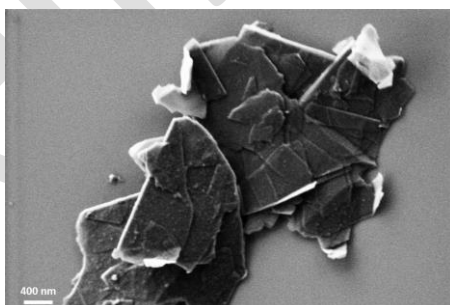


Figure 1. FE-SEM micrograph of amino-functionalized graphene nanoplatelets.

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References

- [1] Possenti D., Olivo G., *ChemCatChem*, 2024, **16**, e202400353.
- [2] Amato F., Possenti D., Daino M., Giaccari L., Marino R., Lucianatelli M., Motta A., Olivo G., Marrani A. G., *Carbon*, 2026, **253**, 121447.

Fe(III)-carboxythiolate MOFs and CNT-based composites for electrocatalytic applications

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Metal–organic frameworks (MOFs) have emerged as a versatile class of porous materials due to their high surface area, structural tunability, and the possibility of incorporating a variety of metal centers and organic linkers. Their relevance in chemistry has increased, culminating in the Nobel Prize 2025. These features make them particularly appropriate for applications in electrochemistry, where the accessibility and density of active sites and the ability to change their chemical environment are really important factors. However, although their potential, the practical application of MOFs in electrocatalysis is normally impeded by their intrinsically low electrical conductivity.

To resolve conductivity issues, nanocomposite materials are developed by using carbon nanotubes (CNTs), which are expected to improve charge transport and enhance the exposure of active sites. The resulting materials are characterized using complementary physicochemical techniques in order to achieve information about structure, morphology, and electrochemical behaviour [1].

In this context, Fe(III)-based MOFs containing redox-active centres represent promising candidates, because they can participate in electron transfer processes. In particular, this work describes the synthesis of three different layered Fe(III)- MOFs based on 2,5- disulfydrylbenzene-1,4-dicarboxylic acid (DSBDC) as ligand, which cation-sulphur bond can produce an improvement in electronic transport, that may enhance their electrochemical activity. The full characterization of the Fe(III)-carboxythiolate MOFs showed a crystalline structure based on anionic {Fe(DSBDC)} layers that are separated by different cations DMA⁺, Na⁺ and K⁺. Preliminary results showed the electroactivity, particularly of the sodium derivate. Ongoing studies are now being performed on the DMA⁺ and K⁺ materials [2]. At the end, this work aims to evaluate the potential application of these materials as electrocatalysts and to explore strategies to overcome their limitations.

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References

- [1] D. D. Chronopoulos, H. Saini, I. Tantis, R. Zbořil, K. Jayaramulu, and M. Otyepka, “Carbon Nanotube Based Metal–Organic Framework Hybrids From Fundamentals Toward Applications,” Jan. 01, 2022, *John Wiley and Sons Inc.* doi: 10.1002/sml.202104628.
- [2] N. Gedikoglu *et al.*, “Fe(iii)-carboxythiolate layered metal-organic frameworks with interest as active materials for rechargeable alkali-ion batteries,” *J. Mater. Chem. A Mater.*, vol. 11, no. 44, pp. 23909–23921, Oct. 2023, doi: 10.1039/d3ta05353a.

Piezoelectric Polymer-Coated Magnetic Nanodiscs for Remote Electrical Stimulation

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The development of non-invasive neuromodulation strategies remains a major challenge in biomedical engineering, particularly in achieving remote, spatially controlled stimulation of neuronal activity without the need for implanted electrodes. Smart magnetic nanomaterials (SMNs) have recently emerged as promising candidates, as they can transduce externally applied magnetic fields into local mechanical or thermal stimuli [1]. However, the conversion of these signals into localized electrical stimulation at the nanoscale is still largely unexplored.

In this context, this work aims to engineer magnetic nanodiscs (MNDs) as multifunctional actuators by integrating magneto-mechanical motion with piezoelectric polymers, enabling the generation of local electric fields under magnetic excitation.

To achieve this objective, two complementary functionalization strategies were developed. The first approach relies on the non-covalent coating of MNDs with poly(vinylidene fluoride) (PVDF) and PVDF-based copolymers via a phase separation method, allowing the formation of the polymer shells [2]. The influence of polymer content on coating efficiency and colloidal stability was systematically investigated. However, the intrinsic hydrophobicity of PVDF limits its applicability in aqueous environments.

To address this limitation, a second strategy based on covalent grafting-from polymerization was explored using the piezoelectric polypeptide poly(γ -benzyl-L-glutamate) (PBLG). Surface-initiated ring-opening polymerization from amine-functionalized MNDs yielded polymer-grafted nanohybrids with improved compatibility in aqueous media [3]. Ongoing work focuses on the development of amphiphilic block copolymers (PBLG-b-PEG) to further enhance dispersion stability [4].

The resulting nanohybrids were characterized by spectroscopic and colloidal techniques, confirming successful polymer deposition and tunable surface properties. In addition, piezoresponse force microscopy (PFM) was employed to investigate the electromechanical behavior of the polymer coatings. Point-and-shoot measurements on PVDF-coated nanohybrids showed promising responses consistent with piezoelectric activity [5].

Overall, this work provides new insights into the design of magneto–piezoelectric nanohybrids and establishes a foundation for the development of remotely actuated nanosystems for neuromodulation.

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References

- [1] L. Signorelli, S.- A. Heschem, A. Pralle and D. Gregurec, *iScience*, 2022, 25, 105401.
- [2] Yujang C., Jaeseon J., Minseok Choi, Gyunpyo Baek, S. Park, H. Choi, S. Ahn, S. Cha, T. Kim, D.S. Kang, J. Bae, J. J. Park, *Chemical Engineering Journal*, 2022, 427, 1, 131030.
- [3] Dong L., Yi L., Jianping D., Wantai Y., *Reactive and Functional Polymers*, 2011, 71, 10, 1040.
- [4] Jing Huang, Xingliang Liu, Zhen Yuan, Tianjian Yang, Yu Zhao, Yao Lin, Ziyuan Song, and Jianjun Cheng, *Macromolecules* 2025, 58, 9692.
- [5] Shubhra Jyotsna, Ashima Arora, Jagmeet S. Sekhon, and Goutam Sheet, *Journal of Applied Physics*, 2014, 116, 104903.

Anilate-Based Ultramicroporous MOFs: Physisorbent Materials for Environmental Applications

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Atmospheric CO₂ capture is a critical challenge in mitigating global temperature rise, and Metal-Organic Frameworks (MOFs)—which were awarded the 2025 Nobel Prize in Chemistry—have emerged as candidates for this task due to their high porosity and tunable structures.

In 2021, we synthesized, *via* hydrothermal approach, a new ultramicroporous MOF, [Co(trz₂An)]*n*·2.5H₂O (**1**),¹ combining 3, 6-*N*-ditriazolyl-2,5-dihydroxy-1,4-benzoquinone (trz₂An, An=anilate=2,5-dihydroxy-1,4-benzoquinone), with Co^{II} metal node in a 1:1 stoichiometric ratio. **1** exhibited high selectivity, adsorption capacity and regenerability, acting as a molecular sieve against larger molecules, such as methane or nitrogen. In this work, we report the synthesis, crystal structure and performance studies of three new microporous MOFs obtained by combining trz₂An with Cu^{II}, Zn^{II} and Fe^{II} metal nodes, formulated as [Cu(trz₂An)]*n*H₂O (**2**),² Zn(Trz₂An) 3H₂O (**3**) and Fe(Trz₂An) 3H₂O (**4**). **2**, **3**, **4** are physisorbent, ultramicroporous MOFs characterized by pore sizes of 3.46 Å, 3.8 Å, 3.6 Å, respectively, suitable for CO₂ adsorption. Notably, **2** exists in two polymorphs: monoclinic and orthorhombic. The orthorhombic one form exhibits a 9.5 ° rotation of the triazolil ring; however, this difference in pore diameters does not affect its influence in the adsorption performance. Pore analysis of compounds **3** and **4** indicates that both the maximum pore diameter (3.8 Å) and the pore limiting diameter, corresponding to the narrowest pore aperture, exceed those observed for compounds **1** and **2**.

Static and Dynamic Adsorption Measurements revealed *i*) remarkable carbon dioxide uptake, *ii*) high selectivity in CO₂/N₂ and CO₂/CH₄ gas mixtures, *iii*) easy regeneration in mild conditions and *iv*) enhancement of CO₂ (~65%) performance in humid conditions attributed to transient pore opening due to guest-induced linker flexibility. Furthermore, *i*) CO₂ electroreduction studies showed a good capability of (**2**) to convert carbon dioxide into ethylene and *ii*) adsorption test removal, performed on (**3**) and (**4**) revealed a good performance to remove Cd^{II} and Pb^{II} well known as highly toxic heavy metal ions, at different pH range and concentrations. In conclusion, trz₂An is a strategic organic linker, which combined with different transition metal ions, gave rise to a novel thermal stable, robust, microporous 3D MOFs family employing for environmental quality.

References

- [1] M. Mercuri, M. L.; Coronado, E. et al. A Thermally/Chemically Robust and Easily Regenerable Anilate-Based Ultramicroporous 3D MOF for CO₂ Uptake and Separation. *J. Mater. Chem. A* 2021, 9 (44), 25189–25195. <https://doi.org/10.1039/D1TA07436A>.
- [2] Oggianu, M.; MaGalán-Mascaros, J. R.; Masciocchi, N.; Mercuri, M. L. et al. A 3D Polymorphic Cu-Based Ultramicroporous MOF Capable of CO₂ Uptake and Conversion. *J. Mater. Chem. A* 2026, 14 (16), 9301–9315. <https://doi.org/10.1039/D5TA09255H>.

Mechanochemically synthesised MOFs as supercapacitor materials

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Metal–Organic Frameworks (MOFs) constitute a versatile class of crystalline hybrid materials in which metal nodes and organic linkers assemble into extended architectures with finely tunable structural and chemical features. Their versatility enables precise control over pore environment, connectivity, and electronic structure, making them an ideal platform for designing functional materials with targeted properties.[1] Among the various application areas, energy storage has highlighted the importance of MOFs since capable of combining high surface area with efficient charge transport pathways. In this field, two-dimensional π -conjugated conductive MOFs have emerged as structurally significant systems where the interplay between metal-ligand coordination, extended conjugation, and redox-active sites gives rise to promising material for supercapacitor application (Figure 1).[2] A key challenge, from a materials chemistry perspective, is the development of synthetic strategies that allow access to these frameworks in a scalable and environmentally benign manner, while preserving their structural integrity and functional performance. Although solvothermal methods remain the standard route, mechanochemical synthesis has proven capable of generating crystalline MOF phases with reduced solvent use and, in some cases, distinct structural outcomes not attainable in solution.[3] Our group previously demonstrated that mechanochemical conditions can yield phase-pure Cu-HHTP, a copper-catecholate MOF based on the 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) ligand, confirming the robustness of this coordination motif under solvent-minimal conditions and its suitability for its application in supercapacitor devices.[4] Building on these insights, we now report an optimised mechanochemical synthesis of the structurally related, prototypical benchmark 2D conductive MOF Ni-HITP (HITP = 2,3,6,7,10,11-hexaminitriphenylene).

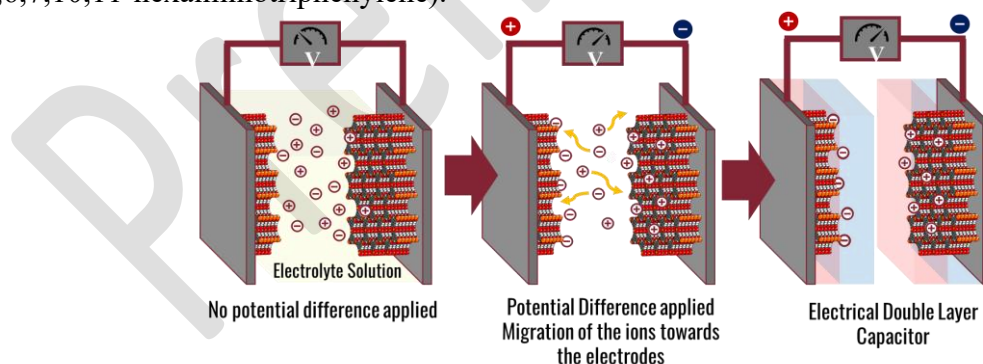


Figure 1: Charge mechanism of a supercapacitor device employing a 2D conductive MOF as the electrode material.

References

- [1] Furukawa H., Cordova K.E., O’Keeffe M., Yaghi O.M. *Science*, 2013, **341**, 6149.
- [2] Mohanty A., Jaihindh D., Fu Y., Senanayak S.P., Schmidt Mende L., Ramadoss A. *J. Power Sources*, 2021, **488**, 229444
- [3] Ardilla-Fierro K.J., Hernández J.G. *ChemSusChem*, 2021, **14**, 2145-2162.
- [4] Marchetti D., Scaravonati S., Anyfanti G., Aversa L., Verucchi R., Riccò M., Massera C., Gemmi M., Pontiroli D., Pedrini A. *J. Mater. Chem. A*, 2026, Advance Article.

Theme E - Energy, Environment and Sustainability

Comparative Analysis of Calcination Strategies for NMC811 Synthesized via Oxalic Coprecipitation

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$\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ (NMC811) has emerged as one of the most promising cathode materials for high-performance Lithium-Ion Batteries (LIBs), due to its high energy density and low cobalt content. Coprecipitation is the conventional synthesis route, thanks its ability to deliver controlled particle morphology, homogeneous atomic-scale mixing and scalability [1]. Recently, oxalic acid has been proposed as a simpler, cost-effective precipitating agent with lower energy demand [2]. Following precipitation, calcination remains a mandatory step that playing a critical role in determining electrochemical performance. However, many works reported a wide range of calcination strategies, making it difficult to identify an optimal approach.

Here, the four most used calcination protocols have been investigated. They are differing in the number of heating steps and lithium addition timing (Figure 1). Comprehensive physico-chemical characterization revealed distinct variations in structure, morphology and surface properties among the resulting NMC811 cathodes. Electrochemical testing further highlighted significant differences in performance, with capacity retention ranging from 42% to 72% after 200 cycles. This comparative analysis provides valuable insights into the structure-property relationships shaped by calcination, clarifying how this critical step governs the overall performance of NMC811.

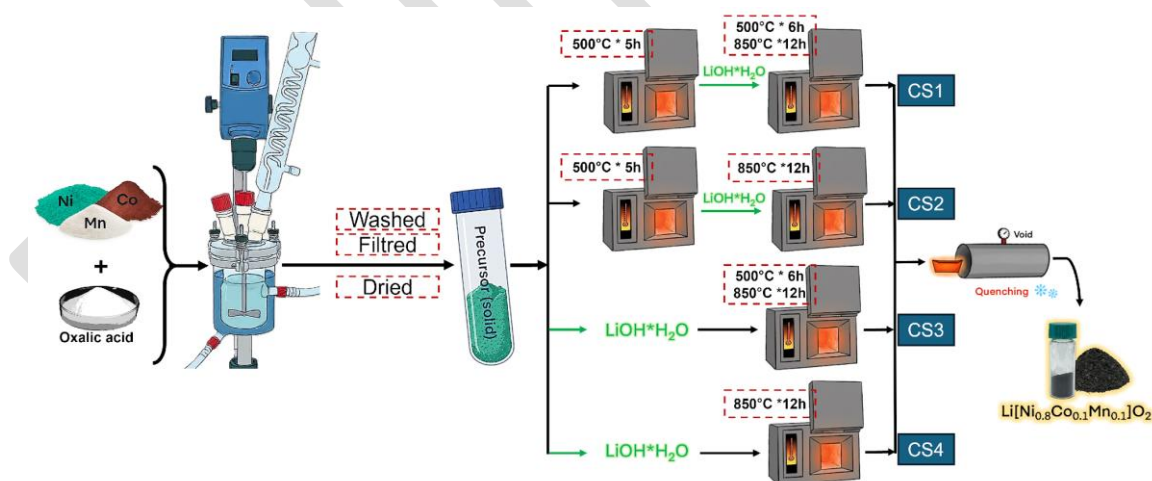


Figure 1. Schematic diagram of four different calcination strategies used to obtain the NMC811 cathode after co-precipitation step.

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References

- [1] M. Malik, K. H. Chan, G. Azimi, *Mater. Today Energy* 2022, **28**, 101066.
- [2] M. Colasanti, C. Gatti et al., *Journal of Power Sources*, 2025, **11**, 657

Innovative strategies for treating residual secondary contamination sources: *in-situ* microemulsification approach

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A critical aspect of NAPLs (Non-Aqueous Phase Liquids) contamination scenarios is the presence of residual free product trapped between the porosity of the aquifer by strong capillary forces with high interfacial tension values. These long-term persistent contamination sources are irrecoverable by normal hydraulic gradients, making remediation targets unachievable, especially when conventional Pump and Treat (*P&T*) approaches are used. A successful strategy in this context is the possibility to use extracting agents, such as surfactants, to reduce interfacial tension and consequently increase the mobility of the organic phase [1].

Micellar solubilization and displacement are the main mobilization mechanisms in surfactant-enhanced aquifer remediation (SEAR). Surfactants can also interact with NAPLs through emulsification, dispersing NAPLs into the aqueous phase as tiny droplets [2]. By optimizing the physicochemical parameters of surfactant solutions, typically by adjusting salinity, it is possible to generate thermodynamically stable systems, called *Winsor III (WIII)* microemulsions, well known for producing ultra-low oil-water interfacial tension values [3]. The microemulsification approach has been widely studied for several applications, such as the advanced oil recovery from depleted reservoirs, but the application for environmental remediation is still marginal. In this regard, this work proposes a systematic laboratory validation of *in-situ WIII* microemulsification mechanism for contamination source depletion.

Taking into account two anionic alkyl-sulphosuccinate (ASSs) surfactants and toluene or trichloroethylene (TCE) as reference NAPLs, the study investigated the optimal solution conditions through a NaCl scan under which stable *WIII* microemulsions can be formed between both toluene and TCE in the presence of both investigated surfactants. Subsequently, a continuous configuration experiment was conducted by setting up several fixed-bed glass columns to replicate saturated porous media with trapped residual pure-phase contaminants. On these systems, a bench-scale soil flushing process was reproduced, evaluating directly the abilities of the investigated surfactants to generate *in-situ WIII* microemulsion. To compare the removal effectiveness between solubilization and microemulsification, the flushing process was divided into two steps: the first one with a sub-optimal NaCl concentration for the sole solubilization mechanism, followed by the second step with the previously determined optimal NaCl concentration to trigger the *in-situ* microemulsification.

This study highlights the remarkable versatility of microemulsions in environmental remediation. Depending on the specific characteristics of the contamination, the surfactant solution's conditions can be precisely adjusted to obtain an optimal formulation for the formation of a stable *WIII* microemulsion. Pumping the formulation through the contaminated zone *in situ* microemulsification mechanism can be triggered, favouring an effective and quantitative depletion of persistent secondary sources, allowing a significant reduction of pollutant mass in very short operating times and offering technical and economic advantages for the remediation and management of polluted sites.

References

- [1] P. Ciampi, C. Esposito, G. Cassiani, G.P. Deidda, P. Rizzetto, M.P. Papini *Environ. Sci. Pollut. Res.* 2021, **28**, 35286–35296.
- [2] L. Huo, G. Liu, X. Yang, Z. Ahmad, H. Zhong *Chemosphere*, 2020, 252.
- [3] T.T. Nguyen, (2019) 983–999.

A Laboratory Study on a Biochar-Carboxymethylcellulose Composite as Injectable Colloidal Suspension for In-Situ Groundwater Remediation

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Groundwater contamination by volatile organic compounds (VOCs), including chlorinated solvents such as tetrachloroethylene (PCE) and trichloroethylene (TCE) and aromatic hydrocarbons as toluene (TOL), remains a major environmental concern due to their persistence, toxicity, and complex subsurface behavior. Traditional pump-and-treat and excavation-based approaches are energy-intensive and often inefficient in deep or heterogeneous aquifers. Injectable Permeable Reactive Barriers (IPRBs) have emerged as a sustainable in-situ alternative, though challenges remain in achieving uniform subsurface distribution in complex aquifers. This study focuses on developing and optimizing a biochar-based colloidal suspension stabilized with sodium carboxymethylcellulose (BC-CMC), designed as an injectable, low-impact reactive medium for groundwater remediation. The biochar employed originates from biomass gasification residues, valorizing a waste material within a circular and carbon-neutral framework.

Composites were prepared by dispersing pine-wood biochar (gasified at 950 °C) in aqueous CMC (10 g L⁻¹) to enhance colloidal stability. The biochar concentration was optimized to deliver effectively the maximum amount of BC while maintaining colloidal stability. The stability of the suspension was evaluated through sedimentation tests and ζ -potential measurements, providing insight into aggregation behaviour. The influence of ionic strength (0–400 mM NaCl) and pH (0.50–12) was systematically assessed. Column distribution experiments using glass-bead packed systems were performed to evaluate the mobility and distribution of the suspension in fine sand aquifers. The effect of the granulometry of the BC-CMC suspension on the efficiency of the column bed retention was studied by feeding unfiltered, 64 μ m-filtered, and 50 μ m-filtered suspensions. The adsorption capacity of biochar and commercial activated carbon (AC) toward PCE and TOL was then compared through batch adsorption isotherms, fitted with the Freundlich equation. Theoretical retardation factors derived from column adsorption tests on the dispersed BC-CMC suspension were then used to estimate the adsorption potential of injectable barriers under field conditions.

The optimized BC-CMC suspension, containing 3 g L⁻¹ of biochar and 10 g L⁻¹ of CMC, exhibited excellent colloidal stability under neutral to basic pH and moderate salinity. This formulation allowed the injection of a higher biochar mass using a lower liquid volume, improving field applicability. Sedimentation and ζ -potential measurements showed that the suspension maintained high stability at pH 9.4, where the modulus of ζ -potential remained highest across all test days. In contrast, increasing ionic strength caused a gradual loss of stability due to Na⁺ induced charge neutralization of CMC carboxyl groups, reducing electrostatic repulsion and leading to aggregate formation and precipitation. Column distribution experiments revealed that pre-filtration of the suspension is crucial to achieve deep-bed retention of the BC-CMC suspension and avoid surface-filtration and cake formation which leads to clogging issues. Adsorption tests analyzed with the Freundlich model demonstrated the biochar's strong affinity toward both toluene (TOL) and tetrachloroethylene (PCE) comparable to commercial activated carbon. Continuous-flow adsorption experiments performed on columns loaded via BC-CMC suspension distribution confirmed that TOL displayed an earlier breakthrough than PCE, consistent with its lower sorption affinity, the calculated retardation factors of 144 ± 4 for TOL and 360 ± 6 for PCE. Overall, these findings confirm that the BC-CMC suspension ensures high adsorption capacity, homogeneous distribution, and environmental compatibility while efficiently immobilizing both chlorinated and aromatic hydrocarbons.

Long-term resilience and biologically driven regeneration of a coupled adsorption–biodegradation reactor treating chlorinated ethenes

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The development of sustainable remediation strategies is increasingly driven by the need to integrate waste-derived materials into treatment systems, reducing environmental impact while maintaining high removal efficiencies. In this context, aquifers contaminated by trichloroethylene (TCE) represent a particularly challenging scenario due to the physicochemical properties of chlorinated solvents (CS), including their density—higher than water—which enables migration below the water table, and their low solubility, which leads to the formation of persistent, low-concentration plumes. In situ biological approaches are frequently limited by insufficient residence time and the lack of suitable electron donors to sustain reductive dechlorination processes. To address these limitations, this study proposes a combined remediation strategy integrating Biological Reductive Dechlorination (BRD) with adsorption onto pinewood biochar (PWB-BC), a waste-derived material obtained from biomass gasification [1]. The system is further enhanced by the use of polyhydroxyalkanoates (PHA)-enriched biomass, produced from the fermentation of the organic fraction of municipal solid waste (OFMSW), acting as a slow-release electron donor to sustain the sequential hydrogenolysis of TCE to cis-dichloroethylene (cis-DCE), vinyl chloride (VC), and ultimately ethylene. The objectives of this work are: (i) to design and operate a mini-pilot reactor (144 cm height, 10 cm diameter) incorporating waste-derived materials; (ii) to evaluate the robustness of the system under varying operational conditions; and (iii) to assess process resilience following depletion of the electron donor, with a view to future scale-up. A long-term experimental campaign was conducted over 934 days, corresponding to 1433 pore volumes, allowing for the investigation of different operational phases. In Phase I, the combined system exhibited stable and complete TCE removal over 220 days (145 pore volumes). This performance highlights the synergistic interaction between biochar adsorption and microbial degradation processes, which effectively delays contaminant migration while sustaining biodegradation. In Phase II, the system was subjected to stress conditions induced by the depletion of the electron donor, as confirmed by the absence of volatile fatty acids (VFAs). Under these conditions, a decrease in degradation kinetics was observed, accompanied by transient accumulation of intermediates and a shift of the TCE adsorption front due to increased flow rates. In Phase III, restoring the initial flow conditions confirmed that the decline in microbial activity was primarily due to electron donor exhaustion. The subsequent addition of a readily fermentable donor (lactate) rapidly reactivated the microbial community, demonstrating the resilience of the system.

References

- [1] M. Abruzzese, L. Lorini, R.G. Cervilla, A. Santos, D. Lorenzo, L. Niccolini, B. Matturro, M.P. Papini, Coupled adsorption-biodegradation of trichloroethylene in groundwater using food waste-derived Polyhydroxyalkanoates (Pha) and pine wood biochar, (2025). <https://doi.org/10.1016/j.jwpe.2025.108972>.

In Operando Synchrotron study of phase evolution in Lithium-rich cathodes

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Lithium-rich cathode materials have attracted increasing attention as promising candidates for the next-generation lithium-ion batteries due to their exceptionally high reversible discharge capacity ($>250 \text{ mA h g}^{-1}$), arising from the combined contribution of conventional transition metal redox reactions and unconventional oxygen anion redox activity [1]. Despite these advantages, their practical application is still hindered by challenges such as sluggish kinetics and voltage fading upon cycling [2],[3]. Nevertheless, their high energy density, together with the possibility of cobalt-free compositions based on abundant elements such as manganese and titanium, makes them highly appealing for the development of more sustainable and cost-effective energy storage systems.

Here, we investigate the impact of the reaction environment during the calcination process on the formation and stability of lithium-rich cathode materials synthesized via a solid-state route using carbonate precursors and planetary ball milling. By systematically tuning the temperature and atmosphere, we demonstrate that the structural evolution of these materials is highly sensitive to the thermal treatment conditions. In particular, annealing at 850°C in air promotes the formation of a layered $\alpha\text{-NaFeO}_2$ -type phase (R-3m), whereas the same treatment under argon leads to the formation of a disordered rock-salt structure (Fm-3m). Increasing the annealing temperature to 900°C under inert atmosphere results in a mixed-phase system composed of disordered rock salt (DRX) and spinel-like domains, indicating a thermally induced structural rearrangement.

To directly probe these transformations, synchrotron radiation scattering techniques were employed for temperature-dependent, in operando, measurements under both air and argon atmospheres. These analyses reveal the presence of distinct phase evolution pathways and provide key insights into phase stability and transformation mechanisms as a function of the reaction environment. Overall, this study highlights the critical role of calcination conditions in governing the crystallographic structure of lithium-rich cathodes and provides fundamental insights into synthesis–structure relationships, paving the way for the rational design of high-performance, cobalt-free materials for advanced energy-density lithium-ion batteries.

References:

- [1] W.He, W.Guo, H.Wu, L.Lin, Q.Liu, X.Han, Q.Xie, P.Liu, H.Zheng, L.Wang, X.Yu, D.-L.Peng, *Adv. Mater.* 2021, **33**, 2005937.
- [2] Zhenfei C., Shuai W., Hekang Z., Xinya T., Yangzhou M., Denis Y.W. Yu, Shihong Z., Guangsheng S., Weidong Y., Youlong X., Cuie W. *Journal of Colloid and Interface Science*, 2023, **630**, 281-289.
- [3] Li, H., Wang, L., Song, Y., Wu, Y., Zhang, H., Du, A. and He, X. (2023), *Small*, **19**, 2302208.

Integrated Black Mass Engineering for Closed-Loop Recovery of Dual Cathode Precursors via NMC Leaching with LFP as Reducing Agent

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The sustainable recycling of lithium-ion batteries is crucial to secure critical raw materials and reduce the environmental impact of the energy transition. Conventional hydrometallurgical processing of Ni–Mn–Co (NMC) black mass relies on external reducing agents, increasing reagent consumption and process complexity. In this work, an integrated hydrometallurgical route is proposed in which spent LiFePO₄ (LFP) cathodes act as internal reducing agents to promote selective NMC dissolution. The leaching stage was optimized by varying solid-to-liquid ratios, achieving high extraction efficiencies of Ni, Mn, and Co without external reductants. Iron and phosphorus released from LFP were recovered as FePO₄ via hydrothermal synthesis directly from the leachate. Subsequently, LiFePO₄/C was regenerated through a solid-state process using Fe⁰ as reducing agent. This dual-stream approach enables the simultaneous valorization of NMC and LFP, reducing reagent use and waste generation. The proposed process provides a resource-efficient pathway for closed-loop battery recycling.

Keywords: battery recycling, hydrometallurgy, circular economy

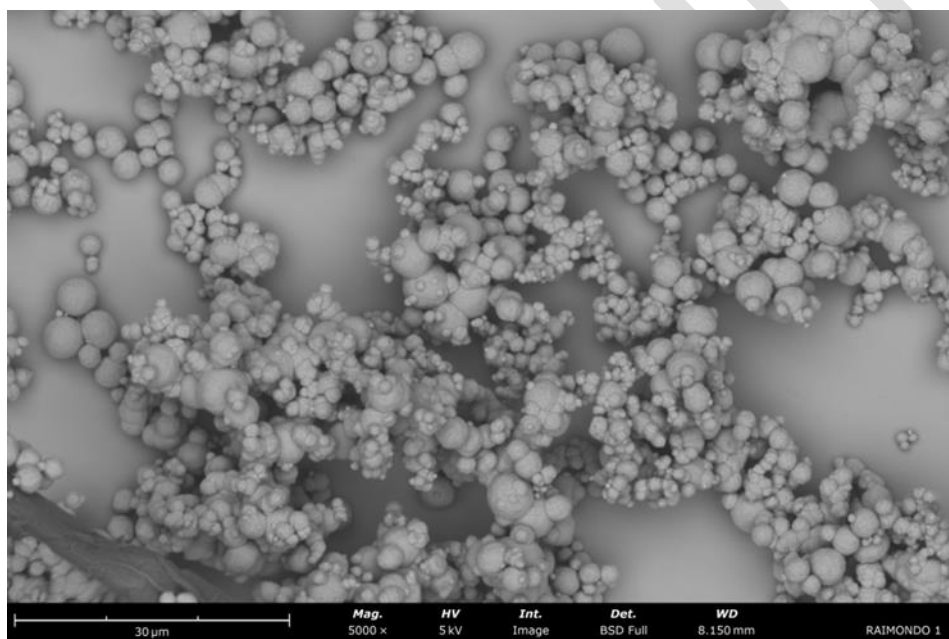


Figure 1: SEM micrograph of recovered FePO₄ particles.

A sustainable mechanochemical approach to the selective oxidation of benzylic alcohols

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The growing interest in sustainable oxidation processes arises from the need to reduce the environmental impact of this kind of reaction [1]. Mechanochemistry has emerged as a powerful tool for conducting reactions in a more sustainable manner [2] and it is increasingly recognized as an innovative approach for catalyst activation [3] and chemical synthesis [4].

This work developed a new sustainable oxidation method for the selective conversion of benzylic alcohols into aldehydes via a solvent-free mechanochemical approach.

The most effective catalyst system consists of copper-supported on an inorganic material in combination with TEMPO. As reported in figure 1, this methodology enables the oxidation of a variety of benzylic alcohols to their corresponding carbonyl compounds. The presence and nature of substituents on the aromatic ring influence the reaction yield.

A green chemistry assessment [5,6,7] demonstrates that this method is more sustainable than the corresponding solution-based process. Additionally, it is less energy and time intensive while providing improved selectivity.

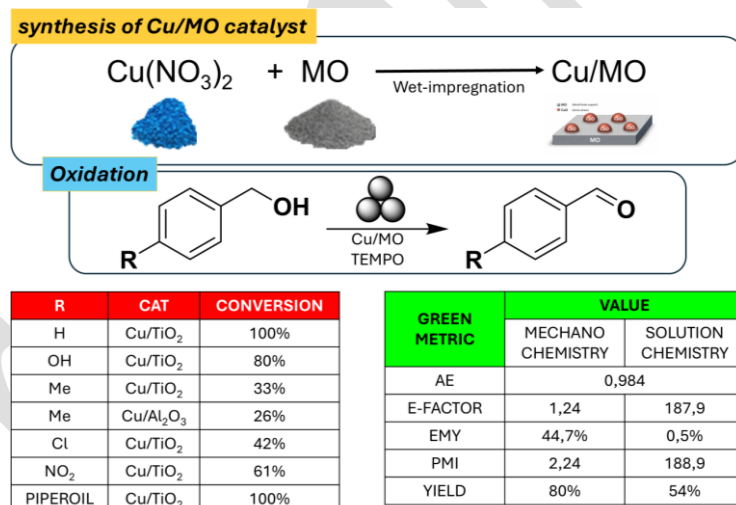


Figure 1 Graphical abstract.

References

- [1] R.A. Sheldon. *Chemical Society Reviews*, 2012, **41**, 1437-1451.
- [2] Robertson J.C., Coote M.L., Bissemer A.C. *Nature Reviews. Chemistry*, 2019, **3(5)**, 290-304.
- [3] Piermattei A., Karthikeyan S., Sijbesma R.P. *Nature Chemistry*, 2009, **1**, 133-137.
- [4] Patulski P., Fernández-Catalá J., Berenguer-Murcia Á., Cazorla-Amorós D. *Journal of CO2 Utilization*, 2025, **94**, 103055.
- [5] McElroy C. R., Constantinou A., Jones L.C., Summerton L., Clark J.H. *Green Chemistry*, 2015, **17(5)**, 3111-3121.
- [6] Andraos J., Sayed, M. *Journal of chemical education*. 2007, **84(6)**, 1004.
- [7] Aneggi E., Campagnolo F., Segato J., Zuccaccia D., Baratta W., Llorca J., Trovarelli, A. *Molecular Catalysis*, 2023, **540**, 113049.

The Other Side of Sustainability: Evaluating Chemical Migration from Alternative Food Contact Materials – The Case of Drinking Straws

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The progressive phasing-out of single-use plastics in food contact applications is a global trend driven by stringent environmental policies and shifting market demands. Alternative materials – such as paper-based products, bio-based materials, and other plant-derived materials – are being rapidly introduced. However, the transition toward more sustainable materials does not automatically guarantee chemical safety. The potential migration of intentionally and unintentionally added substances from these alternatives remains a significant concern for consumer health. This study aims to identify the chemicals released from commercially available alternative single-use straws. Samples made of recycled plastic, plant fibers, and paper were subjected to migration testing in accordance with EU guidelines, ensuring a harmonized framework for simulant selection and test conditions. To cover a wide range of chemical properties, a multi-analytical approach was employed: i) volatile and semi-volatile compounds present in the migration solutions will be analysed using Headspace Solid-Phase Microextraction coupled with Gas Chromatography-Mass Spectrometry, allowing for the screening of compounds originating from raw materials, additives, degradation processes, or production treatments; ii) non-volatile and more polar migrants will be studied using Liquid Chromatography coupled with High-Resolution Mass Spectrometry, applying a non-targeted workflow aimed to detect both known and unknown compounds. Given the growing concern over the potential toxicity of organic pollutants in food contact materials, particular attention will be paid to per- and polyfluoroalkyl substances due to their persistence. A targeted analysis using Liquid Chromatography coupled with Mass Spectrometry will be performed to assess these substances in the selected samples. The results will provide valuable scientific evidence to bridge the gap between environmental sustainability and chemical exposure, supporting future monitoring and regulatory discussions on the safety of “eco-friendly” food contact materials.

Acknowledgements:



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References

- [1] Asensio E., Montañés L., Nerín C. *Food and Chemical Toxicology*, 2020, **142**, 111457.
- [2] Canellas E., Vera P., Nerin C., Goshawk J., Dreolin N. *Food Packag. Shelf Life*, 2024, **41**, 101237.
- [3] Simonetti G., Riccardi C., Pomata D., Acquaviva L., Fricano A., Buiarelli F., Senofonte M., Di Filippo P. *Foods*, 2024, **13**, 645.

A Metal-Free Current Collector Made of Polymer for Anode-Less Lithium-Metal Batteries

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In this work, we coat a LiNO₃–PEO composite onto Cu via hot-pressing to create a stabilizing interlayer that accommodates reversible electrochemical Li-metal plating ¹. This architecture promotes uniform nucleation and dendrite-free cycling. The scalable, low-cost design represents a promising current collector for advanced Li-metal batteries ². The need for improved energy storage has made anode-less batteries a promising option. Unlike conventional batteries, they contain no anode only a bare current collector ^{3,4}. Upon charging, lithium or sodium plates directly onto this collector, forming the anode in situ. This design yields a lighter, more compact, and cheaper battery, while also enhancing sustainability.

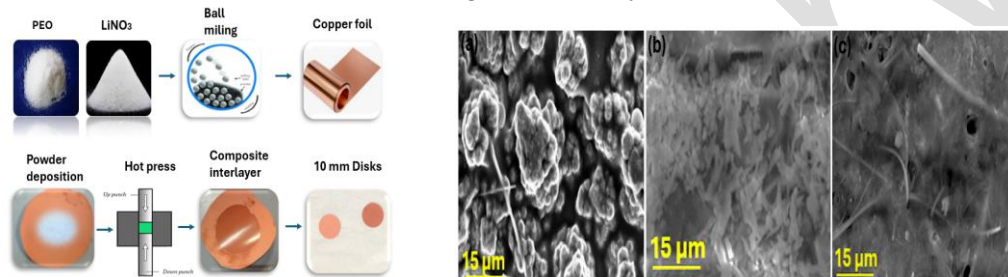


Fig. 1. (Left side) Schematic illustration of the preparation of the interlayer PEO and LiNO₃ were mixed and deposited onto copper foil and directly hot-pressed. The (Right side) The (Right side) SEM P.M Images (b) Cu, (c) PEO@Cu and (d) PEO-LiNO₃@Cu current collectors.

We demonstrate this interlayer's performance in electrochemical cells. Post-mortem studies (SEM spectroscopy) reveal key factors that control lithium plating/stripping reversibility within porous interlayers.

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References

- [1] Chen, S.; Pan, C.; Wang, Q.; Luo, J.; Fu, X. Advancements in Current Collectors for Composite Lithium Metal Anodes. *Adv. Funct. Mater.* **2024**, *34* (51), 2409812.
- [2] Hao, Z.; Li, G.; Zheng, C.; Liu, X.; Wu, S.; Li, H.; Zhang, K.; Yan, Z.; Chen, J. The Dependence of Solid Electrolyte Interphase on the Crystal Facet of Current Collector in Li Metal Battery. *Angew. Chem. Int. Ed.* **2024**, *63* (37), e202407064.
- [3] Jo, S.; Kwon, B.; Oh, J.; Lee, J.; Park, K.; Lee, K. T. The Roles of Nucleation and Growth Kinetics in Determining Li Metal Morphology for Li Metal Batteries: Columnar versus Spherical Growth. *J. Mater. Chem. A* **2022**, *10* (10), 5520–5529.
- [4] (44) Parks, A. Investigation of Morphology and Surface Chemistry of LLZO Garnet in Composite Electrolyte for Lithium Solid-State Batteries. **2025**.

Structural features of a geothermal thermophilic PETase

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The ubiquity of plastics in modern society and their escalating production rates pose a significant environmental threat. Poly(ethylene terephthalate) (PET) is a primary concern due to its high production volume and inherent resistance to natural degradation [1]. Enzymatic biodegradation using specific hydrolases has emerged as a sustainable strategy for PET recycling and upcycling. In this study, we characterize DIEGO (*Depolymerising Isolated Enzyme from Geothermal Origin*), a novel thermophilic PETase identified through geothermal metagenomic screening [2].

DIEGO stands out for its ability to operate at 60°C, enabling PET bioconversion into a single step. The high operation temperature increases substrate accessibility and triggers the spontaneous breakdown of BHET and MHET intermediates, achieving full degradation of post-consumer PET in just 96 hours. Structural analysis, conducted in both solution and crystalline states, confirms that the enzyme adopts a canonical α/β hydrolase fold (Figure 1) involving a central core of nine β -strands flanked by ten α -helices. The enzyme exhibits intrinsic thermostability, with a melting temperature of approximately 89°C. Consistent with other characterized PETases, this stability is further enhanced by the addition of divalent cations Mg^{2+} and Ca^{2+} [3].

The crystallographic study provides the structural basis of DIEGO specific features. Comparative structural analysis between DIEGO, the mesophilic *Ideonella sakaiensis* PETase (*IsPETase*), and the thermophilic Leaf-Branch Compost Cutinase (LCC) reveal unique molecular features. By integrating high-temperature catalytic efficiency with a highly stable protein scaffold, DIEGO represents a promising candidate for biocatalytic applications within a circular PET economy.

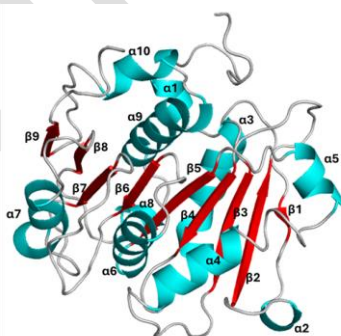


Figure 1: A cartoon representation of the overall DIEGO crystal structure, with secondary structure elements depicted in red and cyan for β -strands and α -helices, respectively

References

- [1] Vincent T., Sophie D., Frédérique G., Henri C., Daniel T., Alain M., and Isabelle A. *Chemical Reviews* 2023 123 (9), 5612-5701
- [2] Marika G., Carmen E., Nicola C., Donato G., Domenico P., Wolfgang R. S., Pablo P. G., Beatrice C. P., Andrea S., Marco M. *Environmental Technology & Innovation*, Volume 40, 2025, 104587
- [3] Jansen S., Rifqi Z. J., Aisy H. R., Safero Hedi A., Resmila R. R., Dwi H. S., Sony S., Rindia M. P., Reza A., and Azzania F. *ACS Omega* 2025 10 (7), 6385-6395

CaZn₂ Alloy as a Stable Counter Electrode for Reliable Evaluation of Calcium-Based Battery Systems

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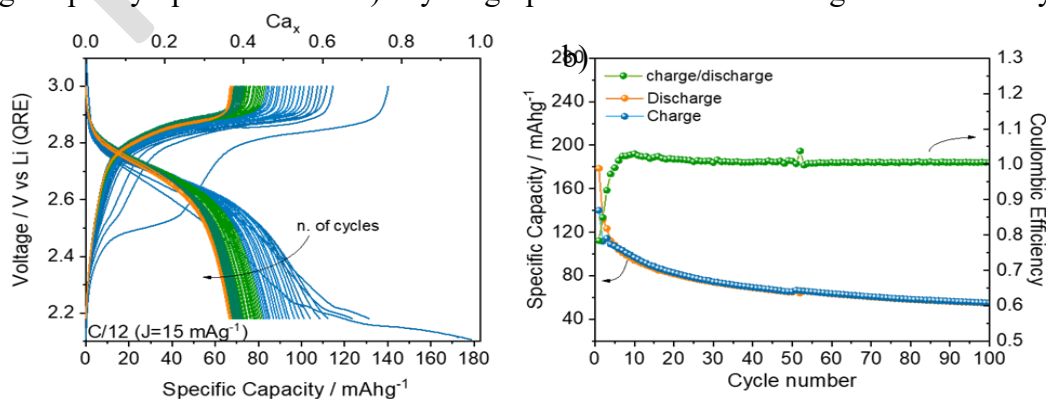
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The development of calcium-ion batteries (CIBs) is hampered by the lack of reliable and standardized counter electrodes for evaluating cathode materials and electrolytes. Metallic calcium, although thermodynamically ideal, exhibits poor reversibility, high reactivity, and unstable interfaces in most organic electrolytes, especially those based on Ca(TFSI)₂, leading to severe parasitic reactions and irreproducible electrochemical behaviour. Here, we introduce a Ca–Zn intermetallic alloy with a nominal 1:2 stoichiometry (CaZn₂), synthesized by arc melting, as a robust and chemically stable counter electrode for CIB research. Structural and compositional analyses confirm the formation of a CaZn₂-rich alloy, with CaZn₃ as a secondary phase and a homogeneous Ca/Zn distribution. Owing to its moderated calcium activity and thermodynamic stability, CaZn₂ displays markedly improved compatibility with a weakly coordinating Ca(TFSI)₂-based electrolyte (0.4 M Ca(TFSI)₂ in G1/G2/TEP, i.e., 1,2-dimethoxyethane, diethylene glycol dimethyl ether, and triethyl phosphate, respectively), enabling stable cycling with lower overpotentials compared to metallic Ca. Symmetric CaZn₂|CaZn₂ cells exhibit well-defined, reversible redox features and sustained galvanostatic cycling, while impedance spectroscopy reveals stable charge-transfer resistance and a gradually evolving interphase. The electrolyte shows an electrochemical stability window of ~3 V vs. CaZn₂, supporting its use in practical full-cell configurations. As a proof of concept, CaZn₂ was paired with an NTCDA-based organic cathode, delivering capacities close to the theoretical value for one Ca²⁺ equivalent in the first cycle and highly reversible cycling with near-quantitative coulombic efficiency over 100 cycles, outperforming analogous cells employing calcium metal. By suppressing deleterious side reactions and enabling reproducible performance benchmarking with a Ca(TFSI)₂ electrolyte, CaZn₂ provides an effective and scalable reference electrode platform for the systematic investigation of CIB components, thereby accelerating the development of practical calcium-based energy storage systems.

a) voltage-capacity profile and b) cycling performance of the galvanostatic cycling of



1,4,5,8naphthalenetetracarboxylic dianhydride (NTCDA) | Ca(TFSI)₂ 0.4M in G1,G2, TEP | CaZn₂.

Synthesis of ZnCu/PTFE electrodes for CO₂ electroreduction

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Electroreduction of carbon dioxide (ERC) is a competitive technology for reducing carbon dioxide emissions and storing energy from renewable sources. Using various metals as catalysts, CO₂ is converted into fuels/chemicals (e.g., carbon monoxide, formic acid, methanol) [1] at the cathode of an electrochemical cell. Major limitations of ERC are the scarce solubility of CO₂ in water, which limits mass transfer in aqueous systems, and the unsatisfactory selectivity and/or costs of available electrocatalysts. To improve mass transfer, electrochemical flow cells relying on the gas-diffusion electrodes (GDEs) can be used. Noble metals such as gold, silver, and palladium can ensure high selectivity (up to 90%) to CO, but they are expensive [2]. For this reason, attention has been devoted to the application of zinc, which is widely available in nature and can provide satisfactory selectivity to CO. However, the catalytic activity of zinc is lower compared to noble metals [3]. This limitation can be mitigated by the application of foam electrodes with high specific surface area. These electrodes can be effectively synthesized by the bubbling electrodeposition method [4], [5]. It has been previously demonstrated that the addition of copper to zinc electrolyte ensures the formation of porous structures and can enhance the catalytic activity for ERC. However, previous studies have not investigated the application of Zn-Cu in flow cell configurations. To this purpose, the introduction of hydrophobic domains within the foam is required to enforce the coexistence of gas and liquid and reduce mass transfer resistance. In this work, the synthesis of composite ZnCu/PTFE foams by electrodeposition from suspensions of PTFE nanoparticles is discussed. We investigate how electrodeposition parameters (current density, charge density, and Zn/Cu ratio in the bath) govern not only the morphology and composition of Zn-Cu foams, but also mass transport and wettability properties through the incorporation of PTFE during synthesis. The structure and morphology of the electrodes were characterized by SEM, XRD, and ICP, while electrocatalytic performance was first evaluated in an H-cell and subsequently in a flow cell. This approach correlates synthesis parameters, structure, and operating conditions, highlighting the role of the gas-liquid-solid interface on activity and selectivity in ERC.

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References

- [1] Feng. L., Kaiwen Z., Lei Z., Yingjie. Z., Yong L., Xueliang S. *Small*, 2021, 17, 2100323.
- [2] Toru H., Kendra P. K., Etosha R C., David. N. A., Thomas. F. J. *PCCP*, 2014, 16, 13814-13819.
- [3] Dong D. Z., Jin L. L., Shi Z. Q. *Advanced Materials*, 2016, 28, 3423–3452.
- [4] García P. M., Schlegel N., Zanetti A., López A.C., Galvez-Vázquez M. J., Dutta A., Rahaman M., Broekmann P. *ACS Applied Materials & Interfaces*, 2018, 10, 31355–31365
- [5] Lamaison S., Wakerley D., Montero D., Rousse G., Taverna D., Giaume D., Mercier D., Blanchard J., Tran H. N., Fontecave M., Mougél V. *ChemSusChem*, 2019, 12, 511 – 517.

Rhodium Porphyrin Catalysts for Efficient Hydrogen Production from Ammonia Borane

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The transition toward sustainable energy systems has intensified interest in hydrogen as a clean energy carrier. Ammonia borane (AB) is a promising hydrogen storage material due to its high gravimetric hydrogen content and good stability;^[1] however, its thermal decomposition requires high temperatures and generates undesirable byproducts. In contrast, catalytic hydrolysis of AB in aqueous media enables controlled and efficient hydrogen production under mild conditions, as described by the reaction:^[2]



Rhodium-based catalysts have proven to be among the most active systems for promoting AB hydrolysis at ambient temperature.^[3,4]

In this contribution, we introduce rhodium porphyrins as a new class of catalysts for the hydrolytic dehydrogenation of AB, moving beyond the conventional use of porphyrins as supports for metal nanoparticles.^[5,6] A series of rhodium complexes was prepared from different porphyrin scaffolds, including both water-soluble (cationic and anionic) and water-insoluble systems, enabling the investigation of both homogeneous and heterogeneous catalytic conditions.^[7]

All the synthesized rhodium porphyrins exhibited catalytic activity under mild conditions, with differences in performance depending on the porphyrin structure and solubility. In particular, the anionic system showed the highest efficiency among the homogeneous catalysts, while the heterogeneous system displayed lower activity but improved stability over multiple runs.

Overall, these results highlight the potential of rhodium porphyrins as versatile catalysts for hydrogen production from ammonia borane, offering insights into the role of porphyrin structure and reaction conditions in tuning activity and stability.

References

- [1] J. Yang, A. Sudik, C. Wolverton and D. J. Siegel, *Chemical Society Reviews*, 2010, **39**, 656.
- [2] M. A. Khalily, H. Eren, S. Akbayrak, H. H. Susapto, N. Biyikli, S. Özkar and M. O. Guler, *Angewandte Chemie International Edition*, 2016, **55**, 12257.
- [3] P. V. Ramachandran and P. D. Gagare, *Inorganic Chemistry*, 2007, **46**, 7810.
- [4] S. Akbayrak, Y. Tonbul and S. Özkar, *ACS Sustainable Chemistry & Engineering*, 2020, **8**, 4216.
- [5] D. Özhava, Y. Çiğdem and S. Ertürk, *International Journal of Hydrogen Energy*, 2023, **48**, 22942.
- [6] N. Zhang, G. Liu, Y. Sun, Y. Wang, J. Yan and X. Liu, *Catalysis Letters*, 2021, **151**, 2272.
- [7] M. Minnucci, I. Barlocco, L. Prati, M. Stucchi, A. Villa, G. Di Carlo and F. Tessore, *Dalton Trans.*, 2026, **55**, 2123-2134

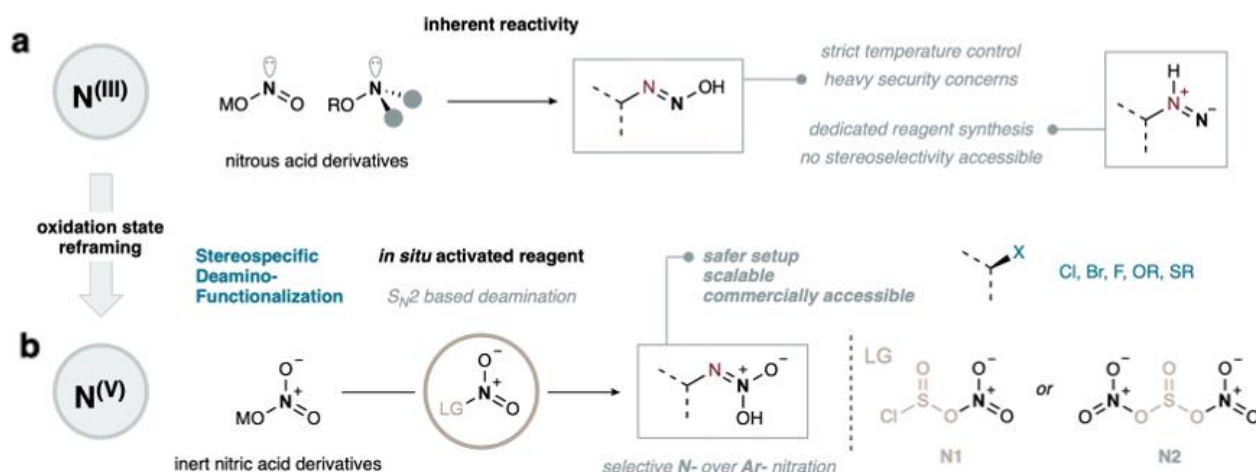
Direct Deaminative Functionalization of Primary Amines through N(V) Activation

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Aliphatic amines are among the most abundant and valuable functional groups in organic synthesis, medicinal chemistry, and chemical biology.^{1,2} Their direct conversion into alternative C(sp³)–X bonds represents an attractive strategy to repurpose readily available amine feedstocks as alkyl synthons.³ However, despite recent advances in direct deaminative functionalization,⁴ the selective replacement of unactivated C(sp³)–N bonds remains challenging, particularly when stereochemical information embedded in chiral primary amines must be preserved. Current strategies often rely on radical pathways or classical nitrosation chemistry,^{5,6} which can limit stereospecificity, functional-group tolerance, or operational generality (Scheme 1a). Herein, we present a conceptually distinct platform for the direct deaminative functionalization of unactivated primary amines based on N(V) activation. In this approach, simple nitrate sources are converted in situ into competent nitrating reagents, enabling the transient formation of N-nitroamine intermediates (Scheme 1b). These species provide access to substitution-competent electrophiles that can be intercepted by external nucleophiles under a polar, stereospecific manifold. The method offers a practical opportunity to access various alkyl derivatives from abundant primary amines, including amino-acid-derived motifs and complex amine-containing scaffolds. More broadly, this work highlights the potential of controlled N-nitration as a general activation logic for C(sp³)–N bond functionalization.



Scheme 1 a) N^{III} approach for deamination reactions b) our approach: activation of N^v with unusual nitrating reagent for selective deamination of alkyl amines.

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References

- [1] Ertl, P.; Altmann, E.; McKenna, J. M. *J. Med. Chem.* 2020, **63**, 8408–8418.
- [2] Berger, K. J.; Levin, M. D. *Org. Biomol. Chem.* 2021, **19**, 11–36.
- [3] Dherange, B. D.; Yuan, M.; Kelly, C. B.; Reiher, C. A.; Grosanu, C.; Berger, K. J.; Gutierrez, O.; Levin, M. D. *J. Am. Chem. Soc.* 2022, **145**, 17–24.
- [4] Durka, J.; Zielińska, B.; Gryko, D. *Angew. Chem. Int. Ed.* 2024, **64**, e202419450.
- [5] Brewster, P.; Hiron, F.; Hughes, E. D.; Ingold, C. K.; Rao, P. A. D. S. *Nature* 1950, **166**, 179–180.

Hydrogen production in a sludge-inoculated MEC: influence of HRT and electrochemical characterization

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Among emerging technologies, Microbial Electrolysis Cells (MECs) represent an innovative approach capable of coupling hydrogen production with organic substrate treatment [1, 2]. These bioelectrochemical systems exploit the metabolic activity of electroactive microorganisms to oxidize organic matter at the bioanode, generating electrons that, through a limited external energy input, are utilized for hydrogen production at the cathode [3]. Compared to conventional electrochemical processes, MECs operate under mild conditions and offer the additional advantage of organic load removal, positioning themselves as a promising technology for integrated energy recovery from wastewater [4, 5].

This study analyzes the performance of a single-chamber MEC equipped with a cation exchange membrane (CEM). The bioanode, consisting of granular graphite (< 4 mm), serves as both the electrode material and the support for biofilm growth. The research objective is to evaluate the influence of the hydrodynamic regime on the system's response. The reactor, inoculated with activated sludge, was tested at different flow rates (from 0.65 L/d to 20.96 L/d), corresponding to variations in hydraulic retention time (HRT from 1.31 d to 0.04 d), to investigate the electrochemical response under conditions of high substrate availability.

Preliminary results demonstrate that increasing the flow rate and the subsequent decrease in HRT significantly enhance cathodic current production (from 19.05 mA to 109.24 mA). Operation at low HRT ensured a constant presence of organic substrate, eliminating any limiting factors for the biofilm. Although this led to high residual COD levels, such a condition was fundamental to ensure that the biofilm operated in a constant substrate saturation regime, nullifying any resistance related to nutrient availability.

To support these findings, cyclic voltammetry (CV) analyses, conducted at various scan rates (5–60 mV/min), confirm the selection of a specific electroactive bacterial population, with a distinct oxidation peak highlighted at 5 mV/min. Overall, the study demonstrates that hydrodynamic optimization is key to overcoming the kinetic limitations of bioelectrochemical systems and maximizing current production. Prospectively, these results lay the groundwork for applying this technology to complex real wastewaters, aiming for sustainable and integrated energy recovery.

References

- [1] Zou, R., et al. (2023). Advances in microbial electrolysis cells for waste-to-hydrogen conversion: A review of reactor designs and operational strategies. *Journal of Cleaner Production*
- [2] Hassan, S., et al. (2024). Bioelectrochemical hydrogen production: Recent trends and challenges in microbial electrolysis cell technology. *Renewable and Sustainable Energy Reviews*
- [3] Wang, L., et al. (2022). Extracellular electron transfer in bioelectrochemical systems: Mechanisms and intensifying strategies. *Bioresource Technology*
- [4] Escapa, A., et al. (2021). Green hydrogen production from wastewater: A technology health check. *Current Opinion in Biotechnology*
- [5] Santoro, C., et al. (2025). Bioelectrochemical Systems for Wastewater Treatment and Resource Recovery: A Roadmap to Commercialization. *Engineering in Life Sciences*.

A diagnostic screening evaluation of dual-cathode MEC performance for waste-derived biohydrogen production

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Microbial electrolysis cells (MECs) are promising bioelectrochemical platforms for simultaneous treatment of organic waste streams and renewable hydrogen production. Their optimization remains a major bottleneck, particularly when real substrates are employed, due to bioanode sensitivity for the substrate heterogeneity, complexity and intrinsic characteristics as pH [1]. This study proposes for the first time a rapid operational screening strategy to evaluate the performance and operational limits of a laboratory-scale dual-cathode MEC under six different hydraulic conditions and organic loading rates (case A, B, C, D, E, F) using several real substrates. The MEC consisted of three identical Plexiglas chambers (0.86 L each). The bioanode chamber, fed in continuous mode, filled with granular graphite (<4 mm), was separated from two cathodic chambers by a CMI cation exchange membrane, allowing selective cation transport. While, each cathodic chamber, fed in batch mode, was equipped with 316 stainless steel sheet electrodes (176.46 cm²). Beyond synthetic feed, used for benchmark purposes, the system was supplied with a dark fermentation effluent derived from organic fraction of municipal solid waste (OFMSW), untreated brewery wastewater (BWV), and untreated dairy wastewater (DWW). The OFMSW effluent exhibited a high fraction of organic acids (82% OA/COD_{sol}) and a low redox potential (≈ -0.278 V vs SHE), indicating strong electron-donating capacity and high suitability for bioelectrochemical conversion. In contrast, raw wastewater showed a more heterogeneous COD composition. The rapid screening approach clearly revealed a trade-off between COD removal efficiency and current generation (and thus hydrogen production). Under the most hydraulic extreme condition (Case F with OLR of 33 gCOD/Ld), COD removal converged to similar values regardless of the substrate type, indicating a critical system operational plateau. This behaviour suggests bioanode saturation, that means the microbial community becomes kinetically limited and unable to further degrade the supplied organic load, independently of substrate composition. Overall, the dual-cathode configuration ensured complete electron recovery into hydrogen (CCE > 100%) with high gas purity across all tested conditions. When comparing with the performance of single-cathode configurations, fed with same synthetic medium, the dual-cathode design enhanced hydrogen recovery and operational robustness: CCE of 95% vs 74%; η_E of 104% vs 83%, comparison with data from Marchetti et al., [2]. However, the results demonstrate that rapid diagnostic screening can serve as a tool to identify system bottlenecks, quickly identifying performance plateaus and bioanodic saturation thresholds, thus accelerating MEC optimization and supporting the practical implementation of sustainable biohydrogen production from heterogeneous waste streams.

References

- [1] Zeppilli M, Paiano P, Torres C, Pant D. A critical evaluation of the pH split and associated effects in bioelectrochemical processes. *Chemical Engineering Journal* 2021;422:130155. <https://doi.org/10.1016/J.CEJ.2021.130155>.
- [2] Marchetti A, Cerrillo Moreno M, Lauri R, Zeppilli M. Optimizing Hydrogen Production Through Efficient Organic Matter Oxidation Performed by Microbial Electrolysis Cells. *Processes* 2025;13:1231.

Recycling Processes for Next Generation Photovoltaics

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Next-generation photovoltaic (PV) technologies, specifically perovskite, kesterite, organic, and dye-sensitized cells, offer cost-effective, scalable alternatives to silicon due to their high-absorption and use of abundant materials¹. Moreover, their layered structure allows for ease of production, which is appealing when scaling up at an industrial level. Despite their potential, their commercialization is hindered by limited lifespans, supply chain vulnerabilities (e.g., indium), and the established market dominance of silicon-based PVs.

As these technologies are pre-commercial, there is a unique opportunity to proactively integrate sustainability via “design-to-recycle” strategies. Recycling serves not only to close the loop, but, within the European Union, it is a regulatory mandate under the WEEE Directive (2012/19/EU). This legislation categorizes PV waste as a specific sub-category of WEEEs, shifting the responsibility for end-of-life management and recovery targets directly to the producers². Outside of the European Union, global regulations remain fragmented, leading to significant data gaps.

Current recycling processes for traditional PVs involve a combination of mechanical, thermal and chemical treatments³. Mechanical pre-treatments, like shredding or milling, aim to expose valuable internal components and reduce particle size of the waste, whereas thermal treatments are used to evaporate the polymeric encapsulant. Finally, chemical treatments allow for separation and recovery of the layered stack. These existing processes must adapt to the new configuration of PVs, whose thin film sandwiched architecture with flexible substrates adds new challenges to recycling⁴.

This work offers a comprehensive analysis of global PV waste regulations alongside an evaluation of the material composition, market value, and recycling potential of next-generation panels. By reviewing state-of-the-art advances in thin-film recycling, the study examines how established methodologies may be adapted to address the complexities of layered architectures. An analogy is also provided with other types of thin-film waste, such as OLED (Organic Light Emitting Diode) displays.

References

- [1] Shah, N., et al. "A review of third generation solar cells." *Processes* 11.6 (2023): 1852.
- [2] Shittu, Olanrewaju S., Ian D. Williams, and Peter J. Shaw. "Global E-waste management: Can WEEE make a difference? A review of e-waste trends, legislation, contemporary issues and future challenges." *Waste Management* 120 (2021): 549-563.
- [3] Chowdhury, Md Shahariar, et al. "An overview of solar photovoltaic panels' end-of-life material recycling." *Energy Strategy Reviews* 27 (2020): 100431.
- [4] Tai Wu, Xiaopeng Gao, Ziheng Liu, Xu Liu, Xiaojing Hao, and Meng Zhang. The recycling of perovskite solar cells: progress, challenges and opportunities. *Science Bulletin*, 2026.

A Solvent-free Mechanochemical Route to Ni-Based Catalysts for Efficient CO_x-Free Hydrogen Production

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In the context of current energy transition challenges, the production of CO_x-free hydrogen represents a promising pathway toward sustainable energy systems. Catalytic methane decomposition (CMD) enables the simultaneous generation of H₂ and valuable carbonaceous nanomaterials (CNM) for various industrial applications. Ni-based and Ni-promoted catalysts prepared via impregnation methods are widely reported in the literature for this purpose [1,2]

In this study, Ni, NiFe and NiCu and Fe catalyst supported over Al₂O₃ were synthesized through a solvent-free mechanochemical approach based on mechanical grinding. This method aims to reduce water consumption while enhancing catalysts porosity and surface area. The catalysts were characterized and evaluated for methane cracking at a relatively low temperature of 700 °C

Experimental and results Catalytic performance was assessed using thermogravimetric analysis, monitoring carbon formation over time. The reaction protocol included a 30 min reduction step (200 mL/min H₂, 500 ml/min N₂) at 700 °C, followed by 3h of reaction under a CH₄/H₂/N₂ mixture (200/100/400 mL/min) at the same temperature.

Among the investigated systems, the NiCu catalyst exhibited the highest carbon productivity (2.59 g_{carb}/g_{met} h) and hydrogen yield (29.00 L/g_{met}). Although the other catalysts showed lower activity, they produced carbon with higher structural quality. These results highlight the versatility of the proposed solvent-free synthesis route in developing catalysts suitable for both efficient hydrogen production and tailored carbon material generation.

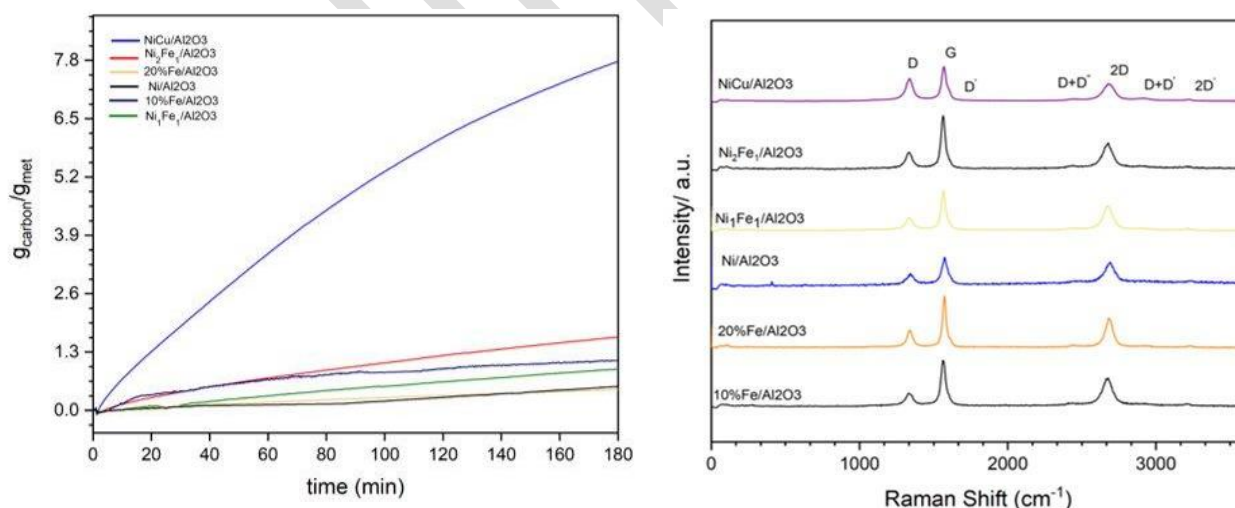


Figura 1 a) Carbon production B) Raman spectra of spent catalysts

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References

- [1] Tom A. J. Welling et al., Phys. Chem. C 2023, 127, 15766–15774
- [2] Cazaña et al., Chem Engineering 2022, 6, 47

High CO₂ Methanation Activity with Low Ni Loading via Enhanced Dispersion on Mesoporous CeO₂

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Due to the increasing concern over global warming, current research is strongly focused on the development of green fuels obtained via the reduction of captured CO₂ (e-fuels) using green hydrogen. Among these, methane represents a prominent example, as it can be produced through the catalytic hydrogenation of CO₂ via the Sabatier reaction. Ni-based catalysts are among the most extensively investigated systems for CO₂ methanation, owing to their high activity and selectivity at relatively low temperatures, as well as their lower cost compared to noble metal-based catalysts. Ni is often combined with supports or promoters such as CeO₂, to enhance catalytic performance [1,2]. In this work, composite catalysts consisting of a NiO active phase dispersed over mesoporous CeO₂ are presented. The use of a mesoporous support promotes a high dispersion of NiO in the form of small nanoparticles, resulting in enhanced catalytic activity while minimizing the amount of active phase required. For comparison, a chemically inert mesostructured siliceous material (SBA-15) was also employed as a support to evaluate the specific role of CeO₂ as a promoter.

NiO was dispersed over the CeO₂ support using an impregnation approach combined with a self-combustion reaction. Three composite catalysts with Ni loadings of 5, 10, and 15 wt% were prepared. A 5 wt% Ni catalyst supported on SBA-15 was synthesized using the same procedure for comparison. XRD analysis indicates that NiO is highly dispersed on the mesoporous support in the form of very small nanoparticles. No diffraction peaks attributable to Ni-based crystalline phases are observed for the 5 wt% Ni sample, while weak and broad peaks appear for the 10 wt% and, more prominently, 15 wt% samples. Elemental mapping obtained by EDX and EELS further shows that decreasing the Ni loading leads to a more homogeneous dispersion of NiO over CeO₂. These findings are consistent with H₂ pulse chemisorption measurements on reduced samples, which reveal an increase in Ni dispersion from 5.3% (15 wt% Ni) to 16.7% (5 wt% Ni). Catalytic activity was evaluated under varying temperature and gas hourly space velocity (GHSV) conditions. All catalysts supported on mesoporous CeO₂ exhibit high activity, with CO₂ conversion ranging from 80 mol% (5 wt% Ni) to 85 mol% (15 wt% Ni), values comparable to or exceeding those reported in the literature for similar systems. In contrast, the catalyst supported on SBA-15 shows significantly lower activity (approximately 10 mol% CO₂ conversion), highlighting the crucial role of CeO₂ not only as a support but also as a strong promoter. Notably, CO₂ conversion is only weakly dependent on Ni loading, indicating that even a low Ni content (5 wt%) can achieve high catalytic performance due to superior dispersion in the form of ultra-small nanoparticles. This aspect is particularly relevant, as it enables minimizing the use of Ni while maintaining high catalytic efficiency.

References

- [1] I. Hussain et al. International Journal of Hydrogen Energy 48(64) (2023) 24663-24696.
- [2] S. Chen et al. Applied Catalysis B: Environmental 366 (2025) 125029.

Synchrotron ex-situ characterization of Li-rich Ni-rich layered oxides materials for application in lithium ion batteries

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Lithium-ion batteries (LiBs) employing Li-rich layered oxide (LRLO) cathodes have attracted significant attention as advanced energy storage systems due to their remarkable theoretical capacities exceeding 250 mAh g⁻¹ and high operating voltages above 4.5 V. Together, these features enable an energy density approaching 900 Wh kg⁻¹. In particular, cobalt-free LRLO materials offer advantages in terms of improved stability and lower cost compared to conventional cobalt-containing cathodes [1]. A representative cobalt-free composition is Li_{1.2}Ni_{0.2}Mn_{0.6}O₂, which enhances lithium content while preserving an optimal Mn/Ni ratio, thereby removing the dependence on cobalt.

In this study, we report the synthesis of nickel-enriched LRLO materials with compositions spanning 0.24 < Ni < 0.40. These materials were systematically evaluated through detailed chemical, structural, and electrochemical characterization to assess their suitability for LiB applications. To investigate structural changes occurring in the Ni-rich LRLO electrodes during electrochemical cycling, ex-situ synchrotron-based techniques were employed, including X-ray Absorption Spectroscopy (XAS) and Resonant Inelastic X-ray Scattering (RIXS). XAS measurements enabled examination of the local chemical environments of the transition metal (TM) species, with data interpretation supported by Principal Component Analysis (PCA). Furthermore, RIXS measurements at the oxygen K-edge were utilized to probe oxygen redox activity within the cathode material framing the work as highly interesting in the ongoing vivid debate over anionic-redox material behavior [2,3].

Acknowledgements:

[1] S. Passerini et al.; Is Cobalt in Li-Rich Layered Oxides for Li-Ion Batteries Necessary?; ChemElectroChem Volume 11, Issue 17 e20240039

[2] P. G. Bruce et al.; The role of O₂ in O-redox cathodes for Li-ion batteries; Nat Energy **6**, 781–789 (2021)

[3] J. M. Tarascon et al., (2025). Clarifying the origin of molecular O₂ in cathode oxides. *Nature Materials*, 24(5), 743-752.



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Valorization of Heterogeneous Bioplastic Waste via Hydrothermal Liquefaction: Experimental Study

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Plastic pollution poses a major global challenge, driving the shift toward alternative materials such as bioplastics. These materials match the mechanical performance of conventional plastics while being biodegradable and derived from renewable sources. Although bioplastics accounted for just 1% of total plastic production in 2024 ^[1], their output is expected to grow significantly by 2029. Legislation incentivizes their use by requiring shopping bags certified under the UNI EN 13432 standard, verifying suitability for industrial composting and disposal with the organic fraction of municipal solid waste (OFMSW). However, these waste streams are often contaminated with fossil-based plastics, and a key challenge arises from the mismatch between certification requirements (90% degradation in six months) and the actual industrial processes, such as anaerobic digestion and composting (approximately 1.5 months) ^[2]. Consequently, large bioplastic fragments are mechanically separated during pre-treatment to prevent blockages and are sent to landfills or incinerators, where their structure and high-water content reduce energy recovery efficiency.

In this framework hydrothermal treatments such as thermal hydrolysis, carbonization, and liquefaction are emerging as viable pre-treatment solutions for contaminated bioplastic waste. Operating in subcritical water, these processes can break down recalcitrant bioplastics. Current studies are scarce or focus primarily on pure bioplastics, and a clear knowledge gap remains regarding the behavior of heterogeneous, contaminated municipal waste streams. In this study, hydrothermal valorization of a real mixed waste stream, containing approximately 44% fossil-based plastics contamination and collected from a composting facility in Viterbo (Italy), was investigated. The waste was characterized by TGA, FT-IR, and elemental analysis and was subjected to HTL at 200, 250, 280, and 300 °C for 30 minutes. Experimental results demonstrated a significant shift in product yields: the solid fraction decreased from approximately 67 wt% at 200 °C to about 35 wt% at 300 °C, while the liquid fraction (aqueous and crude) increased from 20% to 47%. The resulting products were characterized using FT-IR, EA, TOC, and GC-MS. GC-MS of the liquid phase revealed a complex composition, with approximately 30% of the relative peak areas attributed to fatty acids, such as acetic acid, and another 30% consisting of butanediol, the main degradation product of starch-based bioplastics. Furthermore, approximately 20% of the identified compounds were classified as ketone-like species, alongside a significant proportion of phenols, confirming the effective hydrothermal breakdown of the mixed organic and plastic feedstock, with the resulting liquid phase thereby offering significant potential for further valorization. Overall, the findings highlight the potential of hydrothermal liquefaction for the valorization of contaminated bioplastic waste within circular waste management strategies.

References

- [1] The Circular Economy for Plastics A European Analysis, 2024.
- [2] F. Marchelli, L. Fiori, The growing problem of waste bioplastics disposal, and a way to tackle it, Waste Management 201 (2025). <https://doi.org/10.1016/j.wasman.2025.114786>.

Substrate-to-Biomass ratio as a driver of Polyhydroxyalkanoates storage capacity of Mixed Microbial Cultures

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Polyhydroxyalkanoates (PHAs) are biodegradable polyesters produced by over 300 species of microorganisms. Mixed microbial cultures (MMCs) offer a promising, cost-effective alternative, for PHA production and are increasingly studied up to pilot scale, typically using sequencing batch reactors (SBR) [1]. This study investigates the optimization of the accumulation stage in a continuous-flow three-reactor process for MMC-PHA production. The highest average intracellular PHA content (55 ± 2 %, wt/wt) was achieved for the combination of low applied organic loading rate (OLR) to the microbial selection reactors (2.12 gCOD/Ld) and high OLR (6.12 gCOD/Ld) to the accumulation reactor, corresponding to the only condition wherein residual substrate was detected, indicating non-limiting carbon availability. To better interpret the relationship between the substrate fed and biomass concentration, a new operational descriptor, the Specific Organic Loading Rate (SOLR), was introduced and defined as the daily carbon load supplied per unit of active biomass. A strong positive correlation was observed, with average polymer contents increasing from 31 ± 2 % (wt/wt) at $\text{SOLR} < 4 \text{ d}^{-1}$ to 77 ± 2 % (wt/wt) at $\text{SOLR} > 10 \text{ d}^{-1}$, following a Michaelis–Menten-type saturation trend with a plateau at $8\text{--}10 \text{ d}^{-1}$ (**Figure 1**). These results identify SOLR as a key parameter governing storage capacity in continuous-flow MMC systems, integrating OLR and biomass concentration into a single descriptor. Maintaining SOLR at $8\text{--}10 \text{ d}^{-1}$ ensures an optimal balance between substrate availability and microbial response. From an engineering perspective, aligning the OLR for the accumulation reactor with biomass from the selection stage is crucial to operate within this range, enabling intracellular PHA contents above 70% (wt/wt) and improving the productivity of the overall process.

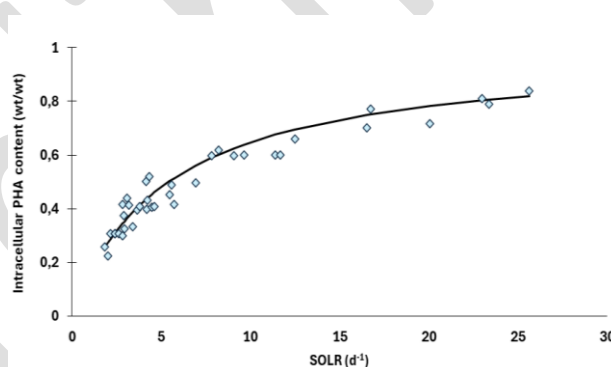


Figure 1 Experimental trend of intracellular PHA content as a function of the specific organic loading rate (SOLR, d^{-1}). Data were fitted using a Michaelis-Menten type model.

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References

- [1] Lorini, L., di Re, F., Majone, M., & Valentino, F. (2020). High rate selection of PHA accumulating mixed cultures in sequencing batch reactors with uncoupled carbon and nitrogen feeding. *New biotechnology*, 56, 140–148.

Bottom-Up Microstripe Patterning of CIGS Thin Films for Semitransparent Photovoltaic Windows

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The integration of photovoltaic functionality into historical and contemporary architectural contexts represents one of the most critical challenges in sustainable building design. Conventional PV solutions impose an inherent trade-off between transparency, aesthetic compatibility, and compliance with cultural heritage regulations, severely limiting their applicability in urban renovation and restoration projects [1].

Here, we present a semitransparent solar cell architecture based on a bottom-up microstripe patterning approach using Cu(In,Ga)Se₂ (CIGS) as the active absorber material. The microstripe geometry achieves average visible transmittance up to 70% and photovoltaic conversion efficiencies approaching 8%, while remaining imperceptible to the human eye at distances exceeding one metre, enabling seamless integration into windows and building façades without altering their appearance. The choice of CIGS as the absorber guarantees long-term stability and efficiency retention, with a projected operational lifetime exceeding 25 years [2]. Incorporation of MXene-based interlayers further enhances device performance through passive infrared reflection and thermal insulation, reducing building cooling demand without compromising optical clarity [3].

The fabrication methodology employs jet-plating of metal electrolytes to define photovoltaic microstripes in a fully additive, bottom-up process. Unlike conventional laser ablation, which destroys active cell material to achieve transparency, our approach fabricates the stripe pattern from the outset, significantly reducing material waste and preserving cell integrity throughout processing. We present in detail the device architecture and the underlying fabrication mechanism, providing a comprehensive framework for understanding how bottom-up patterning decouples transparency from efficiency.

This work positions semitransparent microstriped CIGS solar cells as a disruptive technology with the potential to redefine the boundaries of the photovoltaic market. By enabling solar power provision on surfaces previously inaccessible to conventional PV (glazed façades, heritage windows, high-visibility infrastructure) the technology opens an entirely new addressable market within the built environment, one where aesthetics, regulatory compliance, and energy performance are no longer mutually exclusive.

References

- [1] Li J., Sun S., Wang S., Lu Y., Chen X., Liao X. *Defence Technology*, 2025
- [2] Ramanujam J., Singh U.P. *Energy & Environmental Science*, 2017, **10**, 1306–1319
- [3] Wang Y.-J., Guo B.-F., Peng L.-D., Li Y., Cao C.-F., Zhang G.-D., Gao J.-F., Song P., Shi Y.-Q., Cao K., Tang L.-C. *Advanced Nanocomposites*, 2024, **1**, 217–239.

Composite Anion Exchange Membranes Added with Functionalized Graphene Oxide for Water Electrolyzer Applications

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Alkaline technology, alongside proton exchange membrane water electrolysis (PEMWEs), constitutes one of the two primary low-temperature operation methods, but faces limitations in renewable electricity storage due to poor performance and compatibility issues with intermittent operations. While alkaline water electrolyzers (AWEs) are surpassed by PEMWEs in efficiency, the latter suffer from durability issues and higher costs due to the use of PEMs like Nafion and Platinum Group Metal based catalysts. An emerging alternative, the Anion Exchange Membrane Water Electrolyzer (AEMWE), holds promise by employing non-precious metal catalysts and less expensive and non-perfluorinated membranes, aiming to combine the resilience of AWEs with the performance of PEMWEs. However, the poor hydroxide ion (OH^-) conductivity compared to protons (H^+), as well as mechanical and chemical stability, pose significant challenges in the development of anion exchange membranes (AEMs) [1]. To address them, this study first investigated the incorporation of varying amounts of Graphene Oxide (GO), into the Fumion® FAA-3 ionomer using the solvent casting technique to fabricate AEMs. Then, after proving its beneficial effect on the conductivity and stability of the AEMs [2], the GO was functionalized with quaternary ammonium groups using various straightforward and innovative synthesis methods to obtain different Quaternized Graphene Oxides (QGOs) and further increase the conductivity of the AEMs. The best one of the resulting composite membranes (containing 1%wt of the additive named QGO3) showed a high ion conductivity, increased mechanical stability and higher performances and durability in electrolyzer cell tests respect to the benchmark one (Figure 1).

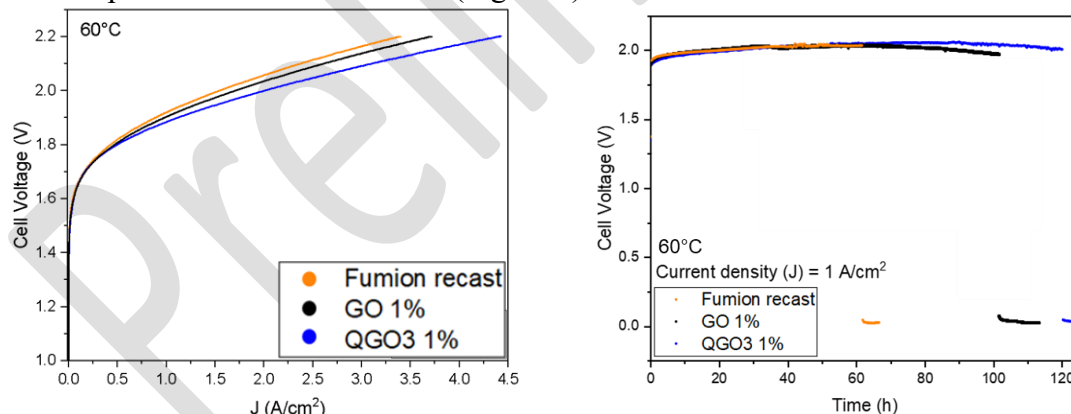


Figure 1: (a) polarization curves and (b) durability test of Fumion AEM (orange), Fumion-GO1% (black) and Fumion QGO3 1% (blue). The tests were performed in a single 5 cm² cell with Ni felt anode and NiFeCo cathode, fluxing 1M KOH

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References

- [1] N. Carboni et al. *Electrochimica Acta* 486, **2024**, 144090
- [2] N. Carboni et al. *J. Mater. Chem. A*, **2026**, 14, 9852-9881

Effect of Wastewater composition on the Performance of a continuous-flow Microbial Electrolysis Cell for Hydrogen Production

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Microbial electrolysis cells (MEC) have emerged as a promising approach for wastewater treatment, as they enable the simultaneous valorization of organic wastes and the generation of renewable energy [1]. Among the possible outputs, hydrogen (H₂) is widely recognised as an attractive energy carrier due to its high energy density. H₂ production, as well as the overall MEC performance, strongly depend on the activity of the biofilm established at the anode which is influenced by the nature and complexity of the feedstock [2].

In this study, effluents supplied by Acquedotto Pugliese (AQP), consisting of drainage wastewater generated from the centrifugation of anaerobically digested of primary (AQP-Effluent 1) and secondary sludge (AQP-Effluent 2), were fed into the bioanode compartments of two identical MECs. The main characteristics of the AQP-effluents used as bioanode feedstocks are shown in Table 1.

The anode of both continuous flow MECs was poised at +0.2 V vs. SHE (Standard Hydrogen Electrode), in order to promote the enrichment of electroactive bacteria on the graphite granules used as electrode materials. The organic loading rate (OLR) was fixed at 1 gCOD (Chemical Oxygen Demand)/Ld, and the current generated at the anode from the COD oxidation was continuously monitored. COD removal efficiency, the fraction of the removed COD converted into current (i.e., Coulombic Efficiency, CE) and H₂ production were determined for both cases. As expected, the lower COD removal efficiency was observed when AQP-effluent 2 was fed to the bioanode (13±1 %) compared to that obtained using AQP-effluent 1 (27±1 %). These findings are consistent with the lower carboxylic acid concentration detected in AQP-effluent 2. Furthermore, CE values of 54±13 % and 28±6 % were determined for AQP-effluent 1 and AQP-effluent 2, respectively; suggesting that the carboxylic acid fraction was readily converted into current. These results demonstrate that the bioanode activity is affected by the heterogeneity of the feedstock, particularly by its carboxylic acid content. This study is currently ongoing, and further investigations are required to optimize the bioanode operating conditions and, in turn, improve the current density and H₂ production.

Table 1. Characterization of the MEC feedstocks

Feedstock	totalCOD (gCOD/L)	solubleCOD (gCOD/L)	NH ₄ ⁺ (g/L)	Carboxylic acids (gCOD/L)	Proteins (gCOD/L)
AQP-Effluent 1	2	1.4±0.1	0.4	0.4	0.3
AQP-Effluent 2	2	1.4±0.1	0.2	0.04	0.3

Acknowledgements:

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References

- [1] Heidrich E. S., Edwards S. R., Dolfing J., Cotterill S. E., Curtis T. P. *Bioresource Technology*, 2014, **173**, 906, 87–95
- [2] Satinover S. J., Rodriguez M., Campa M. F., Hazen T. C., Borole A. P. *Biotechnology for Biofuels*, 2020, **13**, 169.

Decoding Molecular Structure in Sustainable Electrolytes for Ni-Rich Lithium-Ion Batteries

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Ni-rich layered oxide cathodes such as $\text{LiNi}_{0.92}\text{Mn}_{0.04}\text{Co}_{0.04}\text{O}_2$ (NMC92) are promising candidates for next-generation lithium-ion batteries due to their high operating voltage and enhanced energy density. However, their practical utilization requires advanced electrolytes capable of sustaining high-voltage conditions while ensuring safety, low flammability, sustainability, and stable electrode–electrolyte interfaces [1]. Conventional carbonate-based electrolytes often fail to meet these combined requirements, motivating the search for innovative solvent formulations.

In this context, a recently optimized electrolyte formulation based on lithium bis(fluorosulfonyl)imide (LiFSI), lithium difluoro(oxalato)borate (LiDFOB), diethylene glycol butyl ethyl ether (DEGBEE), and bio-derived γ -valerolactone (GVL) outperformed its analogous propylene carbonate (PC)-based counterpart, exhibiting lower viscosity, higher ionic conductivity, enhanced Li^+ transport, and superior long-term cycling stability in NMC92 half-cells [2].

Despite these substantial macroscopic differences, the two key formulations differ only in the substitution of GVL for PC, solvents whose molecular structures vary by only a single oxygen atom. To elucidate the molecular origins of these differences, molecular dynamics (MD) simulations were performed using the previously developed and validated AMOEBA polarizable force field [3,4]. MD results were compared with pulsed-field gradient NMR self-diffusion coefficients of all electrolyte species, as well as with Li^+ transport numbers, showing excellent agreement.

Detailed structural analysis revealed that GVL contributes more effectively than PC to the first Li^+ solvation shell, enhancing Li^+ shielding and reducing Li^+ –FSI[−] association. This promotes greater ionic dissociation and reduced ionic aggregation, consistent with the experimentally observed increase in Li^+ transport number and ionicity index for the GVL-based formulation.

Overall, this integrated computational–experimental approach effectively resolves subtle yet critical molecular-scale differences governing electrolyte performance, establishing a powerful framework for both mechanistic understanding and the rational design of next-generation safe, sustainable, and high-performance electrolytes for advanced lithium-ion batteries.

References

- [1] W. Li, Z. He, Y. Jie, F. Huang, Y. Chen, Y. Wang, W. Zhang, X. Zhu, R. Cao, S. Jiao, *Adv. Funct. Mater.*, 2024, **34**, 2406770.
- [2] J.L. Gómez-Urbano, M. Binder, E.N. Dwiputra, T. Diemant, D. Bresser, A. Pierini, A. Cioffi, E. Bodo, S. Brutti, M. Koželj, T. Gouveia, E. Bremond, A. Ladam, S. Fantini, S. Sananes-Israel, I. Landa-Medrano, I. de Meatza, *Angew. Chem. Int. Ed.*, 2026, e26145.
- [3] A. Pierini, V. Piacentini, J.L. Gómez-Urbano, A. Balducci, S. Brutti, E. Bodo, *ChemistryOpen*, 2024, **13**, e202400134.
- [4] A. Pierini, V. Migliorati, J.L. Gómez-Urbano, A. Balducci, S. Brutti, E. Bodo, *Molecules*, 2025, **30**, 230.

Theme F - Biomaterials and Chemical Biology

***Drosophila melanogaster*: a sentinel for health effects of occupational PM exposure?**

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Airborne particulate matter (PM) represents a major environmental and occupational health concern due to its association with a wide range of adverse health effects. Traditional approaches used to evaluate PM toxicity, including acellular oxidative potential assays and in vitro cellular models, often provide limited insight into the complex biological responses occurring in living systems. In this context, the use of model organisms directly exposed to particulate matter represents a promising strategy to bridge the gap between environmental exposure and biological effects. The aim of this study was to explore the potential of *Drosophila melanogaster* as a model organism for investigating biological responses to particulate matter in occupational settings using an integrated multi-omics approach. *D. melanogaster* is widely employed in toxicology and biomedical research [1,2] due to its well-characterized genetics, short life cycle, and the evolutionary conservation of many metabolic and cellular pathways shared with higher organisms, including mammals. The experimental approach was first developed under controlled laboratory conditions to evaluate the feasibility of the model [3]. Larvae were exposed to brake dust incorporated into the food medium at different concentrations, allowing the assessment of responses to particulate ingestion. Subsequently, the approach was applied in real occupational settings by placing cages containing adult flies in different industrial facilities, enabling direct exposure to airborne particulate matter generated by specific production activities. Following exposure, organisms were analysed through a multi-platform strategy combining ICP-MS for elemental bioaccumulation (ionomics) and untargeted NMR metabolomics to investigate metabolic alterations. Data fusion and chemometric analysis of the resulting datasets revealed clear differences in metabolic and elemental profiles between exposed and control organisms, as well as distinct signatures associated with the different exposure sites within the industrial environment. The observed metabolic alterations mainly involved pathways related to protein synthesis, oxidative stress response, and reactive oxygen species (ROS) scavenging mechanisms. Furthermore, from the bioaccumulation analysis it was possible to correlate some metabolically induced alterations with the bioaccumulation of particular PM components such as potentially toxic elements (PTEs). Overall, the results demonstrate that *D. melanogaster* can effectively capture biologically relevant responses to particulate exposure. The proposed integrated multi-omics approach highlights the potential of this organism as a powerful experimental system for linking particulate matter composition to biological effects and for improving the assessment of health risks associated with environmental and occupational PM exposure.

References

- [1] Cummings, A.; Kavlock, R. A Systems Biology Approach to Developmental Toxicology. *Reprod Toxicol* **2005**, *19*, 281–290, doi:10.1016/j.reprotox.2004.10.001.
- [2] Peterson, R.T.; Nass, R.; Boyd, W.A.; Freedman, J.H.; Dong, K.; Narahashi, T. Use of Non-Mammalian Alternative Models for Neurotoxicological Study. *NeuroToxicology* **2008**, *29*, 546–555, doi:10.1016/j.neuro.2008.04.006.
- [3] De Rosa, M.; Vaccarella, E.; Cerasti, F.; Lucchesi, V.; Marini, F.; Massimi, L.; Mastrantonio, V.; Sciubba, F.; Spagnoli, M.; Porretta, D.; et al. *Drosophila Melanogaster* as Model Organism to Assess Brake Dust Toxicity by a Multi-Platform Approach. *Environmental Pollution* **2026**, *392*, 127661, doi:10.1016/j.envpol.2026.127661.

A computational study of β -cyclodextrin nanosponges as green materials for drug incapsulation

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Cyclodextrin nanosponges are environmentally friendly materials employed in the development of drug delivery systems due to their ability to interact with a wide range of therapeutic molecules¹. In this work we carried out a computational study of a small model of a nanosponge where 9 β -cyclodextrins are crosslinked with epichlorohydrin molecules. Although single β -cyclodextrin molecules can form inclusion complexes primarily with hydrophobic molecules, their crosslinked structures can interact with both hydrophilic and hydrophobic drugs. Due to the lack of suitable parameters available in literature, the full nanosponge structure has been parametrized manually. After model construction (charges were optimized using Gaussian and parameters were generated with ACPYPE), molecular dynamics simulations were carried out at 300 K to investigate the interactions between the nanosponge and various drugs. We studied its interaction with molecules such as doxorubicin (DOXO) and *N,N*-bis (5-ethyl-2-hydroxybenzyl) methylamine (EMD)¹, fisetin², dasatinib³ and camptothecin⁴. All the inclusion complexes formed remained stable throughout the entire MD simulations. A previous thermodynamic⁵ and structural characterization of single β -cyclodextrin complexes highlighted a reversible and stable inclusion mechanism for complex formation, suggesting that β -CDs-based systems may represent promising materials to enhance drug solubility and bioavailability. Doxorubicin, being the least hydrophobic molecule among those considered, preferentially interacts with the hydrophilic surface of the cyclodextrins in the nanosponge. In contrast, the other, more hydrophobic drugs form stable inclusion complexes within the cyclodextrin cavities. Overall, these results highlight the ability of cyclodextrin-based nanosponges to accommodate structurally diverse drugs through distinct interaction mechanisms supporting their potential as versatile structures for drug delivery.

References

1. Thongsom S., Di Gianvincenzo P., Ciattaglia G., Subrati A., DiSilvio D., Birocco A. M., D'Abramo M., Boonla C., Chanvorachote P., Moya S. E. Cyclodextrin-based nanosponge co-delivery of doxorubicin and EMD: synergistic anticancer activity with improved selectivity toward cancer cells. *RSC Pharmaceutics* 2(6), 1514-1532. 2025. <https://doi.org/10.1039/D5PM00183H>.
2. Takaya, K., Asou, T. & Kishi, K. Fisetin, a potential skin rejuvenation drug that eliminates senescent cells in the dermis. *Biogerontology* **25**, 161–175 (2024). <https://doi.org/10.1007/s10522-023-10064-9>
3. Levêque, D., Becker, G., Bilger, K. *et al.* Clinical Pharmacokinetics and Pharmacodynamics of Dasatinib. *Clin Pharmacokinet* **59**, 849–856 (2020). <https://doi.org/10.1007/s40262-020-00872-4>
4. Behera, A., Padhi, S. Passive and active targeting strategies for the delivery of the camptothecin anticancer drug: a review. *Environ Chem Lett* **18**, 1557–1567 (2020). <https://doi.org/10.1007/s10311-020-01022-9>
5. Bò L., Milanetti E., Chen CG., Ruocco G., Amadei A., D'Abramo M. Computational Modeling of the Thermodynamics of the Mesophilic and Thermophilic Mutants of Trp-Cage Miniprotein. *ACS Omega* 7(16), 13448–13454. 2022, <https://doi.org/10.1021/acsomega.1c06206>

Novel Insights on Benzo[*b*]thiophene Analogues for MAO-B Inhibition and Neuroprotection: Design, Synthesis, Molecular Modelling Studies and Biological Activity

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Neurodegenerative disorders pose a growing challenge in ageing societies. In Parkinson’s disease, elevated hMAO-B activity plays a key role in oxidative stress and dopaminergic neurodegeneration, making selective hMAO-B inhibition a relevant therapeutic strategy. Building on previous work with benzofuran and benzothiophene-3-ol *scaffolds*, this study introduces 2-arylbenzothiophene analogues as promising candidates for neurodegeneration-oriented drug discovery. [1] The synthesized compounds have been screened against the hMAO-A and hMAO-B isoforms, identifying derivatives **4**, **11** and **12** as the most promising candidates (**Figure 1**). Based on their inhibitory profiles, compounds **4**, **11**, and **12** were advanced to preliminary cellular studies. Notably, compound **12** displayed an antioxidant-like behavior, significantly reducing basal ROS levels. Finally, molecular modelling studies were conducted to predict the compounds’ binding mode (**Figure 1**). A novel class of 2-arylbenzothiophenes has been identified as selective, nanomolar hMAO-B inhibitors, with potency finely tuned by aryl substitution [2]. Supported by molecular modelling and favourable cellular and redox profiles, this *scaffold* represents a compelling lead for Parkinson’s disease drug discovery.

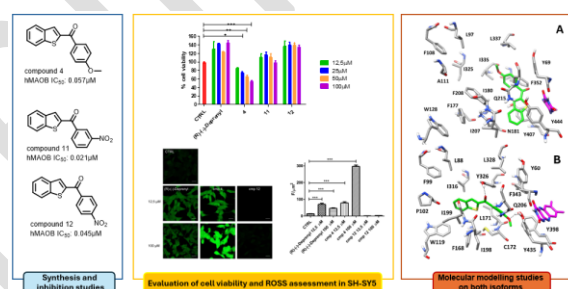


Figure 1. work-flow of the project.

References

- [1] Guglielmi, P. et al. Benzo[*b*]thiophen-3-ol derivatives as effective inhibitors of human monoamine oxidase: design, synthesis, and biological activity. *J Enzyme Inhib Med Chem* 34, 1511–1525 (2019)
- [2] Arrighi, F et al. Novel Insights on Benzo[*b*]thiophene Analogues for MAO-B Inhibition and Neuroprotection: Design, Synthesis, Molecular Modelling Studies and Biological Activity. *Antioxidants* **2026**, 15, 346. <https://doi.org/10.3390/antiox15030346>

Formulation and characterization of estrogenic soft drugs-loaded vesicular carriers: a preliminary study for a nanotherapeutic approach of topical wound healing

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Estrogens play a well-documented role in wound healing; however, their systemic administration raises significant safety concerns. The soft drug approach offers an elegant solution: molecules designed to be pharmacologically active at the site of application but rapidly metabolized into inactive species, thus minimizing systemic exposure. Our previous studies have identified two estrogenic compounds with hydrolyzable ester groups, **1** and **2**, as the most promising candidates for topical application [1,2]. This research work is aimed at: i) developing a more efficient and sustainable synthetic route for **1** and **2**, exploiting one-pot strategies and avoiding unnecessary protecting group manipulations; ii) and designing lipid-based nanovesicular carriers potentially able to enhance skin penetration and local drug accumulation (**Figure 1**).

Liposomes and transfersomes [3] were prepared using a phosphocholine (dipalmitoylphosphatidylcholine, DPPC, or dimyristoylphosphatidylcholine, DMPC) as the main component, in mixture with the estrogen derivative (**1** or **2**) and/or sodium cholate as edge activator. The addition of sodium cholate to transfersome-based formulations imparts greater flexibility to the lipid membrane, a key property that ensures its deformation and penetration through the stratum corneum, thereby making vesicles particularly well-suited for topical administration compared to conventional liposomes. Size, polydispersity, ζ -Potential and colloidal stability over time of liposomes and transfersomes were evaluated by DLS and DELS analysis. The compounds **1** and **2** nanovesicles' entrapment efficiency was assessed by UV-Vis spectrophotometry. In addition, the leakage of the estrogenic compounds from the nanovesicles was monitored over 24 hours.

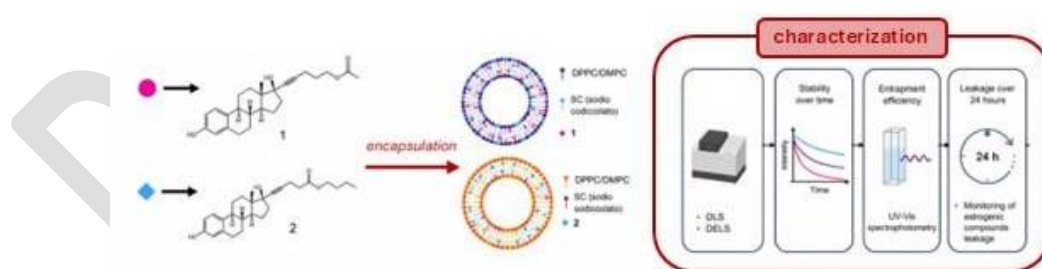


Figure 1: Encapsulation of estrogenic soft drugs **1** and **2** into vesicular carriers and characterization

- [1] Brufani et al., Molecular Pharmaceutics, 2009, 6 (2), 543-556.
- [2] Brufani et al., Scientific Reports, 2017, 7: 2510.
- [3] Hua S., Frontiers in Pharmacology, 2015, 6, 219.

Optimization of a xanthine-based senolytic lead compound

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Cellular senescence is a major contributor to aging and age-related diseases, driving the search for effective senolytic agents.¹ HSP90 inhibitors represent a promising class, although their development is still limited by issues related to formulation, toxicity, and cost. In this context, recent studies identified a xanthine-based compound, K5, as a potent and selective HSP90 α inhibitor with senolytic activity, highlighting this scaffold as a valuable starting point for further optimization.²⁻³ This study describes the design and synthesis of a library of K5-derived compounds. The selection of substitution patterns was guided by computational analyses. Synthetic efforts focused on systematic modification of the benzylic aromatic moiety at position 1 of the xanthine scaffold, introducing hydroxy, halogen, and trifluoroalkyl substituents to modulate electronic and steric properties. Thirteen derivatives were successfully prepared through a modular and reproducible synthetic strategy, enabling efficient access to structurally diversified compounds. Preliminary structure-activity trends indicate that functionalization at the benzylic position is well tolerated and can lead to improved performance compared to the parent compound. Notably, a subset of derivatives exhibits enhanced potency, supporting further development of this scaffold. Overall, this study establishes a synthetic platform for the diversification of xanthine-based HSP90 inhibitors and provides new candidates for next-generation senolytic agents.

References

- [1] McHugh D, Gil J. *J Cell Biol*, 2018, **217**, 65-77.
- [2] Atlante S, Cis L, Pirolli D et al. *Aging Cell*, 2025, **24**, e70047.
- [3] Gaetano C, Atlante S, De Rosa MC et al. Patents WO2023135532A1 and WO2023135533A1

Novel Benzofuran-Donepezil derivatives to dually inhibit monoamine oxidases and cholinesterases: a multifunctional strategy against neurodegenerative diseases

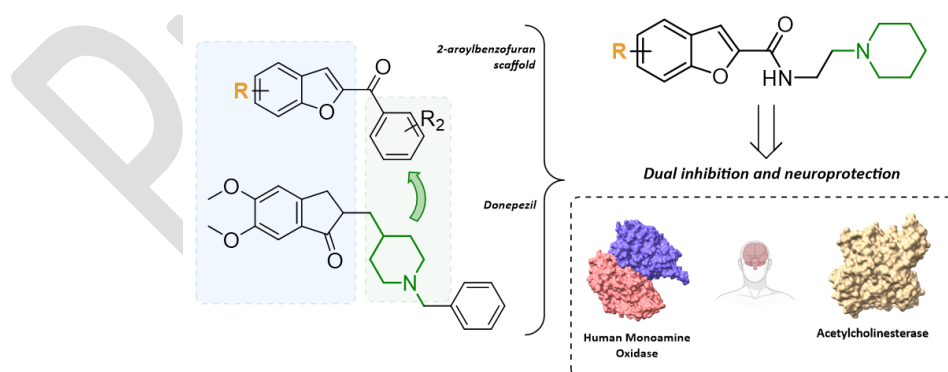
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Neurodegenerative diseases (with Alzheimer's and Parkinson's diseases as the most prominent representatives) are among the heaviest burdens on healthcare systems all over the world and possess complex and heterogeneous pathogeneses, far from a complete understanding [1]. Among the various factors involved, human monoamine oxidases (hMAOs) and cholinesterases (ChEs: acetylcholinesterase, AChE, and butyrylcholinesterase, BChE) occupy a remarkable position. In fact, both classes of enzymes are clinically targeted in the treatment of neurodegenerative diseases, and the development of dual inhibitors has recently emerged as an interesting approach to enhance the therapeutic efficacy of novel drug candidates [2].

For these reasons, we have decided to develop a series of novel compounds to dually inhibit these enzymes. The design of the scaffold (see **Figure 1**) took inspiration from the benzofuran nucleus, which we have successfully employed for the design of potent and selective hMAO-B inhibitors [3]. The benzofuran portion notably resembles the indanone core of the AChE inhibitor donepezil, currently used for the symptomatic treatment of AD. This nucleus was then fused with the piperidine moiety of donepezil through a N-ethyl carboxyamidic linker. The compounds were obtained via a three-step synthetic process and were chemically characterised using ¹H and ¹³C NMR. The inhibitory activity of the derivatives was then evaluated in vitro through spectrophotometric enzymatic inhibition assays against hMAOs and ChEs. The compounds exhibited notable activities against hMAO-B and BChE, hence demonstrating their potential ability to act as multitarget agents in neurodegenerative diseases' treatment.



References

- [1] S.L. Forrest and G. G. Kovacs, *Pathology* (2025); 57, 2, 178-190
- [2] B. Matthew et al. *Arch. Pharm. Chem. Life Sci.* (2019); 352:1900177
- [3] P. Guglielmi and M. Coluccia, et al. *Eur. J. Med. Chem.*(2025), 297

Engineered GO-Based Hydrogels for Controlled Hyaluronic Acid Release in Knee Osteoarthritis Treatment

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Osteoarthritis (OA) is a prevalent chronic pain syndrome and a leading cause of disability worldwide, characterized by progressive deterioration of articular cartilage. This degradation leads to pain, swelling, inflammation, and eventual stiffness as the cartilage wears down, causing bone-on-bone friction. Current medical treatments primarily aim at pain relief; however, many interventions, especially invasive or surgical ones, carry risks of adverse outcomes. Consequently, intra-articular (IA) therapy, particularly hyaluronic acid (HA) injections, is widely adopted as a conservative treatment option. HA plays a crucial role in maintaining joint homeostasis by supporting proteoglycan synthesis and scaffolding, restoring optimal HA concentrations in synovial fluid, and providing chondroprotective and anti-inflammatory effects. In recent years, hydrogels composed of natural and synthetic materials have emerged as promising candidates for OA treatment. Our research focuses on the biosynthesis and characterization of novel hydrogel composites combining short peptide hydrogelators with aminated graphene oxide (a-GO) nanosheets functionalized with HA (a-GO-HA@Hgel). These a-GO-HA@Hgel nanocomposites are designed to facilitate the controlled release of HA into the extracellular matrix, aiming to promote cartilage regeneration and mitigate inflammation. The strategy is to exploit the oxygen-containing functional groups of GO nanosheets to enable covalent coupling or physical adsorption of HA molecules through various chemical approaches. The resulting a-GO-HA are incorporated within hydrogel matrices to achieve sustained and controlled HA release. We study the influence of a-GO-HA on the native hydrogel structure and its viscoelastic properties, which are critical for mimicking the mechanical environment of native cartilage tissue. Through this multidisciplinary approach combining advanced materials science and cellular biology, this work aims to develop innovative nanocomposite hydrogels capable of delivering HA in a controlled manner, enhancing cartilage repair and providing a potential therapeutic strategy for OA management.

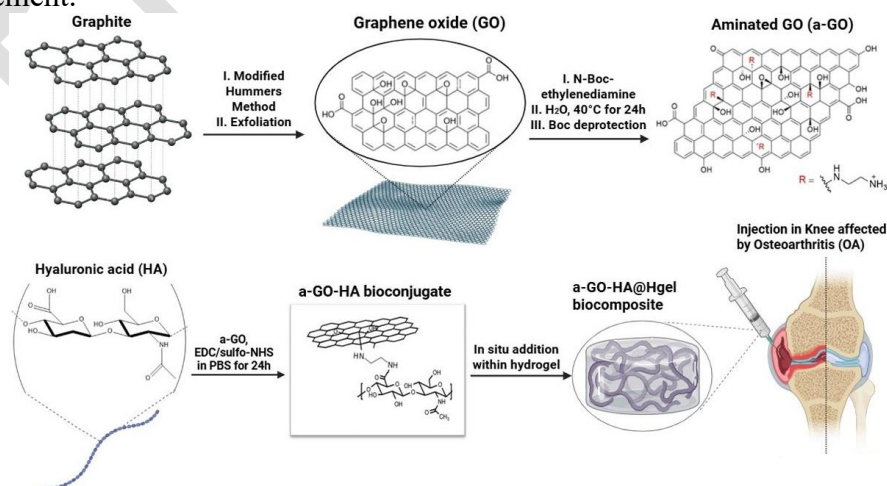


Figure 1: Schematic illustration of the preparation process of a-GO-HA@Hgel.

MDL-800–Mediated Allosteric Activation of SIRT6 Drives Endothelial Epigenetic Remodeling in Hyperglycemia

Antonella Bordin¹, Virginia Pontecorvi¹⁻³, Claudia Cozzolino¹, Vittorio Picchio¹, Erica Floris¹, Dante Rotili⁵, Antonello Mai³, Francesca Pagano², Sebastiano Sciarretta¹, Isotta Chimenti¹⁻⁴ and Elena De Falco¹⁻⁴

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Metabolic disorders such as hyperglycemia contribute to cardiovascular disease by altering epigenetic regulation. Sirtuin-6 (SIRT6), a NAD⁺-dependent histone deacetylase, is a key regulator of chromatin remodeling and vascular homeostasis, representing an attractive target in chemical biology. MDL-800 is a selective allosteric activator of SIRT6 that enhances its deacetylase activity by stabilizing the active conformation of the enzyme. However, its effects in endothelial cells under metabolic stress remain poorly defined.



The aim of this study was to characterize MDL-800 as a chemical probe of SIRT6 activity in human umbilical vein endothelial cells (HUVECs) exposed to hyperglycemia. Cells were treated with MDL-800 (2.5–5 μM, 24 h), and epigenetic modulation (H3K9 acetylation), autophagy (LC3II/LC3I), apoptosis, angiogenesis, secretome, extracellular vesicles, and transcriptomic changes were evaluated.

MDL-800 showed dose-dependent activity. At 2.5 μM, it reduced H3K9 acetylation ($p < 0.05$), enhanced autophagy, and decreased apoptosis in hyperglycemic HUVECs, without affecting basal conditions. At 5 μM, it restored angiogenic and immunomodulatory factors (EGF, Endoglin, PECAM-1, CXCL1/8, MIF-1), improving angiogenic capacity ($p < 0.05$). Transcriptomic analysis revealed modulation of gene clusters involved in angiogenesis, metabolic stress, and cell cycle regulation. MDL-800 also reshaped extracellular vesicle profiles, shifting from large vesicles (>500 nm) to smaller vesicles (<100 nm), consistent with reduced cellular damage and improved intercellular communication.

In conclusion, MDL-800 acts as an effective allosteric activator of SIRT6, promoting epigenetic and functional reprogramming of endothelial cells under hyperglycemic stress. These findings highlight its potential as a chemical tool to counteract diabetes-related endothelial dysfunction.

Acknowledgements: Virginia Pontecorvi was supported by Fondazione Umberto Veronesi.

References

- [1] Claudia Cozzolino, et al. Pharmacological Research, November 2025, 221, 107970
- [2] Antonella Bordin et al, Cell Proliferation, 2022 Nov;55(11):e13312

From Anthelmintic to Anticancer: Mebendazole-Derived Enantiomers in Breast Cancer

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Breast cancer (BC) is the most diagnosed and challenging malignancy due to its biological heterogeneity, variable clinical behaviour, and potential for recurrence and metastasis [1].

Drugs Repurposing in Oncology (ReDO) is a new frontier of translational medical research, leveraging well-established pharmacological agents for new clinical applications. Mebendazole (MBZ), an FDA-approved anthelmintic, has been identified as a potential anticancer candidate due to its ability to interfere with microtubule cytoskeletal polymerisation, thereby inhibiting cell proliferation [2]. However, the clinical use of MBZ is limited by its unpredictable bioavailability. To overcome these limitations, we developed a drug repurposing strategy focused on the main metabolites of MBZ, by a chemical reduction followed by chiral resolution of the resulting species (E1, *S*; E2, *R*) [3], to evaluate whether they can enhance antitumor activity [3].

We tested both enantiomers on MCF-7 breast cancer cells (invasive ductal breast cancer, Luminal A subtype with wild-type BRCA1) and MCF10-A (non-tumorigenic cells, basal B wild type) at experimental concentrations of 0.5 – 1.0 μ M, using MBZ as a positive control.

Cell viability assay, in both normal (MCF10A) and tumour (MCF7) cell lines, shows that E1 at 1 μ M preferentially affect tumour cell viability by 0.74-fold after 48h compared to Control, while not significantly decreasing normal cell viability. Moreover, E1 markedly suppressed the cells' ability to form colonies, halving their colony formation efficiency. Cell cycle analysis revealed that E1 and E2 enantiomers induced a moderate and sustained modulation of cell cycle distribution compared to Mebendazole (MBZ), which caused a marked G2 phase arrest at 24 h. Consistently, Annexin V/PI assays showed a more gradual induction of apoptosis by E1 and E2, suggesting a distinct effect on cell fate. Both enantiomers inhibited MCF-7 cell migration in a similar manner to MBZ after 24 hours ($p < 0.05$). Interestingly, treatment with E1 markedly altered the cancer secretome, leading to the downregulation of soluble factors associated with breast tumour progression, such as ErbB family receptors, including ErbB2, ErbB3, and their associated ligand Amphiregulin (AREG). Overall, these findings highlight E1 as a promising candidate for breast cancer therapy, combining selective anticancer activity with modulation of key processes involved in tumour progression, thus supporting the potential of chirality-driven drug repurposing strategies in precision oncology.

Acknowledgements: Virginia Pontecorvi was supported by Fondazione Umberto Veronesi.

References

- [1] Yin L, et al., *Breast Cancer Research*, 22, **61**, 2020.
- [2] Pantziarka, P., et al., *Ecancer*, 8, **443**, 2014.
- [3] Guglielmi P., et al., *Pharmaceuticals*, 17, **6**, 2024.

Exploiting microbial DNA G-Quadruplexes to Tackle Antibiotic Resistance

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Antibiotic resistance represents one of the most critical global health challenges, driven by the widespread and often indiscriminate use of antibiotics, which has accelerated the emergence of multidrug-resistant (MDR) bacterial strains. Given the limitations of the current antibacterial drug pipeline, the identification of novel targets and mechanisms of action is urgently needed [1]. In this context, microbial DNA G-quadruplexes (G4s) have recently emerged as promising targets, as they are involved in key biological processes such as gene expression, genome stability, and DNA replication. Their presence in regulatory regions of pathogenic bacteria makes them attractive candidates for therapeutic intervention [2,3]. Despite the limited knowledge available on microbial G4s, our previous study investigated the G4-forming sequence TET22 as a structural model in *Pseudomonas aeruginosa*. Although originally derived from the *Tetrahymena* genome, TET22 has been widely used to explore bacterial G4 ligandability. In this context, in vitro screening of known human G4 ligands identified pyridostatin (PDS) as a reference compound capable of binding and stabilizing TET22, showing moderate antibacterial activity against *P. aeruginosa* [4]. Building on these findings, the present work focuses on the design and synthesis of a novel series of small molecules targeting microbial G4s, inspired by the PDS scaffold. Accordingly, the compounds were designed to incorporate key structural features required for G4 interaction, including (i) a planar quinoline core and (ii) flexible aliphatic chains bearing terminal amine groups. Briefly, the synthetic strategy starts from commercially available 2-amino-4-hydroxyquinoline, which undergoes a Mitsunobu reaction with NH-Boc-ethanolamine, previously protected starting from ethanolamine. The resulting intermediate is then reacted with the acyl chloride of appropriately substituted carboxylic acids, affording the protected final products. A subsequent deprotection step yields the target compounds. Overall, the synthetic pathway has been developed and optimized to efficiently access these derivatives in a cost-effective and reproducible manner, enabling the straightforward construction of a library of antimicrobial compounds. These will be further evaluated for their biological activity and their ability to selectively interact with G4 structures.

References

- [1] 2023 Antibacterial agents in clinical and preclinical development: an overview and analysis. Geneva: World Health Organization; 2024.
- [2] Yadav, P. *et al.* (2021). G-quadruplex structures in bacteria: biological relevance and potential as an antimicrobial target. *Journal of Bacteriology*, 203(13), 10-1128.
- [3] Xuan, T. F. *et al.* (2021). Design and synthesis of novel c-di-GMP G-quadruplex inducers as bacterial biofilm inhibitors. *Journal of Medicinal Chemistry*, 64(15), 11074-11089.
- [4] Fiabane, M., *et al.* (2025). Structure-Based Ligandability Exploration of a G-Quadruplex-Forming Sequence from the *Pseudomonas aeruginosa* Genome. *ACS medicinal chemistry letters*, 16(11), 2232–2238.

Microfluidic 3D bioprinting of hierarchical macroporous scaffolds with tailored architecture and composition

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The development of macroporous biomaterials is emerging as an effective strategy in biofabrication to address fundamental limitations in mass transport, oxygenation, and architectural complexity of bioengineered tissues. In this work, we present a microfluidic-assisted 3D bioprinting platform that enables the fabrication of constructs with tunable micro and macroporosity by harnessing structured multiphase material such as colloidal inks (e.g., hydrogels, foams, and emulsions). The proposed approach leverages microfluidics to pattern bioink features prior to extrusion, enabling deterministic control over material composition, cell density, compartmentalization, and filament morphology. Specifically, we designed and characterized a mixer-integrated flow-focusing-based microfluidic printhead directly coupled to a 3D bioprinter, enabling in-line tuning of filament composition and cellular loading. Within this framework, multiphase systems enhance the structural and functional complexity of the printed constructs by introducing controlled porosity and phase organization. To this end, foam-based bioinks were investigated as a strategy to directly introduce tunable macroporosity within printed fibers via microfluidic gas-liquid templating, creating internal niches for localized cell clustering. Unlike conventional approaches, this method enables *in situ* generation of a monodisperse liquid foam during printing, immediately stabilized through rapid ionic crosslinking (i.e., alginate-calcium gelation) at the point of extrusion. This allowed instantaneous immobilization of the foam into solid fibers, preserving monodispersity, spatial organization, and the dynamic tunability of pore size while preventing coarsening and collapse. As a result, this approach enabled real-time modulation of porosity along the printed construct, allowing patterning of architectural gradients to regulate cell behavior in 3D as well as diffusion properties.

Looking forward, this microfluidic-assisted 3D bioprinting paradigm may shift the design focus toward multiphase colloidal architectures, where flow-engineered structure and material chemistry act as complementary design variables. This is extendable to a wide range of bioinks and soft materials, enabling the scalable fabrication of next-generation macroporous constructs. The convergence of microfluidics and 3D bioprinting offers a powerful route toward high-performance biofabrication platforms, where structural precision, transport efficiency, and process integration open new opportunities in tissue engineering and advanced *in vitro* models.

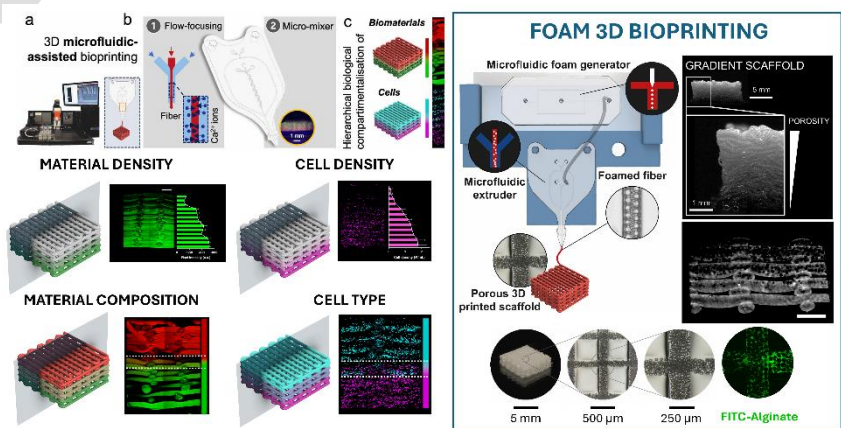


Figure 2 – Overview of the presented work. On the left, image of the experimental set-up consisting of the 3D bioprinter equipped with a mixer-integrated microfluidic printhead for the realization of 3D constructs with different types of gradients in terms of composition and cell distribution. On the right, integration of the printhead with a microfluidic bubble generator to extrude foamed fibers. Realization of a 3D construct with porosity gradient and validation of the gradient formation via microCT scans.

Physicochemical Characterization of Curcumin Delivery Systems Based on Functionalized Cyclodextrins

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Curcumin (CUR) is a natural polyphenol with well-documented antioxidant, anti-inflammatory, antimicrobial, and anticancer properties. However, its biomedical application remains severely hampered by poor aqueous solubility, low bioavailability, and rapid metabolism. In this context, cyclodextrins (CDs) have emerged as highly attractive drug carriers due to their cyclic oligosaccharide architecture, characterized by a hydrophilic external surface and a hydrophobic internal cavity that facilitates the formation of inclusion complexes with poorly water-soluble molecules [1]. Among these, β - and γ -cyclodextrins are particularly relevant due to their favorable cavity sizes and proven pharmaceutical applicability [2]. In this work, β - and γ -cyclodextrins were functionalized with maleic anhydride (β -/ γ -CDM) or succinic anhydride (β -/ γ -CDS) to investigate how pendant carboxyl groups influence their interaction with curcumin, as well as the physicochemical and biological properties of the resulting host-guest systems. The modified CDs were characterized by FT-IR, ¹H-NMR, TGA, and DSC. NMR analysis revealed a degree of substitution ranging from 15% (for γ -CDM) to 40% (for β -CDS). Phase solubility studies, Job plots, and Benesi-Hildebrand analysis confirmed the formation of CUR inclusion complexes in both β -/ γ -CDM and β -/ γ -CDS systems, primarily in a 1:1 stoichiometric ratio, while their performance was further assessed in terms of encapsulation efficiency, antioxidant activity, and antibacterial efficacy, showing a significant improvement in the performance of the host-guest systems. While native β -CD increased curcumin solubility 11-fold, β -CDM and β -CDS yielded increases of approximately 25- and 70-fold, respectively. Notably, γ -CDs exhibited the most remarkable behavior, showing a linear solubility profile and a stability constant (K_s) of $1.66 \times 10^4 \text{ M}^{-1}$, resulting in a 150-fold increase in curcumin solubility. Thermal characterization supported effective encapsulation, evidenced by the disappearance of the curcumin melting endotherm. Inclusion efficiency peaked for γ -CD derivatives, reaching $25 \pm 3\%$ for γ -CDS_CUR. While maintaining antioxidant activity, the functionalized complexes exhibited significantly improved antibacterial activity, with MIC values reduced up to tenfold compared to free curcumin. Overall, these results demonstrate that succinylation is a superior strategy for enhancing the delivery and biological performance of curcumin, positioning γ -CDS as a promising platform for advanced therapeutic applications.

References

- [1] C. Bertoncini-Silva, A. Vlad, R. Ricciarelli, P. Giacomo Fassini, V.M.M. Suen, J.-M. Zingg, *Antioxidants*, 2024, **13**, 331.
- [2] [2] I. Spiridon, N. Anghel, *Molecules*, 2025, **30**, 3044.

Poster Communications

Day 1 - 15th June 2026

N.	Name	Surname	Institution	Abstract Title
Theme A - Advances in Organic Chemistry				
P1	Federica	Di Mascolo	La Sapienza University of Rome	Synthesis of α -(alkoxyimino)alkynones as precursors for bioconjugation reactions towards thiol groups
P2	Francesca	Commmito	University of L'Aquila	Reusable Solid Magnetoliposomes for the Efficient Removal of Polycyclic Aromatic Hydrocarbons from Water
P3	Giorgia	Venanzetti	Sapienza University of Rome	Synthesis and functionalization of imidates via modified Beckmann rearrangement
Theme B – Advances in Physical and Colloids Chemistry				
P7	Marco	Vuolo	Sapienza University of Rome	Lysine rich D,L peptide-based amphiphiles with antimicrobial activity
P8	Laura	Di Rienzo	University of Naples Federico II	Design and characterization of biocompatible albumin nanocarriers
Theme C – Advances in Analytical Chemistry				
P11	Giorgia	Danese	Sapienza University of Rome	A First Step Toward Human Nanoplastic Exposure Assessment: Multimodal AF4 Analysis of Polystyrene Nanoparticles
P12	Gregorio	Lurci	Sapienza University of Rome	Printed electrochemical sensors for the rapid detection of 8-Oxoguanine as a biomarker of oxidative damage
P13	Bianca	Comegna	Università Tor Vergata	Electrochemical Sensor as Smart Device for White Blood Cell Measurement in Synovial Fluid
P14	Fabio	Candiano	Sapienza Università di Roma	Exploratory study of VOC emissions from synthetic textiles using SPME-GC/MS
P15	Andrea	Fricano	Sapienza University of Rome	Microplastics and Additives in Indoor Dust: Integrated Spectroscopic and Chromatographic Characterization
P16	Giordano	Putzolu	Sapienza University of Rome	Rapid Identification of Diesel Adulteration Using Portable MicroNIR Spectroscopy Coupled with Chemometrics
Theme D – Advances in Inorganic Chemistry and Functional Materials				
P23	Luca	Barigelli	University of Camerino	Indium(III) Phosphane Complexes: Green Catalysts for Michael-Type Additions of α -Nitroketones to α,β -Unsaturated Carbonyl Compounds

P24	Immacolata	Mazzuoccolo	University of Naples Federico II	Surface ligand exchange in ultra-small CeO ₂ nanoparticles: a strategy for enhanced colloidal stability in polar media
P25	Ludovica	Mattioli	Sapienza University of Rome	Can a polymer interlayer improve the electrochemical behaviour of metallic lithium?

Theme E – Energy, Environment and Sustainability

P29	Myriam	D'Alù	Sapienza University of Rome	Recovery and Regeneration of Cathode Materials via Direct Recycling
P30	Lorenzo	Pirollo	Politecnico di Torino	In Situ photopolymerized ionogels for safe high-Voltage lithium metal batteries
P31	Alice	Patta	Sapienza University of Rome	Lipases as biocatalysts in biodiesel production: a Molecular Dynamics study
P32	Gaia	Salvatori	Sapienza University of Rome	Green strategy for polyhydroxyalkanoates recovery from a continuous-flow mixed microbial cultures process
P33	Clara	Marandola	Sapienza University of Rome	Boosting Biomethane production via Electrochemical stimulation of Anaerobic Digestion
P34	Lionel	Nguemna Tayou	Università di Roma la Sapienza	Continuous-flow process for agricultural waste valorisation into polyhydroxyalkanoates production with mixed microbial culture
P35	Cheikh Reda	Bernaoui	Sapienza University	Scalable, Low-Cost interlayer Current Collector for Dendrite-Free Anode-Free Lithium Metal Batteries
P36	Cecilia	Petitta	CNR - Sapienza	Halophilic biocathode for bioelectrochemical hydrogen production under hypersaline conditions

Theme F – Biomaterials and Chemical Biology

P46	Antonella	Bordin	Sapienza University of Rome	MDL-800–Mediated Allosteric Activation of SIRT6 Drives Endothelial Epigenetic Remodeling in Hyperglycemia
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Total = 23 poster presentations

Day 2 - 16th June 2026

N.	Name	Surname	Institution	Abstract Title
Theme A - Advances in Organic Chemistry				
P4	Federica	Bonzani	Università di Roma La Sapienza	Computational Modeling of Decarboxylation of ACAs
P5	Gianluca	Pellegrino	Sapienza Università di Roma	Regio- and Stereoselective ring opening of 2,3-Diaryloxiranes: access to aryl-substituted 2,3-Dihydrobenzofuranols
P6	Fiammetta	De Dominicis	Sapienza University of Rome	Synthetic strategies for the preparation of functionalised 2,3-diaryloxiranes, key intermediates in the synthesis of ϵ -viniferine
Theme B – Advances in Physical and Colloids Chemistry				
P9	Fabrizio	Attene	Sapienza Università di Roma	Where Order Blurs: Structural Journeys Across the Fluid–Solid Continuum of Sodium Deoxycholate
P10	Gioia	Lanini	Sapienza University of Rome	Computational study of dynamics and fluorescence of two single-tryptophan mutants of holomyoglobin
Theme C – Advances in Analytical Chemistry				
P17	Marialuisa	Ruocco	Sapienza University of Rome	Study of head-space: an innovative monitoring approach using MicroNIR/Chemometrics
P18	Aurora	Patrizi	Scuola Normale Superiore	Magnetic Fe ₃ O ₄ @PDA Nanoparticles for Enhanced LFA Sensitivity: Human Transferrin as a Model System
P19	Gaia	Rizzo	Sapienza University of Rome	Lipid Based Microparticles of EGCG: Catechin Stabilization, Structural Characterization and Chemometric Validation
P20	Elena	Papa	Sapienza University of Rome	Rapid and innovative analytical platform for the characterization and quality control of e-liquids
P21	Martina	Luziani	Sapienza University of Rome	TGA-FTIR and μ -FTIR for the study of microplastics in atmospheric particulate matter
P22	Francesco Dario	Campana	Sapienza University of Rome	Migration of Hazardous Chemicals from Food Contact Materials: A Multi-Analyte Analytical Approach
Theme D – Advances in Inorganic Chemistry and Functional Materials				
P26	Samuele	Furlanetto	Sapienza University of Rome	Lanthanide-based Metal-Organic Frameworks for Nonlinear Photonics

P27	Federica	Angelini	Sapienza Università di Roma	Transition-Metal MOFs Enable Lanthanide-Free Photon Avalanche Processes
P28	Donata Concetta	Infante	Sapienza Università di Roma	Transition-Metal MOFs Enable Lanthanide-Free Photon Avalanche Processes

Theme E – Energy, Environment and Sustainability

P37	Sara	Colecchia	Sapienza University of Rome	Sustainable Electrochemical Strategies for Selective Lithium Recovery from Brine Resources
P38	Claudia	Masia	University of Padova	Self-assembling donor-acceptor dye that displays off/on photocatalytic H ₂ evolution.
P39	Szymon	Swiatek Brzezinski	University of Gdańsk	Predicting the Environmental Fate of Nanomaterials: A Probabilistic Framework for Sustainable Nano- Innovation
P40	Flavio	Di Carlo	INSTM	n-depth study of cathodic materials for electrochemical use
P41	Laura	Infante	Sapienza University of Rome	Lignohumic Redox-Active Materials Extracted from Wastewater Sludge for Energy Applications
P42	Jorge	Montero	Sapienza University of Rome	Bifunctional ORR/OER Electrocatalysts for Unitized Regenerative Fuel Cell Systems
P43	Francesca	Crupi	Sapienza	From Precursor to Power: Accelerating Lithium-Ion Battery Production
P44	Francesco	Capezzali	Sapienza University of Rome	Functionalized Graphene Oxide as an additive for Anion Exchange Membranes

Theme F – Biomaterials and Chemical Biology

P47	Clarissa	Ciarlantini	Sapienza University of Rome	Preparation and Characterization of Hyaluronic Acid and Arabinogalactan Mixtures for Cosmetic Applications
P48	Beatrice	Di Mattia	Sapienza University of Rome	Semi-IPN hydrogels of poly(2-hydroxyethyl methacrylate) and star-shaped poly-L-lactide for wound healing applications
P49	Pauline Trisha Umali	Cabral	Sapienza University of Rome	Deciphering the role of H565F Mutation and Glycosylation in ErbB3 Conformational landscape and Oligomerization

Total = 25 poster presentations

Theme A - Advances in Organic Chemistry

Synthesis of α -(alkoxyimino)alkynones as precursors for bioconjugation reactions towards thiol groups

F. Di Mascolo^{1,2*}, F. D'Acunzo², M. Nicque³, Johan M. Winne³, P. Gentili^{1,2}

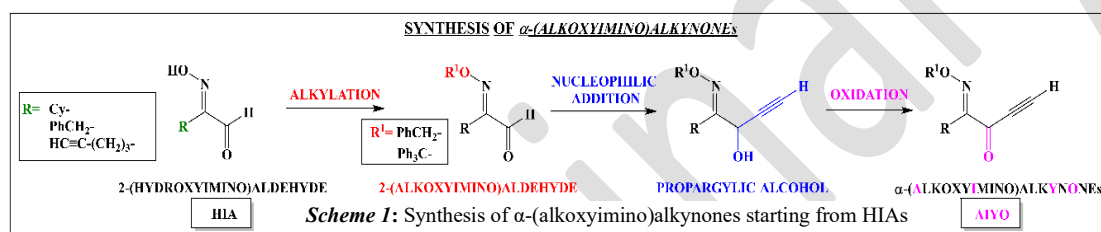
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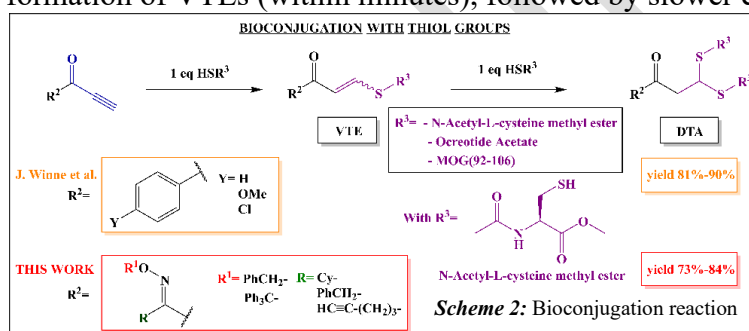
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Oximes and their derivatives, such as oxime esters, have versatile applications in the medical field, showing anti-inflammatory, antimicrobial, antioxidant, and anticancer activities [1]. In recent years, our team has focused on the development of new oxime derivatives based on the 2-(hydroxyimino)aldehyde (HIA) platform, obtained via α -oximation of aliphatic aldehydes [2,3]. This work represents a further step in the exploration of HIAs reactivity toward the formation of a novel class of compounds: the α -(alkoxyimino)alkynone (AIYO), $RC(=NOR^1)C(=O)C\equiv CH$ (Scheme 1). Those derivatives are potentially active in the medical field. Their promising biological properties can



further enhanced through bioconjugation strategies, combining intrinsic bioactivity with selective targeting, improving the drug delivery. Bioconjugation of alkynone derivatives to peptides and proteins has been previously established in the research group of Prof. J. Winne through selective Michael-type addition to cysteine residues, yielding vinylogous thioesters (VTEs) and, upon further reaction, dithioacetals (DTAs) [4]. The newly synthesized α -(alkoxyimino)alkynones showed rapid formation of VTEs (within minutes), followed by slower conversion to DTAs (Scheme 2).



The products were purified and demonstrated good stability in aqueous media, while competition experiments confirmed high selectivity toward thiol groups over lysine residues.

Finally, the ability to reform disulfide bonds in peptides was successfully demonstrated through the rebridging of *Octreotide acetate*, a synthetic analogue

of *Somatostatin*, known for its anticancer activity. In this system, the disulfide bridge is essential for maintaining the cyclic structure required for proper receptor recognition. Overall, these results demonstrate that AIYOs are versatile and efficient tools for peptide bioconjugation, highlighting their potential in the development of targeted therapeutic systems.

References

- [1] Surowiak A. K., Lochy ' nski S., Strub D.J., *Symmetry* 2020, **12**, 575.
- [2] Gentili P., et al., *Chem. Eur. J.* 2018, **24**, 7683.
- [3] D'Acunzo F., et al., *Eur. J. Org. Chem.* 2021, 289.
- [4] Maes D., Nicque M., Iftikhara M., Winne J. M., *Org. Lett.* 2024, **26**, 895.

Reusable Solid Magnetoliposomes for the Efficient Removal of Polycyclic Aromatic Hydrocarbons from Water

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Polycyclic aromatic hydrocarbons (PAHs) are persistent environmental pollutants characterized by high hydrophobicity, bioaccumulation potential, and well-documented toxic, mutagenic, and carcinogenic effects in humans [1,2,3,4]. Their removal from aqueous environments remains a major environmental and public health challenge. Based on these premises, we investigated the efficiency of solid magnetoliposomes (MLs) as magnetic, recoverable nanoplateform for PAHs removal from water. These hydrophobic pollutants tend to accumulate in the scarcely polar lipid portion of MLs. Once repartition of PAHs in lipid bilayer of MLs occurs, they can be easily removed with a magnet before the discharging of wastewater into surface waters takes place: 9 different MLs formulations, differing in the headgroup charge and, for cationic lipids, in the number and length of alkyl chains, were prepared, characterized and tested. These structural variations were designed to modulate membrane packing, hydrophobic domain accessibility, and pollutant affinity. Several PAHs were selected as model contaminants. Removal efficiency was evaluated at different incubation time (1, 2, 3 and 24 h). To rationalize experimental trends, the molecular properties of the hydrocarbons were investigated through molecular dynamics simulations, and the resulting descriptors were incorporated into a design-of-experiments framework to correlate nanostructure features with adsorption performance. An optimized sustainable recycling strategy for MLs was also assessed starting from a previous strategy based on calcination of the lipid bilayer, a process energy-consuming that lead to partial structural degradation and limited reusability [5]. The new milder regeneration protocol allows the selective removal of the outer lipid layer *via* controlled heating for a short time in small amount of organic solvent, thus preserving the magnetic core without compromising removal efficiency. The key objective of this study was a structure–property–performance correlation for determining the key factors that governs PAHs removal and thus paving the way for sustainable nanomaterial-based remediation of hazardous hydrophobic pollutants.

References

- [1] Samanta E. C., Singh O., Jain R. K. J. Environ. Sci. Health C, 2002, 20, 55–89.
- [2] Srogi K. Water Air Soil Pollut., 2007, 181, 139–164.
- [3] IARC Working Group IARC Monogr. Eval. Carcinog. Risks Hum., 2010, 92, 1–853.
- [4] Ravindra K., Sokhi R., Van Grieken R. Atmos. Environ., 2008, 42, 2895–2921.
- [5] Allegritti E., Palumbo C., Battista S., D'Orazio F., Aschi M., Mattera M., Commito F., Cravello B., Giansanti L. ACS Applied Materials & Interfaces, 2025, 17, 3489–3502.

Synthesis and functionalization of imidates via modified Beckmann rearrangement

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The insertion of nitrogen atoms into carbon–carbon bonds represent a fundamental strategy for the synthesis of biologically and pharmaceutically relevant molecules. A landmark reaction in this direction is the Beckmann rearrangement (BKR), which allows to transform ketones to amides and it still plays a fundamental role in organic synthesis^[1]. Unfortunately, it is a two-steps reaction and requires severe conditions (high temperature and strong acid). Recently, a direct method based on the use of hydroxylamine derivatived reagents, as the N-source, has emerged, providing high yields under mild conditions^[2].

In this context, we employed a specific hydroxylamine aminating reagent (MsONH_3^+) to investigate the effect of different solvents on reaction mechanism and selectivity. Indeed, starting from a general ketone, the corresponding amide was obtained when the reaction was conducted in a ACN/ H_2O mixture. On the other hand, under alcoholic solvent condition (e.g., EtOH, MeOH) the obtained product was an imidate (imino-ethers). Given the importance of imidates in organic synthesis we worked to exploit the reactivity of these imidates for the development of one-pot functionalization reactions.

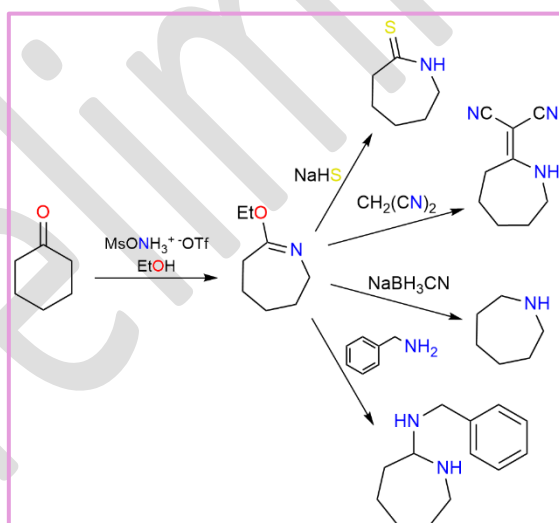


Figure 1: Different functionalization pathways of imidates

Acknowledgements:

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References:

- [1] A. H. Blatt, *Chem. Rev.*, **1933**, 12, 215-260.
- [2] S. Verma, V. Singh, J.L. Jat, B. Tiwari, *J. Org. Chem.*, **2024**, 89, 8201-8207
- [3] R. Thakur, Y. Jaiswal, A. Kumar, *Org. Biomol. Chem.*, **2019**, 17, 9829

Computational Modeling of Decarboxylation of ACAs

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Activated carboxylic acids (ACAs) are defined as abiotic "fuels" that maintain dissipative systems in a functional, out-of-equilibrium state. They have garnered research interest because they can be used to design complex molecular systems. These systems are engineered to persist in a dissipative state as long as the stimulus is present, much like the functions of living systems. Catalysts that can switch between active and inactive states are intriguing in this field. However, this particular aspect is still poorly explored. Building on this, this study aims to investigate the carboxylation reaction of certain ACAs (trichloroacetic acid, tribromoacetic acid, and nitroacetic acid), shown in Figure 1, through a combination of experimental and computational methods[1]. Experimental potentiometric studies were conducted to determine the lifetime of the dissipative state[2] (see Figure 1). Meanwhile, the decarboxylation reaction was modeled using a theoretical-computational hybrid QM/MM approach, the Perturbed Matrix Method (PMM)[3]. We compared the results to gain significant insights into the parameters governing the lifetime of the dissipative state in semiaqueous media.

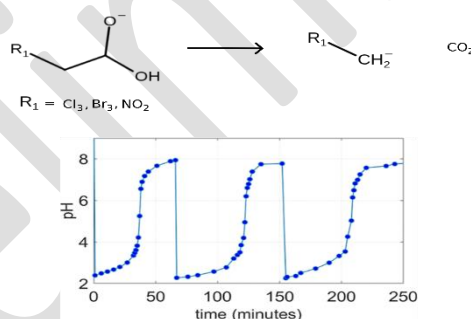


Figure 1. Upper Panel: Schematic representation of the ACAs decarboxylation reaction. Lower Panel: pH versus time profile of a 10 mM potassium carbonate solution in 80% DMSO upon three equimolar consecutive additions of 10 mM TCA each at 25 °C.

References

- [1] Zhou, S., Wang, Y. Solvation Induction of Free Energy Barriers of Decarboxylation Reactions in Aqueous Solution from Dual-Level QM/MM Simulations *JACS Au* 2021, **1**, 233-244.
- [2] Pucciarelli, G., *et al.* Temporally Controlled Supramolecular Catalysts with pH-Dependent Activity *ACS Omega* 2026, **11**, **4**, 6353-6361.
- [3] Zanetti-Polzi, L. *et al.* *Phys. Chem. Chem. Phys.*, 2018, **20**, 24369-24378.

Regio- and Stereoselective ring opening of 2,3-Diaryloxiranes: access to aryl-substituted 2,3-Dihydrobenzofuranols

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The 2,3-dihydrobenzofuran ring-system constitutes the core skeleton of numerous biologically active compounds, displaying a broad spectrum of biological activities including antioxidant, antitumor, and neuroprotective properties [1]. On a synthetic standpoint the 2,3-dihydrobenzofuran nucleus has recently received significant attention to find efficient regio- and stereoselective approaches, which allow the preparation of good quantities of compounds for broad-spectrum biological and pharmacological analysis [2].

As described in the synthetic pathway (Fig. 1), substituted *trans*-2,3-diaryloxiranes can be envisaged as suitable parent compounds for the direct access to regioisomeric aryl 2,3-dihydrobenzofuranols **5** and **6**. In particular, *trans ortho* ethoxymethoxy-2,3-diaryloxiranes were prepared, either *racemic* or in enantiopure form, by the Corey-Chaykovsky epoxidation between substituted protected salicylaldehydes and suitable sulfur ylides, which were generated *in situ* from the parent sulfonium salt in alkali medium. Upon treatment with Amberlyst-15, two competing reaction pathways occurred: 1) acetal moiety was cleaved and direct intramolecular nucleophilic attack afforded dihydrobenzofuranol **6** and 2) Meinwald rearrangement occurred, leading to the corresponding diarylactaldehyde, then, after cleavage of acetal group, intramolecular nucleophilic addition afforded dihydrobenzofuranol **5**. In this investigation, the effect on regio- and stereoselectivity of the reaction by different substituents on aryl groups was evaluated. Using chiral enantiopure sulfonium salts **4** [3], enantioenriched products with good yield and enantiomeric excess could be achieved as well.

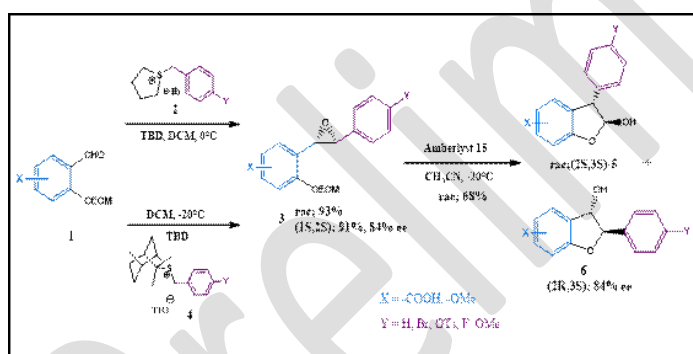


Figure 1: Synthetic pathway

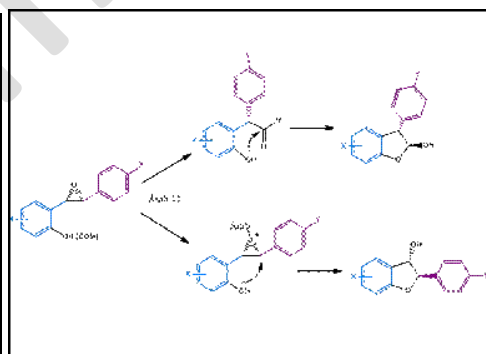


Figure 2: Reaction mechanisms

References

- [1]. Miao, Y.; Hu, Y.; Yang, J.; Liu, T.; Sun, J.; Wang, X. RSC Adv. 2019, 9, 27510
- [2]. Laurita, T.; D'Orsi, R.; Chiumminto, L.; Funicello, M.; Lupattelli, P. Synthesis 2020, 52, 1451
- [3]. Illa, O.; Aggarwal, V. K. et al. J. Am. Chem. Soc. 2013, 135, 11951

Synthetic strategies for the preparation of functionalised 2,3-diaryloxiranes, key intermediates in the synthesis of ϵ -viniferine

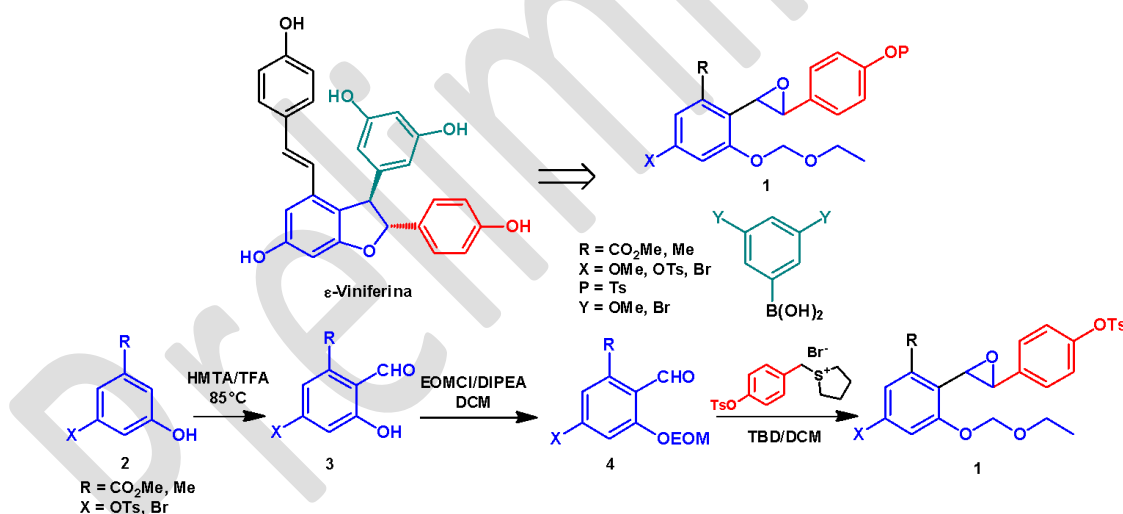
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In recent decades, viniferins have generated a great interest within the scientific community, particularly due to their potential applications in the medical field. Viniferins are resveratrol derivatives and are the most prominent stilbenoids synthesized by plants as phytoalexins. In particular, showed various pharmacological properties as antioxidant, antiinflammatory, antidiabetic, antiobesity and, even, anticancer [1]. Due to its low bioavailability, a variety of approaches for its total synthesis have been explored. This work is part of a project which has identified suitable functionalized *trans* 2,3-diaryl oxiranes as key intermediates for the total synthesis of ϵ -viniferin (Figure)[2]. Various 2,3-diaryloxiranes of type **1** were prepared starting from commercially available phenol derivatives **2**, which were elaborated by selective OH protections, regioselective Duff type formylation and Corey-Chaykovsky epoxidation reaction of the corresponding aldehydes, affording the desired epoxides **1**. Their chemical behaviour upon different arylation conditions and the substituents effects on regio- and stereoselectivity of the reaction, as well as on the chemical stability of the intermediates will be shown and discussed on the poster.



References

- [1] a) Ohara, K. *et al. Biochem. Biophys. Res. Commun.* **2015**, 468(4), 877-882; b) Barjot, C. *et al. Life Sci.* **2007**, 81(23-24), 1565-1574
- [2] a) Laurita, T.; Chiummiento, L.; Funicello, M.; D'Orsi, R.; Sallemi, D.; Tofani, D.; Lupattelli, P. *Eur. J. Org. Chem.* **2019**, 4397-4403; b) Laurita, T.; Chiummiento, L.; Lupattelli, P. *et al. Bioorg. Med. Chem. Lett.* **2021**, 49, 128264

Theme B - Advances in Physical and Colloids Chemistry

Lysine rich D,L peptide-based amphiphiles with antimicrobial activity

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One of the major modern medicine's challenges is laid by the increasing drug-resistance developed by bacteria. Among the many classes of compounds exploited as potential antimicrobials, Antimicrobial Peptides (AMPs)^[1] are natural occurring peptides whose cationic and amphipathic nature leads to self-assembly and bioactivity property. Some of the natural AMPs have a regularly alternated enantiomeric sequence (D,L), which increases their proteolytic resistance, lends special conformation accessibility and may be also responsible for their biological activity. In this context, we have designed a series of peptide amphiphiles to evaluate this stereochemistry effect on both the self-assembling properties and the bioactivity. The hydrophilic region was formed by cationic peptide sequences of increasing length, built by repeating one, two or three times a unit of valine (Val) and lysine (Lys). The Palmitic acid (Palm), chosen as hydrophobic tail, was conjugated to the N-terminus of the di-, tetra- and hexapeptides; obtaining molecules with a different hydrophilicity/hydrophobicity ratio, since this feature seems to be important for antimicrobial activity. For all Palm(D-Val-L-Lys)_n (n=1,2,3) conjugates, the corresponding homoconfigurational (all-D or all-L) sequences were synthesized. The structural characterization carried out with dynamic light scattering, small angle X-ray scattering, scanning electron microscopy and circular dichroism spectroscopy showed that the lipopeptides with homoconfigurational residues self-assembled into fibrous structures stabilized by β -sheet conformation, while the peptides with regularly alternating sequences adopt a random coil conformation self-organizing into fibrous structures at higher pH values and concentrations. Biological test on gram-negative *Pseudomonas. aeruginosa* and gram-positive *Staphylococcus. Aureus* showed that only the tetrapeptide and hexapeptide conjugates with alternated enantiomeric sequence had antimicrobial activity. These findings could be the result of the optimal hydrophilicity/hydrophobicity balance and the higher flexibility of the peptide moiety that allow a better interaction with the bacteria membranes^[2].

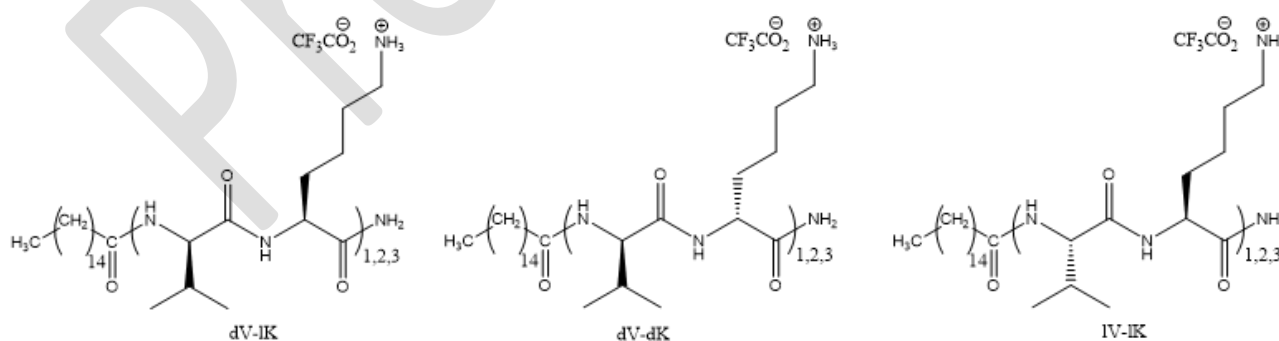


Fig.1: Lipopeptides sequence with heteroconfigurational and homoconfigurational sequence.

References

1. Luofeng Yu ACS Applied Bio Materials 2022 5 (2), 366-393
2. S Barman J. Am. Chem. Soc. 2026, 148, 4544–4556

Design and characterization of biocompatible albumin nanocarriers

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The use of nanocarrier systems for active ingredient delivery represents a promising strategy to enhance efficacy and protect labile compounds from degradation in numerous applications, spanning from pharmacy to agriculture, from detergency to cosmetic. For biomedical and cosmetic applications, the use of highly biocompatible and non-toxic carriers is imperative¹.

In this context, protein-based nanocarriers offer several advantages, including inherent biocompatibility, high biodegradability, and an endogenous origin, supporting safe and physiologically compatible delivery. Among proteins, serum albumins are versatile candidates due to their non-toxicity, high availability, and cost effectiveness. Their unique amphiphilic structure, rich in functional groups, facilitates interactions with a wide range of active molecules through both hydrophobic and hydrophilic domains^{2,3}.

Albumin nanoparticles are usually obtained via desolvation, a process involving controlled precipitation followed by cross-linking to ensure stability and high drug loading. Despite its demonstrated efficacy, concerns persist about residual toxicity associated with organic solvents and cross-linking agents. To overcome these limitations, alternative strategies—such as glucose mediated crosslinking and albumin self-assembly—can be employed to improve both the safety and sustainability of the formulation process⁴.

In this respect here we present the optimisation and characterisation of highly biocompatible albumin-based nanoparticles (NPs), prepared via either desolvation or metal-induced self-assembly, and subsequently stabilised through glucose crosslinking. Moreover, a comparative evaluation is conducted between Bovine Serum Albumin (BSA) and Human Serum Albumin (HSA) as building blocks for nanocarrier formulation. The physicochemical properties of the NPs are investigated using light scattering techniques, while the structural integrity and conformational features of albumins are analysed through spectroscopic methods. Finally, the loading capacity and release kinetics are evaluated by means of UV spectroscopy.

References

- [1] Gressler S., Hipfinger C., Part F., Pavlicek A., Zafiu C., & Giese B., *Journal of nanobiotechnology*, 2025,23,90.
- [2] Gradishar W. J., Tjulandin S., Davidson N., Shaw H., Desai N., Bhar P., Hawkins M., & O'Shaughnessy J., *Journal of clinical oncology: official journal of the American Society of Clinical Oncology*, 2005, 23(31), 7794–7803.
- [3] Qu N., Song K., Ji Y., Liu M., Chen L., Lee R. J., & Teng L., *International journal of nanomedicine*, 2024, 19, 6945–6980.
- [4] Bartlett B., A. Klier J., Razavi S., *Nanoscale*, 2025, 17, 5715–5731.

Where Order Blurs: Structural Journeys Across the Fluid–Solid Continuum of Sodium Deoxycholate

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Sodium deoxycholate (NaDC) displays a rich landscape of concentrated phases whose organization remains only partially understood. In this ongoing study, we want to combine small-angle X-ray scattering (SAXS) with controlled slow dehydration or other controllable experimental variables to track the structural evolution of NaDC as it transitions from highly hydrated aggregates toward increasingly ordered states. The resulting scattering patterns reveal a sequence of mesophase-like arrangements that echo those recently reported when NaDC associates with cationic and block-cationic polymers, suggesting common structural motifs emerging under crowding or charge-compensated conditions.

Our current goal is to establish a structural bridge between four key organizational states of NaDC: the recently resolved crystal structure, the fiber-like assemblies observed in gels and those observed in dehydrated gel samples, and the putative hexagonal phase proposed in concentrated solutions. Preliminary comparisons indicate partial correspondence between the packing features of the solid state and those inferred from SAXS profiles of the dense phases, though significant discrepancies remain.

By placing concentrated NaDC phases, polymer–NaDC coassemblies, and solid-state data on the same structural map, this work aims to clarify how hydration, ionic environment, and confinement shape bile salt ordering. The results presented here represent an evolving effort to connect mesoscopic scattering signatures with molecular-level organization across the NaDC phase diagram.

Keywords: sodium deoxycholate, bile salts, lyotropic mesophase, non-classical crystallization, SAXS.

Computational study of dynamics and fluorescence of two single-tryptophan mutants of holomyoglobin

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Although myoglobin is among the most extensively studied proteins, the experimental characterization of tryptophan fluorescence in holomyoglobin remains challenging because the heme group can efficiently quench the emission of nearby tryptophan residues. In this context, computational approaches can provide valuable insight into the dynamic behavior of holomyoglobin and, at the same time, allow the investigation of how conformational fluctuations of the protein matrix modulate the intrinsic emission properties of the tryptophan chromophores. The computational protocol used in this work is based on Molecular Dynamics (MD) coupled with the Perturbed Matrix Method (PMM)¹, a QM/MM approach that combines the classical dynamics of the system with a quantum mechanical description of the quantum center (QC), here represented by the indole moiety of tryptophan. This method allows the excitation energies to be evaluated while taking into account the local electrostatic environment, particularly the electric field generated by the protein matrix and the solvent. The method was applied to two single-tryptophan mutants of sperm whale holomyoglobin, namely W7Y and W14Y, for which experimental emission maximum wavelengths were available in the literature². The results obtained so far show that, despite a blue-shift in the predicted spectra, the λ_{max} values are similar for the two tryptophan sites, with W7 being slightly more exposed to the solvent, in good agreement with the experimental data.

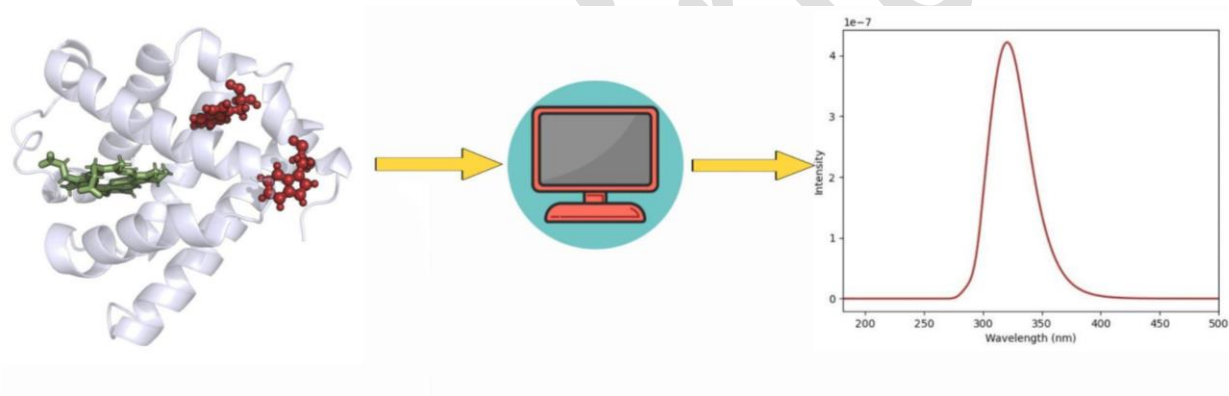


Fig.1: Left: representative snapshot of holomyoglobin (highlighting the two tryptophan residues and the heme group). Right: a typical predicted emission spectrum.

References

- [1] D'Abramo, M., Aschi, M., Amadei A.; *J. Chem. Phys.*, 2014, 140 (16): 164104.
- [2] Stevens, J. A., Link, J. J., Kao, Y. T., Zang, C., Wang, L., & Zhong, D.; *J. Phys. Chem. B*, 2010, 114 (3), 1498-1505.

Theme C - Analytical Chemistry

Preliminary

A First Step Toward Human Nanoplastic Exposure Assessment: Multimodal AF4 Analysis of Polystyrene Nanoparticles

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An analytical method based on Asymmetric Flow Field-Flow Fractionation (AF4) constitutes an innovative approach for the high-resolution separation and investigation of nanoplastics in complex biological matrices. [1] This study describes an optimized methodology for the human biomonitoring (HBM) of polystyrene (PS) nanoparticles in urine and serum. [2] Sample preparation protocols are developed to minimize matrix interferences while preserving nanoparticle integrity and preventing their loss, aggregation, or contamination. The coupling of AF4 with a suite of on-line detectors—including Multi-Angle Light Scattering (MALS), Dynamic Light Scattering (DLS), and ultraviolet (UV) detection—provides simultaneous size information and semi-quantitative analysis. Within this setup, the UV detector specifically enables polymer-specific responses for evaluating PS nanoparticles in the 20 to 200 nm size range. In addition to on-line detection, AF4 allows time-resolved fraction collection, enabling monodisperse nanoparticle populations to be isolated and subjected to complementary off-line techniques. This includes morphological assessment by Field Emission Scanning Electron Microscopy (FESEM), as well as independent confirmation of size and concentration using Nanoparticle Tracking Analysis (NTA) [3] and Single-Particle ICP-MS (SP-ICP-MS) through carbon-13 monitoring. [4] Overall, the results demonstrate the reliability and analytical suitability of this integrated workflow. Ultimately, this research provides a standardized protocol applicable to HBM studies, supporting the generation of reliable exposure data for the assessment of potential human health risks associated with PS nanoparticles.

Acknowledgements: The authors gratefully acknowledge the financial support by the National Plan for Complementary Investments (PNC) project “Biomonitoring of biodegradable micro and nanoplastics: from the environment to humans in a one health perspective (BioPlast4Safe)”.

References

- [1] Battistini B, Petrucci F, Bocca B. In-house validation of AF4-MALS-UV for polystyrene nanoplastic analysis. *Anal Bioanal Chem.* 2021 May;413(11):3027-3039. doi: 10.1007/s00216-021-03238-2.
- [2] Ruggieri F., Battistini B., Sorbo A., Senofonte M., Leso V., Iavicoli I., Bocca B. From food-to-human microplastics and nanoplastics exposure and health effects: A review on food, animal and human monitoring data. *Food and Chemical Toxicology*, Volume 196 (2025) <https://doi.org/10.1016/j.fct.2024.115209>.
- [3] Adkins GB, Sun E, Coreas R, Zhong W. Asymmetrical Flow Field Flow Fractionation Coupled to Nanoparticle Tracking Analysis for Rapid Online Characterization of Nanomaterials. *Anal Chem.* 2020 May 19;92(10):7071-7078. doi: 10.1021/acs.analchem.0c00406.
- [4] Laborda F, Bolea E, Jiménez-Lamana J. Single Particle Inductively Coupled Plasma Mass Spectrometry: A Powerful Tool for Nanoanalysis. *Anal. Chem.* 2014, 86, 5, 2270–2278 Dec. 2013 <https://doi.org/10.1021/ac402980q>

Printed electrochemical sensors for the rapid detection of 8-Oxoguanine as a biomarker of oxidative damage

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8-oxo-Guanine (8-oxoG) is one of the most prevalent oxidative lesions of nucleic acids, generated by reactive oxygen species and widely recognized as a key biomarker of oxidative stress. Reliable quantification of 8-oxoG is essential not only for evaluating oxidative imbalance but also for gaining insight into pathological conditions in which oxidative damage plays a crucial role. Despite its importance, current analytical determination still relies on laboratory-based techniques that are not always compatible with rapid, low-cost, or decentralized analysis. Among conventional analytical approaches, high-performance liquid chromatography coupled with tandem mass spectrometry (HPLC-MS/MS) is considered one of the most sensitive and selective methods for detecting oxidized nucleobases. However, these techniques are limited by expensive instrumentation, the need for highly trained personnel, and complex analytical workflows. Sample preparation steps such as extraction and purification are often time-consuming and can hinder fast or in situ measurements, making these methods more suitable for confirmatory laboratory analysis than for user-friendly applications. In this context, the present work explores the development of electroanalytical sensors based on screen-printed electrodes fabricated on low-cost and flexible substrates, including polyester and paper. Different electrode configurations were evaluated for the detection of 8-oxoG, and carbon black dispersion was employed to modify the working electrodes to enhance sensitivity. The choice of printed platforms is driven by advantages such as low production cost, ease of fabrication, mechanical flexibility, and compatibility with disposable formats, while electrochemical detection enables rapid analysis with relatively simple instrumentation. After optimization of key experimental parameters, including electrode type, supporting electrolyte, and electroanalytical technique, the proposed sensing platform exhibited a reproducible and sensitive response toward 8-oxoG, achieving detection in the micromolar range with good repeatability (ca. 10%). The method was further evaluated in spiked serum samples to assess performance in complex matrices and evaluate matrix effects. Notably, these sensors operate without the need for extensive sample preparation, enabling simple, rapid, and potentially in situ measurements. Although still under development, these results highlight the potential of electrochemical sensors as a practical and user-friendly alternative to conventional methods, offering advantages in terms of cost, speed, and accessibility.

References

- [1] Hahm, J. Y.; Park, J.; Jang, E.-S.; Chi, S. W. *Exp Mol Med* **2022**, 54 (10), 1626–1642.
- [2] Wang, J.; Li, C.; Han, J.; Xue, Y.; Zheng, X.; Wang, R.; Radak, Z.; Nakabeppu, Y.; Boldogh, I.; Ba, X. *J Biomed Sci* **2025**, 32 (1), 1.
- [3] Boysen, G.; Collins, L. B.; Liao, S.; Luke, A. M.; Pachkowski, B. F.; Watters, J. L.; Swenberg, J. A. *A Journal of Chromatography B* **2010**, 878 (3), 375–380.
- [4] Singh, S.; Wang, J.; Cinti, S. *ECS Sens. Plus* **2022**, 1 (2), 023401.

Electrochemical Sensor as Smart Device for White Blood Cell Measurement in Synovial Fluid

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Periprosthetic joint infections (PJI) represent a clinically complex complication of joint arthroplasty, characterized by the interplay between microorganisms, the prosthetic implant, and the host immune system (1). Early diagnosis is essential to prevent severe complications and infection chronicization and to this end standardized diagnostic criteria, such as those proposed by the Musculoskeletal Infection Society (MSIS) (3), identify synovial white blood cell (WBC) count as a key diagnostic marker. Emerging biomarkers, including pH and lactate, have been proposed as complementary parameters, as synovial pH decreases and lactate increases in infected conditions (5). In this work, we propose a paper-based screen-printed electrochemical sensor for the multiparametric detection of PJI biomarkers. The system is based on a paper-based microfluidic platform enabling the simultaneous analysis of WBC, pH, and lactate.

Herein, the preliminary validation was reported for WBC detection using an impedance-based sensor with data analysis supported by chemometric approaches, including Partial Least Squares (PLS) and Principal Component Analysis (PCA).

In detail, 19 capillary blood samples was selected and analysed to enable rapid sample collection, improved repeatability and a higher abundance of WBCs, thereby facilitating the initial validation of the sensing approach. Once satisfactory predictive performance is achieved in blood samples, the same sensing architecture and modelling framework will be transferred to synovial fluid. Initial correlation between solution resistance (R_s) and WBC concentration was observed ($((0.0044 \pm 0.0005) - (1.0 \times 10^7 \pm 0.6 \times 10^7); R^2 = 0.822)$) using only 10 μ L of sample. The pH sensor exhibited a linear response within the physiological range ($y = (-0.044 \pm 0.005)x + (0.310 \pm 0.004); R^2 = 0.970$). Preliminary tests on synovial fluid samples provided WBC consistent with reference laboratory methods. These results demonstrate the feasibility of printed sensing low-cost point-of-care platform for rapid PJI diagnosis.

Acknowledgements: Financial support is recognized under the National Recovery and Resilience Plan (PNRR), Missione 6 – Salute, Componente 2 – Innovazione e ricerca sanitaria, Investimento 2.1 – Valorizzazione e potenziamento della ricerca biomedica del SSN, **Avviso pubblico n. 377**, finanziato dall'Unione Europea – NextGenerationEU – The diagnostic pillar for diagnosis of infections in the orthopedic field: Smart and sustainable paper-based electrochemical point-of-care device assisted by artificial intelligence– PNRR-POC-2023-12378291 CUP E83C23003450007– Decreto di Assegnazione BANDO PNRR M6/C2 2023 26 marzo 2024.



References

- [1] Patel, Robin. "Periprosthetic joint infection." *New England Journal of Medicine* 388.3 (2023): 251-262.
- [2] Parvizi, J., Tan, T. L., Goswami, K., Higuera, C., Della Valle, C., Chen, A. F., & Shohat, N. (2018). "The 2018 Definition of Periprosthetic Hip and Knee Infection: An Evidence-Based and Validated Criteria." *The Journal of Arthroplasty*, 33(5), 1309-1314.
- [3] Müller, Dirk, et al. "Synovial pH, lactate, and glucose as adjunct biomarkers to exclude periprosthetic joint infection in hip and knee arthroplasty: a prospective study." *Journal of Bone and Joint Infection* 10.4 (2025): 293-301.

Exploratory study of VOC emissions from synthetic textiles using SPME-GC/MS

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In recent years, the spread of fast fashion e-commerce platforms, based outside Europe, has led to a consequent increase in the purchase of low-cost clothing items, which often lack clear information about the treatments applied to them and the chemical additives used. In this context, particular attention should be paid to volatile organic compounds (VOCs) released by synthetic fabrics, especially in relation to potential inhalation exposure during everyday use.

To address this issue, an exploratory study investigated the release of VOCs from different types of garments purchased through Chinese e-commerce platforms, including T-shirts, shirts, and other upper-body clothing items. The information reported on the labels, confirmed through μ FTIR analysis, indicated a predominantly polyester-based composition, with smaller amounts of spandex in some garments, always below 10%.

The analysis was performed using solid-phase microextraction (SPME) coupled with GC-MS. The experimental conditions were optimized by considering the amount of fabric, the type of vial used, the exposure time, and the temperature. The samples were finally kept at 80 °C for 45 minutes in order to evaluate the total releasable fraction from the garment (worst-case scenario).

The analysis revealed the presence of different classes of compounds, including aldehydes, ketones, aromatic hydrocarbons, esters, and oxygenated compounds, attributable to production and finishing processes. Although still preliminary, these results represent a first useful reference for the interpretation of subsequent exposure scenarios.

Further work will focus on simulating more realistic use conditions, including lower temperatures and longer exposure times, in order to better approximate daily wearing scenarios. In addition, attention will be given to the variability among garments, the influence of repeated use and washing cycles, and the potential cumulative exposure to VOCs over time. These aspects are essential for refining exposure assessments and for identifying compounds of greatest concern from a toxicological perspective.

References

- [1] Foschi, M., Colantoni, V., Reale, S., Scappaticci, C., D'Archivio, A. A., & Biancolillo, A. (2025). *Analysis of volatile organic compounds in textiles: Insights from GC-MS with metal content assessment using ICP-MS*. Applied Sciences, 15, 1572.
- [2] Qian, W., Guo, Y., Wang, X., Qiu, X., Ji, X., Wang, L., & Li, Y. (2022). *Quantification and assessment of chemical footprint of VOCs in polyester fabric production*. Journal of Cleaner Production, 339, 130628.

Microplastics and Additives in Indoor Dust: Integrated Spectroscopic and Chromatographic Characterization

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Microplastics (MPs) are emerging contaminants of increasing concern due to their high environmental persistence, resistance to biodegradation, and ability to accumulate in environmental matrices and along the food chain. In addition to the polymeric particles themselves, MPs contain a wide range of organic and inorganic additives introduced during manufacturing processes to enhance specific material properties. The coexistence of microplastics, plastic additives, and trace metals in indoor environments represents a relevant environmental and public health issue, particularly considering that settled dust acts as a major reservoir and potential exposure pathway for humans.

This study aimed to develop and apply integrated analytical procedures for the isolation, identification, and quantification of microplastics and associated contaminants in complex indoor matrices. A density-based flotation clean-up procedure was optimized to separate microplastics from denser organic and mineral fractions present in dust samples, improving matrix removal and analytical selectivity.

Method validation was performed using the certified reference material NIST SRM 2585, representing indoor dust collected from residential environments. The efficiency of the separation protocol was assessed by micro-FTIR analysis, which confirmed the enrichment of polymeric particles in the floating fraction (Figure 1) and the absence of detectable polymer signals in the sedimented fraction, demonstrating the robustness of the developed procedure.

In parallel, an analytical method was developed for the determination of 33 organic plastic additives belonging to different chemical classes, including phthalates, alternative plasticizers, and flame retardants. Due to their wide range of physicochemical properties, a selective extraction step was followed by instrumental analysis using GC-MS and HPLC-MS/MS. Elemental characterization of the samples was also carried out by ICP-MS after mineralization of the samples, enabling the quantification of trace metals such as Pb, Cr, Zn, and Fe.

The developed procedures were applied both to the reference material NIST SRM 2585 and to real-world dust samples collected from a tire repair workshop, selected as a representative occupational environment with significant levels of technical particulates. A comparative analysis highlighted significant differences in both the distribution of flotation fractions and the chemical profiles of additives. The NIST sample showed a higher abundance of traditional phthalates and regulated flame retardants, whereas the workshop dust was characterized by a predominance of alternative plasticizers and elevated concentrations of metals associated with mechanical wear and technical materials.

Overall, the results demonstrate the effectiveness of the proposed integrated analytical approach for studying microplastics and associated contaminants in complex indoor environments, providing valuable tools for environmental monitoring and for the assessment of potential human health risks related to indoor and occupational exposure.

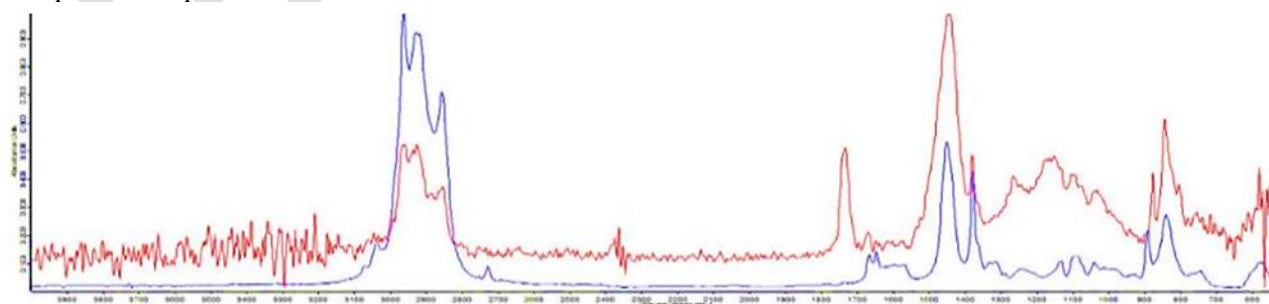


Figure 1: FTIR spectrum of particles detected in dust sample (red) and reference FTIR spectrum of polyisoprene (blue)

Rapid Identification of Diesel Adulteration Using Portable MicroNIR Spectroscopy Coupled with Chemometrics

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Diesel fuel adulteration is an increasing concern across the fuel supply chain, driven by the growing diversification of fuel compositions and the introduction of alternative components such as biodiesel and hydrotreated vegetable oil (HVO). HVO is a paraffinic biofuel obtained via hydrotreatment of vegetable oils or waste fats, characterized by high purity and compatibility with conventional diesel. While it represents a sustainable alternative, its higher market value and favorable taxation make it particularly susceptible to fraudulent practices.

Diesel adulteration is commonly achieved by blending conventional diesel with lower-cost or improperly declared components, including agricultural diesel, waste cooking oil, or undeclared biofuels. These modifications are often carefully tuned to maintain key physicochemical properties (e.g., density, viscosity, cetane number) within regulatory limits, making detection through standard quality control methods difficult. As a result, more sensitive and selective analytical approaches are required to ensure fuel authenticity and compliance.

In this work, a rapid, portable, and non-destructive method based on near-infrared spectroscopy using MicroNIR instrumentation, combined with advanced chemometric techniques, was developed for the detection and quantification of diesel adulteration. Pure diesel samples and blends containing biodiesel, HVO, agricultural diesel, and waste cooking oil were systematically prepared over realistic concentration ranges to simulate common fraud scenarios [1].

Spectral data were analyzed using multivariate methods, including Principal Component Analysis (PCA) for exploratory analysis, Partial Least Squares Discriminant Analysis (PLS-DA) for classification, and Partial Least Squares Regression (PLS-R) for quantification of adulterants. The developed models demonstrated high predictive performance, enabling accurate discrimination of compliant and adulterated samples and reliable quantification even at low concentrations, without evidence of false positives or false negatives [2].

These results demonstrate that the integration of MicroNIR spectroscopy and chemometrics represents a powerful and practical tool for real-time diesel authentication, offering significant potential for on-site applications in regulatory control, supply chain monitoring, and fraud prevention.

References

- [1] Fernanda V. C. V., Paulo F. B. S., Maria F., Márcio J. C. P., Claudete F. P., Using near-infrared overtone regions to determine biodiesel content and adulteration of diesel/biodiesel blends with vegetable oils, 2012, 716, *Analytica Chimica Acta*, 2000, 716, 101-107 Partial least squares discriminant analysis: taking the magic away
- [2] Brereton, R. G., & Lloyd, G. R., Partial least squares discriminant analysis: taking the magic away, 2014, 213-225., *Journal of Chemometrics*.

Study of head-space: an innovative monitoring approach using MicroNIR/Chemometrics

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Volatile organic compounds (VOCs) constitute a broad and heterogeneous class of chemicals widely present in industrial, environmental, and domestic contexts, including solvents, cleaning products, foods, and building materials, with significant implications for human health. Their characterization is traditionally performed using chromatographic techniques coupled with mass spectrometry (HS-GC/MS, HS-SPME-GC/MS)¹, which provide high sensitivity and selectivity but involve sampling and preconcentration steps that may introduce variability and operational complexity. In this context, spectroscopic techniques such as Near-Infrared (NIR) spectroscopy are gaining increasing attention as rapid, non-destructive, and reagent-free analytical tools. Although, NIR spectroscopy doesn't allow direct identification of individual compounds, it provides a comprehensive spectral fingerprint of the sample (associated with overtones and combination bands), which can be effectively interpreted using multivariate chemometric methods to extract qualitative and quantitative information. To date, NIR is predominantly used in an indirect way, where the spectral information is correlated with reference analyses typically performed on the liquid phase, enabling the development of calibration models for predictive purposes.² This work proposes an alternative approach based on NIR spectroscopy combined with chemometric data analysis, directly applied to the headspace for the investigation of VOCs, with particular focus on pure solvents and their mixtures. The experimental protocol was designed to ensure controlled generation of the headspace by optimizing key parameters such as temperature, equilibration time, and system volume, in order to obtain reproducible and representative vapor-phase compositions. NIR spectra were acquired under these controlled conditions and pre-processed to enhance relevant spectral features. Exploratory analysis through Principal Component Analysis allowed discrimination between different solvents and mixtures based on their spectral fingerprints, highlighting the ability of NIR signals to compositional changes in the gaseous phase. In particular, the different solvents were systematically evaluated by analysing their distribution within the multivariate space, examining their clustering behaviour in the scores plot and interpreting their chemical characteristics through the study of loadings plot. The results indicate that, despite the intrinsic complexity and band overlap typical of NIR spectra, the combination with chemometric tools enables reliable extraction of meaningful chemical information. This study represents a preliminary approach that opens the way to multiple future applications, particularly in process monitoring. The investigated solvents serve as relevant model systems for practical applications, suggesting the possibility of extending the methodology to real industrial scenarios where fast, reliable, and non-invasive monitoring of volatile compounds is required.

References

- [1] Lancioni C., Castells C., Candal R., Tascon M. Headspace solid-phase microextraction: Fundamentals and recent advances. *Advances in Sample Preparation*, 2022, **3**, 100035.
- [2] Ye M., Gao Z., Li Z., Yuan Y., Yue T. Rapid detection of volatile compounds in apple wines using FT-NIR spectroscopy. *Food Chemistry*, 2016, **190**, 701-708.

Magnetic Fe₃O₄@PDA Nanoparticles for Enhanced LFA Sensitivity: Human Transferrin as a Model System

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Background: Traditional Lateral Flow Assays (LFAs) based on gold nanoparticles (AuNPs) often rely on the non-specific adsorption of antibodies or require prior functionalization with heterobifunctional linkers. To overcome these, recent research has highlighted the potential of polymeric particles, particularly polydopamine (PDA). PDA has a rich density of catechol and quinone groups, enabling direct bioconjugation with antibodies via Schiff base formation or Michael addition [1]. Integrating these polymers into magnetic core-shell architectures has been shown to significantly improve the Limit of Detection (LOD) [2]. Building on these advantages, this preliminary study compares bare PDA and magnetic Fe₃O₄@PDA nanoparticles as versatile foundational platforms for LFA diagnostics, utilizing human transferrin as a model system

Methods: PDA-NPs were synthesized via oxidative polymerization of dopamine hydrochloride in alkaline conditions (NaOH, 50°C), Fe₃O₄@PDA-NPs were produced through the co-precipitation of iron salts (Fe²⁺/Fe³⁺: 1:2, NH₄OH, 80°C) followed by the deposition of a PDA shell. Both NPs were characterized by Dynamic Light Scattering (DLS), Transmission Electron Microscopy (TEM) and UV-VIS spectrophotometer. LFA cards were assembled with a ~2mm pad overlap; images were processed via ImageJ.

Results: We synthesized PDA-NPs with a hydrodynamic diameter of 108 ± 2 nm (PDI: 0.09 ± 0.1) and Fe₃O₄@PDA-NPs with 100 ± 1 nm diameter (PDI: 0.16 ± 0.01). After 2 h of incubation with Anti-Human Transferrin antibody, the PDA-NPs increased to 145 ± 3 nm (PDI = 0.09 ± 0.01), as confirmed by DLS. Both NPs were tested on LFA, with a transferrin calibration range between 0 and 100.000 ng/mL to investigate the hook effect (Fig.A). In this range, at the same optical density (OD) and transferrin concentration of 1000 ng/mL, Fe₃O₄@PDA-NPs showed a 3-fold higher signal-to-noise ratio (SNR) than PDA-NPs (23.3 vs 7.6). The SNR enhancement is likely due to the higher optical density of the iron core as confirmed by UV-VIS spectra (Fig.B).

Future perspective: Future steps involve using the magnetic core to pre-concentrate samples, to improve SNR and consequently lower the LODs. In conclusion, PDA-iron nanoparticles ensure high visual contrast on nitrocellulose, enabling clear, equipment-free LFA readouts.

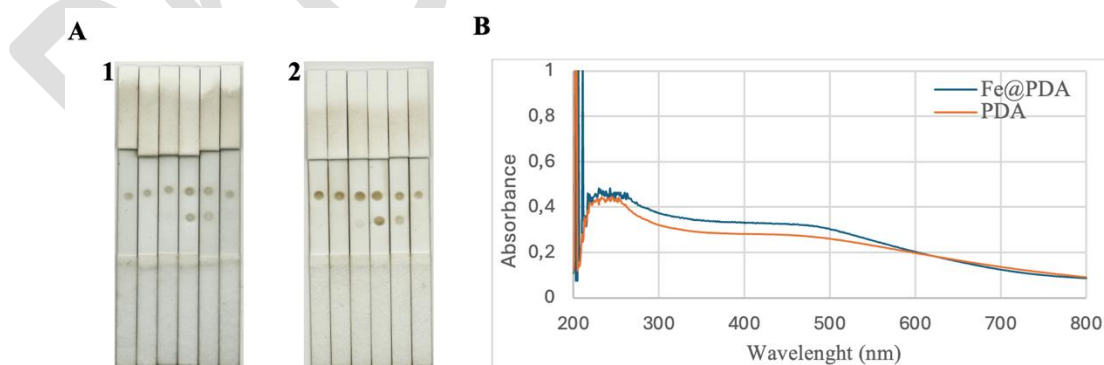


Fig. A: Calibration on LFA for (1) PDA-NPs and (2) Fe₃O₄@PDA-NPs. Legend: 0, 100, 1000, 10000, 100000 ng/mL

Fig. B: UV-VIS spectra of PDA-NPs and Fe₃O₄@PDA-NPs

- References:** [1] Aghaei F, Asgharzadeh F, Kaboudin B, *Langmuir*, 2026
[2] Sun J, Wu Y, Fan X, Peng J, Wang X, Xiong Y, Huang X. *Food Chemistry*, 2025, **465**, 1421s

Lipid Based Microparticles of EGCG: Catechin Stabilization, Structural Characterization and Chemometric Validation

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(-)-Epigallocatechin-3-gallate (EGCG) is the major polyphenol in green tea, where it can account for over 50% of total catechins. EGCG is characterized by marked antioxidant properties due to phenolic hydroxyl groups, with the ability to neutralize approximately 4.16 peroxy radicals (ROO•).^[1] It also presents antioxidant and anti-inflammatory effects, modulation of the lipid profile (reduction of total and LDL cholesterol) and on glycemic regulation. However, EGCG is chemically unstable, subject to self-oxidation and photodegradation, limiting its application.^[2] In this context, microencapsulation represents an effective technological strategy to improve its stability, shelf life and bioaccessibility, modulating the release and protecting the compound from degradation and unfavourable environmental conditions. The aim of this work is to develop a microencapsulation strategy for EGCG by spray congealing, a lipid matrix-based technology, for the formation of spherical microparticles, with controlled release into the gastrointestinal environment. Microparticles were optimized by varying process parameters (nozzle temperature, N₂ pressure, coating type, and coating/EGCG ratio) and characterized by Scanning Electron Microscopy (SEM), Thermogravimetric Analysis (TGA), simulated fluid release tests with ABTS•+ assay, and Near-Infrared (NIR) analysis coupled with supervised and unsupervised chemometric approaches. Stability was assessed for up to 10 months by TGA. Optimal conditions (85 °C nozzle, 2.5 bar N₂, myristic acid) produced homogeneous (~100 µm), spherical and defect-free microparticles, with improved loading at 20% w/w (deformations at 30% w/w and size increase ~200 µm were highlighted). Broido thermokinetic analysis showed an increase in activation energy compared to free EGCG, indicating greater thermal stability of the microencapsulated system. Dissolution tests showed protection in gastric environment and intestinal release, with maintenance of antioxidant activity (~50% scavenging at 0.040 mg/mL) for the 20% formulation. Storage stability did not show significant changes in active content. NIR analyses coupled with a chemometric study showed good sample discrimination and good predictive performance of the PLSr model.

Overall, the obtained microparticles show promising morphological, thermal, and functional properties, highlighting increased stability of EGCG compared to the non-microencapsulated form, maintenance of antioxidant activity, and good controlled release capacity, indicating spray congealing as an effective strategy for highly stable catechin lipid formulations, with potential nutraceutical and food applications.

References

- [1] Valcic, S., et al., Antioxidant chemistry of green tea catechins. New oxidation products of (-)-epigallocatechin gallate and (-)-epigallocatechin from their reactions with peroxy radicals. *Chemical research in toxicology*, 2000, 13.9: 801-810.
- [2] Hou, Z., et al. Mechanism of action of (-)-epigallocatechin-3-gallate: Auto-oxidation-dependent inactivation of epidermal growth factor receptor and direct effects on growth inhibition in human esophageal cancer KYSE 150 cells. *Cancer research*, 2005, 65.17: 8049-8056.

Rapid and innovative analytical platform for the characterization and quality control of e-liquids

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Electronic cigarettes have been developed in recent years as alternatives to conventional tobacco-based products, with the aim of reducing the intake of toxic compounds generated by the combustion process.¹ One of the key factors driving their widespread adoption is the possibility of varying the type and composition of the liquid to be vaporized, allowing users to choose among different flavours and nicotine concentrations. This has prompted the need to develop appropriate analytical methods for quality control and for the comparison of products from different manufacturers, in order to verify compliance with current regulations. With the goal of reducing both analysis and sample preparation times, the present work focused on the development and optimization of spectroscopic methods integrated with statistical analysis.² E-liquid samples from the same manufacturer, differing in nicotine content (0–2%) and flavour composition, were selected. NIR spectra were acquired using a portable MicroNIR instrument directly on the liquid and on an impregnated swab, with analyses performed in triplicate to ensure repeatability and reproducibility. Spectral data processing was carried out through a chemometric approach, applying Principal Component Analysis (PCA) and the Partial Least Squares Discriminant Analysis (PLS-DA) algorithm to build a discriminant model for the classification of different liquid profiles. Concurrently, GC-MS analyses were developed and optimized, performed both by direct injection, to characterize the semi-volatile fraction, and by SPME headspace extraction, for the volatile fraction.³ The GC-MS results were correlated with the spectroscopic data in order to strengthen the chemometric model, identify potential outliers, and detect molecular markers specific to each sample. This integrated approach enabled the development of an innovative, rapid, and selective analytical platform, applicable through in-situ measurements for the determination of e-liquid composition, and representing a potentially valuable tool for fraud detection, comparable in performance to existing reference methods.

References

- [1] Lu F., Yu M., Chen C., Liu L., Zhao P., Shen B., Sun R. The emission of VOCs and CO from heated tobacco products, electronic cigarettes, and conventional cigarettes, and their health risk. *Toxics*, 2021, **10**(1), 8.
- [2] Akhtar Z., Barhdadi S., De Braekeleer K., Delporte C., Adams E., Deconinck E. Spectroscopy and chemometrics for conformity analysis of e-liquids: Illegal additive detection and nicotine characterization. *Chemosensors*, 2024, **12**(1), 9.
- [3] Rantaša M., Majer D., Finšgar M. A review of analytical techniques for the determination of e-liquid and electronic cigarette aerosol composition. *Journal of Chromatography A*, 2025, **1748**, 465859.

TGA-FTIR and μ -FTIR for the study of microplastics in atmospheric particulate matter

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Microplastics (MPs) are ubiquitous contaminants with significant ecological and health impacts. In particular, the study of airborne MPs is highly challenging due to their heterogeneity in terms of shape, size, and chemical composition, as well as their coexistence with the numerous organic and inorganic constituents of atmospheric particulate matter (PM). This complexity makes their selective isolation, identification, and accurate quantification difficult [1]. Among the most widely used analytical techniques are vibrational spectroscopy, thermoanalytical methods, and mass spectrometry, including pyrolysis coupled with gas chromatography/mass spectrometry (Py-GC/MS). By contrast, a still underutilized approach for the study of MPs in PM is the coupling of thermogravimetric analysis with Fourier-transform infrared spectroscopy (TGA-FTIR), which, by combining the thermal properties of polymers with evolved gas IR spectra, can provide detailed information on polymers and additives.

Therefore, the aim of this work is to develop a robust and innovative method for the analysis of airborne MPs in complex environmental matrices, by combining pretreatment processes of PM samples with different particle size fractions collected from a packaging facility, where polyethylene granules are predominantly used as raw material, with subsequent morphological characterization by μ -FTIR and semiquantitative polymer analysis by TGA-FTIR.

Collected PM was mechanically removed from filters, and MPs were separated from the carbonaceous and mineral components of PM by density separation via flotation in a supersaturated saline solution. The supernatant fraction was then digested with H₂O₂ to remove organic contaminants, testing different concentrations, temperatures, and contact times. The treated samples were subsequently filtered using different membrane filters (PTFE, cellulose esters, polycarbonate, etc.). In parallel, the thermal ramps for TGA-FTIR analysis of different polymer standards (PE, PET, PP, PS, PVC) were optimized to verify their separation during thermal decomposition. For each polymer, calibration curves were constructed by correlating characteristic FTIR bands with the amount of polymer used.

The treated PM samples were then analyzed by μ -FTIR in ATR mode to determine morphology, size, and polymer composition, and by TGA-FTIR to estimate the total polymer content present on the filters.

After optimization, the TGA-FTIR method was applied to deposited dust samples and PM fractions with different particle sizes collected at the packaging facility. The results confirmed the predominant presence of polyethylene (PE) in both dust samples and PM fractions, with a higher abundance in the coarser fractions. The method proved to be effective for the characterization and semiquantitative determination of airborne microplastic samples.

Bibliografia

[1] Thurston GD et al. 2017.

Migration of Hazardous Chemicals from Food Contact Materials: A Multi-Analyte Analytical Approach

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A renewed focus on the safety of food contact materials (FCMs), including plates, cups, napkins, and cutlery, has arisen in response to the increasing use of alternative materials derived from bio-based or recycled sources. In this context, special attention is given to contaminants that may migrate into food at relevant concentrations, including PFAS, plastic additives, azo dyes, and aromatic amines, whose presence in FCMs depends on the raw materials used and the processing methods involved.

The migration of these compounds was assessed on a representative selection of FCMs, including both conventional materials and items derived from natural or recycled sources, in order to highlight any differences related to composition and intended conditions of use. Migration tests were carried out in accordance with current European regulations, using food simulants representing fatty and acidic matrices (96% EtOH and 3% CH₃COOH, respectively), under controlled temperature and time conditions (70°C for 2 hours), to reproduce realistic usage scenarios [1-3]. Target analytes were determined using chromatographic techniques coupled with mass spectrometry, such as HPLC-ESI/QTrap for PFAS and GC-EI/MS/MS and HPLC-ESI/MS/MS for additives, aromatic amines, and azo dyes.

The multi-analyte approach revealed significant differences among the various types of FCMs analyzed, with an overall higher migration observed in tests performed using 96% ethanol, suggesting a greater affinity of the compounds for lipophilic matrices. The analyzed samples mainly showed the presence of plastic additives (phthalates and alternative plasticizers) and, in some cases, aromatic amines. The detection of these substances, known for their potential toxicity, highlights the need for systematic monitoring of food contact materials, particularly under realistic conditions of use and with respect to regulatory compliance.

References

- [1] European Commission Regulation. (EU) 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food (Text with EEA relevance). OJ L 2011
- [2] Simonetti, G., Riccardi, C., Pomata, D., Acquaviva, L., Fricano, A., Buiarelli, F., Senofonte, M., & Di Filippo, P. (2024). *Studies of potential migration of hazardous chemicals from sustainable food contact materials*. Foods, 13(5), 64
- [3] Sonego, E., Di Filippo, P., Riccardi, C., Pomata, D., Bannò, A., Simonetti, G., & Buiarelli, F. (2023). *Occurrence and migration study of chemicals from baking paper and aluminium foil*. Food Chemistry, 409, 135260. Name A. (or Editor), Title of the book, 2000, Chapter, page(s), Publisher, City, Country.

Theme D - Advances in Inorganic Chemistry and Functional Materials

Indium(III) Phosphane Complexes: Green Catalysts for Michael-Type Additions of α -Nitroketones to α,β -Unsaturated Carbonyl Compounds

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In recent years, indium has attracted significant interest due to its applications in a wide range of technological devices. Organoindium compounds exhibit Lewis acid behaviour, promoting various organic transformations, such as C–C and C–N bond formation, as well as oxidative coupling and cross-coupling reactions.^[1] Through Michael addition, α -nitroketones can be powerful intermediates in organic synthesis. After C–C bond formation, the nitro group can be readily converted into a variety of functional groups, such as amines, oximes, carbonyl compounds.^[2] In this study, we report novel, efficient and green indium(III)-based catalytic systems for Michael-type reaction of α -nitroketones to α,β -unsaturated carbonyl compounds. Starting from InCl_3 and InBr_3 , four different phosphane ligands were employed to modulate steric hindrance and electronic environment around the metal center (Figure 1). All the novel complexes were fully characterized in both the solid state and in solution, and single-crystal X-ray diffraction analysis was also performed obtaining the crystal structure of complex **1**. Concerning the catalytic studies, a preliminary catalyst screening was carried out by varying reaction parameters such as solvent, temperature, and catalyst loading (%mol). The reactions were evaluated using benzoylnitromethane and methylvinylketone as starting materials. Complex **1** exhibited very high activity, achieving 100% conversion and a 93% yield, affording the pure product without the need for column chromatography. In addition, several substrates were tested using complex **1** as catalyst, resulting in good yields. Lastly, in the context of green chemistry, a low Process Mass Intensity (PMI) value was obtained.^[3]

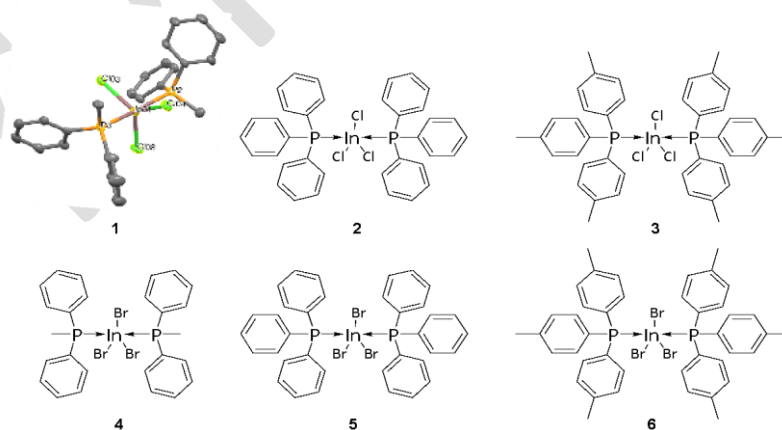


Figure 1. Indium(III) phosphane complexes structures.

Acknowledgements: *Unione Europea – NextGenerationEU (NGEU PNRR, D.M. n. 630/2024 M4C2 I3.3)*

References

- [1] Ajiboye T. O., Ajala O. J., Adeyemi J. O., Dhibar S. *Chemical Papers*, 2024, **78**, 4605.
- [2] Ballini R., Palmieri A. *Nitroalkanes: Synthesis, Reactivity, and Applications*, 2021, Wiley-VCH.
- [3] Barigelli L., et al. *Unpublished results*.

Surface ligand exchange in ultra-small CeO₂ nanoparticles: a strategy for enhanced colloidal stability in polar media

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In recent years, cerium dioxide (CeO₂) nanoparticles (NPs) have attracted increasing attention in the scientific community due to their unique physicochemical properties. In particular, the exceptional oxygen storage capacity and reversible Ce³⁺/Ce⁴⁺ redox cycling make them ideal candidates for a wide range of advanced applications, including catalysis, photochemistry, optoelectronics, and biomedicine [1]. When scaled down to the ultra-small regime (1-2 nm), CeO₂ NPs exhibit a maximized surface-to-volume ratio, which considerably improves their reactivity, but also leads to a strong tendency toward aggregation in polar environment [2]. Achieving long-term colloidal stability of CeO₂ NPs in polar solvents, such as N,N-dimethylformamide (DMF), remains a crucial challenge for their integration into liquid-phase processable systems. As a polar aprotic solvent, DMF is a medium of choice in materials science and the chemical industry.

In the present work, atomically precise propionate-capped CeO₂ NPs, with the dimensions up to ~1.5 nm, were synthesized and subsequently functionalized, through a controlled surface ligand exchange approach [3, 4]. After screening several ligands, cyanoacetic acid was identified as the optimal moiety for ensuring high dispersibility in DMF, while preserving the ultra-small size of the NPs. Fourier Transform Infrared (FTIR) spectroscopy confirmed the successful coordination of cyanoacetic acid to the Ce⁴⁺ core. TEM imaging of the samples stored for one year showed no significant changes in the size or morphology compared to as-synthesized ones. Future investigations will focus on evaluating the colloidal stability over time by means of UV-Vis spectroscopy.

References

- [1] Pansambal, S., Oza, R., Borgave, S., Chauhan, A., Bardapurkar, P., Vyas, S., & Ghotekar, S. (2023). Bioengineered cerium oxide (CeO₂) nanoparticles and their diverse applications: a review. *Applied Nanoscience*, 13(9), 6067-6092.
- [2] Jin, R. (2012). The impacts of nanotechnology on catalysis by precious metal nanoparticles. *Nanotechnology Reviews*, 1(1).
- [3] Mitchell, K. J., Abboud, K. A., & Christou, G. (2017). Atomically-precise colloidal nanoparticles of cerium dioxide. *Nature communications*, 8(1), 1445.
- [4] Calvin, J. J., Brewer, A. S., & Alivisatos, A. P. (2022). The role of organic ligand shell structures in colloidal nanocrystal synthesis. *Nature Synthesis*, 1(2), 127-137.

Can a polymer interlayer improve the electrochemical behaviour of metallic lithium?

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Lithium metal is considered an ideal anode material due to its high theoretical specific capacity (3861 mAh g^{-1}) and low electrochemical potential (-3.0401 V vs standard hydrogen electrode) [1]. However, lithium electrodes suffer from several drawbacks, including dendritic Li growth and the formation of an inhomogeneous and instable solid electrolyte interphase (SEI).

The growth of elongated, branched structures, commonly referred to as “dendrites,” is a critical issue for safe rechargeable batteries. Li dendrites can penetrate the separator and reach the cathode, causing in this way the short circuit. Moreover, the increase in the interfacial area between Li metal and the electrolyte resulting from dendrite formation promotes undesirable side reactions. Indeed, side reactions between electrolyte and fresh Li dendrites lead to continuous electrolyte decomposition and the accumulation of dead Li, causing increased polarization compared to the uniform and dense dendrite-free Li deposits [2].

To solve both problems, here we reported an ASEI (artificial SEI) composed of different layers all plated on copper. The ASEI structure consists of polyethylene oxide (PEO), metallic Li, and a PEO/LiNO₃ composite layer sequentially assembled on copper foil. The procedure starts with the deposition of 0.30g of PEO on the cleaned copper foil, and then we hot press at a temperature of 110° and a pressure of 2 tons. After we place metallic Li and we hot press again, still at 110°, at a pressure of 1 ton. And lastly we deposit the last layer of 0.30 g of PEO and 0.020 g of LiNO₃, and we hot press again at a temperature of 110° at a pressure of 1 ton.

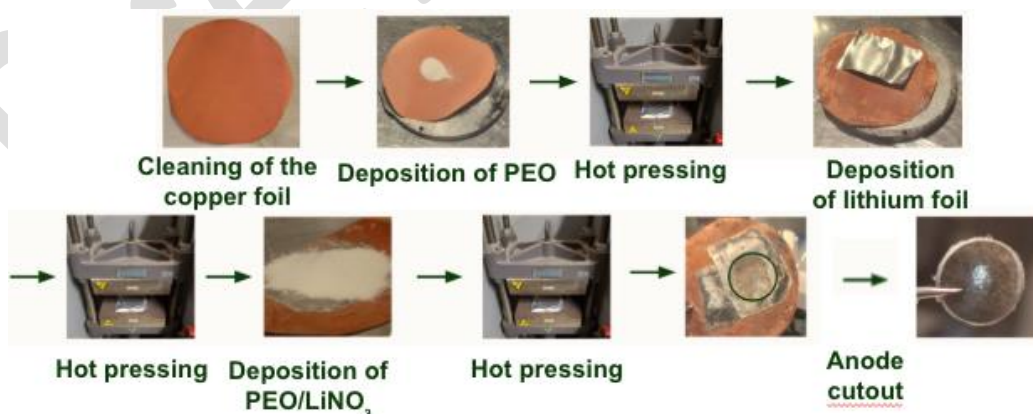


Figure 3 Description of ASEI fabrication procedure

References

- [1] Sheng S. Z., *ACS Appl. Energy Mater.* 2018, **1**, 3, 910–920
Xin-Bing C., Rui Z., Chen-Zi Z., Qiang Z., *Chem. Rev.* 2017, **117**, 15, 10403–10473

Lanthanide-based Metal-Organic Frameworks for Nonlinear Photonics

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Metal–Organic Frameworks (MOFs) are crystalline hybrid networks composed of metal centers interconnected by organic linkers, notable for their tunable architecture and versatile structural properties. [1,2]

Upconversion is an optical process in which low-energy photons are absorbed and converted into a single photon of higher energy, enabling luminescence through mechanisms such as cooperative emission and energy transfer between lanthanide ions. This phenomenon, widely observed in lanthanide-doped materials, has also been demonstrated in lanthanide-based MOFs. [3] In this work, near-infrared excitation is employed to drive the upconversion process.

Among the various upconversion mechanisms, photon avalanche is the most nonlinear, characterized by a sharp onset of emission that occurs when the excitation power surpasses a critical threshold. [4] Here we systematically investigate the upconversion and photon avalanche properties of Yb-based crystals as a function of lanthanide dopant across selected members of the lanthanide series.

A novel crystalline phase of a lanthanide-based MOF, incorporating Yb³⁺ and Eu³⁺ with H₃BTC as organic linker, retains optical properties comparable to those of analogous MOFs obtained under different synthetic conditions, indicating that the photonic behavior is preserved across different structural arrangements.

References

- [1] S. Kitagawa et al, Nat. Chem. 2009, 1, 695-704
- [2] O. Yaghi et al, ACS Cent. Sci. 2020, 6, 8, 1255-1273
- [3] Yao Xie et al, Angew. Chem. Int. Ed. 2023, 62, e202216269
- [4] Huang et al, ACS Appl. Opt. Mater. 2024, 2, 1841–1853

Transition-Metal MOFs Enable Lanthanide-Free Photon Avalanche Process

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Photon avalanche (PA) is a strongly nonlinear optical process characterized by a superlinear dependence of the emission intensity on the excitation power, originating from cooperative mechanisms involving excited-state absorption (ESA), cross-relaxation, and positive feedback between metastable electronic states. Due to the requirement for suitably engineered energy level structures and long excited-state lifetimes, PA phenomena have so far been observed almost exclusively in inorganic nanoparticles doped with lanthanide ions¹.

Recently, we extended the concept of photon avalanche to metal–organic frameworks (MOFs), demonstrating that hybrid porous architectures incorporating lanthanide centers can sustain efficient avalanche dynamics². The high structural modularity of MOFs provides unprecedented control over the coordination environment, interionic distances, and energy-transfer processes, opening new opportunities for the rational engineering of PA-active materials.

In this contribution, we report a further conceptual advancement through the realization of photon avalanche systems based exclusively on transition-metal-containing MOFs. This result demonstrates that avalanche behavior can also be achieved in platforms characterized by electronic configurations and photophysical dynamics profoundly different from those of conventional rare-earth-based systems. Our findings demonstrate that combining the chemical versatility of MOFs with the electronic properties of transition metals enables advanced nonlinear optical processes in lower-cost and potentially less toxic materials, expanding the horizon of active platforms for nanophotonics and optical sensing.

References

- [1] Chen J. et al Nature 2025, 643, 669
- [2] di Gregorio M. C., Oron D., Kazes M. et al ar Xiv:2507.16293

Theme E - Energy, Environment and Sustainability

Recovery and Regeneration of Cathode Materials via Direct Recycling

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The rapid expansion of electric vehicles and portable electronics is driving a sharp increase in lithium-ion battery production, intensifying pressure on critical raw materials (CRMs) and resulting in a growing volume of end-of-life batteries that still contain significant amounts of valuable metals ^[1]. Developing sustainable recycling strategies capable of closing the materials loop is therefore a key challenge for the battery value chain.

Direct recycling has gained increasing attention as it aims to recover cathode materials while preserving their original crystalline structure and functionality. By avoiding complete elemental breakdown, this strategy has the potential to reduce energy consumption, chemical usage, and environmental impact compared to conventional pyrometallurgical and hydrometallurgical routes.

In this work, we investigate the recovery and regeneration of layered oxide cathode materials from spent lithium-ion pouch cells. Different routes were explored to separate the active material from the aluminum current collector, including mechanical and solvent-based delamination methods. All approaches enabled effective recovery of the cathode powder, demonstrating the robustness and flexibility of the separation step, although typical degradation and processing related impurities were observed in the recovered material. Regeneration of the spent cathode was carried out through a solid-state relithiation treatment designed to restore lithium stoichiometry and structural order. Structural and morphological characterization confirmed the re-establishment of the layered crystal structure and the mitigation of secondary phases formed during battery operation and recovery. Electrochemical evaluation demonstrated that the regenerated material recovered a substantial fraction of its original performance, with clear improvements compared to the degraded cathode, indicating successful functional restoration of the active material.

Overall, this study demonstrates the effectiveness of direct recycling for regenerating cathode materials from end-of-life LIBs ^[2]. The results highlight the potential of this approach to support a more circular battery economy by reducing waste, lowering environmental impact, and decreasing dependence on critical raw material supply.

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References

- [1] Wang, T., Liu, T., Sun, H. *Materials Today Energy*, 2023, 3810, 4.
- [2] Chen, M., Ma, X., Chen, B., Arsenault, R., Karlson, P., Simon, N., Wang, Y. *Joule*, 2019, 3, 2622.

In Situ photopolymerized ionogels for safe high-Voltage lithium metal batteries

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The increasing demand for high-energy-density storage systems has accelerated research on lithium metal batteries (LMBs) coupled with high-voltage cathodes such as LMNO and LMFP. However, the practical implementation of these systems remains impeded from one side by the high reactivity of metallic lithium leading to uncontrolled dendrite growth, and to the other side from the limited oxidative stability of most common electrolytes. Two possible answers to these challenges are the use of a polymer based electrolyte to mechanically limit dendrite nucleation and growth and the addition of an ionic liquid to enhance the ionic conductivity and the interfacial contact, while taking advantage of the intrinsically high oxidative stability and low vapor pressure. Hence, we report a novel gel polymer electrolyte (GPE) synthesized via in situ UV-induced radical photopolymerization of butyl methacrylate (BMA) and poly(ethylene glycol) diacrylate (PEGDA) matrix incorporating the ionic liquid 1-ethyl-3-methylimidazolium bis(fluorosulfonyl)imide (EMIMFSI) and lithium bis(trifluoromethylsulfonyl)imide (LiTFSI). Electrochemical characterization demonstrates that the optimized GPE exhibits an electrochemical stability window exceeding 4.5 V vs. Li/Li⁺, rendering it suitable for high-voltage operation. The GPE shows enhanced interfacial stability, slightly higher ionic conductivity compared to the neat ionic liquid electrolyte, and effective suppression of lithium dendrite growth during prolonged plating/stripping tests. Li/GPE/LMFP full cells deliver an initial discharge capacity of 120 mAh g⁻¹ with a Coulombic efficiency of 90% over 50 cycles, and retain a capacity of 100 mAh g⁻¹ after 100 cycles. These results highlight the potential of ionogel-based electrolytes as safe and stable candidates for next-generation lithium metal batteries.

Lipases as biocatalysts in biodiesel production: a Molecular Dynamics study

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Lipases are hydrolase enzymes whose natural catalytic role is the hydrolysis of ester bonds in triglycerides, yielding fatty acids and glycerol. In non-aqueous media, however, lipases can promote synthetic reactions, such as esterification and transesterification, making them valuable biocatalysts with broad industrial relevance. Among their emerging applications, lipase-catalyzed biodiesel production has attracted considerable attention in recent years.[1] Biodiesel consists of a mixture of short-chain fatty acid esters, usually fatty acid methyl esters (FAMES) and fatty acid ethyl esters (FAEEs), produced by the esterification of free fatty acids and the transesterification of triglycerides with short-chain alcohols. Industrial biodiesel production currently relies on homogeneous chemical catalysts, such as NaOH and H₂SO₄, which offer high reaction rates but require energy- and cost-intensive purification processes. Lipases represent a promising alternative, enabling the process to be carried out under milder conditions and with higher selectivity. However, their large-scale application remains limited by high production costs and sensitivity to operating conditions. Enzyme immobilization on solid supports has emerged as a key strategy to address these drawbacks, enhancing enzyme stability and enabling multi-cycle reuse, making the process overall more sustainable from both an environmental and economic point of view.[2]

Recent experimental findings have shown that *Candida Rugosa* lipase can be immobilized on aminated graphene oxide sheets through covalent bonding and that this system is highly promising from an industrial perspective, although it exhibits lower catalytic activity than the free enzyme.

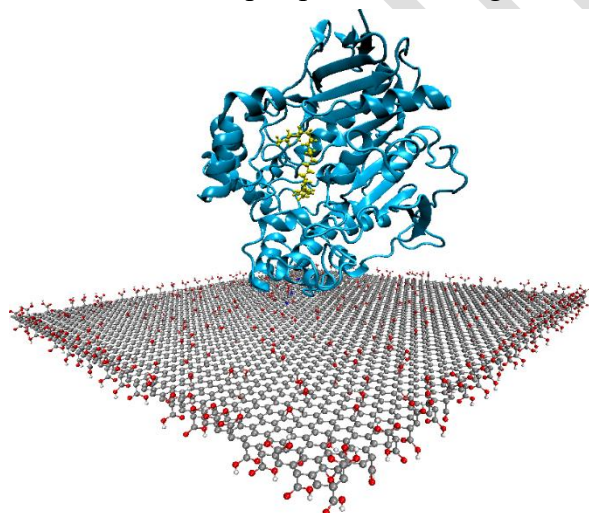


Figure 4: *Candida Rugosa* lipase (blue) in complex with *p*-nitrophenyl palmitate (yellow) immobilized on aminated graphene oxide (grey).

To rationalize this behaviour and provide a detailed molecular-level description, also with the aim of optimizing biodiesel production processes, we carried out a Molecular Dynamics study of immobilized *Candida Rugosa* lipase (**Figure 1**). To gain deeper insight into its behaviour, we compared its structural and dynamic properties with those of three additional systems: the free enzyme in its open conformation, the free enzyme in its closed conformation, and the open conformation in complex with *p*-nitrophenyl palmitate, a standard substrate used in lipase activity assays. Comparative analysis of the four systems revealed that the main differences lie in their dynamic behaviour, particularly in the *lid* region, a flexible structural element that regulates access to the active site and is closely associated with catalytic competence.

References

- [1] A. Mehta, U. Bodh and R. Gupta, *Journal of Biotech Research*, 2017, 8, 58.
- [2] S. Xia, J. Lin, S. Sayanjali, C. Shen and L.-Z. Cheong, *Biofuels, Bioproducts and Biorefining*, 2024, 18, 291–309.

Green strategy for polyhydroxyalkanoates recovery from a continuous-flow mixed microbial cultures process

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Polyhydroxyalkanoates (PHA) production with Mixed Microbial Cultures (MMC) is a promising and cost-effective alternative to pure culture processes. However, the downstream processing remains the most economical impactful stage of the entire process. Among the PHA recovery strategies, Non-Polymer Cell Mass (NPCM) disruption methods are renowned for enabling good PHA purity and recovery rate at moderate low cost [1]. Herein, we proposed an oxidative treatment for PHA recovery using a novel green chemical and compared its performance with the well-established hydrolyzing treatment with NaOH [2]. The PHA-enriched biomass employed in this work was collected from a lab scale continuous flow MMC process. The culture feeding was characterized by a synthetic mixture of carboxylic acids enriched into caproate, resulting in the accumulation of a poly(hydroxybutyrate-co-valerate-co-hexanoate) (PHB-co-HV-co-HH) terpolymer. To identify the optimal operating conditions in terms of effects of oxidant concentration, biomass loading, and reaction time on PHA purity, a factorial design with response surface methodology was adopted (Figure 1). The oxidant concentration was positively correlated with PHA purity whereas biomass concentration showed no significant impact. Furthermore, reaction time exhibited a plateau after 6 hours indicating that an extended duration did not further enhance the recovery efficiency. The operative condition tested for both hydrolyzing and oxidative treatments were comparable in terms of reaction time (ca. 5 h), whilst the reagent concentration was 0.30 M and 0.75 M, respectively for hydrolyzing and oxidative, as well as biomass concentration (20 and 10 g/L). Both treatments allowed to reach high PHA purity (up to 90%, wt/wt) and recovery ($71\pm3\%$ and $84\pm3\%$, respectively for hydrolyzing and oxidative treatments) and a comparable molecular weight (ca. 1000 kDa) with low polydispersity index (PDI, below 3). In addition, the terpolymer composition was not affected by the novel oxidative treatment, suggesting that this strategy could be a promising alternative for PHA recovery.

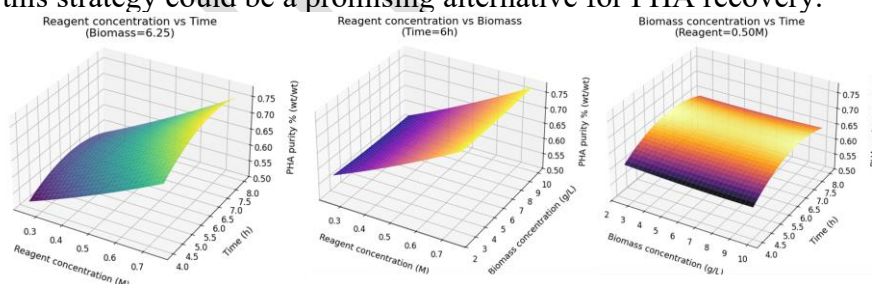


Figure 1: Response Surface analysis

Acknowledgements: This work was supported by the Horizon Europe Project AGRIFOOP: pushing the frontier of circular agriculture by converting residues into novel economic, social and environmental opportunities. AGRIFOOP (2022–2026) was funded by the European Union’s HEU research and innovation program, the UK Research and Innovation Fund under the UK government’s HEU funding guarantee (GA No. 101081776), and The National Key Research and Development Funds of China. The views and opinions expressed are those of the author(s) only and do not necessarily reflect those of the European Union. Neither the European Union nor the granting authority can be held responsible for them.

References

- [1] Pagliano G., Galletti P., Samorì C., Zaghini A., Torri C. *Frontiers in Bioengineering and Biotechnology*, 2021, **9**, 624021.
- [2] Salvatori G., Alfano S., Martinelli A., Gottardo M., Villano M., Ferreira B. S., Valentino F., Lorini L., 2023. *Industrial & Engineering Chemistry Research*, **62**(43), 17400-17407.

Boosting Biomethane production *via* Electrochemical stimulation of Anaerobic Digestion

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Electrochemical stimulation of anaerobic processes is emerging as a promising strategy to enhance CO₂ conversion into value-added products. In this framework, bioelectrochemical systems (BES), and in particular Microbial Electrolysis Cells (MECs) enable the production of reduced gaseous biofuels such as H₂ and CH₄. In methane-producing MECs, electrochemically generated hydrogen works as an electron carrier, supporting the biological reduction of CO₂ to CH₄.

The key advantage of the MEC technology compared to conventional water electrolysis relies on its lower energy demand. Indeed, when organic substrates such as acetate are oxidized at the MEC anode, H₂ evolution at the cathode can theoretically occur at cell voltages (ΔV) as low as 0.12 V, significantly below the value of 1.23 V required for water splitting [1]. This feature makes MECs particularly attractive for integration into anaerobic digestion (AD) processes, where *in-situ* hydrogen production could be exploited to upgrade biogas to biomethane (CH₄ $\geq$ 98%, v/v) [2]. To investigate this potential, the present study evaluated the role of reactor configuration and electrochemical control in driving CH₄ enhancement into the biogas. Three operational strategies were tested across single- and two-chamber MECs: (i) anodic potentiostatic control at 0.20 V (vs SHE) in a single-chamber MEC; (ii) application of fixed cell voltages ($\Delta V = 0.90$ and 1.10 V) in a single chamber MEC; and (iii) cathodic potentiostatic control at -0.60 V (vs SHE) in a dual-chamber MEC. Under anode control strategy (i), an increase in the CH₄ percentage (from 25% to 66%, v/v) and volumetric production was observed, with CH₄ yields consistent with the theoretical H₂ production estimated from current measurements. In contrast, the application of a ΔV (ii) did not significantly modify the gas composition, although CH₄ production rates increased by approximately 15%. The dual-chamber configuration (iii) enabled to increase the CH₄ content in the biogas up to 90% (v/v), but required higher overall cell voltages. Also in this case, CH₄ production trends were consistent with the amount of H₂ theoretically generated, assuming 100% Cathode Capture Efficiency (CCE, %).

Overall, these findings demonstrate that both reactor design and electrochemical operation critically influence the pathways leading to CH₄ enhancement. While potentiostatic control strategies promote H₂-driven methanogenesis, the output observed under fixed voltage conditions points toward the possible contribution of alternative electron transfer mechanisms, such as Direct Interspecies Electron Transfer (DIET)-like interactions.

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References

- [1] Rousseau, R., Etcheverry, L., Roubaud, E., Basséguy, R., Délia, M. L. & Bergel, A. *Applied Energy*, 2020, **257**, 113938.
- [2] Angelidaki, I., Treu, L., Tsapekos, P., Luo, G., Campanaro, S., Wenzel, H. & Kougias, P. G. *Biotechnology Advances*, 2018, **36**, 452–466.

Continuous-flow process for agricultural waste valorisation into polyhydroxyalkanoates production with mixed microbial culture

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The agricultural sector faces critical challenges from plastic pollution and inefficient waste management [1]. This study proposes a circular bioeconomy solution through the integrated valorization of fermented wine lees into Polyhydroxyalkanoates (PHA) production with a continuous-flow Mixed Microbial Cultures (MMC) process. The system here proposed consists of three reactors operated in series to enable microbial selection (1L Tubular Feast Reactor and 5L CSTR Famine Reactor) and PHA storage (2L CSTR Accumulation Reactor) [2]. The process was initially operated using a caproate-rich synthetic feedstock mimicking the fermented wine lees composition before transitioning to the real agro-industrial waste. As showed in Table 1, the transition from the synthetic feedstock to the fermented Wine Lees did not significantly affect the performance of the accumulation reactor. Comparable PHA accumulation was achieved, with intracellular polymer contents up to 50% (wt/wt), storage yields up to 0.50 gCOD/gCOD, and productivities up to 1.7 gCOD/L·d for both feedstocks. Overall, a poly(hydroxybutyrate-co-valerate-co-hexanoate) (PHB-co-HV-co-HH) terpolymer was produced with potential applications in the agricultural sector. In conclusion, the developed continuous-flow MMC process demonstrates a viable path for the agricultural sector to transition toward circularity by converting agro-waste into high-value bioplastics.

Table 1: Performance of the PHA accumulation reactor

Operative conditions	Operation days	Intracellular PHA content (%, wt/wt)	Storage yield (gCOD/gCOD)	Productivity (gPHA/Ld)	HV content (%, wt/wt)	HH content (%, wt/wt)
Synthetic feedstock	80	51 ± 8	0.53 ± 0.24	1.74 ± 0.78	5 ± 2	4 ± 1
Fermented Wine Lees	30	58 ± 6	0.66 ± 0.23	2.04 ± 0.93	5 ± 1	5 ± 1

Acknowledgements: This work was supported by the Horizon Europe Project AGRIFOOP: pushing the frontier of circular agriculture by converting residues into novel economic, social and environmental opportunities. AGRIFOOP (2022–2026) was funded by the European Union’s HEU research and innovation program, the UK Research and Innovation Fund under the UK government’s HEU funding guarantee (GA No. 101081776), and The National Key Research and Development Funds of China. The views and opinions expressed are those of the author(s) only and do not necessarily reflect those of the European Union. Neither the European Union nor the granting authority can be held responsible for them.

References

- [1] Perdana, T., Kusnandar, K., Perdana, H. H., & Hermiatin, F. R. (2023). Circular supply chain governance for sustainable fresh agricultural products: Minimizing food loss and utilizing agricultural waste. *Sustainable Production and Consumption*, 41, 391-403.
- [2] Nguemna, L. T., Marzulli, F., Scopetti, F., Lorini, L., Lauri, R., Pietrangeli, B., Crognale, S., Rossetti S., Majone M. & Villano, M. (2023). Recirculation factor as a key parameter in continuous-flow biomass selection for polyhydroxyalkanoates production. *Chemical Engineering Journal*, 455, 140208.

Scalable, Low-Cost interlayer Current Collector for Dendrite-Free Anode-Free Lithium Metal Batteries

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In this work, we used a hot-pressing machine to sequentially deposit a layer of PEO, a lithium metal film, and a PEO/LiNO₃ composite onto a copper current collector, forming a multilayered structure. The resulting interlayer stabilizes the electrode–electrolyte interface, enabling reversible electrochemical lithium metal plating against various cathodes, including LFP and NMC [1,2]. This novel electrode design ensures uniform Li nucleation and dendrite-free cycling. Its scalable and low-cost fabrication makes it a promising current collector for advanced lithium metal batteries. Anode-free batteries have emerged as a compelling solution for next-generation energy storage. Unlike conventional designs, they lack a pre-existing anode and instead rely on a bare current collector [3,4]. During charging, lithium (Calcium, sodium) plates directly onto this collector, forming the anode in situ. This approach yields a lighter, more compact, and more affordable battery while also improving sustainability.

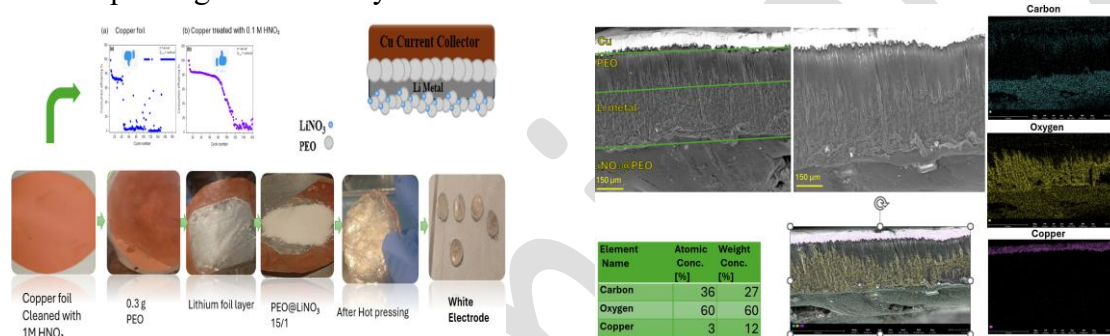


Fig. 1. (Left side) Images illustration of the preparation of the interlayer and deposited onto copper foil and directly hot-pressed. The (Right side) SEM images on the layer deposited layers on the Cu current collectors.

Our results confirm the successful synthesis of the interlayer deposited onto the copper substrate, as well as the uniform deposition of the individual layers, each exhibiting a clearly distinguishable appearance.

Acknowledgements:

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References

- (1) Li, S.; Liu, T.; Yan, J.; Flum, J.; Wang, H.; Lorandi, F.; Wang, Z.; Fu, L.; Hu, L.; Zhao, Y. Grafting Polymer from Oxygen-Vacancy-Rich Nanoparticles to Enable Protective Layers for Stable Lithium Metal Anode. *Nano Energy* **2020**, *76*, 105046.
- (2) Gao, Y.; Yan, Z.; Gray, J. L.; He, X.; Wang, D.; Chen, T.; Huang, Q.; Li, Y. C.; Wang, H.; Kim, S. H. Polymer–Inorganic Solid–Electrolyte Interphase for Stable Lithium Metal Batteries under Lean Electrolyte Conditions. *Nat. Mater.* **2019**, *18* (4), 384–389.
- (3) Lopez, J.; Pei, A.; Oh, J. Y.; Wang, G.-J. N.; Cui, Y.; Bao, Z. Effects of Polymer Coatings on Electrodeposited Lithium Metal. *J. Am. Chem. Soc.* **2018**, *140* (37), 11735–11744.
- (4) Zhao, Z.; Pan, Y.; Chen, H.; Wang, X.; Huang, Y.; Yi, S.; Niu, B.; Long, D.; Zhang, Y. A Lithium-Affinitive Covalent Organic Polymer Network Functionalized Separator for Dendrite-Free and High-Durability Lithium–Sulfur Batteries under Harsh Conditions. *Adv. Funct. Mater.* **2024**, *34* (37), 2402182.

Halophilic biocathode for bioelectrochemical hydrogen production under hypersaline conditions

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Microbial Electrolysis Cells (MECs) are emerging as a promising technology for the simultaneous treatment of wastewater and sustainable hydrogen production. In MECs, electroactive microorganisms oxidize organic substrates at the anode, releasing electrons that are transferred to the cathode, where hydrogen is produced. Despite their potential, MECs can be limited by the proliferation of hydrogenotrophic methanogens that consume the produced H₂, reducing the process efficiency. In this context halophilic bacteria represent a promising strategy, as they are adapted to saline environment and maintain metabolic activity under conditions, that inhibit methanogens.

A halophilic hydrogenotrophic sulfate-reducing enrichment culture was obtained from sulfidogenic sediments collected in Chott El-Jerid, a hypersaline lake in Tunisia, and employed as inoculum for a microbial biocathode. Short-term bioelectrochemical experiments (6 h) were conducted, in H-type cells, testing different cathode potentials ranging from -0.6 to -1.2 V vs. SHE. At -1.0 V the H₂ production rates reaching ~75 $\mu\text{mol L}^{-1} \text{h}^{-1}$, almost one order of magnitude higher than abiotic control. Moreover, long-term operation (212 h) at -1.0 V demonstrated stable hydrogen evolution (~80 $\mu\text{mol L}^{-1} \text{h}^{-1}$) together with negligible methane formation, while approximately 50% of the consumed electrical charge was recovered as H₂. To confirm that the electrocatalytic activity was mainly associated with intact microbial cells rather than soluble redox mediators, cyclic voltammetry analyses performed. Microbial characterization revealed a strong enrichment of *Desulforadii* spp. (>75% relative abundance), supporting the key role of hydrogenotrophic sulfate-reducing bacteria in promoting efficient H₂ evolution under hypersaline conditions.

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Sustainable Electrochemical Strategies for Selective Lithium Recovery from Brine Resources

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The global transition toward sustainable energy and electric mobility has positioned lithium as a critical strategic resource. As the primary component of lithium-ion batteries (LIBs), the demand for high-purity lithium is projected to increase significantly over the next decade. Currently, lithium production relies heavily on hard-rock mining and solar evaporation of continental brines; however, these traditional methods are often associated with slow production rates, high environmental footprints, and significant water consumption [1]. In this context, geothermal brines have emerged as a promising alternative source. The primary challenge in recovering lithium from complex aqueous matrices is achieving high selectivity over competing ions, such as sodium and magnesium, while maintaining the structural integrity of the recovery materials [2]; thus, this work investigates the application of an electrochemical process designed to selectively extract lithium from geothermal-like solutions. The objective is to evaluate the technical feasibility of using olivine-structured materials for efficient capture and release cycles, focusing on system longevity and chemical stability. In fact, the research employs lithium iron phosphate (LiFePO_4 , **Figure 1**) as the active material for the electrochemical recovery process, and the methodology involves the characterization of the intercalation/deintercalation mechanisms [3]. A fundamental aspect of this study is the optimization of the electrochemical cell configuration, with particular attention to the role of the counter-electrode (CE): by appropriately selecting and modifying the CE, it is possible to control the chemical environment of the electrolyte, allowing for a detailed study of both pH variations and the overall selectivity of the recovery process [4].

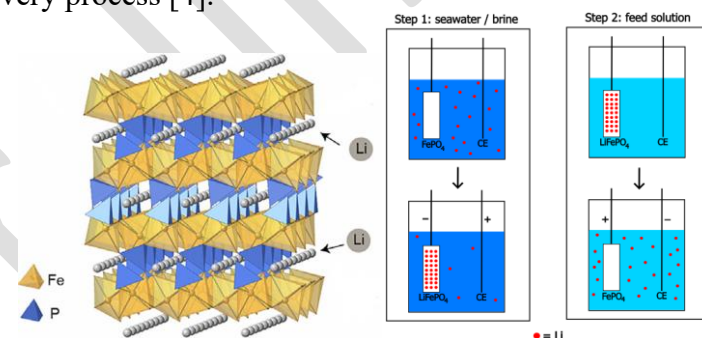


Figure 1: left, olivine structure of LiFePO_4 ; right, stepwise scheme of the lithium intercalation / deintercalation process.

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References

- [1] Liu C., et al., *Joule*, 2020, **4**, 1459-1469.
- [2] Takagi T., et al., *Materials Chemistry and Physics*, 2020, **238**, 122-128.
- [3] Novikova S. A., et al. *Russian Journal of Inorganic Chemistry*, 2017, **62 (13)**, 1681-1704.
- [4] Zhao Z., et al., *Cells Reports Physical Science*, 2020, **1**, 100113.

Self-assembling donor-acceptor dye that displays off/on photocatalytic H₂ evolution

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The development of photocatalytic systems for sustainable solar fuel production is a rapidly growing field, driven by the urgent need to replace fossil fuels. Central to these systems are photosensitizers capable of absorbing visible light and initiating photochemical processes.

Organic chromophores, already widely used in applications such as photodynamic therapy and photovoltaic devices, are promising candidates as photosensitizers.¹ In particular, donor-acceptor (D-A) dyes offer several advantages, including tunable electronic properties, low cost, and strong intramolecular charge-transfer character.² However, D-A systems once photoexcited can change the molecular geometry, leading to the formation of a twisted intramolecular charge transfer (TICT) state, which is usually lower in energy and thus becomes photoredox inactive.³

In this work, a designed D-A molecule was investigated as photosensitizer in a photocatalytic system for hydrogen production, using ascorbic acid as a sacrificial donor and platinum nanoparticles as co-catalyst. In homogeneous solution, no hydrogen evolution was observed, which was ascribed to TICT formation. To overcome this, aggregation of the D-A molecule was induced via charge screening upon addition of salt. Under these conditions, hydrogen production reached 140 mmol·g⁻¹. The aggregation was found to suppress intramolecular rotation and promotes intersystem crossing, favoring the population of long-lived triplet excited states responsible for efficient photocatalysis. These results position chromophore rigidification as a general strategy for photocatalytic applications and stimulate the re-assessment of overlooked organic dyes for production of solar fuels.⁴



Figure 1. Schematic representation of molecular versus aggregated photocatalytic process.

Acknowledgements:

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References

- [1] Leung, C.-F. & Lau, T.-C. Organic Photosensitizers for Catalytic Solar Fuel Generation. *Energy Fuels*, 2021, 35, 18888–18899.
- [2] Wang, L. & Zhu, W. Organic Donor-Acceptor Systems for Photocatalysis. *Adv. Sci.*, 2024, 11, 2307227.
- [3] Zhu, K. et al. Limiting Molecular Twisting: Upgrading a Donor–Acceptor Dye to Drive H₂ Evolution. *Adv. Sci.*, 2024, 11, 2403454.
- [4] Barbieri, M. et al. Supramolecular dye polymers for aggregation-induced photocatalysis. *Nat. Chem.*, 2026, in press. DOI: 10.1038/s41557-026-02151-4.

Predicting the Environmental Fate of Nanomaterials: A Probabilistic Framework for Sustainable Nano-Innovation

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Engineered nanoparticles (ENPs) drive modern chemical innovation, but their sustainable use requires a clear understanding of their environmental footprint. In aquatic ecosystems, heteroaggregation is a key process that controls the mobility and persistence of ENPs. However, the role of aggregation varies greatly across different materials - a knowledge gap that may complicate the development of Safe-by-Design nanomaterials.

In this study, we propose a quantitative metric, the probability of aggregation dominance (D_{agg}), to assess environmental stability [1]. We combined classical DLVO theory with Monte Carlo simulations to account for the dynamic variability of natural waters, including fluctuations in ionic strength and natural particle concentrations. This enabled the evaluation of kinetic competition between aggregation and other removal processes, such as sedimentation and dissolution, using a multimedia fate modeling approach [2].

Our findings reveal that aggregation dominance is not universal - its probability ranges from a few percent to 100% depending on the specific material. We demonstrate that the core material's Hamaker constant fundamentally drives this behavior: high-polarizability metals consistently aggregate, while the behavior of certain metal oxides remains highly variable. For these materials, environmental fate can shift drastically due to subtle variations in particle size and surface charge.

To bridge the gap between fundamental colloid science and environmental sustainability, we developed the CLUMP classification scheme - a five-tier framework for grouping nanomaterials based on their environmental persistence [1]. By providing a predictive tool for both the Safe-by-Design process and risk assessment, CLUMP empowers researchers to innovate responsibly, while assisting environmental regulators in ensuring that new nanomaterials are environmentally compatible.

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References

- [1] Swiatek Brzezinski S. et al. *Environ. Sci.: Nano*, 2026, **13**, 979.
- [2] Meesters J.A.J. et al. *Environ. Sci.: Nano*, 2019, **6**, 2049.

In-depth study of cathodic materials for electrochemical use

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In the context of the energy transition, lithium batteries are currently the most promising electrical storage devices in terms of conversion efficiency, flexibility, and high energy density. Although lithium-ion batteries have numerous advantages over other storage systems, the price of lithium may somewhat hinder its widespread adoption, especially in stationary applications[1]. Therefore, research needs to be conducted on cheaper secondary batteries, such as sodium-ion batteries.

Sodium is much more abundant than lithium, which guarantees a significantly lower price. Since sodium is the lightest alkali metal after lithium, its use should not excessively lower the energy density of devices. Among the many materials studied as cathodes for this type of battery, Prussian Blue Analogues (PBAs) are among the most interesting in terms of cost-effectiveness and low toxicity[2], while still maintaining good cycling performance. In this work, several samples were synthesized, of which three are the most promising: PB15, PB16, and PB19. Two of these, PB15 and PB19, were synthesized by co-precipitation and one, PB16, by ball milling. The main synthesis methods were compared with the synthesized samples, making appropriate modifications to the method in order to improve the electrochemical properties of the material.

The aim of the work was therefore to optimize the synthesis of PBA in order to obtain more regular and larger crystals, to ensure greater performance within the electrochemical cell.

To do this, a technique different from those proposed in the literature was applied to PB19, where the synthesis of the sample, similar to that of PB15, was repeated several times, using the powder synthesized in the previous step as a storage center for subsequent syntheses.

This ensured that the PB19 sample had a higher degree of crystallinity compared to PB15, which made it possible to obtain a specific capacity value similar to that obtained with PB16, obtained by ball-milling, with an additional advantage in terms of cyclability, performing 300 cycles with a 30% fading at the fiftieth cycle.

References

[1] ENEA - Report RdS/PAR 2016/150, P.P. Prosini, A. Aurora, M. Carewska, C. Cento, L. Della Seta.

[2] Bingxing Xie, Baoyu Sun, Tianyu Gao, Yulin Ma, Geping Yin, Pengjian Zuo, Recent progress of Prussian blue analogues as cathode materials for nonaqueous sodium-ion batteries, *Coordination Chemistry Reviews*, Volume 460, 2022, 214478, ISSN 0010-8545,

Lignohumic Redox-Active Materials Extracted from Wastewater Sludge for Energy Applications

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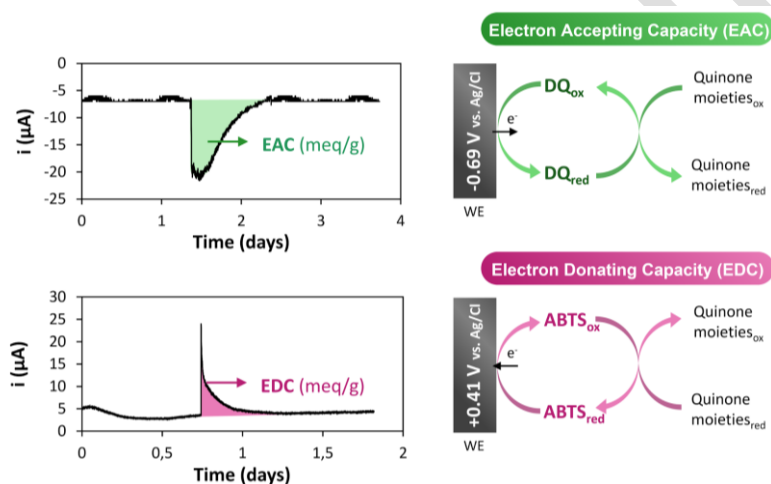
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Within the framework of circular economy strategies, the valorization of wastewater treatment sludge into functional materials is a promising pathway to recover value from waste streams. In this study, lignohumic materials were extracted from wastewater sludge of different origins, including primary, secondary, cellulosic-rich streams, as well as anaerobically and aerobically digested sludges. The extracted materials were characterized through elemental analysis (C, H, N, S), Fourier-transform infrared spectroscopy (FTIR), and nuclear magnetic resonance (NMR). The extracted materials were investigated for their potential application in bioelectrochemical, and photoelectrochemical systems.



In this context, their functionality is typically associated with the presence of redox-active moieties, in particular quinone groups, that can mediate electron transfer processes.

To quantitatively assess their redox properties, a dedicated electrochemical protocol based on mediated assays was developed, enabling the determination of both electron accepting capacity (EAC) and electron donating capacity (EDC) (Figure 1).

Figure 1. Typical mediated electrochemical assays to quantify EAC and EDC of lignohumic substances.

The obtained results demonstrate that the extracted lignohumic materials exhibit EAC and EDC values (up to 5 meq/g) comparable or even higher than those of benchmark carbon-based materials such as biochar. These properties make them particularly attractive for energy-related applications, such as additives to enhance electron transfer efficiency in H₂-producing microbial electrolysis cells (MECs), or as functional supports for photocatalysts aimed at H₂ production. Overall, these findings highlight the yet unexplored potential of sludge-derived lignohumic substances as sustainable and low-cost redox mediators, contributing to improved process performance while supporting resource recovery and circular economy principles.

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Bifunctional ORR/OER Electrocatalysts for Unitized Regenerative Fuel Cell Systems

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Unitized regenerative fuel cells (URFCs) are electrochemical energy conversion devices capable of operating alternately as water electrolyzers and conventional fuel cells. They employ the same pair of electrodes for both electrolysis and power generation, offering advantages in terms of compact design, cost-effectiveness, and operational flexibility [1]. During electrolysis mode, the positive electrode must efficiently catalyze the oxygen evolution reaction (OER), while in fuel cell mode it must promote the oxygen reduction reaction (ORR). Unfortunately, for now they underperformed specialized devices due to large overpotentials between both modes, which significantly reduce their energy efficiency [2]. Present state-of-the-art electrocatalysts are precious metals and metal oxides such as Pt, IrO₂ and RuO₂. These materials are expensive, naturally scarce, and have insufficient durability for practical applications [3]. In this context, low-cost and earth-abundant electrocatalysts are essential for the widespread implementation of OER/ORR-based devices.

This work will focus on the synthesis of bifunctional ORR/OER electrocatalysts to improve long-term stability while reducing noble metals with cost-effective alternatives for their use unitized regenerative fuel cells.

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References

- [1] I. Vincent, N. Almenara Perez, D. Minudri, F. Fernandez-Carretero, E. Fernandez Gesalaga, A. Garcia-Luis and H. Kim, *Sustainable Energy Fuels*, 2025, **9**, 5772.
- [2] K. Dutta, D. Rana, H. S. Han, P. P. Kundu, *Fuel cells*, 2017, **17**, 736.
- [3] P. P. Machado Pico, J. Montero, A. Tsurumaki, S. Passerini, M. A. Navarra, *Sustainable Energy & Fuels*, 2025, **10**.

From Precursor to Power: Accelerating Lithium-Ion Battery Production

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The field of lithium-ion batteries (LIBs) is currently flourishing, driven by both scientific advancement and geopolitical necessity. The European Union is actively incentivizing the transition toward electric vehicles (EVs) to reduce the environmental impact of private transportation. Beyond the common concerns typically raised regarding this transition, such as vehicle costs, charging infrastructure availability, and electricity sourcing, lies a critical, often overlooked vulnerability that may become a primary challenge in the near future: Europe's lack of industrial capacity in this sector, as exemplified by the recent struggles of ventures like Northvolt. Despite this, the transition remains inevitable, especially given the rising share of energy generated from renewable sources (which currently accounts for **41%** of Italy's total electricity consumption). Addressing and resolving this industrial gap is essential.

To this end, the authors have spent the past several years developing a chemical process to optimize the production of LIB cathode materials [1-3]. The process consists of two steps: a precipitation reaction that yields a mixed oxalate precursor of nickel, manganese, and cobalt; and a thermal treatment that converts this precursor into the final cathode material (NMC). While grounded in established industrial processes, this novel approach utilizes oxalic acid as the precipitating agent instead of sodium hydroxide. This modification improves productivity by increasing the reaction rate 24-fold while simplifying operations. Unlike current methods, it requires fewer reagents and eliminates the need for an inert atmosphere or pH control. However, the significantly higher reaction speed demands a more in-depth study of nucleation and aggregation phenomena to ensure precise control over the final product's characteristics.

In this study, various operating conditions were evaluated during the precipitation reaction, with a focus on three key parameters: temperature, turbulence, and time. The precursors and cathode materials were chemically characterized using ICP-OES (PerkinElmer Avio 220 Max) and morphologically analyzed using a particle size analyzer (Malvern Panalytical Mastersizer 3000), SEM (Phenom ProX). Finally, the materials' performance was evaluated through electrochemical testing.

This research correlates the operating conditions of the initial precipitation stage with the final collected product. By identifying how structural characteristics (such as particle and aggregate dimensions, porosity, pore tortuosity, crystal order and chemistry) affect material performance, this study addresses the limitations that have historically made this highly productive process unattractive to the industry.

References

- [1] Di Veroli, M. et al. Coprecipitation-driven memory effect: Linking precursor precipitation conditions to NMC811 cathode performance. *J. Power Sources* 665, 239058 (2026).
- [2] Giarrizzo, A. et al. Simulating the influence of Cu impurities on the performance of NMC811 cathodes for re-synthesis from recycling. *Chemical Engineering Journal* 518, 164686 (2025).
- [3] Colasanti, M. et al. Untangling the variables: Operational parameters and metrics in NMC cathode synthesis by Co-precipitation. *J. Power Sources* 657, 238132 (2025).

Functionalized Graphene Oxide as an additive for Anion Exchange Membranes

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The electrolysis of water using anion exchange membranes (AEMs)-based systems for hydrogen production, as an alternative to the proton exchange membranes (PEMs) ones, is currently the subject of extensive research due to its contribution to environmental sustainability. Anion exchange membrane water electrolyzers (AEMWEs) can in fact employ non-fluorinated membranes and make use of non-noble metal catalysts, significantly reducing costs. Among the main challenges that limit the industrial-scale deployment of this technology is the aggressiveness of the alkaline environment, which affects the durability and mechanical properties of the membranes. Another limitation arises from the lower conductivity of the OH⁻ ion compared to the H⁺ [1].

The incorporation of graphene oxide (GO) into the polymer matrix of the membranes has proven effective not only in enhancing the stability of AEMs but also in improving their conductivity [2]. To further amplify these benefits, quaternary ammonium was grafted onto GO using a Selectfluor-derived reagent, yielding quaternized graphene oxide (QGO_DABCO⁺).

Composite membranes were then prepared via solvent casting technique using a doctor blade technique starting from the Fumion ionomer solution enriched with 1% QGO_DABCO⁺, and compared with AEMs prepared the same way but without the additive.

The additive was characterized with: FTIR-ATR for bonds detection; XPS for the quantification of total amount of nitrogen and to confirm the presence of the quaternary ammonium; SEM for morphology analysis. The additivated membranes and the benchmark one were characterized by SEM, water uptake, ion exchange capacity (IEC) for the evaluation of the number of charge groups per mass of the polymer and conductivity tests. An increase in IEC and ionic conductivity of the composite AEMs, with respect to the Fumion membrane without the additive, was observed.

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References

- [1] N. Carboni et al. J. Mat. Chem. A 14, **2026**, 9852
- [2] N. Carboni et al. Electrochimica Acta 486, **2024**, 144090

Theme F - Biomaterials and Chemical Biology

MDL-800–Mediated Allosteric Activation of SIRT6 Drives Endothelial Epigenetic Remodeling in Hyperglycemia

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Metabolic disorders such as hyperglycemia contribute to cardiovascular disease by altering epigenetic regulation. Sirtuin-6 (SIRT6), a NAD⁺-dependent histone deacetylase, is a key regulator of chromatin remodeling and vascular homeostasis, representing an attractive target in chemical biology. MDL-800 is a selective allosteric activator of SIRT6 that enhances its deacetylase activity by stabilizing the active conformation of the enzyme. However, its effects in endothelial cells under metabolic stress remain poorly defined.



The aim of this study was to characterize MDL-800 as a chemical probe of SIRT6 activity in human umbilical vein endothelial cells (HUVECs) exposed to hyperglycemia. Cells were treated with MDL-800 (2.5–5 μM, 24 h), and epigenetic modulation (H3K9 acetylation), autophagy (LC3II/LC3I), apoptosis, angiogenesis, secretome, extracellular vesicles, and transcriptomic changes were evaluated.

MDL-800 showed dose-dependent activity. At 2.5 μM, it reduced H3K9 acetylation ($p < 0.05$), enhanced autophagy, and decreased apoptosis in hyperglycemic HUVECs, without affecting basal conditions. At 5 μM, it restored angiogenic and immunomodulatory factors (EGF, Endoglin, PECAM-1, CXCL1/8, MIF-1), improving angiogenic capacity ($p < 0.05$). Transcriptomic analysis revealed modulation of gene clusters involved in angiogenesis, metabolic stress, and cell cycle regulation. MDL-800 also reshaped extracellular vesicle profiles, shifting from large vesicles (>500 nm) to smaller vesicles (<100 nm), consistent with reduced cellular damage and improved intercellular communication.

In conclusion, MDL-800 acts as an effective allosteric activator of SIRT6, promoting epigenetic and functional reprogramming of endothelial cells under hyperglycemic stress. These findings highlight its potential as a chemical tool to counteract diabetes-related endothelial dysfunction.

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References

- [1] Claudia Cozzolino, et al. Pharmacological Research, November 2025, 221, 107970
- [2] Antonella Bordin et al, Cell Proliferation, 2022 Nov;55(11):e13312

Preparation and Characterization of Hyaluronic Acid and Arabinogalactan Mixtures for Cosmetic Applications

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The cosmetics industry represents a vast global market, generating billions of dollars in annual revenues. The production of cosmetic formulations requires a wide range of ingredients, including preservatives, colorants, stabilizers, emulsifiers, and thickeners, to confer the desired properties to the final product. In recent years, biopolymers have garnered growing interest in the cosmetics industry owing to their cost-effectiveness, stability, and versatility. At the same time, increasing consumer awareness of the detrimental environmental impact of synthetic polymers is encouraging the transition toward naturally derived alternatives. Among these, polysaccharides serve as functional moisturizing agents and effective rheology modifiers. While Hyaluronic Acid (HA) is established as a gold standard in cosmetic formulations [1], its interaction with Arabinogalactan (AG), a polysaccharide known for its immunostimulatory activity, remains an area of emerging scientific interest. This study investigates the potential synergistic effects between HA and AG to develop innovative cosmetic systems. HA/AG mixtures were prepared at various molar ratios and characterized by FT-IR spectroscopy, thermogravimetric analysis (TGA), circular dichroism (CD), and Small Angle X-ray Scattering (SAXS). These techniques elucidate the intermolecular interactions, macromolecule conformation, and supramolecular organization of the systems. Notably, SAXS analysis identified an optimal 1:3 HA/AG ratio, which promotes the formation of a stable three-dimensional network suitable for industrial scaling. Rheological measurements revealed that the addition of AG reduces the overall viscosity, thereby enhancing the mixture's workability, a critical factor for industrial manufacturing and consumer texture preference. Specifically, the 1:3 blend significantly improved processability while maintaining the system's characteristic "filamentous" feel and favorable film-forming properties upon skin application. Furthermore, antioxidant evaluation via DPPH test [2] demonstrated a synergistic free-radical scavenging effect. The 1:3 ratio provided a superior balance between functional performance and economic sustainability, avoiding the unnecessary costs associated with higher AG concentrations. These findings suggest that HA/AG blends are promising candidates for high-performance cosmetic formulations, combining optimized rheology with enhanced antioxidant activity.

References

- [1] Yao, Y.; Xu, B., Polysaccharides 2022, **3**, 818-830.
- [2] Turcov, D.; Zbranca-Toporas, A.; Suteu, D.; Int. J. Mol. Sci. 2023, **24**, 17517.

Semi-IPN hydrogels of poly(2-hydroxyethyl methacrylate) and star-shaped poly-L-lactide for wound healing applications

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Chronic wounds are characterized by a persistent inflammatory state and excessive oxidative stress, which significantly impair the natural healing process and hinder tissue regeneration. In this context, the use of hydrogel-based dressings is particularly advantageous due to their ability to maintain a moist environment and support localized therapeutic delivery [1]. Hydrogels are crosslinked three-dimensional polymer networks with high water retention, widely used for their biocompatibility and tissue-like properties. However, achieving an optimal balance between mechanical and biological performance remains challenging

In this context, interpenetrating polymer networks (IPNs) have gained attention due to the possibility of combining the favorable properties of each polymeric component of the IPNs leading to a new system with properties that often differ from those of the two single components [2].

In this work, semi-IPNs composed of poly(2-hydroxyethyl methacrylate) (PHEMA) and maleic-anhydride functionalized star-shaped poly-L-lactide (MA-ssPLLA) were investigated, leveraging the synergistic combination of PHEMA's hydrophilicity and biocompatibility with the biodegradable, mechanically reinforcing of MA-ssPLLA to obtain wound dressings with enhanced structural integrity and controlled bio-interactivity. Star-shaped PLLA was synthesized *via* Ring-Opening Polymerization (ROP) using diglycerol as an initiator, as previously reported [3]. The IPN hydrogels were obtained *via* UV photopolymerization and crosslinking (365 nm) of HEMA, MA-ssPLLA and ethylene glycol dimethacrylate (EGDMA), using Irgacure 2959 as the photoinitiator.

The resulting networks were utilized as matrices for the incorporation of phenol-based Deep Eutectic Solvents (DES) to confer radical scavenging properties to the system and decrease the oxidative stress in chronic wounds. The systems were characterized in terms of thermal and mechanical properties, surface wettability, and swelling kinetics in buffered solutions at different pH levels. The DES loading efficiency was also evaluated, and the antioxidant activity of the hydrogel-DES systems was assessed by DPPH assay. Furthermore, phenol-based DES could pave the way to future applications by acting as co-solvents to enhance loading and delivery of hydrophobic bioactive compounds.

References

- [1] V. Gounden, M. Singh. *Gels*, 2024, **10**, 43
- [2] S. Potorac, M. Popa, L. Verestiuc, D. Le Cerf. *Materials Letters*, 2012, **67**, 95–98
- [3] B. Brugnoli, C. Frezza, A. Mariano, P.L. Jacob, A. Diacono, D. Irvine, E. Axioti, A. Del Giudice, L. Galantini, A. Piozzi, A. Scotto d'Abusco, V. Taresco, I. Francolini. *Polymer*, 2026, **356**, 129963.

Deciphering the role of H565F Mutation and Glycosylation in ErbB3 Conformational landscape and Oligomerization

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The Epidermal Growth Factor Receptor (EGFR/ErbB) family comprises four receptor tyrosine kinases involved in key cellular processes. Overexpression of ErbB2 and ErbB3 is associated with tumour progression and resistance to conventional therapies. Heterodimerization has been identified as the crucial step for the activation of ErbB receptors. Interestingly, it has been proven that ErbB3 can be found in different oligomeric states which are hypothesized to form an “autoinhibition reservoir”.

Here, we investigate the conformational dynamics of ErbB3 through Molecular Dynamics (MD) simulations, focusing on the role of glycosylation and a single point mutation (H565F). In particular, we performed 1 μ s Molecular Dynamics simulations of four ErbB3 variants: glycosylated and deglycosylated wild-type, and glycosylated and deglycosylated H565F mutant. Trajectory analysis like RMSD and RMSF calculations revealed major differences in protein flexibility across the variants, while PCA showed non-overlapping clusters suggesting that both glycosylation and H565F mutation strongly influence the conformational landscape of the receptor. These findings provide a structural basis for understanding the conformational states that may govern ErbB3 self-association and lay the groundwork for future docking studies aimed at characterizing the homodimerization mechanism.

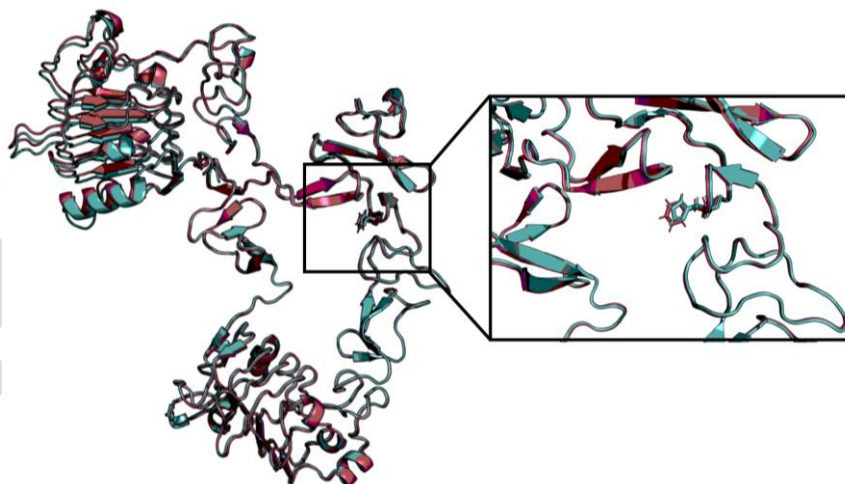


Figure 1 Structure of ErbB3-WT (PDB 1M6B) and ErbB3-H565F (PDB 3OYO, in hold for publication) extracellular domains, with a focus on the mutation site.

References

- [1] Hyun-Soo Cho, Daniel J. Leahy, “Structure of the Extracellular Region of HER3 Reveals an Interdomain Tether”, *Science* **297**, 1330–1333 (2002).
- [2] Kaibo Ma, Xiaojie Ma, João F. Shida *et al.*, “ErbB family receptor dimerization dynamics and dysregulation via long-term single-molecule imaging”, *Cell* (2026).