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CHEMISTRY For the FUTURE

International Conference

28 Jun | 30 Jun 2023

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BOOK OF ABSTRACTS

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SCIENTIFIC PROGRAM

Chemistry for the Future 2023

Wednesday – June 28th

14:00 - 14:45 **Registration**

14:45 - 15:00 **Welcome and Opening**

Session 1_Chair: Dario Frassi & Giulia Caroti

15:00 - 15:40 **Stefano Corni** (Università di Padova) – Manipulating photochemistry by light-molecule strong coupling

15:40 - 16:05 **Tommaso Nottoli** (36° cycle DSCM, Università di Pisa) - Cholesky decomposition technique for the computation of energy and properties at a correlated level of theory

16:05 - 16:30 **Giacomo Salvadori** (36° cycle DSCM, Università di Pisa) - Development of multiscale approaches for photochemical processes in complex environments

16:30 - 17:00 ***Coffee Break***

Session 2_Chair: Adele Ferretti & Giulia Caroti

17:00 - 17:40 **Peter Vandenabeele** (Ghent University) – Mobile Raman Spectroscopy: an ideal tool for the investigation of cultural heritage

17:40 - 18:05 **Tommaso Nacci** (36° cycle DSCM, Università di Pisa) - Multianalytical approach for the life cycle assessment of biodegradable commercial products

18:05 - 18:30 **Elena Eremeeva** (36° cycle DSCM, Università di Pisa) - Molybdenum-Indium oxide based chemoresistive sensor for a selective ammonia sensing

Happy hour

Thursday – June 29th

Session 3_Chair: Elisabetta Rosadoni & Chiara Saviozzi

9:00 - 9:40 **Jess Wade** (Imperial College London) - Chiral functional materials as a platform for emerging technologies

9:40 - 10:05 **Andrea Taddeucci** (36° cycle DSCM, Università di Pisa) - Electronic Circular Dichroism Imaging of Chiral π-conjugated Materials in Thin Film

10:05 - 10:30	**Oliver George Willis** (36° cycle DSCM, Università di Pisa) - The Beauty of Invisible Light: Exploring Near-Infrared Circularly Polarized Luminescence
10:30 - 11:00	***Coffee Break***

Session 4_Chair: Fabiana Cordella & Elisa Della Latta

11:00 - 11:40	**Alain Dufresne** (Grenoble Institute of Technology) - Polysaccharide nanomaterials and potential applications
11:40 - 12:05	**Edoardo Cignoni** (36° cycle DSCM, Università di Pisa) - Machine Learning Exciton Hamiltonians in Light-Harvesting Complexes
12:05 - 12:30	**Flash poster presentations:** Sara Benetti, Piermarco Saraceno, Lorenzo Bonaldi, Alberto Cerchiai, Marco Bazi
12:30 - 14:00	***Lunch Break***

Session 5_Chair: Angela Gilda Carota & Zahraalsadat Yousefniayejahromi

14:00 - 14:40	**Claudia Bonfio** (University of Strasbourg) - Shaping early life: primitive cells, primitive membranes
14:40 - 15:05	**Alessio Lenzi** (36° cycle DSCM, Università di Pisa) - Mass spectrometry-based assay for the determination of natriuretic peptides in biological samples
15:05 - 15:30	**Asia Botto** (36° cycle DSCM, Università di Pisa) - Precision Proteomics of Pancreatic Adenocarcinoma
15:30 - 16:00	***Coffee Break***

Session 6_Chair: Elisa Della Latta & Greta Biale

16:00 - 16:30	**Flash poster presentations:** Elena De Gregorio, Francesca Nerli, Andrea Giovanelli, Ivan Giannì, Patrizia Mazzeo, Alessando Cesaro
16:30 - 16:55	**Noemi Landi** (36° cycle DSCM, Università di Pisa) - Solid-State NMR methods for the study of Lead Halide Perovskites
16:55 - 17:20	**Thantip Roongcharoen** (35° cycle DSCM, Università di Pisa) - Catalysts design by predictive Modelling of Aqueous Phase Reforming of Liquid Renewable Feedstocks
17:20 - 17:40	**Giada Silvi** (INEOS Inovyn) – Failure investigation on polymer materials: metallographic laboratory approach
17:40 - 19:00	**Poster Session**
	Social dinner

Friday – June 30th

Session 7_Chair: Chiara Saviozzi & Dario Frassi

9:00 - 9:40	**Enzo Alessio** (Università di Trieste) – What did we learn from 50 years of medicinal inorganic chemistry?
9:40 - 10:05	**Ester Giorgi** (36° cycle DSCM, Università di Pisa) - Gold-based cytotoxic complexes for targeted anticancer treatments
10:05 - 10:30	**Carlo Marotta** (36° cycle DSCM, Università di Pisa) - New Pt(IV) anticancer prodrugs: synthesis, studies and encapsulation in PLGA-PEG nanoparticles
10:30 - 11:00	***Coffee Break***

Session 8_Chair: Rosaria Lorè & Elisabetta Rosadoni

11:00 - 11:20	**Daniel Toncelli, Sara Taddei** (INEOS) - Experimental activities and assets of the INEOS Olefins and Polymers research and development pilot plant FEX
11:20 - 12:00	**Patricia Benito Martin** (Università di Bologna) – Electrocatalytic conversion of biomass-derived compounds over 3D catalysts
12:00 - 12:25	**Andrea Roggi** (36° cycle DSCM, Università di Pisa) - Polymeric anion exchange membranes for green hydrogen production
12:25 - 12:50	**Gianni Pecorini** (36° cycle DSCM, Università di Pisa) - Biotechnological Polymers for Advanced Technologies and Applications
12:50 - 13:30	**Closing of the conference and final remarks**

ABSTRACTS

ORAL COMMUNICATIONS

What did we learn from 50 years of medicinal inorganic chemistry?

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At the end of the 1960's Barnett Rosenberg announced the astonishing discovery that a simple Pt(II) coordination compound, *cis*-$[PtCl_2(NH_3)_2]$, later to be universally known as *cisplatin*, had unprecedented anticancer activity. The serendipitous "discovery" of *cisplatin*, that became the most widely used anticancer compound worldwide, opened the way to modern inorganic medicinal chemistry and to decades of intense research in this thriving field.

More than 50 years after this scientific and medical cornerstone, the conference will critically address the different typologies of metal-based drugs (both for diagnosis and for therapy), and will try to fathom the future developments of this field.

Electrocatalytic conversion of biomass-derived compounds over 3D electrocatalysts

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The electrocatalytic conversion (hydrogenation or oxidation) of biomass-derived compounds is a fully sustainable alternative to thermo-catalytic processes and a path for the storage of renewable energy into chemicals and liquid fuels. It usually operates at mild conditions, room temperature and pressure (avoiding the use of molecular H_2 or O_2), and may control the selectivity of the process, a challenging task in highly functionalized biorefinery molecules. Although highly promising, the electrochemical route is in its infancy and more knowledge is required to develop selective electrocatalysts able to convert concentrated electrolytes and to achieve a high productivity. 3D electrocatalysts with nanostructured coatings are an option to reach the aim of enhanced productivity due to the large electroactive surface area.

This talk will focus on the electrocatalytic hydrogenation of biomass-derived compounds [1]. After a brief overview of the state-of-the-art, the electrocatalytic hydrogenation of 5-hydroxymethylfurfural (HMF) will be described as an example [2,3]. The electrocatalytic reduction of the HMF platform molecule can produce a biopolymer precursor such as 2,5-bishydroxymethylfuran (BHMF), Figure 1a. This electrocatalytic route is highly selective at pH = 9.2, diluted HMF solutions (0.02 M), and low current densities. While the electrodimerization becomes important when the HMF concentration is increased (Figure 1a). Herein, 3D catalysts based on Cu open-cell foams coated by Ag through electrodeposition (Figure 1b) are proposed to enhance the BHMF production from 0.05 M HMF electrolytes at moderate current densities (Figure 1c).

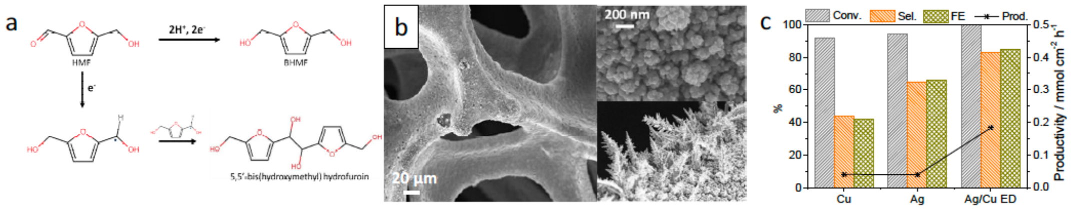

Figure 1. a) Schema of the HMF electroreduction; b) SEM images of AgCu foam catalyst; c) catalytic performance (HMF 0.05 M; 0.5 M borate buffer, pH = 9.2; -0.51 V vs RHE; 241 C)

Key aspects in the preparation and characterization of the catalysts and the reaction mechanism will be presented. The main challenges to overcome to further develop this and other related electrocatalytic processes will be finally underlined.

References:

[1] S. A. Akhade, N. Singh, O. Y. Gutiérrez, J. Lopez-Ruiz, H. Wang, J. D. Holladay, Y. Liu, A. Karkamkar, R. S. Weber, A. B. Padmaperuma, M.-S. Lee, G. A. Whyatt, M. Elliott, J. E. Holladay, J. L. Male, J. A. Lercher, R. Rousseau, V.-A. Glezakou, *Chem. Rev.*, 120, 11370−11419 (2020).

[2] G. Sanghez de Luna, P. H. Ho, A. Sacco, S. Hernández, J.-J. Velasco-Vélez, F. Ospitali, A. Paglianti, S. Albonetti, G. Fornasari, P. Benito, *ACS Appl. Mater. Interfaces*, *13*, 23675–23688 (2021).

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Shaping early life: primitive cells, primitive membranes

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The complexity of modern biochemistry suggests that a systems biochemistry approach is required to understand and potentially recapitulate the network of prebiotic reactions that led to the emergence of life.

Early cells probably relied upon interconnected chemistries to link nucleic acids, peptide-based catalysts and membranes. In this context, I will discuss our recent advancements about:

- what, how and when membrane-based compartments appeared on early Earth;
- whether primitive membranes could be compatible with prebiotic chemistries and metal-driven catalytic processes;
- what biophysical or biochemical mechanisms could enable primitive cell cycles to retain continuity of function.

Addressing all these points can help us to elucidate the prebiotic pathways that led to the emergence of populations of functional primitive cells and, from there, the rise of life as we know it.

References:

[1] R. Rubio-Sanchez, A. Wang, D. O'Flaherty, F. Coscia, G. Petris, L. Di Michele, P. Cicuta, C. Bonfio, *J. Am. Chem. Soc.*, 143, 16589-16598 (2021).

[2] C. Bonfio, D. A. Russell, N. J. Green, A. Mariani, J. D. Sutherland, *Chem. Sci.*, 11, 10688-10697 (2020).

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Manipulating photochemistry by light-molecule strong coupling

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Electronic excitations in molecules can be strongly coupled to electromagnetic modes of resonant cavities. The properties of the resulting hybrid states are different than those of the original electronic states. In particular, the resulting photochemistry depends on the features of the excited molecular states, and can therefore be modified by entering the strong coupling regime. Focusing mainly on single molecules hosted in nanoplasmonic cavities, in collaboration with the group of M. Persico and G. Granucci in Pisa we have extended well-established semiclassical approaches developed for photochemical processes [1] to simulate photochemistry in the strong-coupling regime [2,3]. Moreover, in a collaboration with H. Koch's group (SNS Pisa and NTNU Trondheim) we have investigated changes of the electronic ground and excited electronic states induced by strong coupling with localized surface plasmons [4,5]. In this talk I will describe the theoretical models underlying these developments, and the relevant results for the field of polaritonic (or more specifically, plexcitonic) chemistry.

References:

[1] G. Granucci, M. Persico, A. Toniolo. *J. Chem. Phys.,* 114, 10608 (2001)
[2] J. Fregoni, G. Granucci, E. Coccia, M. Persico, S. Corni. *Nat. Commun.,* 9, 4688 (2018)
[3] J. Fregoni, G. Granucci, M. Persico, S. Corni. *Chem,* 6, 250 (2020)
[4] J. Fregoni, T.S. Haugland, S. Pipolo, T. Giovannini, H. Koch, S. Corni. *Nano Letters,* 21, 6664 (2021)
[5] M. Romanelli, R.R. Riso, T.S. Haugland, E. Ronca, S Corni, H Koch *Nano Letters* in press

Polysaccharide nanomaterials and potential applications

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There has been an explosion of interest in the use of biomass as a source of renewable energy and materials. This has led to a concurrent increase in the research activity on the biosynthesis, isolation, and properties of cellulose, the key structural component in plant cell walls. One focus of this activity has followed from the recognition that, by suitable chemical and mechanical treatments, it is possible to produce fibrous materials with one or two dimensions in the nanometer range from many naturally occurring sources of cellulose [1]. As is usually the case when a new field is developing, the terminology is somewhat confused, but the term “nanocellulose” is now used to cover the range of materials derived from cellulose with at least one dimension in the nanometer range. Nanocellulose-based materials are carbon neutral, sustainable, recyclable, and nontoxic; they thus have the potential to be truly green nanomaterials with many useful and unexpected properties. What is not to love? Multiple mechanical shearing actions can be used to release more or less individually cellulose microfibrils [2]. This material is usually called microfibrillated cellulose (Figure 1A). Longitudinal cutting of these microfibrils can be achieved by submitting the biomass to a strong acid hydrolysis treatment, allowing dissolution of amorphous domains [4]. The ensuing nanoparticles occur as rod-like nanocrystals (Figure 1B). Similar acidic treatment carried out on starch granules allows obtaining platelet-like nanoparticles. Impressive mechanical properties and reinforcing capability, abundance, low weight, and biodegradability of these nanoparticles make them ideal candidates for the processing of polymer nanocomposites. With a Young’s modulus around 130 GPa and a surface area of several hundred $m^2.g^{-1}$, they have the potential to significantly reinforce polymers at low filler loadings [6]. However, as for any nanoparticle, the main challenge is related to their homogeneous dispersion within a polymeric matrix.

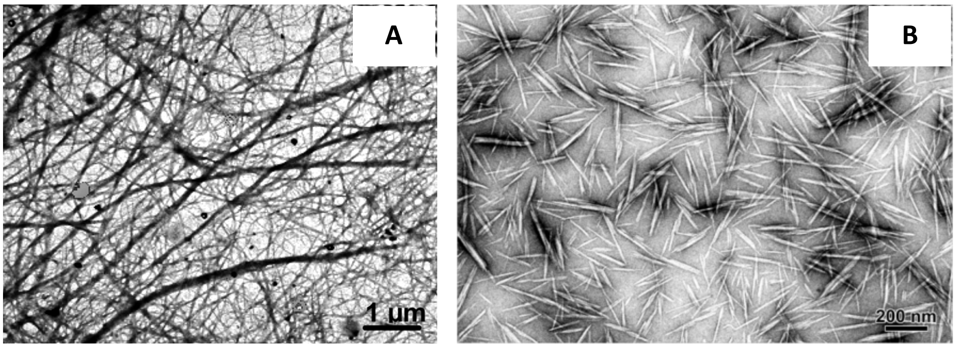

Figure 1. TEM from a dilute suspension of (A) cellulose nanofibrils from *Opuntia ficus-indica* fibers [3], and (B) cellulose nanocrystals from ramie fibers [5]

References:

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Mobile Raman Spectroscopy: an ideal tool for the investigation of cultural heritage

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Raman spectroscopy is widely recognized as a valuable technique for analysing cultural heritage objects. Its non-destructive nature, rapid analysis, and straightforward interpretation are key advantages of this method. Additionally, it enables the study of both inorganic and organic materials by examining their molecular spectra. Furthermore, when using a Raman microscope, highly detailed Raman spectra can be captured with spatial resolution reaching as low as 1 µm. By conducting multiple point measurements consecutively, a Raman map can be generated, a commonly used approach for studying small samples of an object. This facilitates the acquisition of molecular distribution images at a microscopic scale. Moreover, portable instrumentation allows us to bring the instruments to the artefacts, and allows to perform *in situ* measurements. These instruments typically use a fibre optics probe head that can be easily positioned in front of the object being studied. Also, using long working distance zoom lenses can be very useful (Figure 1).
To combine the advantages of mobility and the capability to generate molecular images a macro-Raman-mapping device was developed. This device comprises a mobile Raman spectrometer mounted on three perpendicular translation stages. To position the probe head accurately, various cameras and a triangulator are integrated, using software that is programmed in Matlab. With this system, we can capture Raman mappings of areas spanning several hundreds of square centimeters. By implementing appropriate data processing techniques, we can obtain meaningful images.

Figure 1. The use of a zoom lens for the *in situ* analysis of a polychrome sculpture

References:
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[2] P. Vandenabeele, A. Rousaki, *Anal. Chem.*, 93, 15390-15400 (2021).

Chiral functional materials as a platform for emerging technologies

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The use of organic semiconductors as low-cost, lightweight, easy-to-process active layers in optoelectronic devices has attracted considerable research and technological interest for over thirty years. Chiral organic semiconductors (i.e. organic semiconductors that exist as left- and right-handed non superimposable mirror image pairs) offer unparalleled opportunity to control electron and photon spin, due to a combination of their unique optical, electrical and magnetic properties. Their functional properties, including the absorption and emission of circularly polarised light or the transport of spin-polarised electrons, are highly anisotropic. As a result, the orientation of chiral molecules critically determines the functionality and efficiency of chiral devices. We have developed a strategy to control the orientation of helicenes, prototypical chiral small molecules. Our approach forces the helicenes to adopt a face-on orientation and self-assemble into upright supramolecular columns oriented with their helical axis perpendicular to the substrate, or an edge-on orientation with parallel-lying supramolecular columns, which can independently switch on and switch off low- and high-energy chiroptical responses. Our templating methodologies provide a simple way to engineer orientational control and, by association, anisotropic functional properties of chiral molecular systems for a range of emerging technologies.

Precision Proteomics of Pancreatic Adenocarcinoma

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Pancreatic ductal adenocarcinoma (PDAC) has a very poor prognosis, with less than 10% of patients alive five years after diagnosis. The prognosis of cancer patients is much improved through earlier detection. A recent study reported 5- and 10-year survival rates of 49% and 31%, respectively, for T1-2, N0, and R0 tumors [1]. Earlier diagnosis would enable treatment to begin when the tumor is in its earlier stages, and so improve patient prognosis. This aim would be achieved by developing a method able to isolate and identify characteristic markers of PDAC.

PDAC is characterized by a robust fibroinflammatory response, widespread vascular collapse, and hypoperfusion that make the tumor highly hypoxic and nutrient deprived. This microenvironment promotes tumor invasion, and progression leads to chemotherapy or radiotherapy resistance and eventual mortality.

To isolate newly synthesized protein from hypoxic cells we developed and optimize a protein labeling approach that is cell-type/phenotype-specific, and enables the solation through the labeledproteins. Bio-orthogonal non-canonical amino-acid tagging (BONCAT) is a technique that labels proteins with an azido moiety.

The azido moiety is introduced during protein synthesis using methionine surrogates, then with asimple click chemistry reaction, only the proteins that contain the azido moiety will be enriched [2]. Cell-specific BONCAT labeling can be achieved using azidonorleucine (ANL) as the Met surrogate.ANL is only incorporated into proteins by a specific mutant form of the protein methionyl-tRNAsynthetase (MetRS*). Accordingly, ANL labeling can be restricted to cells equipped with thismutant form. The DNA of MetRS* is introduced into cells by transduction, using specific promotersto target specific cell phenotypes (e.g. HIF1α for hypoxia). Once ANL has been added to the mediaall methionines in the newly synthesized proteins from MetRS* transfected cells will be substitutedfor ANL.

Here we will show progress in method development, including results showing the incorporation of BONCAT labels into PDAC tumor cells and their enrichment by optimization of the click chemistry reaction.

References:

[1] H. Seppänen, et al., *Scand. J. Surg.* 106, 54–61 (2017).
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Machine Learning Exciton Hamiltonians in Light-HarvestingComplexes

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Light-harvesting complexes (LHCs) are of fundamental importance for carrying out photosynthesis [1]. Fine-tuning of their properties holds the promise of improving crop yields [2], stimulating researchers to investigate their excitation transport properties [3]. Still, the computational investigation of these complexes is considerably expensive, as many quantum mechanical (QM) calculations are needed to describe the excited states of the many pigments embedded in the LHCs [4]. We present a machine learning (ML)-based strategy for an inexpensive calculation of excitonic properties of LHCs [5,6]. The strategy uses classical molecular dynamics simulations of LHCs in their natural environment combined with ML predictions of the excitonic Hamiltonian of theembedded aggregate of pigments. The proposed ML model can reproduce the effects of geometrical fluctuations together with those due to electrostatic and polarization interactions between the pigments and the protein. The training is performed on the chlorophylls of the major LHC of plants, but we demonstrate that the model is able to extrapolate well beyond the initial training set. Moreover, the accuracy in predicting the effects of the environment is tested on the simulation of the small changes observed in the absorption spectra of the wild-type and a mutant ofa minor LHC.

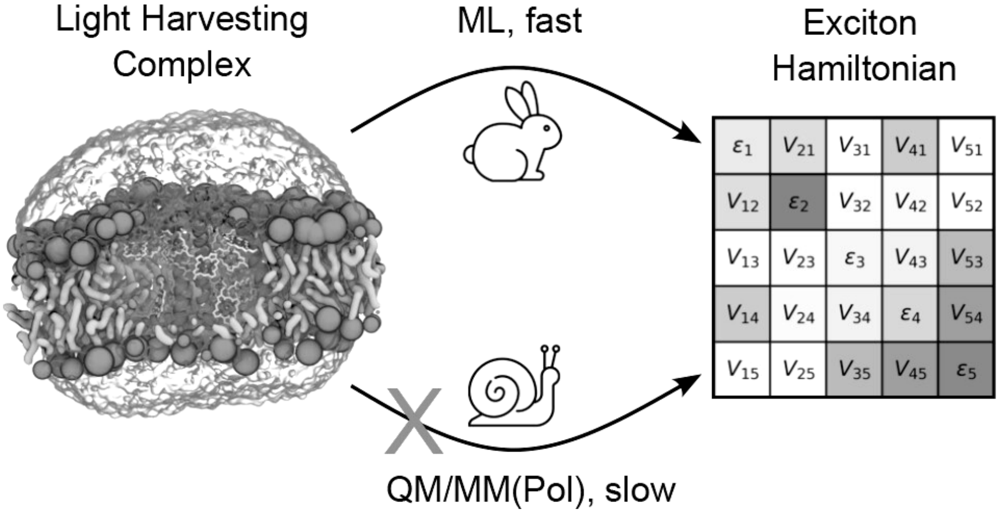

Figure 1. Conventional polarizable QM/MM calculations are computationally demanding for computing theexcited states of chromophores. We bypass their cost by adopting a machine learning strategy, while still retaining their accuracy.

References:

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Molybdenum-Indium oxide based chemoresistive sensor for a selective ammonia sensing

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The detection of ammonia in exhaled human breath can provide information regarding human health. It is known that subjects suffering from kidney and liver disease may have breath ammonia levels up to 820-14700 ppb, whereas healthy people have 400-1800 ppb [1]. However, the lack of fast, non- invasive, and easy-to-use sensors is forcing scientists to conduct studies in this direction [2]. Among the available sensor technologies, metal oxide-based chemoresistive sensors proved to be effective for the analysis of gases thank to their, adaptability, low power consumption, fast response, and sensitivity.

In this work we developed a chemoresistive ammonia sensor based on molybdenum oxide (MoO_3) an n-type semiconductor with a band gap of 3.2 eV. MoO_3 has been shown to be an atractive material for the development of gas sensors due to its unique morphology, custom selectivity for various analytes, and bulk thermal stability [3,4]. MoO_3 sensors were fabricated by directly depositing nanostructured highly porous structures on an interdigitated electrode using flame spray pyrolysis. Figure 1 shows the response of the sensor to several gasses (acetone, ethanol, methanol, ammonia, hydrogen, nitrogen monoxide) performed with a relative humidity of 90 % to beter reproduce human breath composition. The sensor a higher response for ammonia (1 ppm) at an indium content of 1$\%_{wt}$.

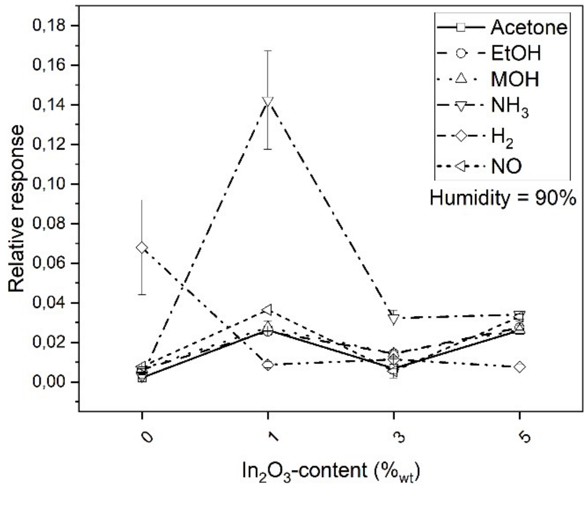

Figure 1. Average sensor response as a function of In_2O_3 content to 1000 ppb acetone (square), ethanol (circle), methanol (triangle), ammonia (reverse triangle), hydrogen (diamond) and nitrogen oxide (triangle pointing left) in humid (90%) air at 400°C. Error bars indicate the response variability toat least three identical consecutive analyte exposures.

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Gold-based cytotoxic complexes for targeted anticancer treatments

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In recent decades, the attempts to repurpose auranofin as a possible anticancer agent have triggered growing interest in Au-based complexes as promising candidates in the search for new anticancer therapeutic strategies [1]. Although the mechanism of action for which gold-based compounds cause cellular apoptosis in cancer cells has not been completely clarified yet, is commonly accepted that the inhibition of thioredoxin reductase (TrxR) plays a pivotal role [2]. At the physiological level, this mitochondrial enzyme maintains the redox homeostasis of the cell, and interestingly it is often overexpressed in tumour cells. The mitochondrial-mediated apoptosis induction presents several advantages, including the potential overcoming of resistance that often occurs after treatment with conventional Pt-based drugs. In order to selectively and specifically deliver therapeutic agents to the desired site or target within the body, targeting strategies are a valid approach to be explored. Targeting involves the identification of specific molecular biomarkers that are particularly present in cancer cells and designing drugs that can interact specifically with them, to obtain a preferential drug's accumulation and selective activity on cancer cells. During this PhD project, new Au(I)-based complexes were synthesized, characterized, and then conjugated to different molecules able to target cancerous cells, according to different targeting strategies. In particular, three targeting molecules have been implemented in the conjugates. Two gold(I) complexes were firstly conjugated with 2,3,4,6-tetra-O-acetyl-1-thio-β-D- glucopyranose, a biomimetic glucose substrate, potentially able to increase the metal-complex uptake in tumour cells by exploiting the overexpressed GLUT-mediated transport (Warburg effect) [3]. Fluorescence and ESI-MS experiments showed the interaction of the new gold(I) conjugates with human serum albumin (HSA), suggesting the possibility of an HSA-mediated transport in the bloodstream to reach the tumour site. Biological tests on A2780 ovarian cancer cell lines showed a significant enhancement in the cytotoxicity of the complexes when conjugation with 1-thio-β-D-glucose tetraacetate is present. Accordingly, cellular localization experiments by confocal microscopy highlighted the increased accumulation of the Au(I)complexes in the cancer cell when the thiosugar moiety is present. Another approach that has been employed is the conjugation of the same gold(I) complexes with two targeting peptides: C-βAla-RGD, which targets the overexpressed integrin receptors on the A2780 cell line (ovarian cancer), and CrFrFrF, a mitochondria-targeting peptide which allows the drug to accumulate in this organelle, where TrxR is mainly present. Biological tests to evaluate the cytotoxicity of the latter conjugates are currently ongoing.

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Solid-State NMR methods for the study of Lead Halide Perovskites

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In the past years, Lead Halide Perovskites (LHPs), with general formula $APbX_3$ (A = methylammonium MA^+, formamidinium FA^+, Cs^+; X = Cl^-, Br^-, I^-), have received great levels of attention due to their remarkable optoelectronic properties, easy processability, abundant constituent elements, and wide compositional tunability [1]. Recent progress is mainly attributed to the exploration of various crystal engineering strategies (*i.e.* compositional and dimensional engineering) aimed at pushing the efficiencies higher, tuning properties, and overcoming stability issues. In 3-dimensional (3D) perovskites, the use of mixed-ion structures, obtained by introducing dopants into the perovskite structure, results in higher perovskite solar cell performance. Lowering the dimensionality of perovskites from 3D to 2D (by sandwiching organic cations, called spacers, between perovskite conductor layers) improves ambient stability, although at the expense of efficiency. Similarly, all-inorganic perovskite nanocrystals (where A is usually Cs^+) show higher thermal stability and higher photoluminescence quantum yields with respect to bulk perovskites, although efficiency in solar cells is lower.

Solid-State Nuclear Magnetic Resonance (SSNMR) stands out as characterization technique for LHPs for its ability to study ion dynamics, compositional variations and ion incorporation, chemical interactions, and degradation mechanisms, and can therefore be used to advance our understanding of these multifaceted materials [2].

In this study, a multiple-cation lead mixed-halide perovskite $Cs_{0.05}FA_{0.81}MA_{0.14}PbI_{2.55}Br_{0.45}$[3], 2D Ruddlesden-Popper phases containing butylammonium (BA) as spacer ($BA_2MA_{n-1}Pb_nI_{3n+1}$ with n=1-4, Figure 1), and $CsPbBr_3$ nanocubes [4] were investigated by a range of multinuclear SSNMR techniques. ^{133}Cs, ^{207}Pb, ^{1}H, and ^{13}C spectra were recorded under Magic Angle Spinning and static conditions; variable temperature measurements of ^{13}C and ^{1}H spin-lattice relaxation times (T_1) allowed dynamic properties of the organic cations in the series of samples to be investigated. The obtained structural and dynamic features of these systems have been compared with those of 3D pure $MAPbI_3$ and discussed in relation to very recent literature.

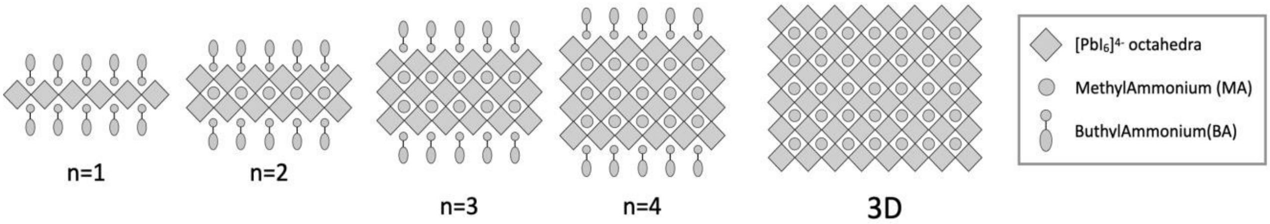

Figure 1. Schematic structure of 2D Ruddlesden-Popper perovskites $BA_2MA_{n-1}Pb_nI_{3n+1}$ for n=1, 2, 3, 4, andof the corresponding 3D perovskites $MAPbI_3$.

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Mass spectrometry-based assay for the determination ofnatriuretic peptides in biological samples

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“Omics” techniques, among which proteomics and metabolomics are the most studied, represent the main tool for the identification and quantification of biomolecules and allowing to gain insights into molecular processes within living organisms. On the other hand, “peptidomics” has not been extensively studied yet, and deals with the identification and quantification of endogenous peptides present at a defined time point in an organism [1]. Peptides (with a molecular weight <15 kDa) are considered key regulatory molecules in several clinical contexts, but the lack of well-defined studies in this field reflects the challenging nature of peptidomics analysis. In complex biological samples, peptides have very low concentrations (from ng/mL to pg/mL) and show widely heterogeneous physicochemical properties [1]. Besides, given their low molecular weight, sample pre-treatment procedures do not inherently involve the use of enzymatic digestion, allowing less time-consuming procedures. However, based on these characteristics, the determination of native peptides by mass spectrometry may be challenging compared to the analysis of tryptic peptides deriving from protein enzymatic digestion.

This research aims to the development of an innovative analytical procedure based on microextraction by packed sorbent (MEPS) coupled with liquid chromatography-tandem mass spectrometry (UHPLC-MS/MS) instrument for the determination of native natriuretic peptides (NPs) in plasma samples. NPs consist of a family of low molecular weight hormones (<4 kDa) released during an impairment of the physiological activity of the heart muscles. Among these, B-type natriuretic peptide represents one of the golden biomarkers for prognosis and diagnosis of heart failure [2]. In the medical field, NPs are commonly monitored in blood using commercially available immunoassay kits even though these approaches are affected by cross-reactions with several NPsforms that share homologous structures [3]. In this context, the ability to rapidly quantify multiple molecular species with high specificity and accuracy makes mass spectrometry a suitable techniquefor determining a panel of seven NPs forms.

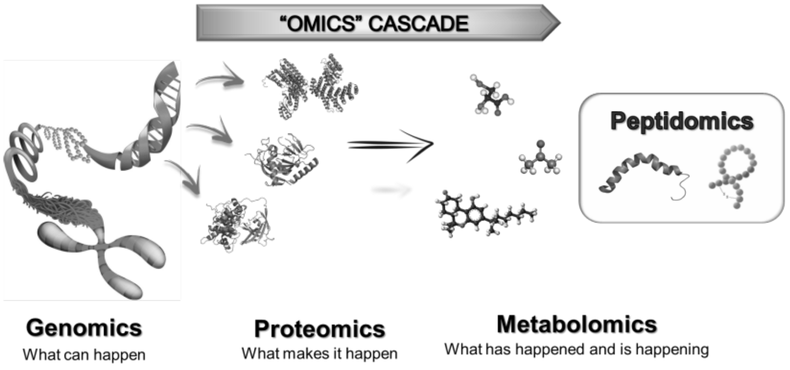

Figure 1. The “omics’ cascade”.

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New Pt(IV) anticancer prodrugs: synthesis, studies and encapsulation in PLGA-PEG nanoparticles

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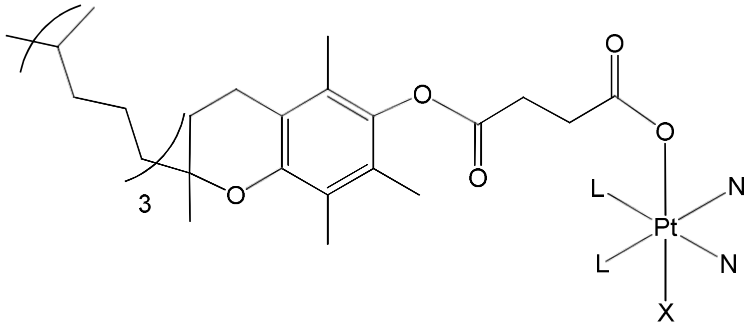
Nowadays, despite the in-depth research that has been carried out, cancer is still a very serious disease with a high-rate mortality. Since its FDA approval in 1978, cisplatin has been the cornerstone in the treatment of this illness. Subsequently, other Pt(II) drugs have been approved by the FDA, namely carboplatin and oxaliplatin, all of which exert their anticancer action by targeting the DNA [1]. However, in spite of their usefulness, their numerous side effects and the development of resistance by cancer cells considerably limit their clinical benefits [2]. Therefore, there is a high need for new drugs with an improved pharmacological profile with respect to traditional Pt drugs. In this frame, a very promising field is represented by Pt(IV) complexes. Indeed, being more kinetically inert, they undergo fewer off-target reactions during their circulation in the body, and thus cause less side effects with respect to traditional Pt(II) drugs [3]. Moreover, their octahedral geometry grants them two additional axial positions which can be functionalized with bioactive molecules, thus obtaining new compounds with an improved pharmacological action [4]. In this context, α-tocopherol succinate (α-TOS) is an interesting molecule to functionalize the axial position of these drugs. Indeed, α-TOS, by inhibiting some anti-apoptotic proteins, is capable of disrupting the mitochondrial functionality, thus leading to apoptosis [5]. Therefore, a Pt(IV) prodrug based on the oxidised form of traditional Pt(II) drugs and functionalized in the axial position with α-TOS would be a dual-targeting anticancer drug, capable both of interfering with the mitochondrial activity and of damaging the DNA. Moreover, these prodrugs can also be encapsulated in PLGA-PEG nanoparticles, thus creating a delivery system that can potentially further increase the overall pharmacological action.



L = Leaving group
N = Non-leaving group
X = OAc, OEt, α-TOS

Figure 1. General structure of the synthesized α-TOS-bearing Pt(IV) complexes.

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Multianalytical approach for the life cycle assessment of biodegradable commercial products

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In the last few years, biobased and biodegradable polymers have been considered a potential solution to the increasing problem of plastic pollution in the environment [1]. However, both the properties of the material and the environment in which it needs to biodegrade influence the biodegradation process. The complexity of biodegradation calls for the development of reliable analytical methods to investigate and characterise biodegradable polymers and their lifecycle, and to follow their degradation in the environment [2,3,4].

The present work was carried out in collaboration with the University of Plymouth - International Marine Litter Research Unit, Dr. Francesca De Falco and Prof. Richard Thompson - and aims at investigating the potential of analytical pyrolysis coupled to mass spectrometry in the study of the life cycle assessment of commercial wet wipes and agricultural mulch films in the environment. The extensive use of wet wipes as single-use sanitary products and the recent "flushability" policy in the UK has increased the concern about microfibre pollution and possible release of additives to the environment. Moreover, the introduction of biodegradable mulch films in the market was not accompanied by a thorough investigation of their potential environmental impact. Both cases highlight the limitations of the current international policies to assess and regulate the massive production and application of biodegradable polymers.

In the first part of this research, different samples of flushable-labelled and conventional commercial wet wipes from the UK market were investigated by scanning electron microscopy (SEM), evolved gas analysis-mass spectrometry (EGA-MS), and multi-shot pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS). Subsequently, a multianalytical methodology for studying the degradation pathways of wet wipes immersed in water and artificially aged in different conditions was developed. The adopted approach consisted in the fibre analysis by SEM, EGA-MS, and Py-GC-MS, while possible organic leachates in water were detected by high performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS). The results showed an increase in the amount of additives and microfibres released in time, and highlighted different degradation pathways of the polymeric structures based on wipe composition.

In a parallel study, two biodegradable mulch films were exposed to open environment along with a conventional mulch film made of polyethylene. Subsamples were collected at different times of exposure and subjected to SEM and Py-GC-MS analysis. The formation of holes and visible damages on the surface of the degraded bioplastic mulch films was observed. Py-GC/MS highlighted the disappearance in the pyrograms of additives, originally observed in the pristine materials, suggesting a possible leaching in the environment. No significant change in the morphology or pyrolytic profiles was detected for the conventional mulch film.

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Cholesky decomposition technique for the computation of energy and properties at a correlated level of theory

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In the last few years, rank-reducing techniques have emerged in quantum chemistry as a mathematical tool able to speed up calculations, and thus being able to extend the range of application of quantum chemical methods to larger molecular systems. In this context, we exploit the Cholesky decomposition (CD) of the electron repulsion integrals (ERI) matrix [1-3]. Such technique is capable of compressing the information stored in the ERI matrix by decomposing it in lower dimensionality tensors, therefore reducing the overall computational cost. The decomposition may be truncated in such a way that the error is always bound to be lower than a chosen threshold, thus providing a robust control over the accuracy.

We exploited the CD in two quantum chemical methods, namely the complete active space self-consistent field (CASSCF) and coupled-cluster with singles and doubles excitations (CCSD), which are customarily used to treat multi-reference and single-reference systems, respectively. For CASSCF, we present a CD based implementation of NMR shieldings [4,5] also showing a real application on medium-large porphyrinoids systems. For what concerns CCSD [6,7], we propose an implementation that in addition to CD can also exploit point-group symmetry, thus offering the possibilty to study larger (symmetric) molecules. In particular, the joint effort given by the CD, the exploitation of point-group symmetry, and the parallelization of the code allowed us to perform a (frozen-core) calculation on fullerene ($C60$) with 1800 basis functions.

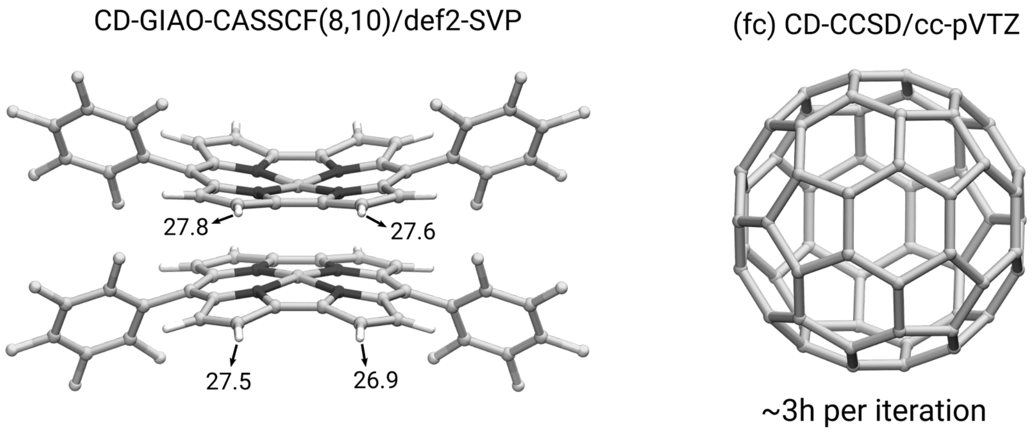

Figure 1. On the left, the NMR shielding computation at the CASSCF level of theory (the absolute values for a few representative isotropic proton shieldings are reported in ppm). On the right, the frozen-core (fc) CCSD calculation on fullerene (C_{60}) of D_{2h} symmetry.

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Biotechnological polymers for advanced technologies and applications

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Biotechnological polymers are sustainable materials produced by means of fermentation processes. They can be employed for the development of novel high-valuable biomaterials with application in many fields, such as pharmaceutical and biomedical products [1].

In this contribution, different 3D printing (3DP) materials with potential biomedical application were developed through chemical functionalization and physical blending of biotechnological polymers, as well as their loading with bioactive agents (i.e., inorganic fillers and phytochemical drugs).

Different bio-based polyesters, i.e., poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV), poly(3-hydoxybutyrate-*co*-3-hydroxyexanoate) (PHBHHx), and poly(D,L-lactide-*co*-glycolide) (PLGA), were studied for the fabrication of scaffolds for tissue engineering. In particular, PHBHHx scaffolds obtained through a melt-extrusion 3DP technique were studied for the regeneration of cartilage tissue, while PHBV-, PHBV/PLGA-, and PLGA-based scaffolds, obtained through a solution-extrusion 3DP technique, referred to as computer-aided wet-spinning (CAWS) [2], were studied for the regeneration of bone tissue. The scaffolds fabricated by CAWS were loaded with osteoinductive ceramics, such as hydroxyapatite (HA) and β-tricalcium phosphate (β-TCP), to obtain composite materials with increased mechanical and biological properties. To further increase the compatibility between the polymeric and ceramic phases and the tunability of the mechanical properties of the composite scaffolds, surface functionalization of HA, through PLGA grafting, was evaluated. PHBV and PLGA were also employed for the development of different devices for the controlled release of flavonoids (i.e., naringenin and quercetin). In particular, naringenin-loaded PHBV microrods for intravitreal implantation in the treatment of ocular diseases were fabricated by means of melt-spinning and wet spinning. In addition, quercetin-loaded electrospun PLGA meshes and 3D printed scaffolds were fabricated as potential biodegradable devised for bone tissue engineering. Chitosan hydrogels were also fabricated employing CAWS and loaded with HA to increase their mechanical properties and make them suitable for bone tissue engineering applications. The morphology of the developed samples was analyzed by scanning electron microscopy (SEM), and their mechanical properties through tensile and compression tests. The kinetics of release of bioactive phytochemical drugs was determined incubating the samples in phosphate buffered saline (PBS) solution (pH 7.4 and 37 °C) and analysing it by means of UV/Vis spectroscopy and high performance liquid chromatography (HPLC). The *in vitro* degradation kinetics of the PLGA samples was determined incubating the samples in PBS and measuring the polymer molecular weight at different incubation times using size exclusion chromatography (SEC). Finally, *in vitro* biological tests were carried out to characterize the fabricated scaffolds employing different cell lines, e.g., the murine preosteoblastic cell line MC3T3-E1. The selected cells were seeded on the scaffolds and cell viability and differentiation were evaluated at different culture times.

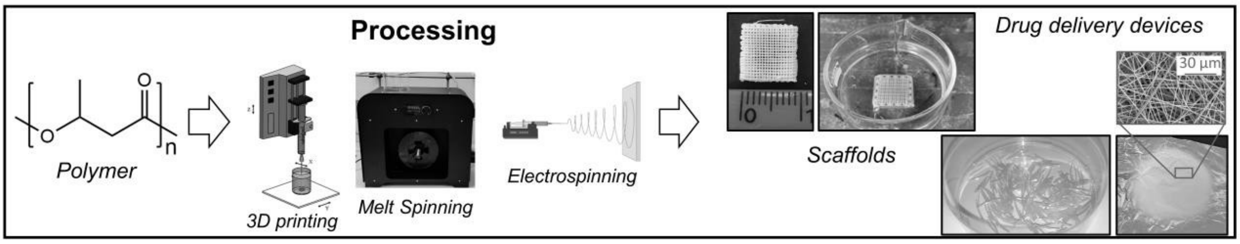

Figure 1. Schematic representation of the fabrication of polymeric devices.

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Polymeric anion exchange membranes for green hydrogen production

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Anion exchange membrane water electrolysis (AEM-WE) currently appears as the most promising technology for green hydrogen production, combining the positive aspects of both alkaline water electrolysis (AWE) and proton exchange membrane water electrolysis (PEM-WE). In particular, AEM-WE merges the use of cheaper materials for the fabrication of cell components (e.g., bipolar plates and electrocatalysts) as in AWE with the advantages of PEM-WE, which include higher current density, the possibility to work with a discontinuous electrical supply and with a diluted supporting electrolyte solution or pure water, as well as a compact cell design [1]. However, AEM-WE early-stage development limits such technology to small-scale production, and the design and preparation of high performing and cost-effective AEMs, in which the chemical, mechanical and electrochemical requirements are combined and optimized in a synergistic way, still represents a challenging task [2,3]. The present work was, therefore, aimed at addressing several unique features of AEMs for the implementation in an industrially scalable and sustainable energy-production process through a suitable synthetic strategy that involves the post-modification of a commercially available and relatively cheap poly(styrene-*b*-butadiene) (SB)-based block copolymer by grafting vinylbenzyl chloride (VBC). The synthesized SB-*g*-VBC graft copolymers were, therefore, used for the fabrication of AEMs by solution casting followed by quaternization reaction with a tertiary amine in order to effectively convert the CH_2Cl groups into cationic sites. The obtained films were thermally, mechanically and electrochemically characterized. By varying the VBC functionalization degree of the copolymers it was possible to modulate the ionic exchange capacity, conductivity, water uptake and mechanical properties of the membranes derived therefrom. The effects on the AEM properties of the inclusion of a polyamine in the quaternization reaction as well as the incorporation of hydrophilic moieties in the grafting reaction and the blending with a mechanically resistant commercial polymer were also investigated. The most promising AEMs were selected for testing in electrolytic cells (Figure 1) and were found to resist to real operating conditions for prolonged time with excellent *in-situ* performance.

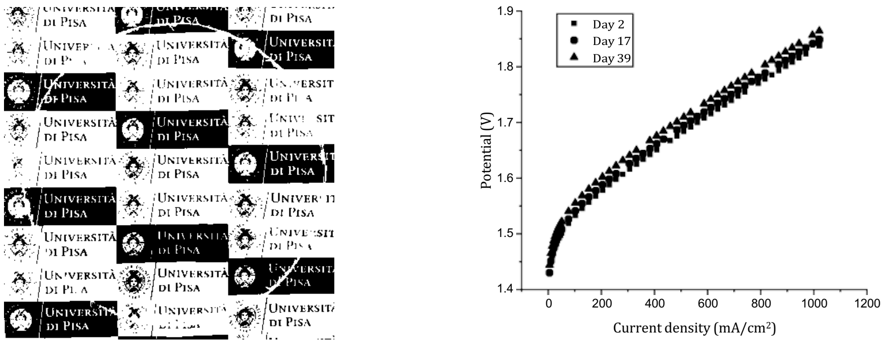

Figure 1. SB-*g*-VBC based AEM (left) and polarization curves of the AEM as a function of residence time in an electrolytic cell (KOH 1 wt % at 55 °C) (right).

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Catalysts design by predictive Modelling of Aqueous Phase Reforming of Liquid Renewable Feedstocks

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We present a computational study of the energetics and mechanisms of oxidation of Pt– Mn systems. We use slab models and simulate the oxidation process over the most stable (111) facet at a given Pt_2Mn composition to make the problem computationally affordable, and combine Density-Functional Theory (DFT) with neural network potentials and metadynamics simulations to accelerate the mechanistic search. We find, first, that Mn has a strong tendency to alloy with Pt. This tendency is optimally realized when Pt and Mn are mixed in the bulk, but, at a composition in which the Mn content is high enough such as for Pt_2Mn, Mn atoms will also be found in the surface outmost layer. These surface Mn atoms can dissociate O_2 and generate MnO_x species, transforming the surface-alloyed Mn atoms into MnO_x surface oxide structures supported on a metallic framework in which one or more vacancy sites are simultaneously created. The thus- formed vacancies promote the successive steps of the oxidation process: the vacancy sites can be filled by surface oxygen atoms, which can then interact with Mn atoms in deeper layers, or subsurface Mn atoms can intercalate into interstitial sites. Both these steps facilitate the extraction of further bulk Mn atoms into MnO_x oxide surface structures, and thus the progress of the oxidation process, with typical rate-determining energy barriers in the range 0.9–1.0 eV. Next, we extensively investigate full methanol aqueous-Phase reforming (APR) mechanisms at high coverage condition of hydrogen on bimetallic Pt-Mn (111) and Pt (111) facets. Water dissociation is the rate-determining step for CH_3OH-APR on Pt (111). Remarkably, the Mn atoms on the surface layer help to alleviate the energy barrier for H_2O dissociation to produce OH* + H* and promote hydrogen evolution. Overall, the Pt-Mn shows a better performance for methanol-APR with the activation energy barrier of 0.82 eV which is smaller than that on pure Pt (0.96 eV).

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Development of multiscale approaches for photochemical processes in complex environments

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Phytochromes are photoreceptors responsible for sensing red and far-red light in plants, fungi, and bacteria [1,2]. They can switch between the resting state (Pr) and the biologically active state (Pfr), which differ in both chromophore stereochemistry and protein structure (Figure 1). Their photoactivation is initiated by the photoisomerization of an embedded chromophore, which triggers large conformational changes in the entire protein [3]. Despite decades of studies [4-7], a comprehensive understanding of the photoactivation mechanism of phytochromes is still far from being achieved.

In previous computational work [7], we obtained atomistic details on the photoactivation mechanism of *Deinococcus radiodurans* bacteriophytochrome through an integrated multiscale approach of nonadiabatic and adiabatic molecular dynamics and IR spectroscopy simulation. In particular, we investigated the ps-timescale mechanism of chromophore photoisomerization and we showed howa histidine residue can control the kinetics of the process. The initial photoproduct evolves rapidly into an early intermediate (early Lumi-R) that relaxes on the ns-to-μs scale to a late intermediate (late Lumi-R), characterized by a more disordered binding pocket (Figure 1).

The transition to the Meta-R intermediate occurs on a timescale of tens of microseconds [5,6]. Therefore, we relied on enhanced-sampling methods to investigate such a mechanism and the role of the environment. Our simulations show how the stability of our putative Meta-R is strongly influenced by the interactions between the chromophore and the nearby residues.

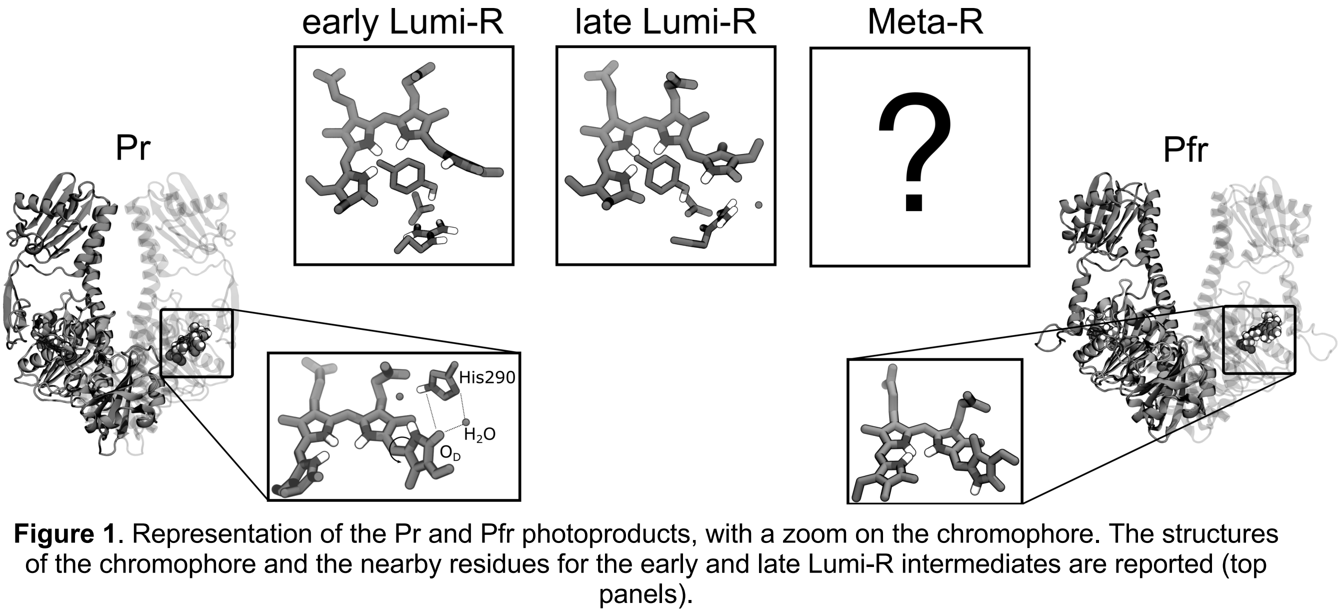

Figure 1. Representation of the Pr and Pfr photoproducts, with a zoom on the chromophore. The structures of the chromophore and the nearby residues for the early and late Lumi-R intermediates are reported (top panels).

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Electronic Circular Dichroism Imaging of Chiral π-conjugated Materials in Thin Film

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Organic π-conjugated systems are nowadays adopted as active layers in various kinds of new generation optoelectronic devices. The introduction of chiral elements in the covalent structure can guide their aggregation in the solid state [1], providing an important tool to modulate optoelectronic properties of thin films. Besides, chirality is able to promote detection [2] or emission [3] of circularly polarized light in devices and increase their performances thanks to the control of electrons' spin (chiral-induced spin selectivity) [4].

In general, the homogeneity of the active layer has a profound impact on charge mobility and overall device efficiency [5], that is why identifying inhomogeneities associated with local domains can lead to a more appropriate choice for the active material to be used in the device or to define the optimal protocol for its deposition. Optical and electron microscopies are the primary tools to investigate thin film textures, but they may not capture and cannot account for differential supramolecular order of the constituent molecules. To this end, spatially resolved chiroptical spectroscopies using highly collimated synchrotron radiation, such as Diamond Light Source B23 Electronic Circular Dichroism Imaging [6] (ECD*i*), has been demonstrated to be able to furnish insights on the distribution of possibly diverse supramolecular structures.

Herein, we will present the ECD*i* study of different chiral π-conjugated molecular systems in thin film, pointing out differences between localized and global properties. Moreover, we will introduce the development and first utilisation of Circularly Polarized Microscopy (CPM), a new technique to map ECD properties of thin layers.

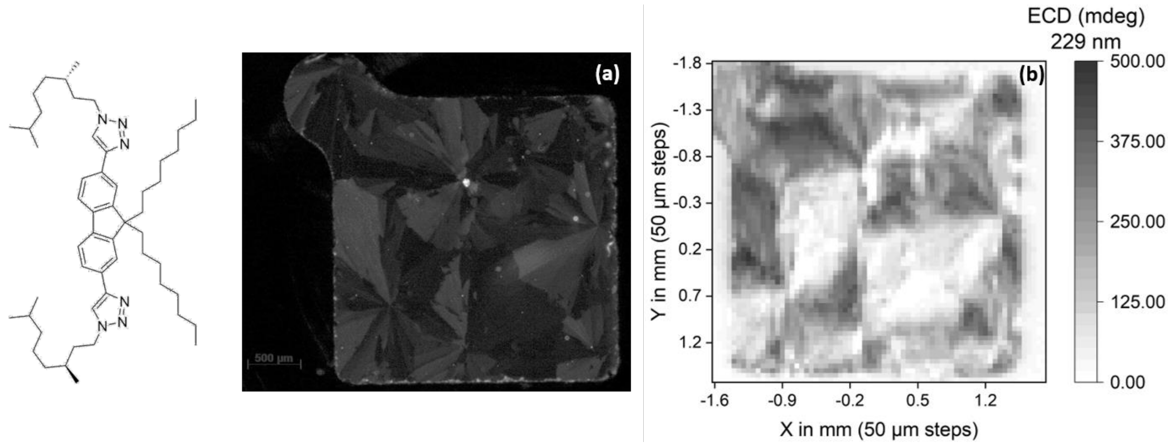

Figure 1. a) Polarized Optical Microscopy (POM) of the fluorene-based molecule reported in thin film. b) Single-wavelength ECDi map of the fluorene-based molecule reported in thin film.

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The Beauty of Invisible Light: Exploring Near-Infrared Circularly Polarized Luminescence

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In recent years, circularly polarized luminescence (CPL) has undergone a renaissance, owing to its increased popularity as a spectroscopic technique and greater accessibility to instrumentation. Novel, efficient CPL emitters have been developed, and a plethora of applications, ranging from electronic devices to microscopy, have been proposed. While most examples of CPL fall within the visible range, only a handful of cases of near-infrared (NIR) CPL-active complexes are available [1]. NIR-CPL compounds may find utility in the telecommunication industry, electronic devices, and bioassays. Due to the nature of f-f transitions, lanthanide complexes have been shown to be effective in displaying significant chiroptical properties.
A novel chiral Er complex based on a pyridine bis-oxazoline (PyBox) derivative with extended conjugation was found to exhibit strong near-infrared circularly polarized luminescence (CPL) within the 1400 to 1600 nm spectral region under 450 nm irradiation [2]. In addition, circularly polarized luminescence (CPL) was successfully measured for homo- and heteroleptic Er complexes in the same wavelength range, achieving discrimination of the left and right circularly polarized components and yielding high dissymmetry values in emission.[3] Discrimination of the left and right circularly polarized components was achieved using inexpensive optics and a commercial fluorimeter.

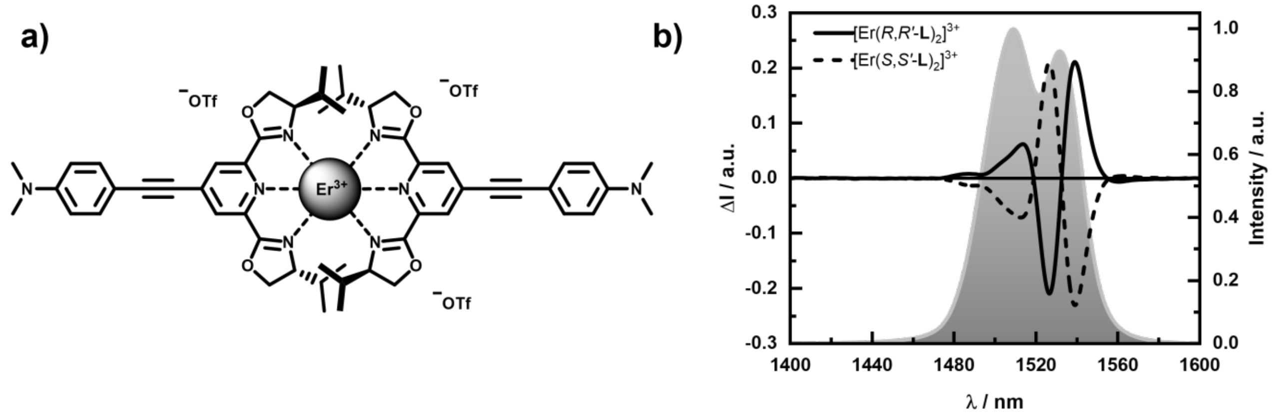

Figure 1. a) Structure of [Er(*R*,*R*-**L**)$_2$]·3OTf. b) NIR-CPL spectra of both [Er**L**$_2$]·3OTf enantiomers with the normalized emission traced in the background.

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Experimental activities and assets of the INEOS Olefins and Polymers research and development pilot plant FEX

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INEOS is a global manufacturer of petrochemicals, speciality chemicals and oil products which are supplied by our 36 separate businesses. These products form the basis of industries that touch much of our daily life - from medicines to mobile phones; agriculture to automotives; construction to technology and textiles. Even the components essential for renewable energy.[1]

Established since 2005 in Rosignano, INEOS Manufacturing Italia is part of the INEOS GROUP, multinational with headquarters office in Rolle, Switzerland, and production sites in 16 different countries worldwide. This business works as part of INEOS Olefins & Polymers Europe, one of the 18 businesses that make up the Group founded in 1998.

The Rosignano INEOS site’s flagship is the Fabrication EXpérimentale (FEX), a group resource engaged in defining and implementing corporate research and development plans in the polyolefins sector. The polyolefin research unit consists of a pilot plant for the polymerization of Polyethylene (PE) and Polypropylene (PP). The unit works within the Brussels-based Ineos polyolefins technology organization.

The pilot plant of Rosignano plays a key role in the development of new products and processes, including product simulation experiments prior to their transposition in industrial systems. The role of the pilot plant is to experiment, on reduced productions (order of magnitude 1 / 100-1 / 1000), the conditions or processes developed in the basic research phase and then verify, under very similar polymerization conditions (first continuous process step) to those of industrial plants if the transition to the production phase can be successfully achieved.

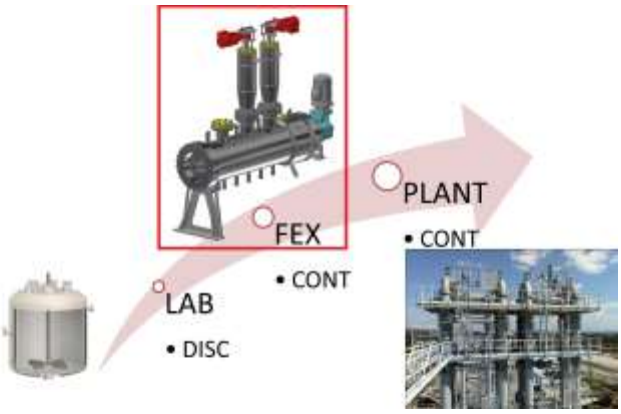

Figure 1. The key intermediate role of FEX between Lab discontinuous scale and continuous plant technology

References:
[1] https://www.ineos.com/

Failure investigation on polymer materials: metallographic laboratory approach

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INEOS is a global chemical, manufacturing and energy company (36 individual business together with a number of consumer brands). INEOS makes the raw ingredients for the products that enable and improve everyday life, harnesses science and technology to solve complex problems, on a local and global scale, thrives on challenge and pushing the limits of what's possible and encouraging people to do the same. INEOS employees are resourceful and creative; constantly learning, whilst setting bold goals and making things happen.

Among overall business, in 2015 was born INEOS Inovyn, Europe's leading producer of vinyls and in the top three worldwide, about 4,200 employees and manufacturing, sales and marketing operations in 8 countries across Europe. Our portfolio consists of an extensive range of class-leading products arranged across General Purpose Vinyls, Specialty Vinyls, Organic Chlorine Derivatives, Chlor Alkali, Hydrogen and Vinyls Technologies.

Italy is one of the Europe countries where INEOS Inovyn is present, Rosignano is the main production site. We're a leading chemicals producer of Chlor Alkali, Organic Chlorine Derivatives including research, technologies and innovation development.

Electrolysis Research Unit, so called URE, is based in Rosignano site and it gives support to all INEOS Inovyn sites having an Electrolysis plant. Within URE, in 2016 was established the Metallographic Laboratory, one of its main activities consists of performing expertise of both metallic and non-metallic materials, by means of failure analyses.

Failure analysis is referred to an extensive study of samples, that relies on collecting information and components for subsequent examination, by using a wide array of methods, such as destructive tests, microscopy and spectroscopy. The main goals of failure investigation on industrial equipment (such as tanks, pipelines, valves, gaskets…) consist of lifetime assessment and/or damages root cause(s) establishment.

This presentation reports the Metallographic laboratory approach used during the execution of failure analysis on specific cases for polymer materials, together with the potential difficulties linked to lack of standardization in comparison with metallic materials.

Based on what reported above, such activity (performing failure analysis) is considered as fundamental and strategic for all INEOS Inovyn sites, since it plays an important role to contribute to the safety of the installations and to the reliability of the plants, avoiding the possible occurrence in similar system/equipment; at the same time improvement of the fabrication quality and material selection is also ensured.

POSTER COMMUNICATIONS

The photochemical mechanism of the activation of Orange Carotenoid Protein

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Orange Carotenoid Protein (OCP) [1] is a photo-responsive protein found in cyanobacteria, responsible for their photoprotection. OCP activates in response to light absorption, going from the dark-adapted form (OCP^O) to the light-adapted one (OCP^R). Once in the active conformation, OCP is able to bind the phycobilisome (PBS), the light-harvesting apparatus of cyanobacteria, and quench the excess of energy in a process know as non-photochemical quenching (NPQ).

The series of conformational changes of OCP in its activation cycle is triggered by the light-absorption and consequent excited state evolution of the chromophore bound to OCP, a ketocarotenoid named canthaxanthin (CAN). The photochemistry following the initial excitation of the carotenoid is still unclear, and there is debate on how light absorption can trigger the conformational changes of OCP. In particular, there is no clear evidence of the molecular mechanism constituting the very first step of this process [2].

In this work, QM/MM nonadiabatic dynamics were employed to simulate the excited state decay of CAN bound to OCP [3]. We found that the $S_1 \rightarrow S_0$ conversion is characterized by multiple timescales, related to the ground-state conformational heterogeneity of the ketocarotenoid, particularly regarding the puckering conformation of the β_1 ring [4]. Our simulations also revealed a hula-twist isomerization observed in a small portion of the trajectories, which could be the atomistic mechanism of the initial trigger to the photoactivation of OCP.

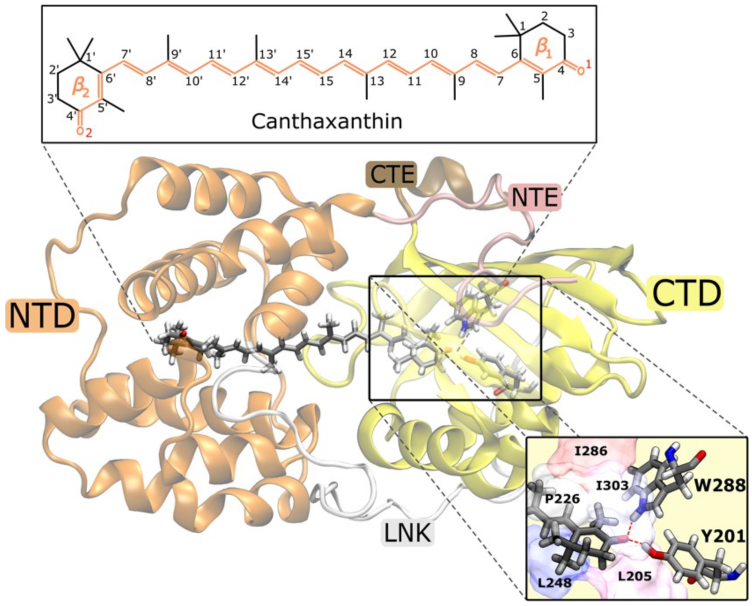

Figure 1. Representation of CAN and OCP^O structures.

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Development of different immobilzed KRED samples for the biocatalyzed reduction of BTAP to (*S*)-BTPE in a flow system

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Chiral alcohols produced through biocatalytic reduction of prochiralketones constitute important building-blocks for the synthesis of Active Pharmaceutical Ingredients (APIs) [1]. Thanks to the expansion of the enzymes market and the research in protein engineering, ketoreductase (KREDs) have proved to be suitable for applications in industrial-scale processes [2]. However, the application spectrum of this type of enzyme is often hampered by their low operational stability due to inactivation (e.g. by organic solvents, reagents and products) and by the difficulties of recovery and reuse of the biocatalyst. In recent years the immobilization of KREDs has emerged as a valid tool to obtain stable and recyclable biocatalysts [3]. In this work, a commercial KRED, produced by Enzymaster (Ningbo) Bio-Engineering Co. Ltd, was immobilized on a set of commercial organic carrier from Purolite® with different functional groups and on silica gel form Silicycle®. The immobilized enzyme samples were employed for the enantioselective reduction of 3',5'-bis(trifluoromethyl)-acetophenone (BTAP) to (*S*)-1-(3,5-bis(trifluoromethyl)phenyl)ethanol (BTPE). BTPE is an important chiral intermediate for example for the synthesis of NK-1 receptor antagonist Aprepitant. The reaction was conducted with the immobilized enzyme sample packed in a PEEK column and inserted in a flow system using a 90:10 IPA:water solvent mixture at 30°C. Five consecutive reaction cycles were performed and the conversion was monitored by HPLC. Complete conversion was reached in 24 hours and the product was recovered as a crystalline white solid for simple solvent evaporation, without further extraction. BTPE was the only product obtained with an ee>99.9% for the (S) enantiomer.

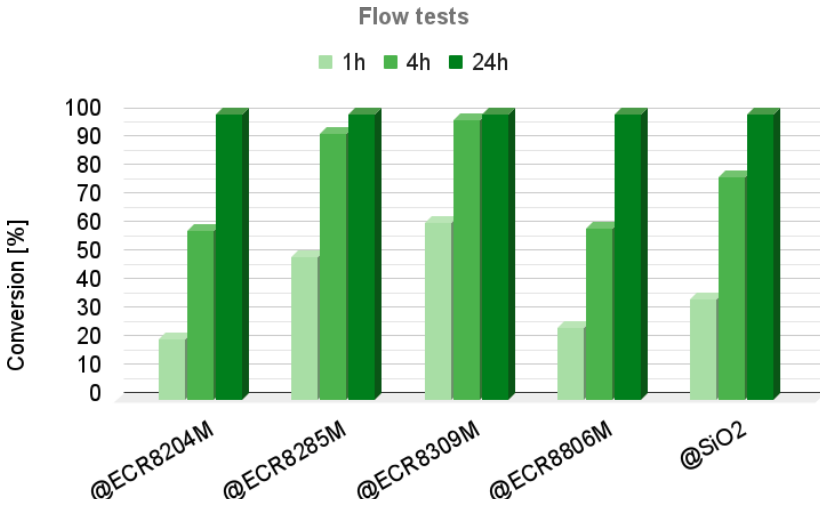

Figure 1: Conversion of BTAP to BTPE obtained in the first cycle of five consecutive cycles, performed with different immobilized samples under flow conditions and monitored at 1, 4 and 24 hours. Similar results were obtained after 5 recycles.

References:
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Multianalytical characterization of bio-microplastic after accelerated aging in artificial seawater

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Microplastics (MPs) are considered one of the most important pollutants for ecosystems worldwide. MPs are plastic debris with dimensions less than 5 mm. They can be divided in “primary microplastics”, intentionally produced as microparticles, and “secondary microplastics”, resulting from environmental degradation of larger plastic debris, as effect of mechanical degradation and photo-oxidation. In the environment, MPs can release low-molecular weight degradation products, additives, and adsorbed organic pollutants. To limit plastic pollution new types of materials have been developed: bioplastics. The term bioplastic is used for a polymer that is biodegradable and/or comes from bio-based materials or fossil sources. In this work, we evaluated changes in the chemical and thermal properties of two bioplastic materials, polylactic acid (PLA) and Mater-Bi®, after accelerated photo-oxidative aging; and we evaluated their leaching in artificial seawater. Thermal properties have been studied by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and evolved gas analysis-mass spectrometry (EGA-MS). The organic fraction leached in water has been analysed by gas chromatography–mass spectrometry (GC-MS) after solvent extraction from aqueous phase and derivatisation. Changing of chemical components after artificial aging has been evaluated by pyrolysis–GC-MS (Py–GC-MS). TGA, DSC and EGA-MS enabled us to determine changes in thermal properties of PLA and Mater-Bi® as glass transition temperature, melting temperature and thermal degradation temperature. In particular, EGA-MS profiles of Mater-Bi® showed a decrease of 10°C on the temperature of the maximum of the thermal degradation peak of the PLA fraction after four-week of artificial ageing, compared to unaged Mater-Bi®. The temperature of the maximum of the thermal degradation peak of the PBS fraction of Mater-Bi® remained constant (Figure 1). GC-MS analysis allowed us to identify the leachates resulting from photo-oxidative aging of bioplastics in artificial seawater.

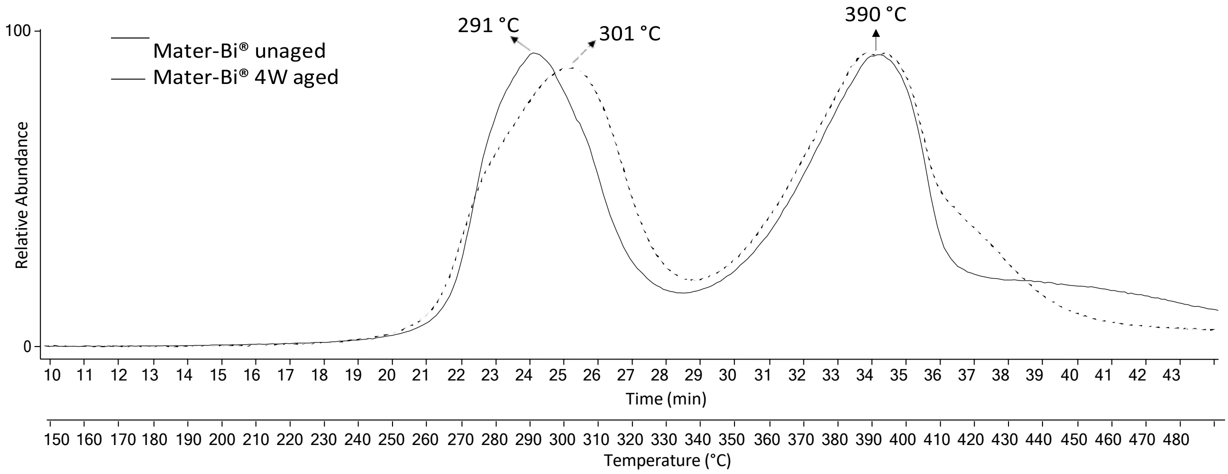

Figure 1. EGA-MS profiles of Mater-Bi® unaged (dotted line) and four-week aged (solid line).

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Mononuclear Rare-Earth metallo-ligands for the synthesis of Pt/RE heterometallic complexes

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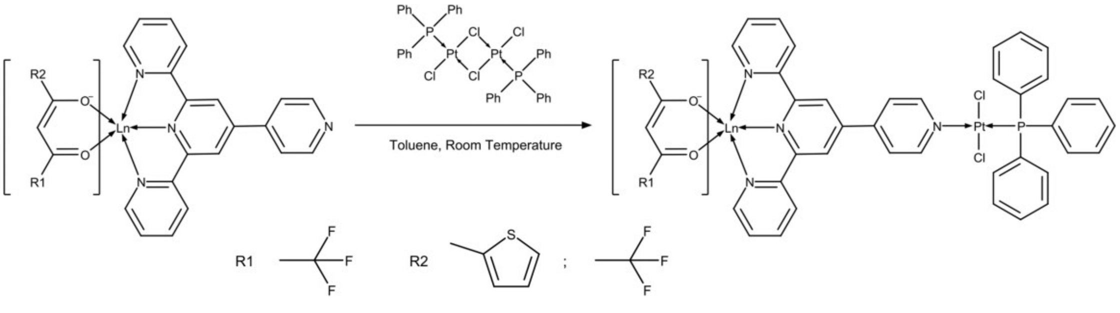
The interest towards convenient syntheses of heterometallic *d-f* complexes is continuously growing in the literature for the relevance they have in many different fields [1]. The use of preformed independently characterized molecular complexes as building blocks may guarantee a better control of the synthesis, than a coordination-driven self-assembly approach [2]. Although *d* transitionmetallo-ligands are relatively common [3], only a few *f* metallo-ligands have been used so far [4], since control of the coordination sphere of lanthanide centers is complicated by their tendency to high and variable coordination numbers and by the high lability of their compounds often involving scrambling of ligands. The divergent ligand 4'-(4-pyridil)-2,2':6',2"-terpyridine (pyterpy) has been largely employed in the synthesis in molecular compounds or coordination polymers for *d* metals [5], nevertheless for lanthanide metals only a couple of complexes have been reported [6]. Pyterpy has been shown to be able to bridge two different *d* transition metal centers, but no heterometallic *d*/*f* complex have been reported. Rare-earth *tris*-diketonato pyterpy complexes [RE(dike)$_3$pyterpy]were prepared reacting at room temperature [RE(dike)$_3$dme] (dike = tta$^-$ with Htta = 2- thenoylacetone and RE = Y, **1**; La, **2**; Eu, **3**; Dy, **4**; or dike = hfac$^-$ with Hhfac hexafluoroacetylacetone, and RE= Eu, **5**; Tb; **6**, Yb; **7**) with 4'-(4-pyridil)-2,2':6',2"-terpyridine (pyterpy). The crystal structures of **2**, **5** and **6** revealed mononuclear neutral complexes with the rare-earth ion in a coordination number nine, with the ligand coordinated only through the terpyridine unit leaving the pyridine moiety uncoordinated. Reactivity studies show that the new compounds are able to behave as metallo-ligands for complexes with a single coordination site in a square planar geometry. These metallo-ligands, **1**, **2**, **3**, **5**, **7,** promptly react at room temperature in few minutes with [Pt(μ-Cl)Cl(PPh$_3$)]$_2$ to yield the heterometallic complexes [RE(dike)$_3$pyterpy(PtCl$_2$PPh$_3$)] (dike = tta$^-$, RE = Y, **8**; La, **9**; Eu; **10**; dike = hfac$^-$, RE = Eu, **11**; Yb; **12**). In each complex, platinum centre is coordinated selectively through the pyridine moiety, leaving the rare-earth core intact during the coordination.



Scheme 1. Synthesis of heterometallic Pt/RE complexes

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Surface modification of cellulose: new methods to achieve hydrophobic and oleophobic paper

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Due to the necessity to reduce the consumption of traditional fossil-based materials and to improve the recyclability of disposable products by the choice of more environmental-friendly and sustainable processes, in recent years paper has attracted significant attention and interest for packaging applications [1]. To this purpose bio-polymers, including cellulose, can be investigated to formulate new materials with hydrophobic and oleophobic properties and low environmental impact. Existing methods about surface modification of paper report the use of multilayered, organosilane and fluorinated coatings with optimal repellence [2] but, due to the environmental persistency and potential harm for humans [3] of fluorinated compounds, they have been progressively restricted at international level. Here, two fluorine-free different approaches are proposed to functionalize microcrystalline cellulose (MCC) in order to reduce the surface hydroxyl groups. In the first method, a direct esterification reaction with long chain carboxylic acids is investigated with and without the use of solvents. In parallel, the second method aims to fabricate cationic cellulose through tosylation and nucleophilic substitution with quaternized or equivalent ammonium compounds in order to improve the affinity between the non-fluorinated compounds and the cellulosic pulp precursor in the papermaking process. Thus, in this work in collaboration with Fedrigoni company, we investigate the possibility to obtain new sustainable materials specifically designed to this purpose.

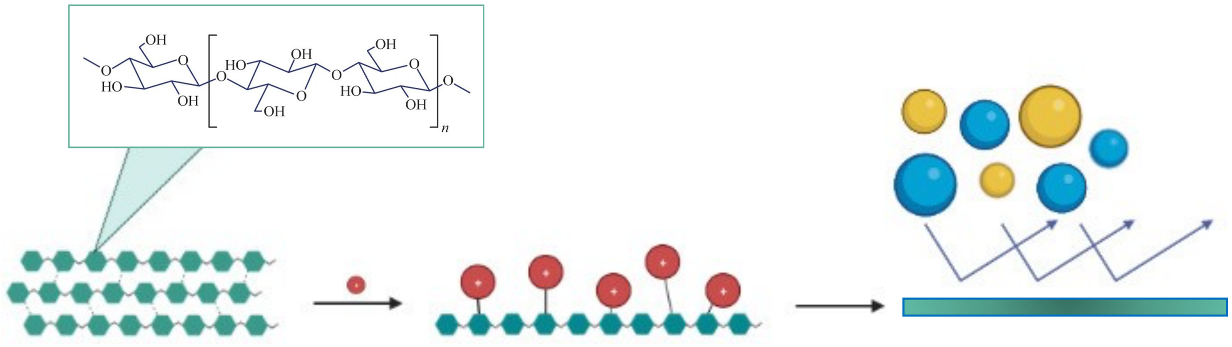

Figure 1. Schematic representation of the functionalization of cellulose to achieve hydrophobicity and oleophobicity

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Fe-coordinated Functionalized Ferrabenzenes from Diiron Precursors

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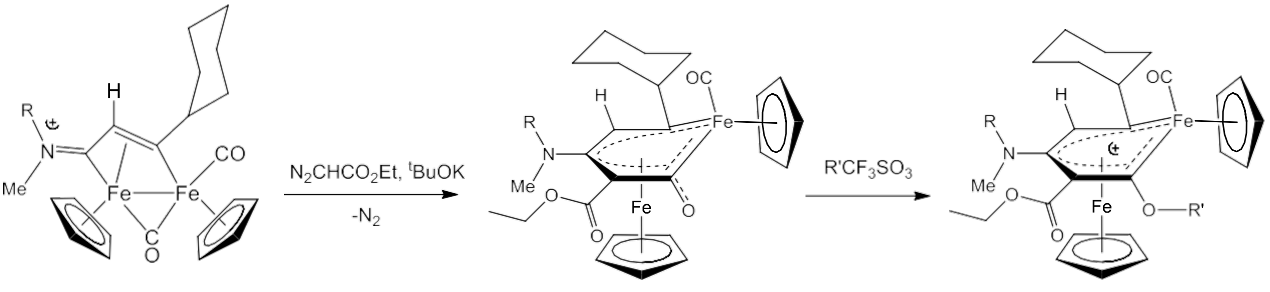
Metallabenzenes have been widely studied over the years for their unique properties and reactivity associated with the aromatic character [1,2]. While a variety of, inter alia, ruthenabenzenes and osmabenzenes have been reported, displaying in some cases a coordinating behaviour towards an external metal centre, a very limited number of ferrabenzenes are known [3]. By exploiting the advantages provided by cooperative effects offered by dimetallic complexes [4], we synthetised a new class of substituted ferrabenzenes η^6-coordinating another iron centre (**1**) via an unusual three-component reaction (Figure 1). Complexes **1** are prone to alkylation giving the cationic derivatives **2**. The identification of **1** and **2** relied on analytical and spectroscopic techniques, and single crystal X-ray diffraction studies. Computational studies were carried out to evaluate the degree of aromaticity of the six-membered ring.



1

2

Figure 1. Synthesis of iron-coordinated ferrabenzenes via carbene-aminocarbene-CO coupling on a diironscaffold. R = Me, $4\text{-MeOC}_6\text{H}_4$, 2-naphthyl; R' = Me, Et.

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Oxylipin monitoring in dried blood spot samples of Heart Failure patients

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Oxylipins are lipid mediators derived from the enzymatic or non-enzymatic oxidation of ω-3/ω-6 polyunsaturated fatty acids (PUFAs). The family of oxylipins includes hundreds of structurally and stereochemically distinct species [1], which are involved in pathophysiological and physiological processes, such as inflammation and oxidative stress.

Heart Failure (HF) is a complex clinical syndrome caused by a wide range of cardiovascular disorders, such as structural or functional abnormalities of the heart. It is a chronic and progressive condition in which the heart muscle does not pump enough blood to meet the body's needs for blood and oxygen. Oxidative stress and inflammation are deeply involved both in the acute phase of the disease and during chronic cardiac remodelling. Therefore, oxylipins can be potential markers for preventive intervention as well as reduction in hospitalizations.

Oxylipins are detected in both conventional (e.g., plasma) and unconventional biological fluids, such as saliva and dried blood spots (DBSs) [2,3]. These latter consist in collecting a few drops of capillary blood from a finger (in adults) or heel (in infants) puncture, depositing them onto a specific card, and storing away from sources of moisture after drying at room temperature. DBS sampling is minimally invasive, and it is a useful tool when venous blood drawing is impractical such as performing a cardiopulmonary exercise testing (CPET).

In our work, we propose a powerful analytical platform that couples the micro-extraction by packed sorbent (MEPS) technique to the UHPLC-ESI-MS/MS instrument for the quantitation of sixty oxylipins and PUFAs in DBS samples. DBSs were collected from HF patients and control subjects before, at maximum, and after CPET at S. Chiara hospital (Pisa).

Preliminary results suggest a different oxylipin profile between HF patients and healthy controls when they are monitored before the exercise. In addition, we observed a higher ratio between pro-inflammatory ω-6 PUFAs and anti-inflammatory ω-3 PUFAs in HF patients than controls, suggesting an unsolved inflammatory status typical of a failing heart condition. Generally, the CPET did not induce any significant change in the oxylipin levels of the recruited subjects, thus excluding a lipid profile alteration with respect to exercise.

A lipid rearrangement typical of the failing heart was clearly evidenced from our preliminary results. The targeted regulation of the inflammatory storm could be the most successful approach for the management of HF in the near future.

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UV-accelerated aging tests of beeswax found as additive in multi-component archaeological adhesives

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The use of adhesive materials marked a significant turning point in the behavioural evolution of prehistoric men. The ability of joining two different parts together to create composite tools was a major advancement in the evolution of stone tools and it paved the way for numerous possibilities for further developments of adhesive technologies [1,2]. Over time, the base materials, generally resins (either in their natural form or as tar and pitch), needed improvements and additives to meet specific and diverse requirements. Ochre and beeswax, for instance, were added to manipulate the physical and chemical properties of adhesives, including malleability, plasticity and adhesive performance [3,4]. The interaction between different components of the adhesives could significantly alter the mechanical properties of the adhesives [5]. Therefore, it is important to study how the simultaneous presence of different components could impact the aging process of each material. As already known in the literature, beeswax is susceptible to the UV radiation [6−8]. Starting from this point, we studied the modifications provided by photo-ageing on the beeswax and if the presence of a resinous material could affect this process. For that aim, double step pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) was performed using an online UV irradiator, in order to directly analyze the compounds that are generated during the exposure of the sample to UV radiation. The experiments were performed both on beeswax samples and reference mixture of beeswax and pine resin. These mixtures were also heated to simulate the most common ancient processes used in adhesives manufacturing. The gas chromatographic analysis highlighted that the terpenes of pine resin did not act as antioxidant on the beeswax components, which underwent chemical degradation to produce short-chain alkenes and aldehydes, as well as other oxidized species.

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Sustainable synthesis of biomass-derived sulfonated hydrochars and pyrochars for the production of 5-(hydroxymethyl)furfural

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Lignocellulosic biomass is one of the most important renewable bioresources containing cellulose, hemicellulose and lignin and represents a valid feedstock for producing renewable fuels and platform chemicals [1]. Various processes can cause the biomass deconstruction and among them, the hydrothermal carbonization treatment (HTC) plays a crucial role to synthesize "high-quality" carbon-based materials, named hydrochar [2]. In particular, HTC is a promising technique that promotes the deoxygenation of biomass in water under subcritical conditions and it can be applied to various biomass types, including wet and waste ones, without the need for any pre-drying step. The obtained hydrochars show potential applications, such as adsorption, energy storage, CO_2 sequestration, catalysis etc. In this last context, within the project PRIN 2020 LEVANTE "LEvulinic acid Valorization through Advanced Novel Technologies", different hydrochars have been synthesized starting from model compounds (glucose and xylose), cellulose and hazelnut shells as real lignocellulosic biomass to be used as precursors for the preparation of biomass-derived catalysts. The effects of the main reaction parameters, such as temperature, reaction time and cellulose loading, on hydrochar yield were studied through a chemometric approach, revealing that both the hydrochar yield and its reactive functionalities are mainly dependent on reaction temperature and time, with a modest effect due to cellulose loading. In particular, the multivariate analysis identified the optimal reaction conditions (220 °C, 5 hours with 20 wt% of biomass loading) to maximize both the hydrochar yield and its reactive functionalities. The obtained systems were characterized by elemental analysis, SEM, EDS, FT-IR, TGA and total acidity. Subsequently, pyrochars resulting from the pyrolysis of the obtained hydrochars have been synthesized and all the produced chars, hydrochars and pyrochars, were sulfonated with sulfuric acid and tested in the acid-catalyzed hydrothermal synthesis of 5-(hydroxymethyl)furfural, adopting microwave irradiation [3]. The achieved high yields of about 40 mol% are in agreement with the best data obtained for the same reaction in the literature with sulfonated biochars and with commercial resins, thus confirming their promising potential as heterogeneous green acid catalysts.

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P10

Evaluation of matrix interference in the analysis of microplastics in sediments by means of Py-GC-MS

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Microplastic (MP) pollution is acknowledged as an environmental and social issue. Nowadays an increasingly large number of studies are focused on determining MPs in different environmental matrices. When approaching MP analysis in environmental samples by analytical pyrolysis-based techniques (pyrolysis-gas chromatography-mass spectrometry, Py-GC-MS), sample pretreatment is crucial, and it frequently implies time-consuming procedures. These procedures usually consist of subsequent purification steps such as physical separation, digestion, and extraction prior to the actual analysis, with the aim of isolating MPs from the undesired organic and inorganic fractions of the matrix. Optimization of such pretreatment procedures and evaluation of their actual necessity for the different environmental matrices has great potential to lead to significant improvements in MP analysis, by reducing the amount of time and reagents required for sample preparation.

In this work, we evaluated the interference of inorganic and organic matrix components on the quantitation of synthetic polymers by Py-GC-MS. Marine sediment samples were taken as reference matrix and subjected to a multi-step sample preparation procedure which included pre-oxidation with H_2O_2, density separation with aqueous $ZnCl_2$, buffered multi-enzymatic digestion, and catalysed Fenton oxidation [1]. Some of the samples were subjected to the full pretreatment procedure, while others underwent only some of the steps. Three matrix fractions were obtained in this way, as shown in Figure 1: the inorganic fraction, the untreated organic fraction, and the fully treated organic fraction. Moreover, two sets of these fractions were distinguished, by either performing or skipping the initial H_2O_2 pre-oxidation step.

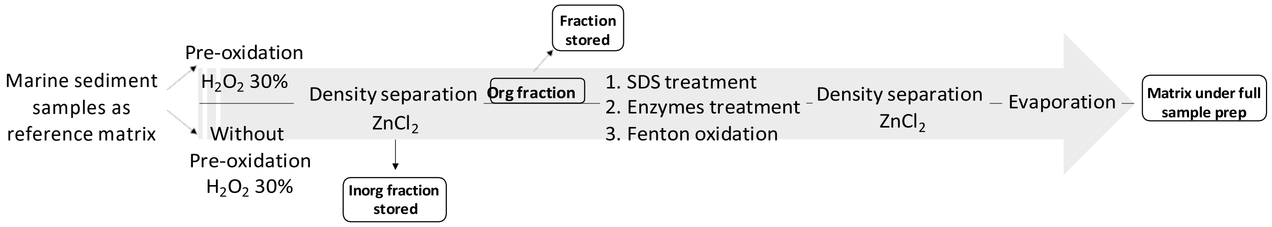

Figure 1. Sample preparation protocol applied to marine sediment samples.

The matrix fractions were spiked with six reference polymers (polyethylene, polypropylene, polystyrene, polyethylene terephthalate, nylon-6,6, polyurethane) and calibration curves were built by Py-GC-MS analysis. These calibration curves were compared with external ones to evaluate matrix effects. Polyolefins were less affected by the presence of the matrix fractions compared to polycondensation polymers. The results of this study will help to evaluate the effect of different steps of the procedure, when approaching Py-GC-MS analysis of marine sediment samples for MPs, and to obtain a better understanding of matrix effects in different environmental samples.

This study was supported by the North Atlantic Microplastic Centre (NAMC, https://namc.no/), a research consortium coordinated by NORCE (Norway) of which the University of Pisa and Aalborg University are partners.

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Integrated valorization of marine residue *Posidonia Oceanica* balls for the production of value added chemicals

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Posidonia Oceanica balls (POb) are fibrous residues that are difficult to degrade and tend to accumulate in an uncontrolled manner on Mediterranean beaches, thus causing various environmental problems. Most of this marine residue is conferred in landfills and disposed into incinerators [1]. Therefore, greener alternative treatments aiming at their valorisation simultaneously overcoming the environmental problems related to their accumulation would be very urgent. The chemical conversion of POb into high value products could represent a sustainable and innovative solution. On this basis, in the present study, the composition of washed POb was initially evaluated highlighting a discrete amount of extractives (3.3 wt%), mainly formed by steroid derivatives, ingol derivatives and fatty acids, which could find application as antioxidants, antimicrobials and anti-inflammatories. Moreover, a remarkable amount of cellulose (28.2 wt%), which represents a potential source of platform chemicals, monomers and bio-fuels, has been found. In particular, in this work, the cellulose fraction has been exploited for the synthesis of a highly interesting product, such as *n*-butyl levulinate (BL), one of the most promising bio-fuel blending additives for Diesel engines [2]. Hence, raw POb were employed as low cost feedstock in the direct alcoholysis, adopting *n*-butanol as a green reagent/reaction medium and sulfuric acid as a cheap homogeneous catalyst. The reaction was performed under microwave heating, an alternative and more efficient system than the traditional one [3]. The optimal alcoholysis conditions have been found by properly tuning the temperature, the biomass loading and the sulfuric acid loading. However, solutions of sulfuric acid below 1.3 wt% could not be used due to the partial neutralization effect of the ashes (12.4 wt%). The highest BL yield of 42 mol% was achieved with a biomass loading of 5 wt% at 190 °C after 30 min. Noteworthy, physical pre-treatment (ball-milling) was investigated to increase the accessibility of cellulose, thus allowing the reaching of analogous BL yield under the same reaction conditions but using a higher biomass loading (14 wt%) of paramount importance to produce concentrated BL streams. Also, the alkaline pre-treatment of POb has been preliminarily investigated, aiming at the removal of the lignin fraction, responsible for the recalcitrance of the cellulose conversion. In particular, this approach could allow the recovery of a cellulose-enriched residue, much more prone towards the alcoholysis, and lignin that can find applications as protective UV-absorbent, batteries, resins, etc. In conclusion, for the first time, an integrated valorization of POb has been proposed giving mainly antioxidants, antimicrobials and anti-inflammatories compounds, as steroids and ingol derivatives, bio-fuels, as BL, and lignin.

Acknowledgements: The authors are grateful to the European Union and Italian Ministero dell'Università e della Ricerca for the financial support provided through the PNRR project NEST. Project code PE0000021, Concession Decree No. 1561 of 11.10.2022 adopted by Ministero dell'Università e della Ricerca (MUR), (CUP I53C22001450006) Spoke n. 3 BIOENERGY & NEW BIOFUELS FOR SUSTAINABLE FUTURE.

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Collagen-Grafted 3D Poly(ε-Caprolactone) Scaffolds for Tendon Tissue Engineering

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The tendon is a dense connective tissue connecting muscles to bones and transmitting the forces that allow movement. Tendon has a complex structure characterized by a precise hierarchical organization, where the main component present in the form of well-ordered fibres is collagen type I. As human lifespan expands and sedentary lifestyle increases, tendon injuries affecting the quality of life of individuals of all ages are approximately 30 million new cases per year. Tissue engineering strategies recreating the native biochemical microenvironment have a high potential for obtaining *in vitro* tendon cell models [1]. In this work, poly(ε-caprolactone) (PCL) scaffolds fabricated via an additive manufacturing (AM) technique based on a computer-aided wet-spinning (CAWS) process were investigated [2]. A grafting procedure for covalently bonding to PCL matrix two types of collagen (I or III) by means of N-ethyl-N′-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC)/N-hydroxysuccinimide (NHS) was optimized in order to mimic the native and altered extracellular matrix (ECM) composition of tendon tissue, respectively. Both collagen type I and type III grafting neither altered the scaffold stiffness nor the polymer thermal behaviour. Instead, the surface morphology of the PCL scaffold was affected by the presence of collagen, by masking the typical microporosity of scaffolds obtained through CAWS and increasing the scaffold fibre diameter. Human tendon-derived cells (hTDCs) seeded on these biomimetic scaffolds proliferated faster and deposited higher levels of proteins, including those typical of the ECM, in comparison to what achieved with non-functionalized PCL scaffolds (Figure 1).

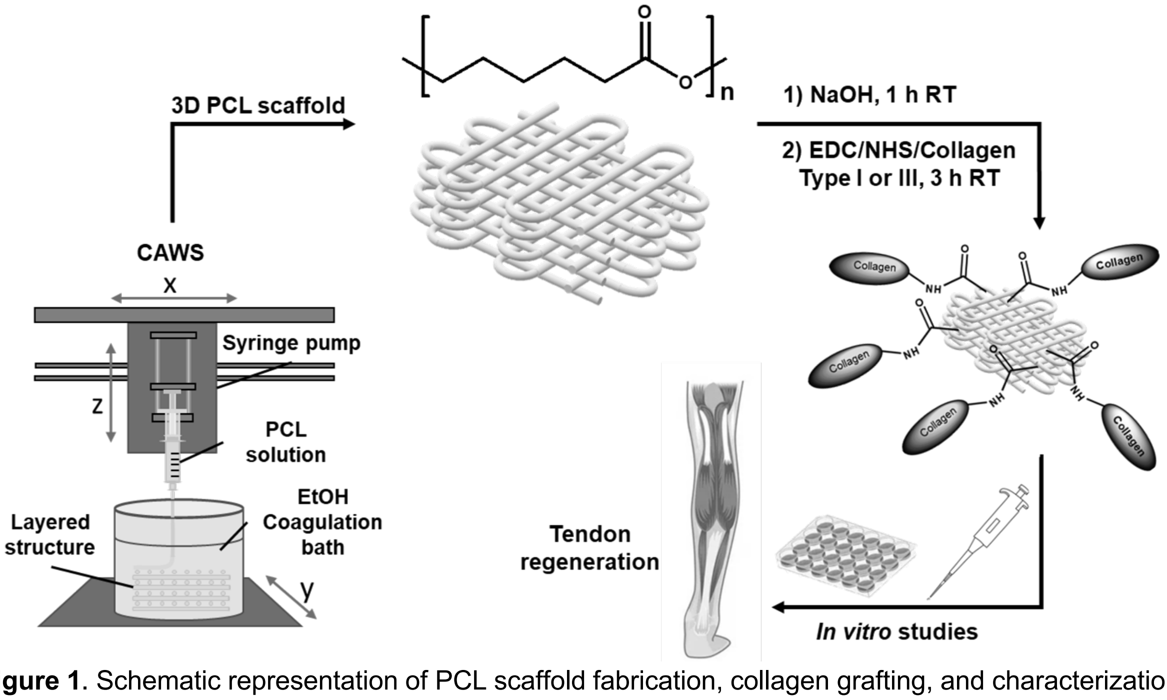

Figure 1. Schematic representation of PCL scaffold fabrication, collagen grafting, and characterizations.

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FT-IR Spectroscopic Analysis in tandem with chemometric tools for the characterization of Cecal Content of Mice: Effects of High Fat Diet and Beer

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Metabolite profiles associated with the gut microbiota offer valuable insights into the influence of lifestyle and dietary factors on both health and diseases in animal models and in humans. In recent years, infrared spectroscopy has been demonstrated to be a valuable tool to investigate fecal and cecal content [1-5]. This study focuses on investigating the metabolite composition of mice cecal content using a fast and novel Fourier-transform infrared spectroscopy (FT-IR) method that involves the deposition of samples onto polypropylene sheets, enabling efficient analysis and characterization of metabolites and offering advantages such as requiring small sample quantities and minimal preparation steps [6]. Experimental procedures included extracting the cecal content, preparing the sample, and depositing it onto polypropylene sheets before and after filtration in 3 kDa microfiltration units. The FT-IR spectra were acquired using a high-resolution FT-IR spectrometer equipped with an attenuated total reflection (ATR) accessory. Preliminary results of principal component analysis (PCA) of the FT-IR spectra demonstrate the feasibility and efficiency of the method to characterize low molecular weight (LMW) metabolites and biomolecules in mice cecal content. Distinctive spectral features corresponding to various metabolites were observed in four groups of mice reared for 10 weeks in the following conditions: they were fed with standard diet (19% proteins, 6% fibers, 7% minerals and vitamins moisture, 64% carbohydrates and 4% fats), high-fat diet (26% proteins, 6 % fibers, 7% minerals and vitamins moisture, 26% carbohydrates and 35% fats); standard diet + 0.23% beer; high-fat diet + 0.23% beer**.** Our findings suggest diet-induced variations in the high and low molecular weight metabolite profiles and showcase the potential of the developed method for studying the impact of diet on gut metabolism. Further analysis and the interpretation of FT-IR spectra will be conducted using also other complementary techniques to identify specific metabolites and elucidate their variations among the different diet groups. FT-IR method with the deposition on polypropylene sheets provides a valuable tool for the efficient, low-cost, and reliable characterization of cecal content metabolites, eventually contributing to the understanding of the effects of healthy lifestyles on gut composition and metabolism.

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P14

Method development for the full derivatisation of catechols in Asian lacquers using Py(HMDS)-GC/MS coupled with Online Micro Reaction Sampler

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Asian lacquers are made from the sap of trees belonging to the *Anacardiaceae* family, mainly *Toxicodendron vernicifluum*, (China, Japan, and Korea) *Toxicodendron succedaneum* (Vietnam and Taiwan) and *Gluta usitata* (Myanmar, Cambodia, and Thailand). The main chemical components are mixtures of long-chain alkylcatechols referred to as urushiol, laccol and thitsiol, respectively. These have chemical differences that enable the differentiation of the three types of lacquer to be obtained, so that questions about object provenance can be answered. This work focuses his attention on urushi and thitsi lacquer formulations with the aim to investigate the trimethylsilylation of catechols using HMDS, which is needed for gas chromatographic analysis of these compounds. Mock-up samples were prepared and analysed by Py-GC-MS at both 600°C and 400°C as well as Py-GC–MS coupled with a micro-reaction sampler (MRS). The MRS allows to seal the sample in a capsule with the derivatizing agent so that the residence time can be extended. The results showed that the instantaneous in situ derivatization occurring during traditional Py-GC-MS mostly yields monoderivatised catechols for steric hindrance reasons. By contrast, by extending the residence time of the sample/HMDS system to 12 s using MRS, catechols are fully derivatized, thus reducing the complexity of the pyrogram. The study confirms the time-dependency of trimethylsilylation and the suitability of MRS to improve the quality of Py(HMDS)-GC-MS data in the field of lacquer analysis.

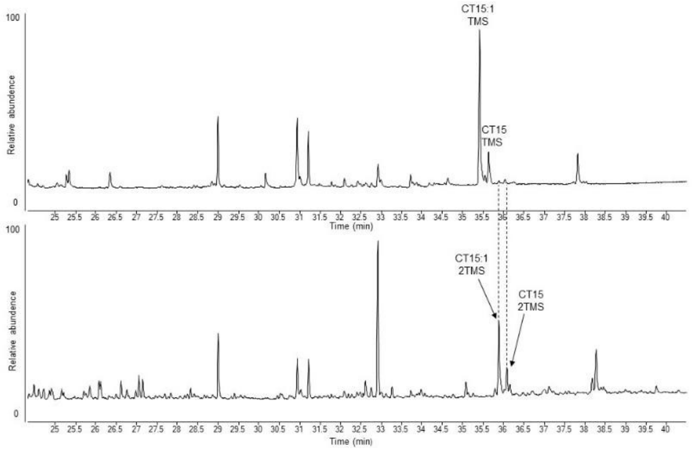

Figure 1.TIC obtained by Py(HMDS)-GC–MS and by MRS-Py(HMDS)-GC–MS analysis of urushi lacquer

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Attractive chiral azole-based chromophores for optoelectronic applications

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Chiral π-conjugated molecules represent attractive starting materials for the preparation of several optoelectronic devices such as Circularly Polarized Organic Light-Emitting Diodes (CP-OLEDs) and CP-laser [1]. For these purposes, conjugated molecules are typically studied in the form of thin films. The electronic properties (e.g. absorption and emission profile, HOMO-LUMO band gap) that emerge in thin films depend not only on the chemical structure of the molecules but also on their organization in the solid state. In such respect, the presence of chiral elements in the starting material may result in the formation of chiral supramolecular architectures and ultimately affect the properties of the film [2].

A potential approach for introducing chirality in π-conjugated molecules consists in decorating the chromophore with enantiopure moieties derived from the chiral pool [3]. Based on this strategy, in this work we synthesized several azole-based π-conjugated molecules, decorated with (S)-β-citronellol as the chiral aliphatic moiety (Figure 1).

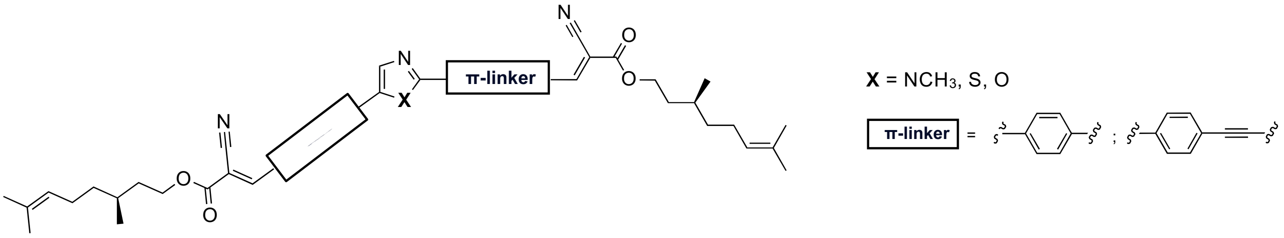
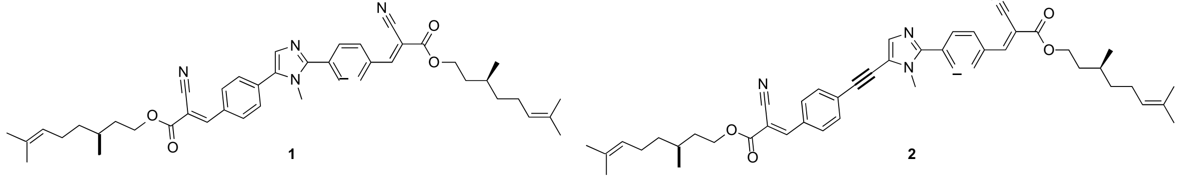


Figure 1

In the preliminary part of this study, we prepared 2,5-diarylazole nuclei through palladium-catalyzed direct arilation and added (S)-β-citronellol to these scaffolds using a Knovenagel condensation [4]. Then, we evaluated their optoelectronic properties and the film deposition techniques: during this screening, N-methyl-1H-imidazole emerged as the most promising heteroaromatic core (**1**, Figure 2). Subsequently, we focused our attention on imidazole core with the aim of optimizing its properties through modifications to the conjugated system. To this end, one-pot sequential bromination and Sonogashira coupling or palladium-catalyzed dehydrogenative alkynylation were employed [5,6].

The introduction of an acetylene moiety in C-5 position of the azole resulted in an improvement of both electronic properties and film preparation method (**2**, Figure 2).



g_{lum}= -0.13
film deposition by drop casting

g_{lum}= -0.22
film deposition by spin coating

Figure 2

References:
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Innovative biorefinery process for the fractionation and conversion of giant reed to carotenoids and triglycerides

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In the last decades the increase in the use of fossil resources contributed to several environmental issues. The replacement of traditional refineries with innovative biorefinery is necessary to reduce the impact of human activities [1]. Biorefinery processes convert low or negative value biomasses into energy, materials and bioproducts. Lignocellulosic biomasses, such as giant reed, are renewable feedstock that does not interfere with food industry, mainly composed of lignin, cellulose and hemicellulose. The last two fractions are biopolymers that can be used as starting material for the production of fermentable sugars or other platform chemicals by chemical and/or biological catalytic approaches. *Rhodosporidium toruloides* is an oleaginous yeast able to convert sugars into carotenoids and triglycerides [2]. Carotenoids are high added-value molecules employed in different fields, such as food industry, human health and semiconductors [3]. Triglycerides are platform chemicals that can find applications in several industry sectors related to human health, nutraceutical, biosurfactant and biopolymers. From an industrial point of view production, microbial triglycerides and carotenoids are a sustainable alternative respect to vegetable oil or carotenoids extracted from plants and/or food. In this context, the aim of this work is to design, develop and optimise an innovative multi-step process for the fractionation of giant reed and conversion of its holocellulose fraction to carotenoids and triglycerides, according to the following steps: i) hydrothermal pretreatment of giant reed in the presence of dilute imidazole for removing lignin; ii) enzymatic hydrolysis of the polysaccharides-rich pretreated solid to glucose and xylose by the industrial enzymatic mix Cellic® CTech 3; iii) fermentation of hydrolysates to carotenoids and lipids. Pretreatment is affected by several parameters (concentration of imidazole, temperature, reaction time, solid to liquid ratio) which were optimised in the present work. Under the optimised reaction conditions for pretreatment and hydrolysis, about 60 wt% of lignin removal was achieved, together with glucose and xylose yields of 99 and 82 mol%, respectively. Also the fermentation process with *Rhodosporidium toruloides* was optimised both adopting synthetic media and raw biomass hydrolysates, investigating the effect of C/N ratio, inoculum size, nutrients composition and process kinetics. Under the optimised process conditions, the carotenoids and lipids productions were 103 mg/L and 1.1 g/L, respectively, a promising value for next studies.

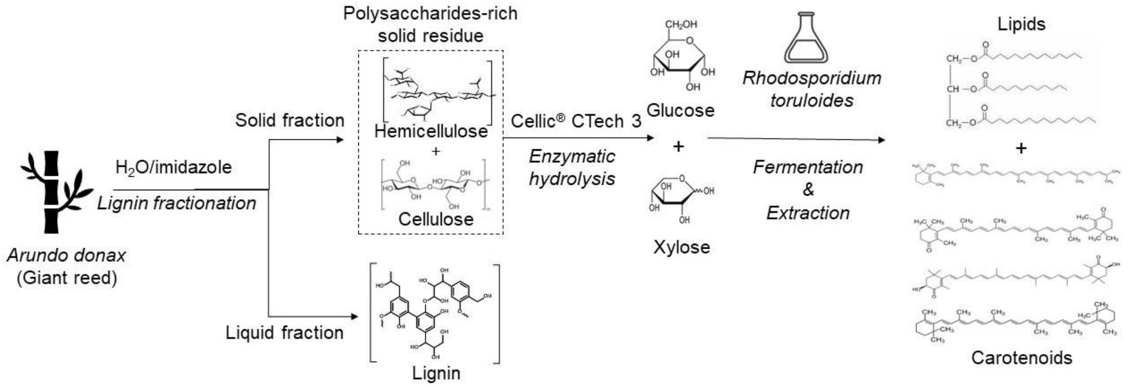

Figure 1. Process layout of the innovative biorefinery process developed in the present study.

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Electrochemical biosensor based on CRISPR/Cas technology for the detection of waterborne pathogens

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Water resources contaminated with pathogen microorganisms are a vectors for the propagation and transmission of diseases, especially in developing countries. Traditional techniques are time consuming, expensive and require highly trained personnel. Biosensors represent a valid alternative, because of their low-cost, portability, ease of use and availability for point-of-need applications [1]. Thanks to its programmability, selectivity and specificity, the newly discovered Clustered Regularly Interspaced Short Palindromic Repeats (CRISPR) and CRISPR associated protein (Cas) system can be used to recognize a specific portion inside of a nucleic acid target, developing a new class of biosensing [2]. In this work, the CRISPR/Cas12a system is integrated with isothermal Recombinase Polymerase Amplification (RPA) method, to develop a portable, low-cost and highly specific point-of-need electrochemical biosensor for the detection of bacteria in drinking water. In particular, a rationally designed ssDNA reporter labeled with methylene blue (ssDNA-MB) is functionalized on the working electrode surface and detected by using Square Wave Voltammetry (SWV) electrochemical technique. Once the CRISPR/Cas12a system specifically detects the pathogen target sequence, the trans-activity is triggered and the reporter ssDNA is cleaved, causing the decrease of the SWV MB associated signal (Figure 1). The cleavage ability of the enzyme for both gold disk and screen printed gold electrodes is compared in different conditions, such us different incubation times, concentration of target DNA and ssDNA-MB.

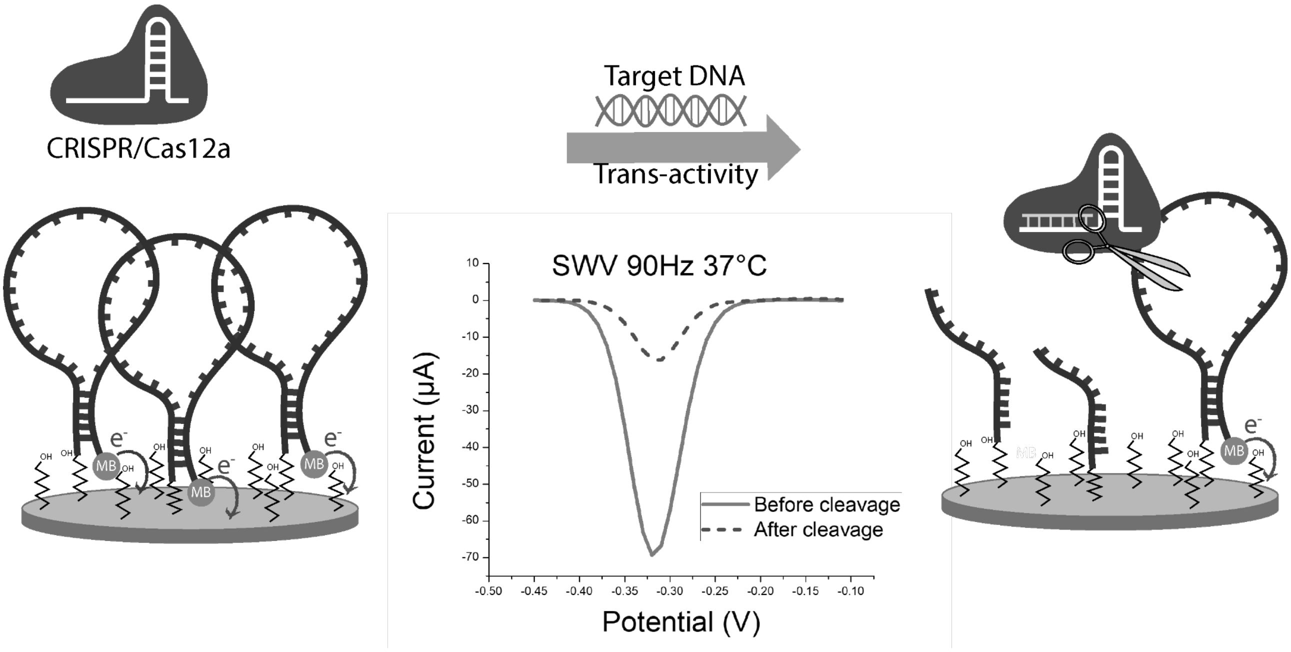

Figure 1. Working principle of the sensing system: recognition of the target DNA, cis-activity and trans-activity by CRISPR/Cas12a on the electrode surface.

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Chemistry for the Future - 2023

Curing of ultramarine blue oil paints: the effect of different characteristics of the pigment

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Ultramarine blue is a deep blue inorganic pigment. It’s a sodium aluminium sulfosilicate with approximate formula $Na_{6\text{-}8}Al_6Si_6O_{24}S_{2\text{-}4}$, where the proportions of Al, Si and O are fixed, while those of Na and S are variable [1]. Originally, this color was made by grinding lapis lazuli, a precious stone known since the Egyptians, and purifying it with a complex process. Starting from the 19th century, ultramarine blue has been artificially produced by heating kaolin, soda, sulfur and coal at high temperatures (800°C) [2]. The chemical composition of artificial ultramarine blue is variable and depends on the ratio between the raw materials and on the experimental conditions of the preparation.

A previous study [3] demonstrated that synthetic ultramarine blue in an oil paint has the tendency to favor the oxidative degradation of the organic binder over cross-linking. This may have consequences on the stability of the paint layers produced, as they can be quite polar and poorly cross-linked. The aim of this study is to understand how the origin and the characteristics of different ultramarine blue pigments influence the effect exerted by the pigment in the curing of an oil paint layer.

To this aim, we selected different artificial ultramarine blue pigments and a sample of natural ultramarine blue from lapis lazuli. The pigments differ for particle size distribution and types of additives. The pigments were characterized by SEM and XRD to investigate the particle characteristics and mineralogical composition. Model paints were prepared with linseed oil, and were analyzed using ThermoGravimetric Analysis (TGA), Rheological Analysis and Evolved Gas Analysis – Mass Spectrometry (EGA-MS). This approach enabled the systematic comparison of the rheological properties, curing kinetics, oxidative behavior of the paints, and the molecular characteristics of the paint films.

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A didactic sequence about Uv-vis Spectroscopy inspired by the historical evolution of spectroscopic instruments

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Teaching and learning sequences (TLSs) represent a relevant inquiry in the field of chemical education since the 1980s. TLSs involve the design and implementation of topic specific sequences in order to address specific topic-related learning problems [1,2].

In this work, we'll focus on teaching and learning UV-Visible spectroscopy at high school level and first introductory undergraduate courses. This topic and how it is presented to students raises several issues that were investigated by a priori epistemological analysis within the theoretical framework of Johnstone's triangle [3] and actual developments in chemistry education.

One of the relevant issues is related to the introduction to high school students of the absorption of light by matter underlining all phenomenological aspects [3], in order to promote a meaningful, and not rote, learning [4]. The design of a research inspired topic-oriented sequence, proposed in this work, is based on the study of historical instruments and fundamental experiments that date back to the earlier days of emission and absorption spectroscopy. The characteristics of these instruments and related experiments of being visual, optical and photographic devices was deeply investigated. Taking advantage of the presence of real historical instruments (located at the Department of Chemistry of the University of Pisa and at the Department of Chemistry of the University 'La Sapienza' of Rome) key experiments based on their operation principles were designed. A selection of instruments is reported in Figure 1.

The didactic sequence is organized in a not linear, but systemic map [5] pointing out the crosslinks between different activities and/or concepts. Part of the sequence was already validated in a pilot study involving high school students and undergraduate students. Further validations are in progress in order to have a more quantitative analysis of the obtained results.

Figure 1. Two models of color comparator or visual colorimeter, from left to right, a Wolff's colorimeter (University of Pisa) and a Duboscq's colorimeter (University "La Sapienza" of Rome).

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Synthesis, chemical characterization and biological evaluation of new hydrophilic gold(I) and silver(I) N-heterocyclic carbenes as potential anticancer agents.

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Metal NHC complexes have been extensively investigated as anticancer candidates due to their advantageous features of stability, which allow a better transport and distribution to cancer cells, and versatility, which offers the possibility to fine-tune their electronic and steric properties [1]. Despite silver(I)-NHCs being investigated mainly for their antimicrobial activity, their antiproliferative properties have recently emerged, raising interest in them as new anticancer candidates [2]. Gold(I)- NHCs, on the other hand, have been widely studied for their cytotoxic effect, which is often related to their ability to inhibit the selenoenzyme thioredoxin reductase. Besides the cytotoxic activity against cancer cells, one of the pivotal aspects to consider in designing novel drugs is the correct balance of lipophilicity/hydrophilicity properties in the final molecule. Indeed, the solubility in aqueous media is crucial to guarantee adequate stability and concentration of the drug in the systemic circulation [3], but the molecule should also have the proper lipophilic character to allow the cellular membrane crossing and the consequent metal uptake [4]. In this context, we synthesized and characterized a series of novel gold(I) and silver(I) complexes of N-heterocyclic carbenes bearing a 1-thio-β-D-glucose-tetraacetate moiety, in an attempt to improve water solubility and to exploit the Warburg effect to increase the overall selectivity for tumor cells. Solution studies of interactions of these species with biologically relevant proteins, such as human serum albumin (HSA) and superoxide dismutase (SOD), have been conducted via UV-Vis absorption spectroscopy and high- resolution ESI mass spectrometry. Inhibition studies of the selenoenzyme thioredoxin reductase (TrxR) have been carried out. In addition, the cytotoxicity of the synthesized compounds has been evaluated in the ovarian cancer cell lines A2780 and A2780/CDDP-R (cisplatin-resistant) and in the healthy cell line HSkMC (human skeletal muscle cells).

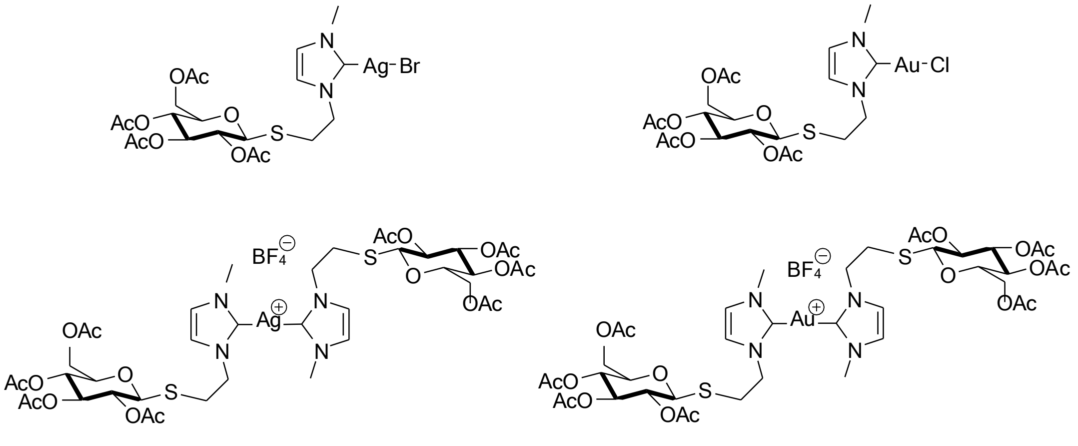

Figure 1. Structures of the new Au(I) and Ag(I) NHC-complexes.

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Cellulose nanocrystals based-materials for circularly polarized luminescence

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The development of new materials from renewable resources represents an important challenge to reduce the dependency from fossil reserves. In this context, cellulose represents one of the most interesting natural materials for its applications in many areas, such as in the fields of electronics and bio-electronics [1]. Cellulose nanocrystals (CNCs), crystalline rods with average length between 100 and 500 nm and diameter ranging from 5 to 50 nm, are able to self-assemble into a cholesteric phase, with the chiral macrostructures being preserved in solid films. These films show interesting chiroptical properties, namely a different transmission of left and right polarized light [2,3]. Due to this property, when suitably doped with luminescent compounds, CNCs films can give rise to intense circularly polarized luminescence (CPL) [4].

In this communication, we present the production of sulphated CNCs, their functionalization with fluorophores and ligands for emissive lanthanides and the preparation of multi-layered CNCs films with both achiral and chiral luminescent lanthanide complexes. The functionalized CNCs and the multi-layered films were then characterized by means of optical and chiroptical technique and in particular CPL spectroscopy.

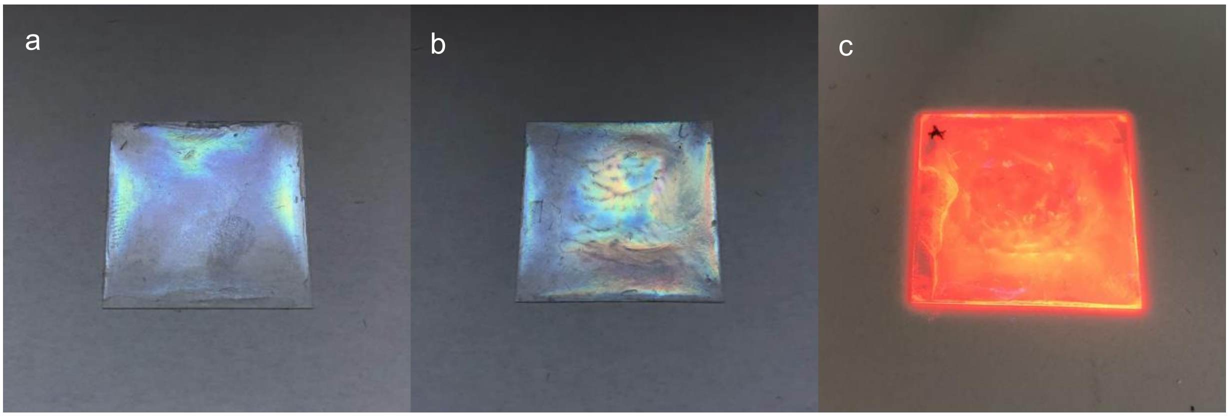

Figure 1. a) CNCs film; b) CNCs/glycerol film multi-layered with Eu(TTA)$_3$(R,R)^{i}Pr-PyBox under normal light and c) under UV light.

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Highly sensitive chemoresistive sensors based on Cu/Pd-doped CeO_2 for hydrogen detection at room temperature

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Hydrogen is considered the most promising energy vector of the future, capable of replacing fossil fuels. Its use is expected to significantly increase in the next decades, but several safety issues have to be dealt with. In fact, hydrogen is a potentially dangerous gas, especially in the event of leaks, due to its high diffusive coefficient and wide explosion limits in air (4 – 75 % v/v) [1]. For these reasons, the development of reliable and accurate sensors for the detection of leaks will play a crucial role in fostering and supporting a larger use of this gas. Additionally, a breath hydrogen test is widely used to diagnose bacterial infections or lactose intolerance [2], as it can be found in intolerant individuals due to the production through the metabolic processes of bacteria in the digestive tract. In this work, we present a chemoresistive sensor based on pure or Pd/Cu-doped CeO_2 synthesized through Flame Spray Pyrolysis (FSP), a technique that allows the synthesis of nanoparticles through the combustion of organic metal precursors using a methane-fed flame [3]. Pure and Pd/Cu doped cerium oxides were characterized by XRD and BET, and directly deposited via FSP on interdigitated electrodes on Al_2O_3 substrates. The resulting CeO_2 layers were porous and thermally, chemically, and mechanically stable. After the annealing at 500°C for 5 h, the sensors were tested with different gaseous analytes. Sensors with pure CeO_2 were selective for MeOH over EtOH and for xylene over toluene and benzene. On the other hand, Pd-doped CeO_2 sensors proved to be sensitive to hydrogen, able to work at room temperature and not affected by any known interferents. Furthermore, thanks to the ability to detect extremely low concentrations of hydrogen in the air, down to 150 ppbV, the Pd-doped CeO_2 sensor is suitable for use both for the preventive detection of hydrogen leaks and for the diagnosis of food intolerance via breath analysis.

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DNA technologies for new CRISPR/Cas12-based biosensing platforms

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Clustered Regularly Interspaced Short Palindromic Repeats (CRISPR) and CRISPR-associated proteins (Cas) are systems that have revolutionized molecular biology as powerful gene editing tools after their discovery in bacteria and archaea, where they act as a defence mechanism against viral infections. Due to their programmability and specificity, CRISPR/Cas systems can be employed in biosensing platforms [1]. In particular, Cas12 is an endonuclease enzyme that can be programmed to recognize and bind a target DNA sequence upon complexing with a guide-RNA strand (gRNA). After binding to the target DNA and cleaving it as a molecular scissor, the Cas12/gRNA complex shows a collateral activity consisting in an indiscriminate cleaving of any single-stranded DNA (ssDNA) in solution. This activity can be exploited for the generation of a readout signal by using a reporter molecule (e.g. a ssDNA labeled with a fluorophore and quencher at both ends). The detection of genetic material of pathogens with biosensing approaches still requires a preamplification step, and this limits the practical application of these devices. New amplification strategies are investigated to improve CRISPR/Cas systems for pathogens detection [2].

In this work, we propose a simple DNA circuit able to amplify the response profile of Cas12 enzyme upon DNA target detection. The reporter DNA structure has been engineered to obtain an exponential amplification of the fluorescence readout signal. The circuit was analytically characterized and kinetic and thermodynamic properties were investigated, testing new theoretical models.

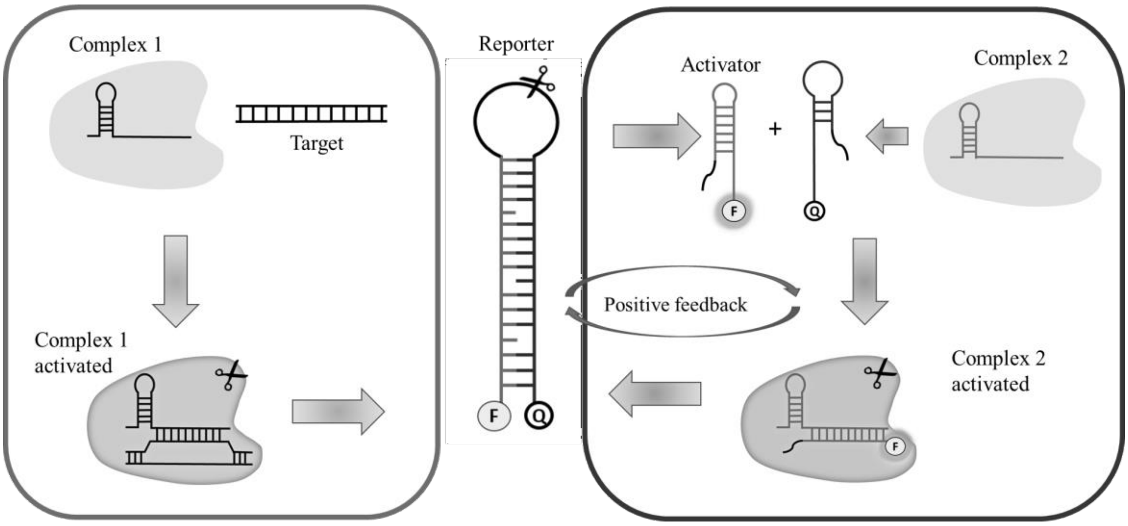

Figure 1. Scheme of the DNA circuit. In the centre, there is the hairpin reporter structure. The filaments that make up the duplex will be released after bulge cleavage and one of them will be the activator of another gRNA/Cas12 complex.

References:

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(*S*)-(-)-INDOLINE-2-CARBOXYLIC ACID: A REACTIVITY STUDY FOR THE SYNTHESIS OF OLIGOMERS WITH NEW SECONDARY STRUCTURES

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(*S*)-indoline-2-carboxylic acid ((2S)-Ind), both a mimetic of proline and phenylalanine, possesses remarkable conformational properties when involved in an amide bond, showing a strong tendency toward the *cis* amide isomer when dissolved in polar solvents.[1] This behavior is opposed to the general preference of proline for the *trans* isomer, making (2S)-Ind a good candidate for the design of different secondary structures like polyproline I.[2] However, one of the main limits of (2S)-Ind is its low reactivity toward traditional peptide couplings, which makes challenge its insertion in longer sequences. Indeed, for the synthesis of (2S)-Ind homoligomers extensive optimization of reaction conditions was necessary because the peptide coupling reaction doesn't work with common peptide coupling activating agents, even though the type and equivalents of base, solvent, and reaction temperature varied. The reaction showed satisfactory results only with 2-chloro-1-methylpiridinium iodide (Mukaiyama reagent) as a coupling activating agent (Fig. 1 A). However, the optimized conditions allow (2S)-Ind reactivity problems to be only partially overcome because further optimization was required for the synthesis of hetero-oligomers based on (2S)-Ind and natural amino acids. Indeed, depending on the amino acid chosen, either the product could not be isolated due to poor conversion rate or the desired product with poor yield was obtained. In further optimizing the synthesis, we saw that the choice of protecting groups of reaction partners for the synthesis of hetero-dimers also plays a key role both to drive the coupling reaction toward product formation, probably due to steric and conformational reasons and to avoid the formation of side reaction (diketopiperazine formation) during the following deprotection reaction on the amino function to give a product which can be used as starting materials in the convergent synthesis of longer hetero-oligomers (Fig. 1 B). The diketopiperazine formation was also registered for the homodimer of (2S)-Ind regardless of the protecting group on the amino group and the protected or free carboxylic acid.

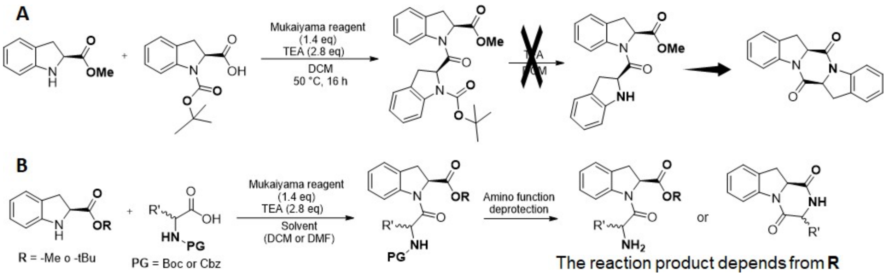

Figure 1. A) Peptide coupling reaction for the homodimer synthesis and deprotection reaction; B) Modification of protecting groups for the hetero-dimers synthesis and deprotection reaction

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Multifunctional thermoresponsive fluorinated polymer networks for self-healing and high durability Luminescent Solar Concentrators

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The constant growth of energy use and the progressive decrease of fossil sources make clear that renewable electricity will be the basis of a future sustainable energy world, and this energy transition will be the most critical challenge for upcoming generations. Among all the available renewable energy sources, solar can potentially provide for the entire energetic need of our society, and the research in the optimization of photovoltaic (PV) devices is constant. Luminescent Solar Concentrators (LSCs) are polymeric films – or slabs – with an embedded fluorophore able to absorb the solar light reaching their surface and concentrate it through photoluminescence on their borders, where a coupled PV cell converts the incident photons into electricity (Figure 1). Since they don't require external concentrating systems and can operate in diffuse light conditions, LSCs can be a valid alternative to common silicon PV panels; at the same time, thanks to their wide range of sizes, shapes and colours, they are suitable for environmental and in building integration, for example as windows. Integrating photovoltaic cells in architectural features, in part or entirely, is a promising way to develop electrical energy self-sustaining buildings [1]. Looking for optimization in LSCs' performances and longevity to give them a lifetime relatable to common silicon PV panels, developing new host matrix materials that can assure LSCs to be more performing and durable devices in harsh outdoor conditions is desirable. In this view, fluorinated polymers can be a promising way to achieve high weathering resistant surfaces [2], and their use in smart materials, such as thermally responsive polymeric systems [3], can ultimately lead to the production of smart LSCs that can adequately react to whatever detrimental effect they can experience in outdoor usage, at the same time promoting a longer lifetime of these devices given by the thermal regeneration of their surface.

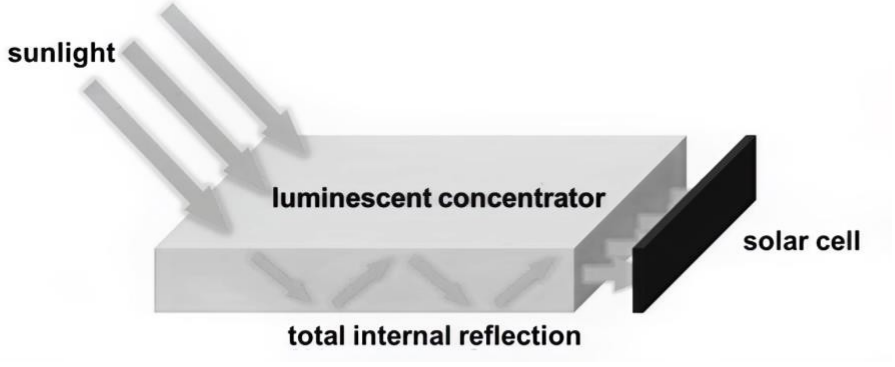

Figure 1. Scheme of a luminescent solar concentrator

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Chemistry for the Future - 2023

Optimization of pre-treatment conditions for natriuretic peptides quantification in plasma specimens

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Natriuretic peptides (NPs) are cardio-specific and sensitive biomarkers normally used to diagnose and monitor heart failure disease [1]. However, their analysis is challenging, mainly due to the limitations of immunoassay kits, such as the high cross-reactivity with structurally similar species [2]. The present work discusses the importance of optimizing a reliable plasma sample pre-treatment procedure for the determination of low-abundant (unit-tenths of pg/mL) intact NPs, specifically atrial natriuretic peptide (ANP), B-type or brain natriuretic peptide (BNP_{1-32}, BNP), C-type natriuretic peptide (CNP), and some of their degraded forms (ANP_{4-28}, ANP_{5-28}, BNP_{3-32}, and BNP_{5-32}), in human plasma. The novel antibody-free procedure is based on salting-out of plasma proteins with saturated ammonium sulphate combined with microextraction by packed sorbent (MEPS) technique and ultra-high performance liquid chromatography-electrospray ionization-tandem mass spectrometry (UHPLC-ESI-MS/MS) instrument.

The use of MEPS technique, which allowed the simultaneous sample clean-up and analyte pre-concentration, allowed to accurately determine NPs in human plasma at low pg/mL levels.

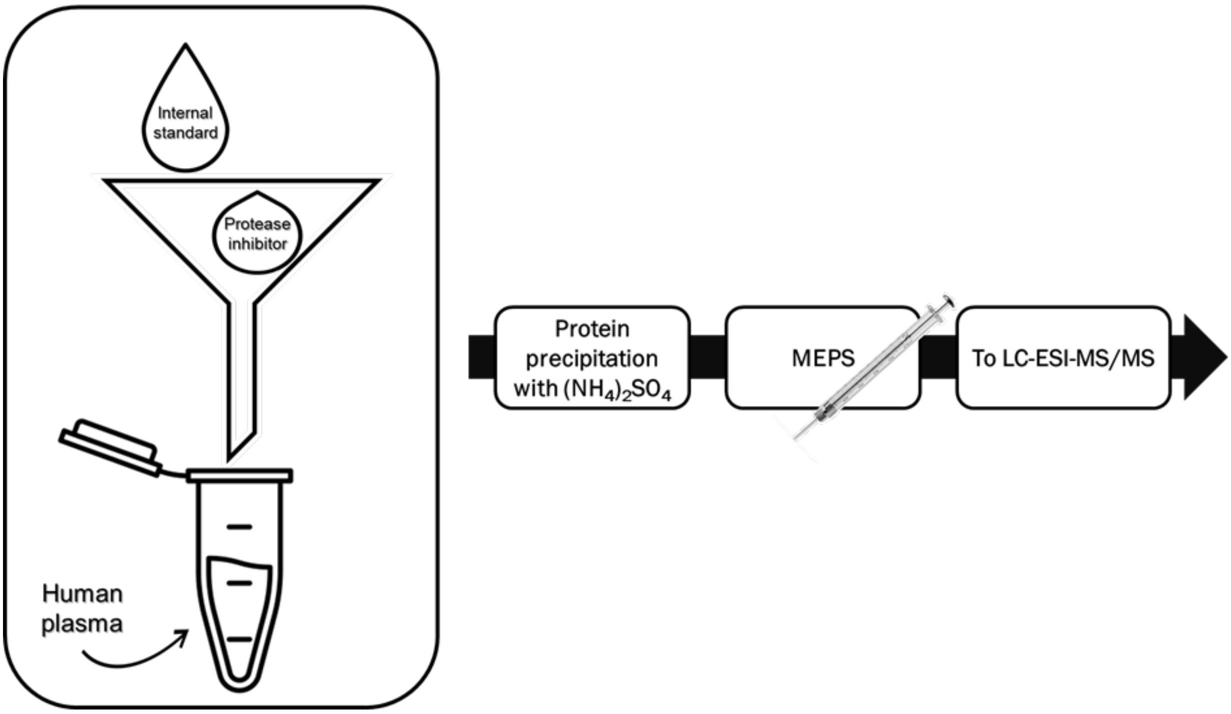

Figure 1. Workflow of the developed procedure based on the salting-out of proteins coupled with MEPS for the analysis of natriuretic peptides.

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2D nanomaterials for biological applications

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Early diagnose is a crucial step to improve the patient's expectancy of life and the quality of the treatment. This is particularly true in the case of tumours, where "circulating tumour cells" (CTCs, i.e. tumoral cells that can move through the cardiovascular and the lymphatic systems) elicit the growth of metastases even years after the surgical removal [1]. The identification of CTCs is of great interest for the definition of an early treatment; however, CTCs detection is challenging because of their low concentration (about 1–100 cells/mL) and small size (tens of µm on average) [1]. 2D nanomaterials have been widely studied in the last decades because of their large surface area and peculiar optical, mechanical and electrical properties [2], which make them suitable for improving biosensing performance. Among 2D nanomaterials, Transition Metal Dichalcogenides (TMDCs) and MXenes have gained great attention in the clinical field as highlighted by the constant growing of published papers [2,3]. Our work aims at tuning the electrical properties of semiconducting (WS_2 and MoS_2) and conducting materials ($Ti_3C_2T_x$) for fabricating immuno- field-effect transistors (immunoFETs) capable of detecting CTCs in blood samples. Since the delamination procedure strongly influences the conduction properties of 2D nanomaterials [4,5], we investigated the thickness and structure of the synthesised materials by means of SEM, XPS and XRD techniques. UV-vis spectroscopy was employed to estimate the bandgap of WS_2 and MoS_2 in solution (Figure 1), yielding results comparable to those reported in literature [5,6]. Preliminary tests on cell adhesion to different surfaces (functionalised glass and gold screen printed electrodes) were performed to study the capability of tumoral cells of sticking on artificial surfaces.

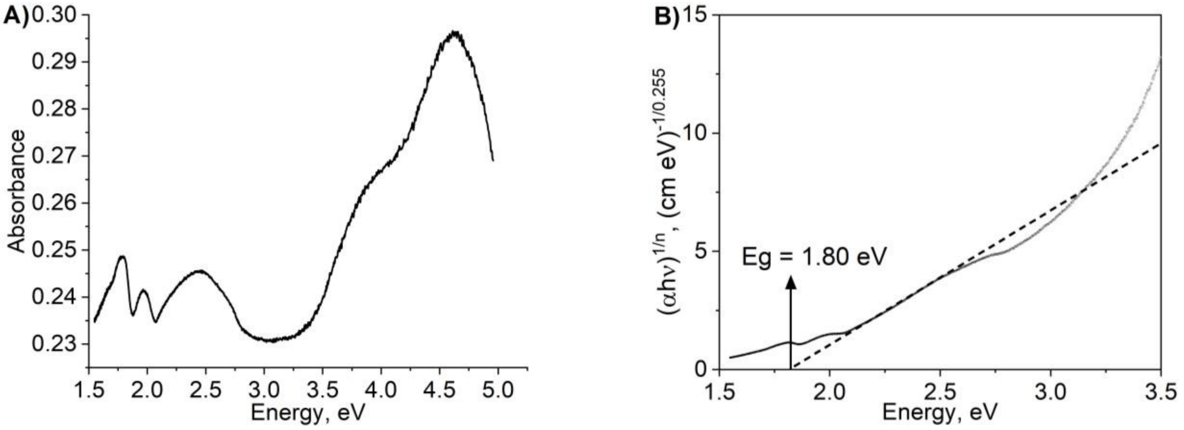

Figure 1. A) UV-vis spectrum of MoS_2 dispersion; B) Tauc plot of MoS_2 dispersion and bandgap estimation.

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Structure and free carrier parameters in ITO Nanocrystals probed by Solid State NMR and optical spectroscopy.

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In the last decades, plasmonic nanocrystals (NCs) have been subject of intense research due to their strong optical response. Indeed, the electric field of light induces a coherent oscillation of conduction electrons, known as "Local Surface Plasmon Resonance" (LSPR), which leads to a strong absorption peak typically in the UV-Vis – near IR (NIR) regions [1,2]. Among plasmonic NCs, degenerately doped *semiconductors* are particularly interesting for infrared plasmonics. In these NCs conduction electrons are generated by introducing aliovalent dopants. Among this class of materials, Tin-doped Indium Oxide (ITO) is an n-type semiconductor in which the aliovalent doping consists in the partial substitution of In^{3+} cations in the bixbyite In_2O_3 crystal structure with Sn^{4+}. ITO NCs show a resonant peak in the NIR region, tunable by varying the dopant content (Sn%) [3]. Thanks to their infrared plasmonic properties, ITO NCs have been proposed in many different fields such as magnetoplasmonics and smart materials activated by NIR light [4,5]. The correlation between free electron parameters and the presence of dopant-related structural defects is an important task in the rationalization of the optical properties of these materials, and it is still far from being completely understood. Solid State NMR (SSNMR) appears particularly attractive for this scope [6-8], as the presence of free electrons affects several NMR properties of the nuclei. In this work, we present a SSNMR investigation on ITO NCs stabilized with oleic acid, containing an increasing amount of Sn. ^{119}Sn SSNMR spectra and spin-counting experiments allowed us to identify different Sn species, correlated with different electronic properties. Further information was obtained by measuring ^{119}Sn spin-lattice relaxation times (T_1) at different temperatures. Optical and magneto-optical spectroscopies were also employed to extract free electrons parameters and correlate the parameter obtained with the structural information provided by SSNMR.

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Europium labeling of proteins in Quattrocento’s paint replicas

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This study employed a derivative of 2-Thenoyltrifluoroacetone-Eu complex for protein labeling in modern replicas of historical paints, to enable the investigation of paint microstructures.
The 15th century has been a transitional period during which Italian artists experimented with siccative oils in addition to traditional binders, mostly based on egg, casein, and animal glue. These developments led to the adoption of new painting techniques, including tempera grassa [1] (an emulsion of protein binder and oil) and oil paint with protein-coated pigments [2].
Previous studies demonstrated that the preparation method plays a crucial role in determining the chemical and physical properties of the paints and had, consequently, hypothesized that different methods of preparation would result in distinct microstructures [2]. The objective of our study was to characterize the microstructure of paints based on drying oils and proteinaceous media prepared using different formulations and preparation methods.
To this aim, replicas of ancient paints were produced using known amounts of lead white, as the pigment, and egg white and linseed oil, as the binders. Proteins were labelled with a luminescent tag by treating the egg white firstly with 5-(4,4,4-trifluoro-3-oxobutanoyl)thiolane-2-sulfonyl chloride, which substitutes its chloride group with a free aminic group of the proteins (usually form the lateral chain of the lysine amino acids) and then Europium, which is complexed by the previous reagent [3]. The labelled egg white was then used to prepare the following paint replicas: egg tempera with lead white, egg tempera grassa with linseed oil and lead white and linseed oil paint with lead white pigment coated in egg white.
Subsequently, the resulting paints were applied onto glass slides and examined with optical reflection microscopy using both dark field and UV illumination. The approach allowed to successfully discriminate the different paint microstructures resulting from different methods of preparation.

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Characterization of exhaled breath in heart failure patients

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Heart failure (HF) is a complex syndrome that results from a structural or functional impairment of ventricular filling or ejection of blood. Given the high rate of hospitalization, HF is considered a global epidemic affecting more than 64 million people worldwide [1]. To improve the early diagnosis and the patient management, clinicians are seeking new approaches focused on biomarkers [2]. Breath analysis has proven to be a valuable tool for this purpose since the chemical composition of exhaled breath reflects the metabolic status of the patient, possibly allowing a distinction between healthy and diseased states. Sampling procedures are easy, effective, non-invasive, and painless. Nevertheless, controlled sampling is mandatory since sampling protocols may alter the breath composition [3].

In this work, we monitored mixed breath samples collected from eighty patients with different severity levels of HF at the University Hospital of Pisa, before and during the cardiopulmonary exercise testing (CPET). Breath was collected using a sampling case (Figure 1) that allows to control the sample volume accurately. A CO_2 infrared sensor differentiated exhalation and inhalation phases during breathing, allowing the collection of mixed breath samples. An aliquot (250 mL) of breath was transferred at 50 mL/min into a solid-phase extraction tube packed with 250 mg of TenaxGR. Samples were analyzed with a thermal desorption unit (TD) coupled with gas chromatography and mass spectrometry (GC-MS) instrument. Ambient air was also analyzed during the test to exclude possible contaminations. ^{8}D-Toluene was used as an internal standard for analyte determination.

Preliminary results confirm the central role of breath acetone as an indicator of disease severity.

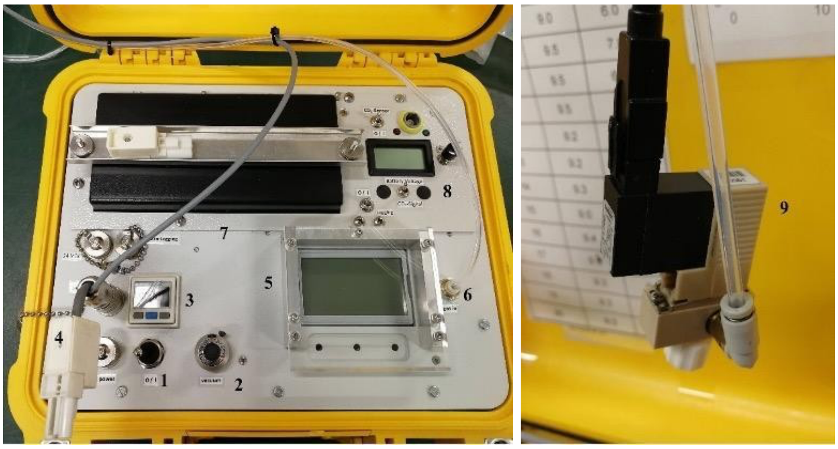

Figure 1. Sampling case used to transfer an accurate volume of breath sample in the SPE tube.

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Revealing the composition of modern inks: optimisation of a LC-DAD-MS^2 method suitable for acid dyes analysis

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In the late 19th century, the introduction of synthetic organic pigments (SOPs) onto the market brought manufacturers into a new and fascinating landscape for ink's production [1]. The main SOP's components of modern inks can be classified into three groups: acid, basic and solvent dyes [2]. In particular, acid dyes are water-soluble anionic compounds containing acidic groups, such as -SO_3H and -NO_2 functionalities, which have been widely used in modern inks due to their range of colours and versatility. When the analysis targets are modern inks, i.e. complex mixtures of SOPs, highly selective and ultra-sensitive methods are necessary to fully characterize their composition, and to detect minor components such as possible degradation markers or synthetic by-products. Thus, liquid chromatography coupled to diode array or tandem mass spectrometric detectors is the technique par excellence for revealing the SOPs composition of modern inks. However, the presence of acidic SOPs in ink formulations complicates their chromatographic separation by producing chromatographic fronting [3], leading to loss of selectivity.

To improve the chromatographic behaviour of acid dyes, in the present work a previously developed LC-DAD-MS^2 method was specifically optimised. In order to propose a universally valid method for both historical and modern inks, the optimisation was carried out using standard natural dyes (carminic acid, alizarin and purpurin), standard and reference SOPs belonging both to acid (cotton scarlet, amido naphthol red G, and naphthol yellow S) and basic groups (methylene blue, methyl violet, and fuchsine). Starting from an optimised chromatographic gradient for natural dyes analysis [4], different flow rates (0.4 and 0.6 mL/min) and formic acid percentage in mobile phase (0.1%, 0.3% and 1%, v/v) were tested to determine the optimal conditions in terms of both number of theoretical plates (NTP), ionisation efficiency (IE), limit of detection (LOD) and limit of quantification (LOQ). The optimised method was finally applied to the analysis of a collection of modern inks produced in France in the late 19th- early 20th century, proving effective in improving both sensitivity and selectivity.

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Photoisomerization dynamics of spiropyrans

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Spiropyrans are a broad class of compounds widely used in materials science due to their pronounced photochromic properties. The excitation of spiropyrans in the UV range converts them into the open and colored merocyanine form. Despite the large use of these molecular switches, the exact mechanism of the photoisomerization reaction is not fully understood and appears to be strongly dependent on the substituents and the environment [1].

For these reasons, we want to study the excited-state dynamics of two spiropyrans labeled as BIPS and nitro-BIPS (Figure 1) through "on the fly" surface hopping nonadiabatic dynamics simulations using the FOMO-CI method in a semiempirical AM1 framework [2,3].

To bring the solvent effects out on the BIPS excited state dynamics, we ran simulations in three different environments (chloroform, methanol, and ethylene glycol) and we compared these results with previous simulations carried out in vacuo [4].

Furthermore, we also considered the modifications of the lowest-lying excited state PESs of BIPS induced by nitro substitutions, and their impact on the nonadiabatic dynamics.

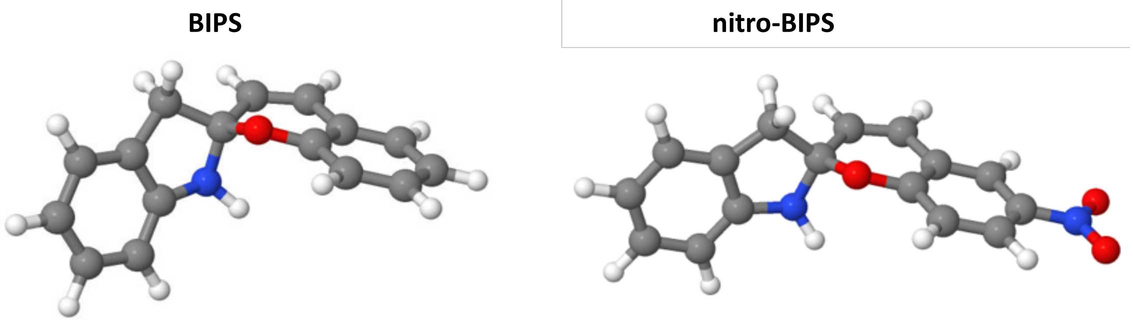

Figure 1. Spiropyrans labeled BIPS and nitro-BIPS.

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Degradation processes and leaching of wet wipes by means of chromatographic and mass spectrometric techniques

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Commercial wet wipes have a wide range of applications that make them easy to use in everyday life [1]. They have also been employed for house cleaning, childcare, facial, and intimate cleansing, for about 25 years now [2]. Wet wipes are disposable nonwoven fibre materials pre-moistened with a specifically formulated solution or emulsion. Wet wipes can be differentiated according to their chemical composition and suggested disposal practices into non-flushable and flushable [1,2]. Non- flushable wet wipes are incompatible with most sewage systems and consequently are expected tobe disposed of with solid waste. Flushable wipes are designed to disintegrate into small pieces anddisperse into sewage systems, and they are claimed suitable to be disposed of through the toilet. However, the environmental impact and risk of such practice deserve specific attention [3]. Recently, the intensive use of wet wipes as a consequence of the global COVID pandemic, together with the diffusion on the market of flushable wipes is increasing the concern about the release of microfibers and additives when introduced in the sewage system and the environment [4,5].

In this work, non-flushable and flushable wet wipes were subjected to two different types of artificial degradation. A set of samples was sonicated in deionised water to simulate the mechanical degradation occurring in the sewage waters, while a second set of samples was soaked in deionized water and subjected to UV-vis radiation in Solarbox to simulate an outdoor photodegradation. After each degradation cycle, the water was filtered on quartz filters to collect released microfibers. The residual tissue and the quartz filters were analysed by multi-shot pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS). Samples of the water which the wipes were immersed during the treatments, were analysed by high-performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS) to detect organic leachates (organic compounds). The Py-GC-MS analysis of the filters confirmed the presence of higher levels of microfibers in samples aged longer and an effect of the ageing conditions. Double-shot Py-GC-MS of the leftover tissues highlighted a decrease of additives (e.g. 2-phenoxyethanol, benzoic acid) with ageing time in the first shot. As for the second shot, an increase of cellulose degradation products (e.g. levoglucosan) was observed for the flushable wipes, whereas no significant changes were detected for the non-flushable wipes. The above was confirmed by HPLC-MS/MS data.

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Ionically crosslinked carboxymethyl chitosan scaffolds by additive manufacturing

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Carboxymethyl chitosan (CMCS) is a chitosan (CS) derivative with enhanced aqueous solubility and high potential for biomedical applications, such as tissue engineering, controlled drug delivery, and gene therapy, thanks to its excellent biocompatibility. In comparison to CS, it also showed enhanced antimicrobial activity and hemocompatibility, as well as improved control over biodegradation kinetics. CMCS is known to promote osteoblasts and fibroblasts adhesion, growth, and differentiation. CMCS ampholytic character allows its crosslinking using small oppositely charged molecules or by polyelectrolyte complexes formation, without altering its biocompatibility [1]. In this work, CMCS was obtained by CS reaction with monochloroacetic acid, using isopropanol as solvent in a strongly alkaline medium. The derivative was soluble in water, with an isoelectric point of 3 and a high degree of substitution (1.2-1.3; O-substitution: 1.07), which was verified by means of FT-IR, NMR spectroscopy, and titration. CMCS scaffolds were fabricated using the additive manufacturing technique Computer-aided Wet-spinning (CAWS) [2] and stabilized in physiological environment through zinc sulphate crosslinking (Figure 1). A physicochemical characterization of the obtained scaffolds by means of FT-IR spectroscopy, differential scanning calorimetry (DSC), and swelling kinetics test, is currently ongoing to investigate the composition, cross-linking, and properties of the developed material.

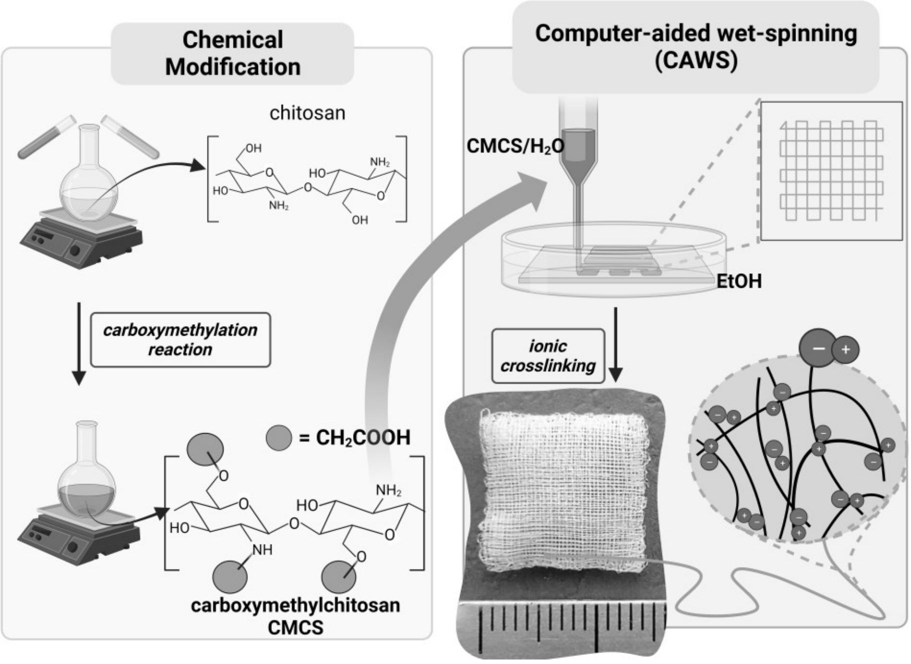

Figure 1. Preparation, processing, and crosslinking of CMCS.

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Development and optimization of an analytical procedure for the characterization of organic residues from archaeological potsherds

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Ceramic has been one of the most common materials used by ancient people for the preparation, storage, cooking and transport of several products. Ceramic can preserve organic substances over time and the extraction and analysis of organic residues can provide answers to a variety of archaeological questions about diet, food storage and processing, trade and the use of commodities. This can contribute to disclose crucial hints about daily life of ancient societies [1]. Commonly, organic residues occur as invisible absorbed material within the porous unglazed ceramic vessel wall. Several studies have been performed to optimize the extraction, detection and quantification of organic residues within archaeological pottery [2-4].

In this research, a procedure for the extraction and characterisation of organic residues from ceramic was optimized to improve the recovery of the analytes of interests and maximize the information achievable from a micro-sample. As preliminary approach, the study was focused on lipid residues. Reference samples were prepared by spiking virgin ceramic with standard solutions of triacylglicerides (TAGs) and fatty acids (FAs) and subjected to artificially ageing to simulate the reactions occurred over time. The organic fraction was extracted from ceramic by microwave-assisted extraction. A Box-Behnken experimental design was used was performed for the extraction optimization. The effects of temperature and extraction mixture composition were investigated using the concentration of TAGs and FAs as responses. The extracts were analysed by methods based on chromatography and mass spectrometry. The optimized procedure was then used to study the organic residues collected from archaeological ceramics provided by “Museo delle Navi di Pisa”.

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Combining CASSCF with MBE-FCI to treat large active spaces

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To this day, the *de facto* standard method to study MR systems is the Complete Active Space Self Consistent Field (CASSCF) [1]. Unfortunately, the application of CASSCF requires to solve multiple times a Full CI (Configuration Interaction) problem, whose size grows factorially with the dimension of the active space chosen. Such limitation sets the maximum treatable size of the active space to 16 electrons to be correlated in 16 orbitals, restricting the application of CASSCF only to smaller systems. During the last few years, some approximate strategies to circumvent this prohibitive scaling have been devised, such as QMCFCI [2], DMRG [3] and selected CI methods, like HCI [4].
In this work, we propose an algorithm which couples CASSCF with an approximate CI solver, namely the MBE-FCI (Many-Body Expansion) [5] solver. The main idea of MBE-FCI is to approximate a property of the exact wavefunction, by expanding it in a series of increments arising from the correlation of any possible subset of the active orbitals. This expansion is appropriately truncated by a screening protocol that neglects the minor terms. We have exploited an implementation of MBE-FCI inside the PyMBE package, to produce the quantities required for a standard first order CASSCF orbital optimization i.e., the Reduced Density Matrices and the Generalized Fock Matrix, from which the orbital gradient is computed. To integrate the CASSCF code with the PyMBE package, an explicit interface was built.
After a first calibration of the MBE parameters, we exploited this new algorithm to perform two MBE-CASSCF calculations with a large 22 electrons in 22 orbitals active space, to evaluate the triplet-quintet gap in a Fe(II)-porphyrin, which is, by now, a classic problem where theory and experiment disagree.

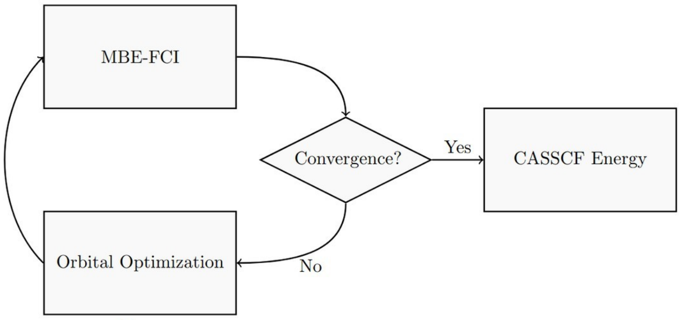

Figure 1. Scheme of the proposed MBE-CASSCF algorithm

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Structural Properties, Dynamics and Phase Separation of a Benchmark Anion Exchange Membrane

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The urgent need of a green transition requires new strategies for the production and conservation of energy. Among different solutions, the so called green hydrogen is gaining extreme attention because of the high availability of water.

Anion Exchange Membranes (AEMs) are vital components of alkaline water electrolyzers because they allow the transfer of hydroxyl ions from cathode to anode while acting as an electric insulator. In recent years, Fumatech GmbH developed a new class of membranes based of FAA-3, a ionomer deriving from the functionalization of Poly-Phenylene Oxide (PPO) with an undisclosed quaternary ammonium group. Because of their improved characteristics and reduced costs, these membranes are commonly used as a benchmark material to compare the properties of new AEMs. However, these materials have been characterized only in a handful of works and some aspects are still unknown [1-3].

Solid state NMR (SSNMR) could serve as a powerful tool for the characterization of these materials because it can allow to focus the attention on different aspects of membrane, such as structure, phase separation and dynamics.

In this work, we performed a multinuclear SSNMR analysis of a commercially available membrane know as FAA-3-PK-130. This membrane is based on FAA-3, which is responsible for the anion conductivity, and is reinforced with Poly-Ether-Ether-Ketone (PEEK) to improve mechanical properties and dimensional stability.

^{1}H and ^{13}C spectra and 2D maps have been used to characterize the structure of these two polymers and to try to identify the nature of the undisclosed quaternary ammonium group. Moreover, ^{19}F NMR has been used to probe the presence of fluorine in the membrane since it has previously been reported [4].

Phase separation between PPO and PEEK has been investigated by spin diffusion by measuring proton spin-lattice relaxation times at 500 MHz through an inversion recovery-cross polarization sequence (IR-CP).

Moreover, low field NMR has been used to unravel the effect of water adsorption on side-chains dynamics and on the separation of ionic channels, which has previously been reported for FAA-3 by means of atomic force microscopy [1]. In order to investigate this aspect, the membrane has been analyzed in its dry form and after hydration in a controlled environment.

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Protein deposit typing in cardiac amyloidosis by S-trap-based microproteomics workflow

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Cardiac amyloidosis is a disease characterized by the deposition of proteinaceous material in the extracellular space of cardiomyocytes, which cause heart muscle function disruption and cardiac disfunction. Transthyretin (ATTR) and immunoglobulin light chain (AL-λ or AL-κ) amyloidosis are the most common amyloidosis types presenting cardiac involvement. Amyloid typing is crucial for patient management since ATTR and AL are characterized by different treatments and prognosis. Endomyocardial or subcutaneous fat biopsies are needed to identify the constituent proteins of the amyloid deposit, for which proteomics has quickly become the gold standard for amyloid typing [1]. Here we present a laser-capture microdissection/microproteomics workflow based on S-Trap to characterize protein deposits in cardiac amyloidosis [2].

Endomyocardial biopsies were collected from 13 cardiac amyloidosis patients, fixed in formalin, and embedded in paraffin. 8 μm thick sections were mounted on glass slides and stained with Congo Red to highlight amyloid deposits. Congo Red positive areas were isolated by laser-capture microdissection and processed with a modified S-Trap protocol. Immunohistochemistry (IHC) was performed on consecutive sections.

A microproteomics workflow for the typing of cardiac amyloidosis was developed. The protocol included FFPE endomyocardial biopsies sectioning, Congo Red staining, and the isolation of protein deposit by Congo Red autofluorescence-guided laser-capture microdissection. A modified S-Trap bottom-up microproteomics workflow was applied to the samples. Peptides were analyzed by nLC coupled with an Orbitrap Fusion mass spectrometer. The protein forming the amyloid deposit was defined by the most abundant amyloidogenic protein in the sample. 10 out of 13 samples showed a concordance between proteomics and immunohistochemical validation, with 8 ATTR cases, 1 AL-λ case and 1 negative case. Only 1 of the remaining 3 cases were discordant (ATTR according to IHC and AL-λ according to proteomics); for the remaining 2 cases either IHC or proteomics were inconclusive. ApoE, ApoA-IV and SAP, known to co-precipitate in the deposit and described as a characteristic amyloid protein signature, were detected in all samples. The principal advantage of the S-trap microproteomics workflow is that it is fast, sensitive, robust to co-factors that may be introduced during routines clinical sample handling, and does not require highly trained personnel.

We used for the first time a microproteomics workflow to characterize amyloid deposit in cardiac amyloidosis, demonstrating its full compatibility with typing of amyloidosis patients.

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The making of transparent wood from fir wood and its woodworking waste material

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Transparent wood is a fascinating material that has the potential to revolutionize the way we think about building and interior design, energy efficiency, and sustainability at large. In recent years, significant progress has been made in the development of transparent wood, which is a composite material created by removing/modifying the lignin from natural wood and replacing it with a transparent polymer matrix with a refractive index in the range of that of cellulose fibers (n ~ 1.53). The resulting material, besides being transparent to visible light, is resistant, lightweight and could have excellent thermal insulation properties compared to inorganic glass [1].

The main objective of this work was the realization of transparent wood composites from fir wood. The production of transparent wood involves typically three steps, *i)* bleaching, *ii)* polymer infiltration, and *iii)* curing [2]. The bleaching process entails removing, at least partially, the lignin from pristine wood samples, which is accomplished through a chemical treatment. Different chemical approaches were evaluated in order to obtain delignified wooden templates with high structural integrity and appropriate size, under mild conditions. The chemical modification of the samples in terms of loss of hemicellulose and lignin was assessed by FT-IR ATR spectroscopy. The resulting delignified cellulose templates were then infused under vacuum with a transparent polymer, such as poly(methyl methacrylate) or epoxy, which fills the voids of the preserved wood internal structure. Finally, the polymer is cured, resulting in a clear and durable material that depending on the conditions could also retain the natural grain pattern of the original wood for added aesthetic value. In parallel, the process was extended also to wood particles and sawdust that are a waste product of fir timber woodworking. In this case the delignification process resulted in loose cellulose fibers that can be easily blended with the polymer matrices as a filler, in different polymer/fiber ratios.

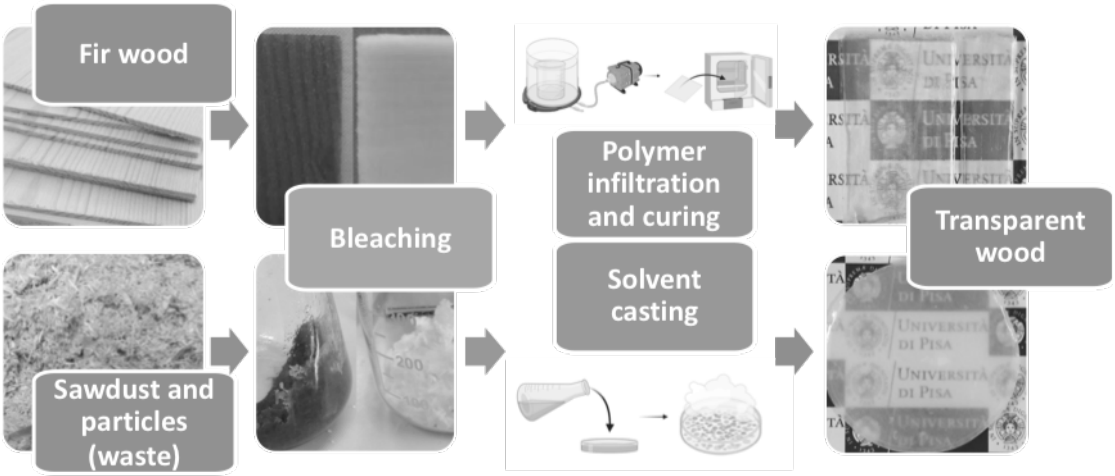

Figure 1. Schematic representation of the preparation of transparent wood from fir timber and sawdust with photos of the different steps.

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Virgin and photodegraded microplastics impact the inflammatory response of vascular muscle cells

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Microplastics (MPs) are being recognized as one of the main environmental problems due to their ubiquitous presence in various ecosystems. Humans are continuously exposed to MPs and some recent findings suggest their role as a trigger for vascular inflammation, potentially worsening the cardiovascular patients' clinical condition. Vascular smooth muscle cells (VSMCs) are the main component of medium and large arteries and play important roles in atherosclerosis.

The present study investigates for the first time the effects of MPs on vascular muscle cell behaviour, metabolic activity, pro-inflammatory state aiming to better clarify the MPs biomolecular modulation and their potential to generate a chemical fingerprint during exposure. Micronized powders of polystyrene (PS), high-density polyethylene (HDPE), and low-density polyethylene (LDPE), either virgin or artificially aged (4 weeks photodegradation at 40 °C and 750 W/m^2), were added at a concentration of 1 mg/mL to Human Coronary Artery Smooth Muscle Cells (HCASMCs) culture media and left for 72 hours and 7 days. Cell viability, intracellular ROS, IL-6, TNF-α and caspase-1 were analysed to evaluate the effect of MPs on HCASMCs. Volatile Organic Compounds (VOCs) were also analysed to evaluate the chemical profile over the HCASMCs at 72 hours and 7 days.

Results highlighted that virgin PS, LDPE, and HDPE had a mild to moderate influence on cell viability, which was not evident for the 4-week-processed materials. This suggests an intrinsic toxic effect of these polymers, which perpetuates even after a week of treatment for naïve LDPE and HDPE. Virgin and aged PS 72-hour treatment of HCASMCs led to acute activation of inflammation mediated by caspase-1 and TNF-α. After 7 days, PS 4-weeks aged stimulated the inflammatory response through IL-6 and TNF-α production. LDPE early exposure also induced caspase-1 and a late response with IL-6 production after a week. Oxidative stress was potentiated after 72 hours in HCASMCs media when left in contact with aged LDPE and HDPE (for the latter, even after 7 days) and virgin HDPE. Unprocessed HDPE stimulated an inflammatory response in HCASMCs, mediated by both caspase-1 and IL-6, after 7 weeks. One-way ANOVA ($p\text{-value} < 0.01$) highlighted pentane, acrolein, propanal, and hexanal as the most important features discriminating the conditions under study suggesting a potential link between the VOCs emitted by cells incubated with MPs and the inflammatory response observed.

MP types and degradation grade differently impact HCASMCs biology and have the capacity to trigger a peculiar inflammatory response, suggesting a potential role to potentiate cardiovascular risks.

New poly(lactic acid)/paper mill sludge bio-composite: preparation and characterization

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In recent years, bioplastics are becoming interesting materials as an environmentally sustainable alternative to traditional petrochemical plastics. Poly(lactic acid) (PLA)-based materials play a crucial role in the new generation of bioplastics due to their biodegradability, good performances and suitability for several applications, such as packaging, agricultural, biomedical, electronics and textile applications [1]. In this context, the modulation of PLA's properties could allow the employment of these PLA-based materials in different applications. For this reason, the study of PLA composites is becoming increasingly relevant [2]. At the same time, in this field, an important challenge is the use of waste materials as fillers for polymer composites in order to make them more sustainable. In this context, the papermaking industry produces a large amount of inorganic-rich paper mill sludges (PS) which are currently landfilled, causing environmental and economic problems, making important the development of new sustainable strategies for their valorisation. For this reason, in order to achieve a sustainable waste policy, in collaboration with the Lucart company, the valorisation and reutilization of one of their paper mill sludges (composition: 30 wt% cellulose, 70 wt% calcium carbonate) as a filler/reinforcing agent in PLA composites was evaluated in this research as a green alternative to cellulose and/or other traditional mineral fillers [3]. On this basis, the present investigation aims at the preparation and characterisation of PLA-PS films with a PS loading in the range of 10-40 wt%. The films were first prepared using the solvent casting method to investigate the interaction between the polymer and the filler in the different investigated formulations. Then, melt-extrusion and compression moulding were chosen as the most effective methods for manufacturing solid dispersions, in the perspective of an industrial production scale. A preliminary thermal and mechanical characterisation of the new PLA-PS films prepared by means of the two different investigate methods was performed, and the achieved results were compared with those obtained for neat PLA films. In particular, the thermogravimetric analysis enabled us to investigate the thermal degradation profile and composition of these composites: the observed decrease in the onset temperature of PLA in the new PLA-PS composites can be due to the presence of the inorganic component [4]. Regarding the mechanical properties, toughness, stress/elongation at break and Young’s modulus of the prepared bioplastic films were analysed by means of a tensile test, underlining the higher stiffness and more pronounced brittle behaviour of the final material prepared with the highest PS loading (40 wt%). In this regard, preliminary tests have shown the possibility to overcome this drawback with the addition of plasticizers, such as polyethylene glycol, triethyl citrate and epoxidized soybean oil, paving the way for a massive use of the waste paper mill sludge.

The authors are grateful to Lucart S.p.A., in particular Dott. Pasquini and Ing. Giordano, the European Union and Italian Ministero dell’Università e della Ricerca for the financial support provided through Programma Operativo Nazionale (PON) “Ricerca e Innovazione” 2014-2020 (Azione IV.4 e IV.6) project “Total Green valorization of paper mill wastes through thermo-catalytic route” (PON 2014-2020 Dottorati di Ricerca su tematiche dell'Innovazione e Green (D.M. N.1061/2021), bando 2021, I59J21017690008).

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Additive Manufacturing of Bioactive Chitosan Scaffolds Loaded with Functionalized Magnetite Nanoparticles

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Bone tissue is not able to regenerate spontaneously after a trauma in the case of critical size defects. Advanced tissue engineering approaches based on the fabrication of bioactive scaffolds with magnetic properties are under investigation to enhance bone repair [1]. In this work, magnetic nanoparticles (MNPs) based on magnetite (Fe_3O_4) functionalized with glycine, ulvan, or gallic acid, were synthetized by means of a co-precipitation method, using $FeSO_4$ as precursor and KNO_3 as oxidizing agent. MNPs functionalization was demonstrated by thermogravimetric analysis (TGA), FTIR spectroscopy, and elemental analysis, while their nanometric size was shown by transmission electron microscopy (TEM) and X-ray powder diffraction (XRPD) analysis. The magnetic property of the newly designed MNPs was investigated by magnetometry and their cytocompatibility by *in vitro* cell culture. Then chitosan scaffolds loaded with MNPs (20%, 40%, or 60% w/w) were fabricated by an additive manufacturing technique, referred to as computer-aided wet-spinning (CAWS), based on printing a MNPs suspension in an aqueous chitosan solution, into a non-solvent bath. The developed scaffolds were characterized by FT-IR spectroscopy, scanning electron microscopy (SEM), TGA, water uptake measurements, and tensile mechanical test.

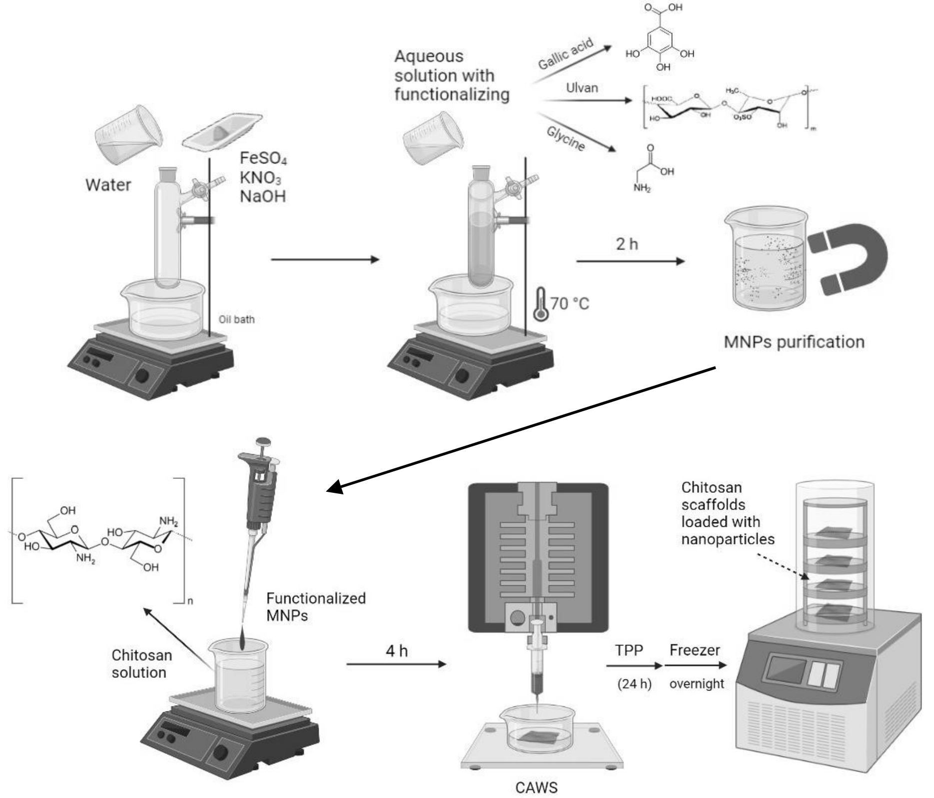

Figure 1. Synthesis of MNPs and fabrication of 3D chitosan scaffolds loaded with MNPs.

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Controlled thermolysis of recycled polymer materials in bitumen for application in "warm asphalt" and with high RAP content

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Bitumen is a non-renewable raw material obtained as a crude oil distillation residue. It’s mainly used as a binder for asphalt production, in combination with inert and filler, thanks to its excellent thermoplasticity, adhesivity, and waterproofing properties. Industrially, asphalt can be produced according to two different procedures that depend on the mixing temperature of these components: the “Hot Mix Asphalt (HMA)” process, which operates at 170/190°C and a more recent one, namely the “Warm Mix Asphalt (WMA)” technique, which operates at 120/140°C [1]. The latter technique is of great interest since the reduction of the working temperature is responsible for several benefits, such as an increased lifespan of the final conglomerate, a reduction in energy consumption and, therefore, in greenhouse gases emission, and lower emission of potentially harmful gases for the environment and workers. An additional related issue concerns the valorisation of End-Of-Life Tyres (ELT). In fact, they represent a significant portion of the waste destined for landfills since the complexity of recycle process severely affects the possibility of any type of energetic or material recovery. Moreover, the chemical composition of tyres makes them extremely resistant to degradation phenomena with a potential long-term permanence in the environment [2]. The work aims to prepare a new bitumen obtained from the thermodegradation in controlled conditions of ELT into the bitumen [3], to produce a bitumen rich in light oils. Thanks to its novel properties, this new bitumen should promote the "WMA" technique and the Reclaimed Asphalt Pavement (RAP) reuse. Starting from this rationale, we prepared a first class of modified bitumen that was characterized chemical-physically and mechanically both before and after the Rolling Thin Film Oven (RTFOT) ageing test. By varying the amount of ELT and by adding a reactive gas (O_2) during the reaction, it was possible to observe different behaviour. The introduction of O_2 leads to a decrease in penetration and the Fraass breaking point, while the addition of a greater quantity of ELT leads to an opposite trend.

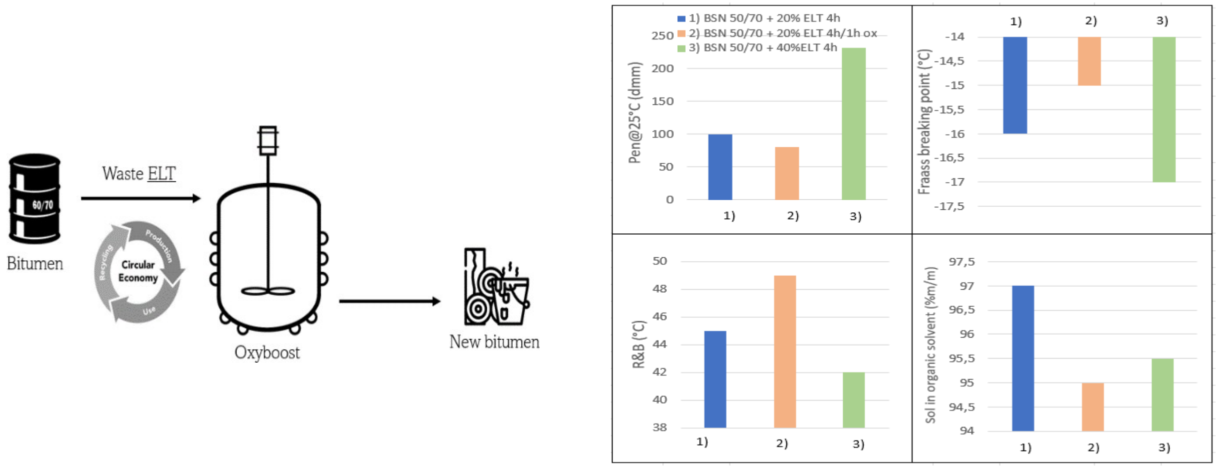

Figure 1. Scheme of the thermodegradation reaction (left) and performance trend of the three different obtained bitumens (right).

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Unraveling the Photoactivation of a Blue-Light Using Flavin Photoreceptor through Excited-State SCF Dynamics

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Blue-Light Using Flavin (BLUF) proteins are photoreceptors with an intriguing activation mechanism. Experiments and computational studies on BLUF proteins suggest a conserved proton-coupled electron transfer (PCET) mechanism [1-3] involving the flavin chromophore (FMN) and the conserved active-site tyrosine (Tyr) and glutamine (Gln) residues (see Figure) [4,5]. Upon blue-light absorption, excited FMN accepts an electron from the Tyr, followed by a double proton transfer from Tyr to FMN mediated by the Gln residue (*forward PCET*), resulting in a Gln imidic acid tautomer. The Gln side chain then rotates, and the diradical intermediate undergoes *reverse PCET*. This process consists of a back electron transfer from the FMN radical to the Tyr radical and of two subsequent proton transfers, ultimately leading to a stable Gln tautomer (see the circles in Figure) [2,6]. However, no direct spectroscopic evidence supports the PCET mechanism in the BLUF domain of the AppA protein from *Rb. sphaeroides*. Indeed, the radical PCET intermediates have not been detected [7], which led researchers to classify AppA as an exceptional case among BLUF domains. Alternative mechanisms were proposed, but none of them has found a robust demonstration [7,8].

Here, by exploiting a combination of a newly implemented method for excited state simulations (polarizable ΔSCF/AMOEBA dynamics) and closed-shell DFT/AMOEBA dynamics, we show that the PCET process is also valid for AppA, supporting Gln tautomer as the light-adapted characteristic feature [9].

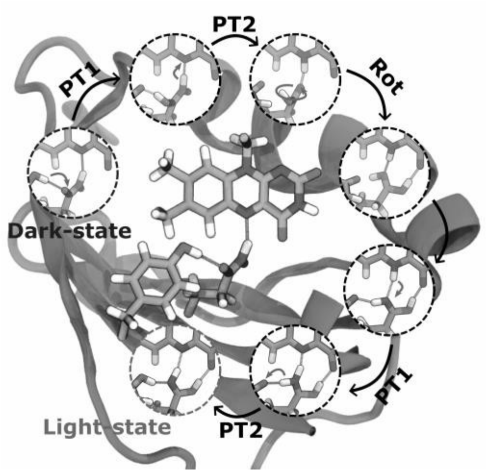

Figure 1. In the background is the dark-adapted geometry of the AppA BLUF photoreceptor. The circles illustrate the complete mechanism of activation.

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Cell-Surface Proteomics of Pancreatic Ductal Adenocarcinoma Cells and Exosomes

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The study of membrane proteins is of particular interest in clinical research, since they are involved in many biological processes such as cellular communication [1]. Their location on the cell surface makes them attractive targets for pharmaceutical intervention, indeed they represent the majority of targets of pharmaceutical drugs [2]. This work is focused on the analysis of PDAC (Pancreatic Ductal Adenocarcinoma) cells and exosomes. PDAC is the most common pancreatic cancer. It has a five-year survival rate below 10% due to the fact that is usually diagnosed at an advanced stage when the available therapies are largely ineffective. It has been estimated that this type of neoplasm could become the second leading cause of death in Western countries [3]. The investigation of PDAC cell surface proteins can lead tothe identification of new drug targets, and the identification of exosome surface proteins specific to PDAC, could enable the development of new biomarker assays for earlier diagnosis. The hydrophobicity of membrane proteins and the embedding of the transmembrane domains within the phospholipid bilayer of the membrane means their extraction is more difficult with respect to the total cellular proteome. For this reason, specific methods of extraction and identification arefrequently employed. The aim of this work was the optimization of a method for cell surface proteomics. The method consists in the use of a cell-impermeable biotinylation agent that chemically derivatizes the lysines of cell-surface proteins. At the end of the reaction and after cell lysis, a neutravidin resin is used to isolation the biotinylated proteins. Finally, biotinylated denatured proteins are converted into peptides after proteolysis using trypsin and bottom-up proteomics analysis performed. This technique has been applied to the PDAC cell lines SUIT 2-028 and PANC 1 and their exosomes. Cell surface biotinylation is well established and the materials needed are readily available. The large number of cells typically used (~ 10^7 cells) [4] makes it difficult to apply to exosomes. The optimization was focused on decreasing the number of cells used in the analysis, so that the methodcould be applied to exosome preparations.

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Development of new fluorinated Cerium based Metal-Organic Frameworks (MOFs) with MIL-140A topology as solid adsorbents for biogas upgrading

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Biogas upgrading involves CO_2 removal from raw biogas to produce biomethane, a sustainable biofuel well aligned with international climate goals. Therefore, the development of efficient and cost-effective CO_2 separation technologies to scale-up the production of biomethane is imperative [1].

In this context, an appealing candidate for a real life application in carbon capture is F4_MIL - 140A(Ce), an ultramicroporous Metal-Organic Framework (MOF) based on Ce(IV) and tetrafluoroterephthalic acid as organic linker. This system exhibits a non-hysteretic step-shaped CO_2 adsorption isotherm, characterized by a steep uptake increase at low pressure (0.2 bar) at 298 K due to a phase-transition occurring upon CO_2 adsorption, whose molecular origin is attributed to a cooperative CO_2 mechanism that involves the concerted rotation of fluorinated aromatic rings [2,3].

To better understand the influence of fluorination of ligands (in terms of symmetry, steric hindrance and fluorine functionalization degree) on the step-shaped adsorption isotherm of F4-MIL_140A(Ce), we herein report a ligand engineering approach targeting the MIL-140A(Ce) topology (MIL stands for Materials of Institute Lavoisier) and involving terephthalic linkers with different degree of fluorination and isomerism.

To this end, we synthesised novel F*x*-MIL_140A(Ce) MOFs by means of both an acetonitrile-based solvothermal synthesis and a milder methanol/water mixed solvent approach. The former route led to highly crystalline MOFs with the major drawbacks of the presence of unreacted linkers and fluoride ions trapped in the pores (suggesting partial decomposition of the ligand during synthesis), while the latter allowed clean and phase-pure materials to be obtained, although with lower crystallinity. The MOFs were characterized by solid-state nuclear magnetic resonance techniques that shed light on their local structure, as well as gas adsorption measurements. No step-shaped CO_2 isotherm was observed, unravelling a strong relationship between the fluorination degree of the linker and the adsorption behaviour of the resulting materials. These results open the way to deeper experimental and computational investigations into structure-property relationship which will guide the design of such advanced materials and rationalize their separation performance.

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Chemistry for the Future - 2023

Double the Fun: Exploring Two-Photon Circularly Polarized Luminescence of Chiral Eu Complexes

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Our group synthesized two unique chiral ligands, namely 2,2'-(4-(phenylethynyl)pyridine-2,6- diyl)bis(4-phenyl-oxazoline) and 2,2'-(4-(phenylethynyl)pyridine-2,6-diyl)bis(4-isopropyl-oxazoline), each with their corresponding enantiomers. These ligands, which are obtained through a multistep synthesis starting from commercial chelidamic acid and enantiopure amino alcohol, have been specifically designed to efficiently sensitize and induce strong chiroptical properties of the corresponding chiral europium complexes. These ligands combine two fundamental properties. Firstly, the ligands contain a pyridine bis-oxazoline core that creates an asymmetric coordination environment, which leads to strong circularly polarized luminescence (CPL). Secondly, adding a phenylacetylenic unit at position 4 of the pyridine helps enhance the sensitization ability of the system via the antenna effect [1]. Most importantly, the extended π-system allows the ligands to be excited by two photons (2P) simultaneously, thanks to their suitable cross-section (σ2). Many systems showing efficient CPL have been developed, while other systems can show emissive properties upon excitation via 2P. However, only one report to date combines these two aspects [2]. In our work, we report novel chiral Eu complexes that, upon excitation between 700 and 710 nm, show strong 2P-CPL using a sophisticated set-up that involved coupling a tunable femtosecond pulse laser to an existing conventional photoelastic-modulator-based CPL spectrometer. These results are of interest in the field of biomedical research, due to the greater penetration depth of the excitation wavelength and limited cell damage. Other applications include photodynamic therapy through the selective excitation of molecules within a specified focal volume.

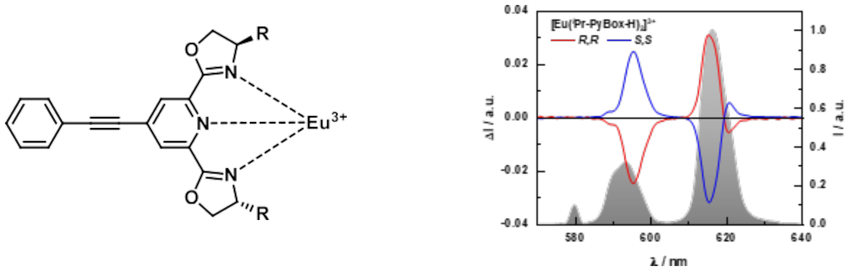

Figure 1. General structure of the Eu complexes (left) used in measuring 2P-CPL (right).

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Mapping Microplastics Pollution in European Coastal and Deep Sea Sediments through the PISA Procedure

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Plastic pollution is currently receiving worldwide attention and represents one of the most urgent environmental problems of the 21st century. Microplastics (MPs) pose a risk to human health and biota, thus it is compelling to optimize and apply analytical tools for the identification and quantification of MPs in natural environments [1]. MPs are ubiquitous pollutants in marine and freshwater bodies and can accumulate in the seabed. The aim of the JPI-Oceans HOTMIC project "*Horizontal and vertical oceanic distribution, transport and impact of microplastics*" (2020 - 2023) is to collect information to support mapping the distribution of MPs -including particles < 10 μm and microfibers- in water, sediment, and biota from coastal ocean to open ocean (Atlantic gyre) and deep sea. In one of the HOTMIC project cruises, benthic sediment samples were collected along the coast of Western Europe, at depths ranging from 10 up to 250 meters. 13 sediment samples were analysed adopting the Polymer Identification and Specific Analysis (PISA) procedure, developed by the University of Pisa [2], as it has the advantage of working directly on bulk samples and being able to identify the mass of individual synthetic polymers present as MP (< 2 mm) pollutants. The PISA procedure (Figure 1) entails solvent extraction/fractionation followed by Py-GC-MS analysis (for polyolefins, polystyrene and their degradation products), and depolymerization followed by HPLC quantification (for polyethylene terephthalate, PET, and polyamides, PAs). The approach has previously been successfully applied to sediment samples and to wastewater treatment plant sludges for the analysis of MPs [3]. The analysis of HOTMIC samples highlighted concentrations of MPs, mainly PP and PET, in the 0.1-3.0 ppm range (roughly equivalent to microparticles generated by 3 mm^2–1.5 cm^2 of a typical 20 μm thick wrapping film/kg sediment). The PISA procedure proved to be an effective method for the identification and mass quantification of MPs, providing complementary information with respect to the more common (but time-consuming and typically limited to particles >20 μm) separation by flotation and particle count procedures.

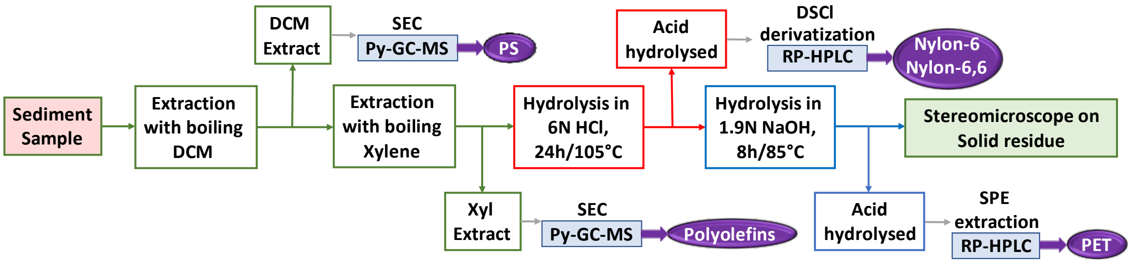

Figure 1. Flowchart of the entire analytical protocol for the separate quantification of the total mass of micro- and nanoparticles of different polymer types [2].

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Cobalt-Copper Bimetallic Catalysts by Urea Precipitation approach for Oxygen Evolution Reaction in Anion Exchange Membrane Water Electrolysis

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The demand for sustainable energy sources has intensified due to increasing concerns about greenhouse gas emissions and rising energy demands. The generation of hydrogen as an energy vector through water electrolysis has emerged as a promising technology to achieve a clean and renewable economy [1]. Anion exchange membrane water electrolysis (AEMWE) is a still in early-stage development but it is potentially economically and environmentally sustainable technology for hydrogen production that combines the advantages of proton exchange membrane water (PEM) electrolysis and traditional alkaline water electrolysis systems [2]. The development of cheap and earth-abundant metal-based catalysts for Oxygen Evolution Reaction (OER) in AEMWE is essential for the large-scale application of this technology. Cobalt oxide-based materials are low cost and available electrocatalysts that often exhibit high activity and stability in strong alkaline media, making them a promising alternative to noble metal-based catalysts [3].

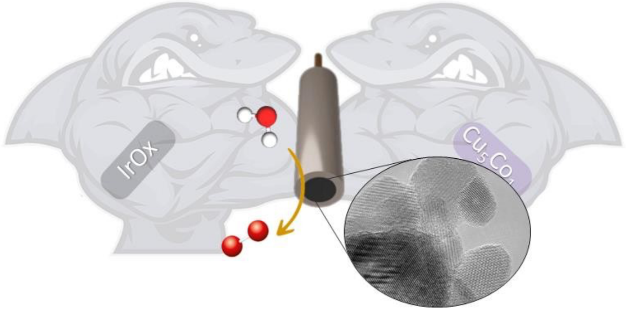

Figure 1. Graphical representation of Oxygen Evolution Reaction (OER) onto a rotating disk electrode and HRTEM image of Co5Cu1 oxide nanopowder (inset).

In this study, we investigated nanostructured Co/Cu-bimetallic oxide systems obtained through a simple and scalable approach, using urea as a precipitating agent (PU). Different Co/Cu molar ratios (7:1, 5:1, 3:1, 1:1) were synthesized and tested both in half-cell experiments and in a lab scale single cell AEMWE setup at Erredue s.p.a. The systems were comprehensively characterized using XRD, TEM, and ICP-OES techniques. Notably, the presence of Cu in the Co/Cu systems significantly contributed to enhance the performance of the monometallic Co system. In particular, the system with a Co/Cu molar ratio of 5 showed a remarkable activity and stability, exhibiting comparable results to a benchmark IrOx material.

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Comparison of thin film microextraction devices to sample human skin volatilome

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Thin Film Microextraction (TFME) is a passive sampling technique introduced in 2003 which consists of a carbon mesh sheet impregnated with one or more sorptive phases. Thanks to the large extraction surface area and volume of the sorptive phase (~190 mm^2 corresponding at about 9 µL of sorbent film), TFME sampling protocols are characterised by a greater sensitivity compared to other commonly used microextraction techniques [1]. These devices are rugged, reusable, flexible, and easy to transport and store, making TFME applications relevant in several fields, including industry, food, environment, and medicine. In this work, we focused on the use of TFME membranes for the analysis of volatile organic compounds (VOCs) emitted from the skin, as body odours play a significant role in chemical communication. We compared different sampling protocols for VOCs emitted from the armpit, which is a gland-rich area extensively studied in the literature. To determine the best sampling procedure, we employed commercially available TFME devices with three different stationary phases: Polydimethylsiloxane (PDMS), Polydimethylsiloxane/Carboxen (PDMS/CAR), and Polydimethylsiloxane/Hydrophilic lipophilic balanced (PDMS/HLB), along with different exposure times (10, 20, and 30 minutes). Sampling was conducted on nominally healthy volunteers recruited at the Department of Chemistry and Industrial Chemistry of the University of Pisa. Each experiment involved an initial cleaning of the sampling area with milli-Q water, followed by placement of the device in direct contact with the skin through the use of hypoallergenic gauze compresses Dermatess Plus. Devices were thermally desorbed with a TD-100 and VOCs analysed using a GC-QQQ (Gas Chromatography-Triple Quadrupole Mass Spectrometry) instrument. To obtain a comprehensive overview of the results, a qualitative screening was performed to identify the sample components. Figure 1A illustrates the number of identified compounds for each phase at different sampling times. To visualise similarities and differences among samples, a principal component analysis (PCA) was performed using the Metaboanalyst software (Scores plot in Figure 1B). Results highlighted that the most promising sorbent materials were PDMS/HLB and PDMS/CAR and the optimal exposure times were 20 and 30 minutes.

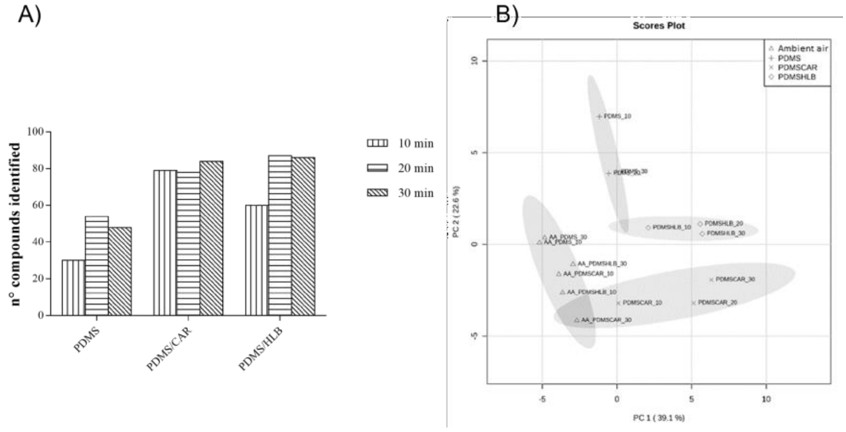

Figure 1. A) Number of identified compounds per phase and exposure time. B) Scores Plot related to the PCA of the compounds from samples collected with different phases (PDMS, PDMS/CAR, PDMS/HLB) on the armpit at various sampling times. In the label: AA = ambient air, 10/20/30 = exposure time.

References:

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Direct C-2 alkylation of imidazole derivatives through decarboxylative coupling

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Imidazole-containing drugs have a broader spectrum of applications in clinical medicine. Based on various literature studies, imidazole derivatives have antibacterial, anti-tuberculosis, antifungal, antiviral, anti-inflammatory, antitumor activity, etc.[1] In particular, a class of imidazoles of considerable interest involves derivatives bearing an alkyl substituent at the C-2 position. In fact, many of the bioactive derivatives containing the imidazole nucleus bear an alkyl substituent at this position. It can be seen from the literature also that functionalized imidazoles and benzimidazoles are usually obtained by cyclization reactions. This type of approach, while generally leading to highyields, requires the preparation of precursors for each derivative, if not commercially available. In addition, complex molecules containing imidazoles and benzimidazoles substituted in position C-2 present the cyclization as one of the first synthetic steps, which represents a disadvantage for drug discovery, since different analogues must be obtained in a simple way.

A key to overcome this issue may be represented by C-H activation reactions, as they allow the functionalization of already preformed nuclei. According to the literature, however, there are only a few examples for the direct C–H alkylation of imidazoles and benzimidazoles, and all of them require harsh conditions. In the last years, radical protocols have been revisited because, in general, these reactions are fast and work under mild conditions. A striking example of radical C-H activation for the formation of sp^2-sp^3 C-C bond is undoubtedly the Minisci reaction, whose original protocol[2] was developed between the 60s and 70s. However, only in the last decades with the advent of novel chemical techniques such as photo- and electrochemistry Minisci protocol has been deeply revisited, leading to the development of a great number of procedures (known as Minisci-like reactions) that refer to the original one. While many radical precursors have been successfully employed in Minisci couplings, relatively few heteroarenes undergo successful coupling. Among these, electron poor 6-membered rings still remain the favorite cores especially when nucleophilic C-centered radicals are employed. On the basis of these considerations, we have instead decided to investigate the reactivity of five-membered electron-rich systems, such as imidazole and benzimidazole derivatives, with carboxylic acid derivatives as radical precursors under Minisci conditions, starting from his pioneering protocols,[2] with the aim of allowing fast molecular exploration in medicinal chemistry.

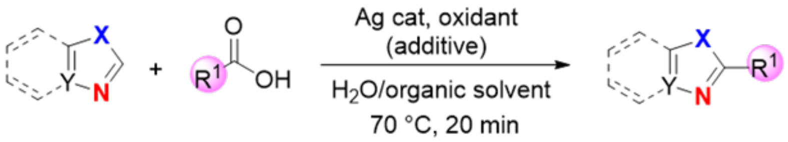

Figure 1. General procedure for the direct alkylation of azoles

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Modeling energy-transfer processes in the light-harvesting complex CP29: first principles simulation of transient absorption spectroscopy

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In photosynthetic organisms, light is absorbed by specialized molecular aggregates called light harvesting complexes (LHCs), protein scaffolds that host multiple photosynthetic pigments. The resulting excitation energy is funnelled from pigment to pigment and from LHC to LHC toward reaction centres, where it is converted to chemical energy.

These processes, called light harvesting, can be studied using transient absorption (TA) spectroscopy. The time-resolved spectral features represent a direct fingerprint of the excited-state dynamics occurring in light harvesting complexes. However, the complexity of the signals, coming from different simultaneous processes, prevents a complete interpretation of spectra.

Computer simulations represent a powerful tool to help spectroscopists map all excited-state processes that occur during TA experiments. However, LHCs are challenging systems for computational chemists. First, LHCs are large systems in which each chromophore experiences a specific and dynamic interaction with the protein environment. The combination of molecular dynamics simulations with *ab-initio* multiscale methods has proven effective in modelling the excitation properties of such dynamic systems [1]. Secondly, simulating light harvesting processes requires strategies to model excitation energy transfer processes and the relative spectroscopic fingerprints. Here we present a first-principles simulation of the TA spectra of the chlorophylls network in the CP29 minor LHC from plants. A comparison with experimental spectra is included [2].

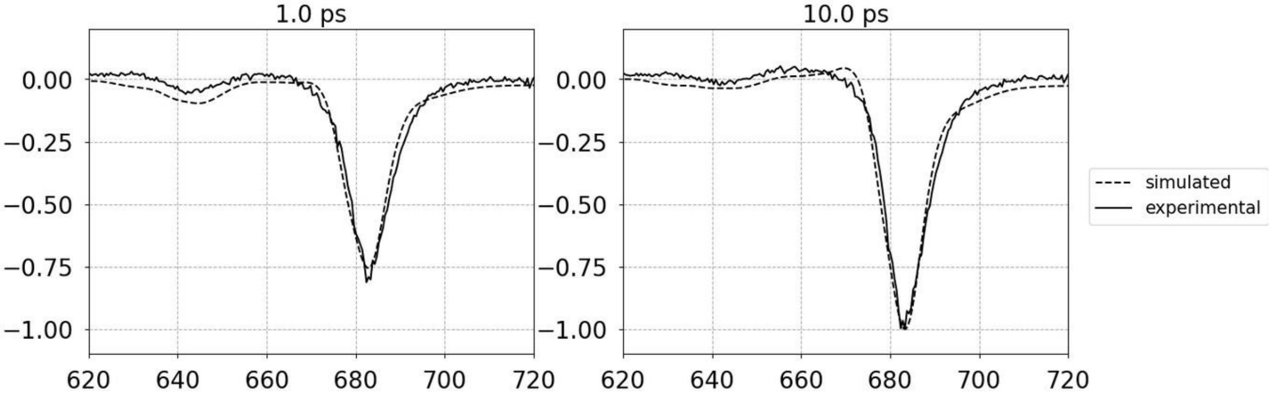

Figure 1. Comparison between simulated and experimental transient absorption spectra (298K). The delay time between the pump and probe pulses is shown above each plot.

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A potentiometric pH sensor for monitoring chronic wounds

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Chronic wounds, namely wounds that do not heal in three months, represent a problem for healthcare system, as they heavily impact both the quality of life of the patients and the resources required for their treatment. Parameters such as pH and temperature are good indicators of the wound state and its healing process (e.g., the pH value of a wound typically decreases as it progresses towards healing) [1]. In this work, a potentiometric pH sensor with integrated thermistors was devised to monitor both pH and temperature in the active site of the wound and on the perilesional skin. In a single platform (figure 1A) attached on the skin, pH is measured through the potential difference between a traditional Ag/AgCl reference electrode, placed on the perilesional skin, and a functionalized graphite electrode as the working electrode, placed directly on the wound. Polianiline was chosen as the pH sensitive material for the functionalization of working electrode, ensuring a quick and sensitive response to pH variation. A Poly-acrylic acid (PAA) based hydrogel was developed to be applied onto the reference electrode to improve its electrical stability and to enhance the adhesion of the sensor to the skin (figure 1B). The sensor showed linear response from pH 3 to pH 10, a range that encompass the possible pH that a wound could manifest in a real situation (Figure 1C). Furthermore, this sensor was able to measure pH of a real sample of wound exudate with an error within ±0.2 points of pH when compared with the results obtained with a reference glass electrode.

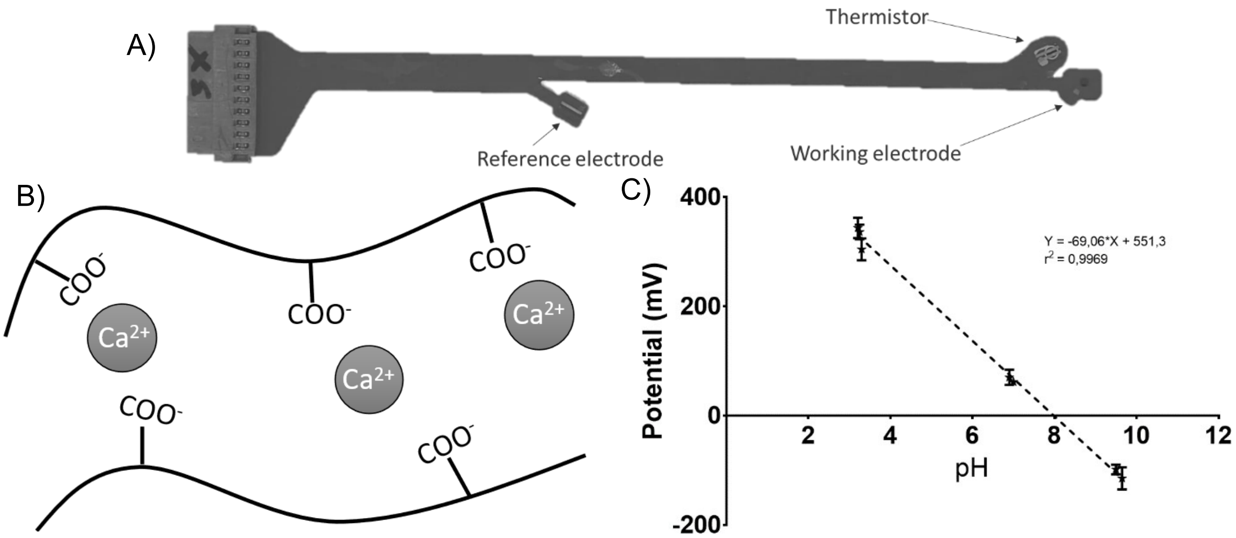

Figure 1. (A) A picture representing the first prototype of the sensor (B) The Calibration curve obtained from triplicate pH measures from 4 different electrodes (N=12) of a solid agar surface used to mimic the consistency of human skin (C) A simplified scheme of the structure of the PAA hydrogel used to stabilize the reference electrode and to make it adhere better on the skin.

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Holistic enzymatic approach to antibacterial cellulose nanocrystals

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Nanostructured materials represent promising substrates for biocatalysts' immobilization and activation. Cellulose nanocrystals (CNCs), accessible from waste and/or renewable sources, are sustainable and biodegradable, show high specific surface area for anchoring a high number of enzymatic units, and have high thermal and mechanical stability. This work presents a holistic enzyme-based approach for fabricating cellulose nanocrystals from Avicel and functional materials by immobilizing enzymes onto sustainable CNCs. Figure 1 describes the use of *Aspergillus Niger* endoglucanase for the enzymatic hydrolysis of Avicel. This approach is greener if compared to acid hydrolysis and successfully yields neutral CNCs. Then, we describe enzyme self-assembly, performed between the lysozyme from chicken egg white and neutral or negatively charged sulphated cellulose nanocrystals. The immobilization reaction of the enzyme on the biodegradable substrate produces interesting biohybrid systems with preserved enzymatic activity.

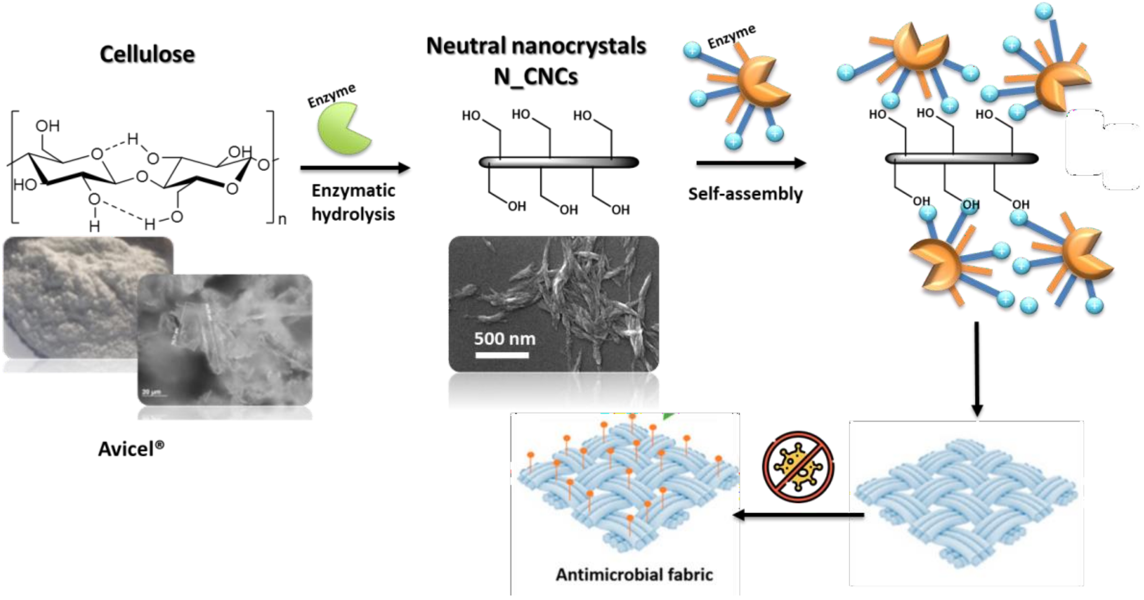

Figure 1. Holistic enzymatic approach to obtain cellulose nanocrystals from Avicel and to functionalmaterials by enzymes immobilizing them onto sustainable CNCs

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Exploiting Self-Association Phenomena to determine enantiomeric composition without chiral auxiliaries: NMR Spectroscopy investigations and implications

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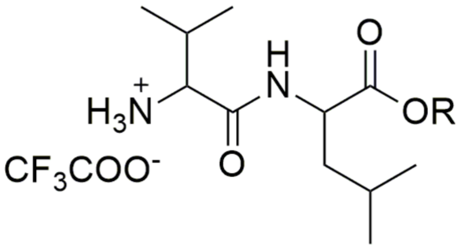
Self-association phenomena may be exploited to determine enantiomeric composition via NMR Spectroscopy without employing any chiral auxiliary. The phenomenon underlying this process is also called SIDA (Self-Induced Diastereomeric Anisochrony) [1]. Due to the interactions among enantiomers, diastereomeric complexes may be formed and some peaks may undergo splitting: the integrated areas of the split signals correspond to the enantiomeric composition [2,3].

Several ester derivatives of dipeptides have been investigated to verify whether they exhibit self-discrimination abilities. Those that showed self-discriminating behaviours (Figure 1) were then subjected to thermodynamic studies (*i.e.,* determination of self-association constants and determination of self-association enthalpy and entropy), to diffusion coefficient measurements via DOSY (Diffusion Ordered SpectroscopY) experiments and to mono- and bi-dimensional NOE (Nuclear Overhauser Effect) experiments. These measurements allowed to gain insight into the fundamental aspects of the SIDA phenomenon.



TFA ValLeuOR
R = -Et, -tBu, -Bn

Figure 1. Chemical structure of the investigated ester derivatives of dipeptides

References:

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New Reactivity Pathways in Ruthenium(II) η^6-Arene Complexes

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Half-sandwich ruthenium complexes with η^6-arene ligands represent an interesting organometallic platform in view of their versatile chemistry and their potential application in catalysis [1] and/or in medicinal chemistry [2]. The {Ru(η^6-arene)}$^{2+}$ moiety is capable of coordinating a wide range of mono-, bi- and tridentate ligands by well-established substitution reactions in mild conditions. The π-backdonation from the Ru(II) center is mostly directed towards the arene ligand, resulting in the electrophilic activation of other unsaturated fragments in the coordination sphere. For the same reason, the ruthenium−arene bond can be cleaved in the presence of competing π-acceptor ligands.

Herein we describe new reactivity pathways enabled by the coordination of alkynes or isocyanides and regulated by the selection of arene ligands with different electronic and steric properties.

The interaction of terminal alkynes with [$RuCl_2(PR_3)(η^6\text{-}C_6Me_6)$] precursors provided new alkoxy(alkyl)carbene complexes, via reactive η^1-vinylidene intermediates. Their subsequent hydrolysis gave access to rare alkyl-carbonyl derivatives (Figure 1a).

Selective coordination of m-xylyl (Xyl) or cyclohexyl isocyanide to the {$RuCl_2(η^6\text{-}C_6H_6)$} scaffold was accomplished via ligand exchange on the labile Me_2S adduct. Next, nucleophilic addition of methylamine on the isocyanide carbon gave an acyclic diaminocarbene ligand, the first to be reported for Ru-arene derivatives (Figure 1b). Instead, the bulkier *p*-cymene ligand was displaced from [$RuCl_2$(XylNC)(η^6-*p*-cymene)] by thermal treatments in the presence of DMSO, affording unprecedented octahedral [$RuCl_2$(XylNC)(DMSO)$_3$] complexes (Figure 1c).

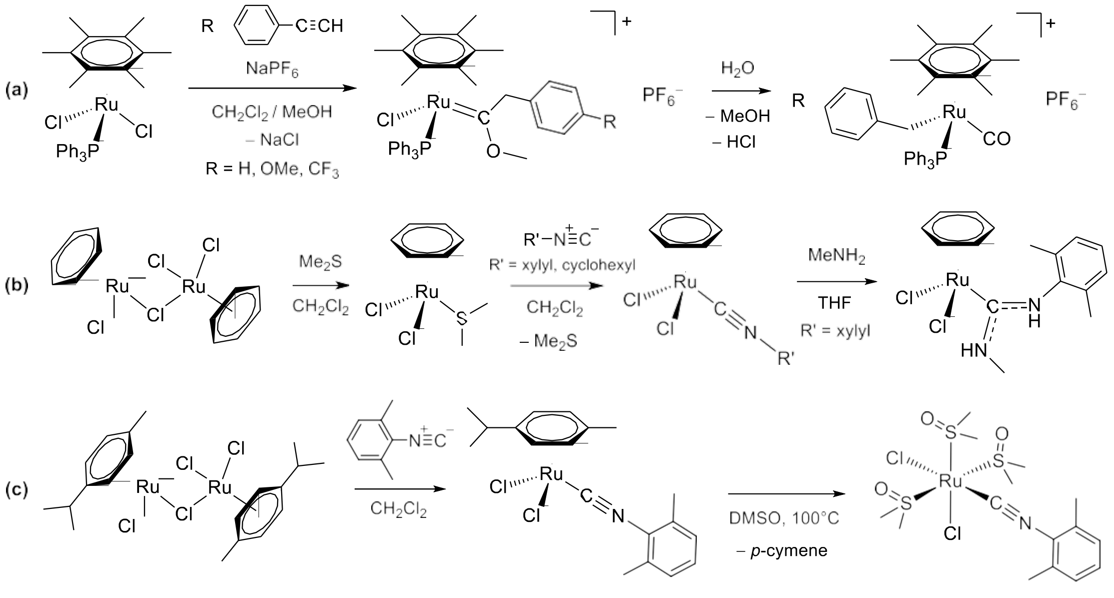

Figure 1. Coordination and/or activation of terminal alkynes (a) or isocyanide(s) (b) on Ru(II) η^6-arene complexes and subsequent *p*-cymene/DMSO replacement (c).

References:
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Anti-Cancer Warfare: A New Hope. ReaxFF MDs Disclose the Stages of Biohybrid Nano Weapons Preparation, Structure, Dynamics, and Final Action.

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Understanding the stability and functionality of nanocarriers in drug delivery systems is crucial to get effective therapeutic outcomes. In this work, we have conducted Reactive Molecular Dynamics simulations based on a tuned force field to investigate the assembly and behavior of a nanocarrier composed of a functionalized zinc oxide nanoparticle (ZnONP) loaded with an anti-cancer drug [1]. Our goal has been to gain new insights into the reactivity of the whole system and its ability to release the drug cargo in a physiological setting. The simulations revealed the intricate dynamics and interactions among the various components: for example, the functional chains (oleic acid) exhibited stable chemisorption on the ZnONP, forming monodentate or bidentate bonds with the metal oxide surface. These chains enhanced the stability and distribution of the lipid cover and acted as a reservoir for the drug molecules. The drug was entrapped within the lipid chains or adsorbed on the exposed surface regions, which could be detrimental to its release. Our findings demonstrated a gradual increase in the aggregate size due to the lipid cover's swelling in response to the aqueous medium. This evolution led to an unpacked structure with extended and separated lipid chains, providing potential pathways for a gradual drug release. This computational strategy successfully described and predicted the dynamics of the nanocarrier during various stages, in agreement with experimental results. It also showed how the possible reactions could be evaluated to predict the behavior of functionalized nano-vehicles in different environments, emphasizing the need to include reactivity for optimizing the nanocarrier design.

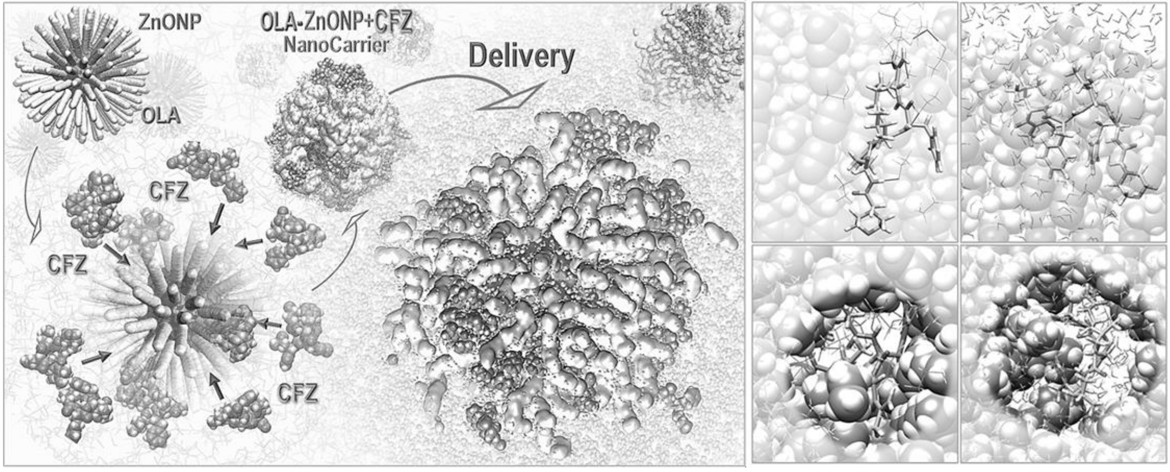

Figure 1. Steps of the simulated processes (from left to right): 1) ZnO nanoparticle (ZnONP) functionalization with oleic acid (OLA); 2) Drug loading (CFZ = Carfilzomib); 3) Study of the dynamics of OLA+ZnONP+CFZ in ethanol; 4) Study of the dynamics of OLA+ZnONP+CFZ in water.

References:

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Energy storage devices: graphite/$LiFePO_4$ batteries and supercapacitors

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Lithium-ion batteries are the leading rechargeable systems on the market today. Their high energy density and power density favoured their use as energy sources in a wide range of applications from portable electronics to electric transport [1]. The $LiFePO_4$ (LFP) cathode, generally considered thermally stable and of low toxicity, presents a theoretical capacity of 170 mAh/g. For that reason, LFP-based cells are considered as promising candidates for application in high-rate devices. However, the safety of lithium-ion battery is still a technical hurdle for same interesting applications, such as in hybrid electric vehicles and electric vehicles. The possible thermal runaway is not only a safety hazard, but also it hampers the performance of lithium-ion batteries. Up to now, literature research is focused on studying batteries under extreme conditions in order to improve their safety. In this work, post-mortem experimental studies have been performed on graphite/$LiFePO_4$ cells designed for power-type applications, investigating a fresh and an abused cell under normal/regular conditions at initial temperature of 40°C after an overcharge test. The main components of both batteries, cathode, anode and electrolyte, were analysed by FTIR spectroscopy, SEM and EDS. The performed analyses displayed some modification of the graphite anode surface after the abuse, such as a rougher surface and increased amount of oxygen, fluorine and phosphorus. On the contrary, regarding the cathode, no relevant differences on the morphology between reference and aged cells were evidenced. Moreover, the exhaust gases from the abused battery were analysed by GC/TCD, revealing the prevailing presence of CO_2, CO and H_2.

Still in the field of energy storage, a highly interesting alternative to batteries are supercapacitors that have gained a lot of attention for their high specific capacitance, long life cycle, high power density and safety, becoming a bridging for the power-energy difference between capacitors and fuel cells/batteries. In particular, literature studies focus on the development of new materials, such as biomass-derived graphene-like carbon ones, to be used in novel energy storage applications [2]. In detail, porous activated carbons (AC) represent promising candidates for electric double layer capacitors, whose high performance is mainly due to the ultrahigh specific surface area ideally located in pores with suitable size. On this basis, in this work, two AC materials were prepared starting from the waste biomass hazelnut shells, using KOH as activated agent [3]. The first one was obtained by activating the raw biomass, whereas the second one by activating the hydrochar achieved by the hydrothermal carbonisation of the same hazelnut shells. Both AC materials were investigated in supercapacitors field and the preliminary cyclic voltammetry and electrochemical impedance spectroscopy measurements have shown promising results in line with reference data reported in the literature.

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Mitigation of Copper corrosion with N-Heterocyclic Carbenes

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Due to its excellent thermal, mechanical and electrical properties, copper is an irreplaceable material in many fields such as power distribution and integrated circuits manufacturing, to name a few. However, when exposed to oxidizing environments or halide-containing solutions, Cu tends to form a superficial oxide layer that is not self-passivating. This phenomenon seriously compromises its performances in most applications, thus making it necessary to protect its surface with inorganic or organic coatings. Organic coating such as Self-Assembled Monolayers (SAMs) of n-alkanethiolates provide excellent short-term resistance against copper corrosion [1,2] but their performances gradually worsen over time [2]. Recent studies [3,4] have shown that N-Heterocyclic Carbenes (NHCs) can strongly bind to copper surfaces forming SAMs. Moreover, it was discovered that NHCs are also able to remove surface oxides and simultaneously functionalize the resulting metallic surfaces [5]. In this work, we investigated how the adhesion of an NHC layer on Cu could act as a possible mitigator of corrosion processes. Adhesion of *NHC-1* (Figure 1*)* was carried out using an electrochemical process [6] which exploits the formation of bases to deprotonate the NHC precursors, producing the corresponding carbenes. Potentiodynamic polarization curve measurements were carried out in a 3.5% (w/w) NaCl solution and Tafel Extrapolation was applied to the cathodic part of the polarization curve to obtain the corresponding corrosion current density at the corrosion potential (Figure 2). Then, by applying Faraday's Law it was possible to convert the current density to its penetration velocity (mm/year). Cu surfaces functionalized with NHC-1 showed a 70% decrease in the corrosion rate with respect to bare Cu, achieving performances similar to short chain thiolate SAMs.

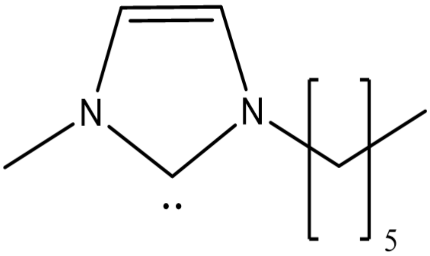

Figure 1. The carbene 1-hexyl-3-methylimidazol-2-ylidene (NHC-1)

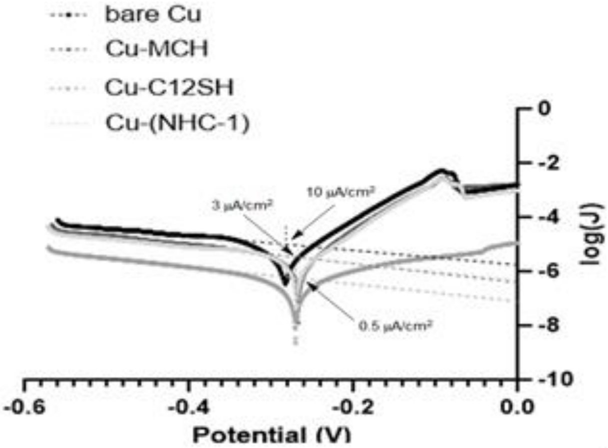

Figure 2. Polarization curves (vs Ag/AgCl electrode) registered on Cu electrodes functionalized with 6-mercaptohexanol (MCH), dodecanethiol (C12SH) and NHC-1

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Development of an aptasensor for the detection of *Escherichia coli*

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The detection and identification of pathogenic microorganisms within public health and food safety is of crucial importance as they pose a major threat to worldwide health system as well as an economic burden. In this context, biosensors represent a valuable alternative to classical methodologies due to their intrinsic low-cost, short response time, and portability [1]. In this work, a screen-printed gold electrode functionalized with two different aptamers (P12-55 and P12-31 [2]) was used for the development of an aptasensor for the detection of *E. coli*. Electrochemical impedance spectroscopy was used to evaluate the change in the charge transfer resistance of the aptasensor upon interaction with the bacterial cells. The aptasensor showed a linear response in the presence of *E. coli* within 7 – 7×10^3 CFU/mL with a limit of detection of 1.4 CFU/mL (Fig. 1A). Additionally, the biosensor proved to be selective for *E. coli* and no response was observed in presence of *Staphylococcus aureus* and *Pseudomonas aeruginosa*. Finally, the sensor was tested in real samples like urine, milk, and tap water (Fig. 1B).

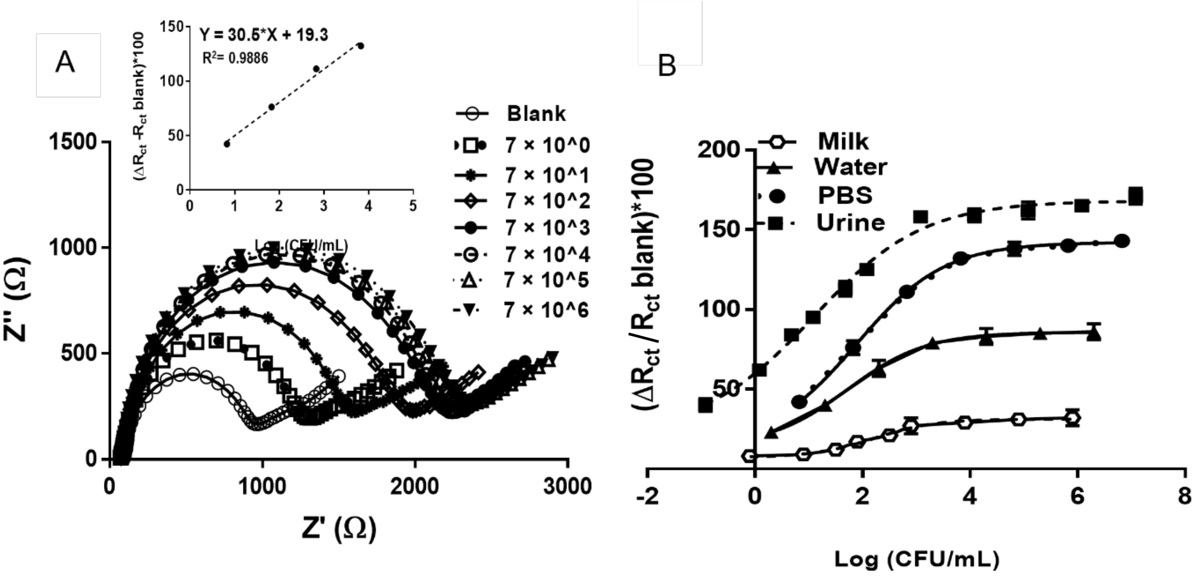

Figure 1. (A) Electrochemical impedance spectroscopy performed in buffer solution containing $K_4Fe(CN)_6$ 5 mM with increasing concentrations of *E. coli* (0 to 10^6 CFU/mL). (B) Difference in the charge transfer resistance of aptamer-based biosensors towards *E. coli* in different matrices.

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Cyano-Amino-Allylidene Diiron Complexes

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A range of diiron complexes derived from $Fe_2Cp_2(CO)_4$ ($Cp=\eta^5-C_5H_5$) have emerged as versatile scaffolds for the building of functionalized organometallic structures: the facile removal of up to three carbonyl ligands and the cooperative effects exerted by the two iron centres allow to assemble small molecular units through unconventional reaction pathways [1]. Cyano-amino-allylidene complexes (**1**) are obtainable in high yields from the commercial precursor through a sequence of regio- and stereo-selective reactions. The synthesis is tolerant towards various functionalities, granting a fine tuning of the substituents (R, R', R''). In **1**, the interaction between the amine lone pair and the terminal carbonyl ligand paves the way to the thermal removal of the CO and its replacement with the amino group in the coordination to the iron (Figure 1a). The resulting hemi-labile system (**2**) exhibits a promising catalytic activity in the coupling reaction of CO_2 with epoxides. When the thermal decarbonylation of a set of complexes **1** (R'' = ferrocenyl) is performed in the presence of an isocyanide, the reaction provides the route to the formation of rare dimetallic species comprising two bridging hetero-hydrocarbyl ligands (**3**) [2].

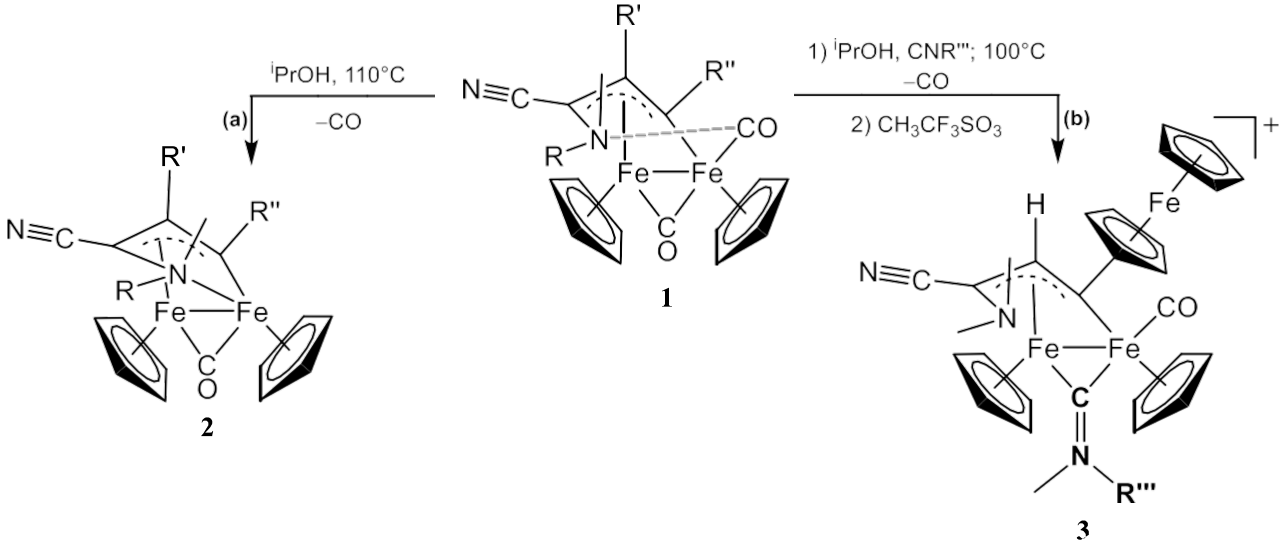

Figure 1. a) Thermal decarbonylation of diiron cyano-amino-allylidene complexes; (b) Two step synthesis of aminocarbyne ligands.

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5 GENDER EQUALITY

Achieve gender equality and empower all women and girls