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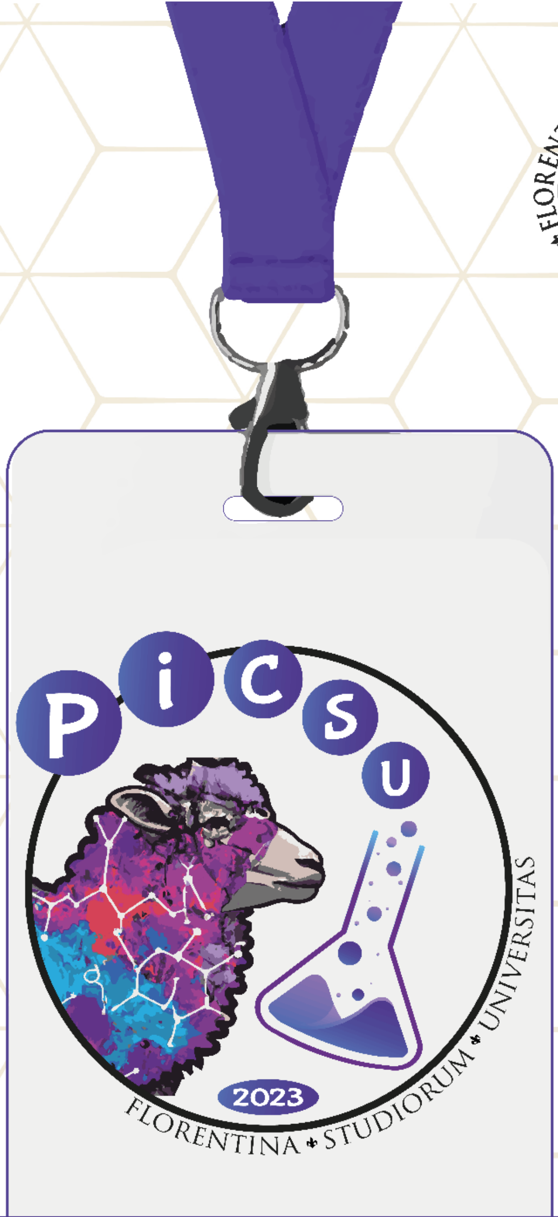

Book of Abstracts

2nd Edition of the Symposium

PhD in Chemical Sciences at UniFi

PiCSU 2023

25-27 January 2023
Wed the 25th: 14:00-18:15
Thu the 26th: 09:00-12:50 and 13:50-16:30
Fri the 27th: 09:00-12:45 and 13:45-16:30

Blocco aule, room 35
Scientific campus of Sesto F.no
Via Gilberto Bernardini 6

2nd Edition of the Symposium

PhD in Chemical Sciences at UniFi

PiCSU 2023

25-27 January 2023, Sesto Fiorentino (FI), Italy

BOOK OF ABSTRACTS

Ideated and edited by:
Anna Maria Papini, Chiara Sarti, Davide Ranieri, Francesca Buco,
Lapo Renai, Lorenzo Pacini, Marco Bonechi, Michael Quagliata,
Michelangelo Fichera, Michele Casoria, Patrick Severin Sfragano,
Saul Santini, Yschtar Tecla Simonini Steiner.

The Organizing Committee

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Michelangelo Fichera

Chiara Sarti

Davide Ranieri

Yschtar Tecla Simonini Steiner

Anna Maria Papini

List of Participants

All PhD students in Chemical Sciences that presented their research projects are listed below in alphabetical order on the basis of their PhD cycle.

XXXV cycle
Agnieszka Staśkiewicz
Arianna Balestri
Debora Pratesi
Giacomo Lucchesi
Giammarco Maria Romano
Gina Elena Giacomazzo
Giulia Mugnaini
Jacopo Cardellini
Jacopo Tricomi
Lapo Renai
Letizia Pontoriero
Lorenzo Briccolani Bandini
Maria Giulia Davighi
Mariagrazia Lettieri
Martina Vizza
Gheorghe Melinte
Stefano Martinuzzi

XXXVI cycle
Andrea Comparini
Davide Ranieri
Francesca Porpora
Gavino Bassu
Kristian Vasa
Lorenzo Baldini
Michela Lupi
Patrick Severin Sfragano
Sara Calandra
Saul Santini
Simi Maria Emilia Mangani
Valentina Vitali

XXXVII cycle
Alessandro Gerace
Alessandro Veneri
Alice Cappitti
Andrea Dali
Chiara Sarti
Daniela Porcu
Fernando Soto Bustamante
Francesca Buco
Laura Vespignani
Lorenzo Bracaglia
Lorenzo Pacini
Lucrezia Cosottini
Marco Bonechi
Margherita Verrucchi
Mert Acar
Michael Quagliata
Michelangelo Fichera
Michele Casoria
Riccardo Spena
Sara Aquilia
Serena Benedetta Cabigliera
Yschtar Tecla Simonini Steiner

XXXVIII cycle
Andrea Geri
Andrea Sodini
Angela Sofia Tino
Benedetta Ciuffi
Chiara Baroni
Chiara Cianci
Chiara Mangini
Elena Mariani
Fabio Biffoli
Francesca Mancusi
Francesca Milano
Giulia Bonaccorso
Giulio Pappaianni
Ilaria Antonia Vitale
Ilaria Chiarugi
Ilaria De Santis
Laura Conti
Laura Sforzi
Leonardo Querci
Leonardo Tacconi
Lorenzo Quadrini
Margherita Marino
Mariano Riccardi
Neri Fuochi
Pietro Gentilesca
Pietro Tordi
Prem Prakash Sahu
Riccardo Gallorini
Sara Pavone
Shagufta Sajjad
Stefano Zineddu

Programme of the Symposium

Wednesday, 25/01/2023

14:00	14:45	**Opening Session**	Opening speech	
			Chair: Michele Casoria, Patrick S. Sfragano	
14:45	15:05	OR01	Giulia Mugnaini	Chemically cross-linked gelatin hydrogels: glutaraldehyde and glyceraldehyde effect on structural, diffusional, and mechanical properties
15:05	15:25	OR02	Letizia Pontoriero	Disentangling the complexity of modular proteins through advanced NMR spectroscopy: preliminary characterization of the full-length Nucleocapsid protein from SARS-CoV 2
15:25	15:45	OR03	Jacopo Cardellini	The nano-bio interface as a platform for technological applications
15:45	15:58	OR04	Sara Calandra	Optimization of the binder selection protocol for radiocarbon dating of historical mortars
15:58	16:30			**Coffee Break & Poster Session**
16:30	16:50	IS 01	Giacomo Becheri, PQE Group	My journey from physical chemistry at Unifi to Manager at PQE Group
16:50	17:03	OR05	Gavino Bassu	Fast and Bacterious: motility drift from super to sub-diffusion behavior
17:03	17:16	OR06	Lorenzo Baldini	Divergent synthesis and chemoinformatic studies of natural product-derived small molecules for biomedical application
17:16	17:26	OR07	Michael Quagliata	Glucopeptides derived from myelin-relevant proteins and hyperglucosylated non-typeable Haemophilus influenzae bacterial adhesin cross-react with multiple sclerosis specific antibodies
17:26	17:36	OR08	Francesca Buco	Gold Nanoparticles as Scaffolds for the Multimerization of Iminosugars: New Multivalent Modulators of the Enzyme GCase
17:36	17:46	OR09	Fernando Soto Bustamante	Optimizing the structure of sustainable hydrogels for nano/microfiltration, selective absorption, and anti-biofouling behavior
17:46	17:56	OR10	Chiara Sarti	Wastewater as a source of emerging micropollutants: occurrence, removal, and future perspectives
18:00	18:15			**End of the 1st Session**

Thursday, 26/01/2023

Chair: Francesca Buco, Lapo Renai

9:00	9:20	OR11	Arianna Balestri	Amphiphilic block copolymers as versatile tools for the design of smart lipid assemblies
9:20	9:40	OR12	Jacopo Tricomi	Rational design, synthesis and pharmacological evaluation of a new generation of β-adrenergic receptors (β-ARs) ligands
9:40	10:00	OR13	Gina Elena Giacomazzo	Ruthenium (II) polypyridyl complexes: versatile tools in the design of light-responsive therapeutic agents
10:00	10:13	OR14	Michela Lupi	Synthesis of enantioenriched hetero[4]- and [5]helicenes through Lewis Base catalysis
10:13	10:26	OR15	Andrea Comparini	Electroplating on Al6082 aluminium: a new green and sustain-able approach
10:26	10:46	IS 02	Marynka Ulaszweska, ThermoFisher	Metabolomics data elaboration: from Features to Compounds
10:50	11:20			**Coffee Break & Poster Session**
11:20	11:40	OR16	Martina Vizza	Electrodeposition and modification of interesting catalytic and technological surfaces
11:40	11:50	OR17	Alice Cappitti	Biomass valorization towards new high-performance biopolymers
11:50	12:00	OR18	Laura Vespignani	Study of new materials with low environmental impact and their use in the protection of wooden artifacts
12:00	12:10	OR19	Sara Aquilia	Development of renewable materials based on proteins and peptides from vegetable sources
12:10	12:20	OR20	Daniela Porcu	Spectroscopic and morphologic investigation of Bronze Disease in Cultural Heritage
12:20	12:30	OR21	Lorenzo Pacini	Optimization of critical parameters to obtain difficult peptide sequences using induction-heat energy on solid phase peptide synthesizer PurePep® Chorus
12:30	12:40	OR22	Alessandro Veneri	Development of flexible molecular and inorganic hybrid solar cells: materials for a sustainable future
12:40	12:50	OR23	Andrea Dali	The role of the propionate interactions in the Listeria monocytogenes coproporphyrin ferrochelatase bound to its physiological substrate
12:50	13:50			**Lunch Break**

Chair: Chiara Sarti, Michelangelo Fichera

13:50	14:10	OR24	Giacomo Lucchesi	Synthesis and characterization of a new lead-free perovskite solar cell

14:10	14:30	OR25	Maria Giulia Davighi	Stimuli responsive inhibitors and pharmacological chaperones for Gaucher disease
14:30	14:50	OR26	Debora Pratesi	Synthesis of N-glycomimetics from low cost and recycled saccharides
14:50	15:10	OR27	Lapo Renai	Development and application of instrumental LC-MS/MS analytical platforms and chemometric data treatment for the study of complex matrices in the environmental and nutritional fields
15:10	15:23	OR28	Simi Maria Emilia Mangani	Archaeometric study of Montelupo Maiolica: a critical analysis of the non-invasive approach chosen
15:23	15:36	OR29	Francesca Porpora	Development of a methodology for characterization and treatment of triacetate cellulose media of historical and artistic interest with a focus on those affected by «vinegar syndrome»
15:40	15:55			**Coffee Break**
15:55	16:05	OR30	Serena Benedetta Cabigliera	Microfibers (MFs): the key to framing the problem and developing systems for their mitigation
16:05	16:15	OR31	Marco Bonechi	Electrochemical characterization of molecular properties and modified surfaces for energy and technological applications
16:15	16:30			**End of the 2nd Session**

Friday, 27/01/2023

9:00	9:30	Prof. Giulietta Smulevich	**January 27 · International Holocaust Remembrance Day**

Chair: Michael Quagliata, Davide Ranieri

9:30	9:50	OR32	Giammarco Maria Romano	Polyamine-based fluorescent receptors for Emerging Pollutants
9:50	10:10	OR33	Lorenzo Briccolani Bandini	Effects of xc-functional choice on the characterization of a reaction mechanism
10:10	10:30	OR34	Agnieszka Staśkiewicz	The role of helical structure in a series of Myelin Basic Protein peptides for antibody recognition in Multiple Sclerosis
10:30	10:43	OR35	Kristian Vasa	Synthesis of Peptide and Protein Drug-Conjugates for Targeted Therapy
10:43	10:56	OR36	Valentina Vitali	Effects of protonated and deuterated environment: towards a detailed distance distribution analysis
10:56	11:26	IS 03	Riccardo Deidda, Janssen	What's next after a PhD? My journey from academia to the pharmaceutical industry
11:26	11:46			**Coffee Break & Poster Session**

11:46	11:59	OR37	Saul Santini	Development of analytical procedures for the determination of emerging organic compounds in environmental matrices
11:59	12:09	OR38	Lorenzo Bracaglia	13C detected NMR spectroscopy applications for the study of multidomain proteins
12:09	12:19	OR39	Margherita Verrucchi	Electrochemical methods to quantify the content of organic additives in complex metrices of copper plating baths
12:19	12:29	OR40	Lucrezia Cosottini	HuHf-Gold(I) compounds bioconjugates
12:29	12:39	OR41	Mert Acar	Smart Autonomous Responsive Materials
12:39	12:49	OR42	Michelangelo Fichera	Production of carbonaceous materials through thermoconversion of sewage sludge, their activation and characterization for application in wastewater depuration
12:49	12:59	OR43	Yschtar Tecla Simonini Steiner	Recognition of emerging pollutants (EPs) with artificial fluorescence chemical sensors: a supramolecular approach
12:59	13:09	OR44	Michele Casoria	Improved Fluorinated Alcohol Force Fields for Molecular Dynamics Simulations of Peptides and Proteins in Biomimetic Media
13:10	14:20			**Lunch Break**
			Chair: Saul Santini, Yschtar Tecla Simonini Steiner	
14:20	14:40	OR45	Stefano Martinuzzi	A Comparative Research on Corrosion Behavior of Electroplated and PVD Chromium Coatings
14:40	15:00	OR46	Mariagrazia Lettieri	Optical-based bioanalytical assays for drugs quality control and diagnostic applications
15:00	15:20	OR47	Gheorghe Melinte	Electrochemical platforms for allergens aptasensing
15:20	15:33	OR48	Davide Ranieri	Paramagnetic Porphyrin Dimers: New Building Blocks for the Development of two Qubit Quantum Gates
15:33	15:49	OR49	Patrick Severin Sfragano	Sewage sludge-derived biochar to design more sustainable electrochemical sensors
15:50	16:05			**Coffee Break**
16:05	16:15	OR50	Alessandro Gerace	Synthesis of new materials to develop innovative permanent magnets: hard/soft coupling
16:15	16:25	OR51	Riccardo Spena	Design and fabrication of micro- and milli- fluidic chip for the development of green industrial formulations
16:25	17:00	**Closing Session**	PhD Coordinator, Prof. Marco Pagliai, Organizing Committee, Awards	
17:30				**Social Event at CUS Bar**

Abstracts of the Oral Presentations

OR01

Chemically cross-linked gelatin hydrogels: glutaraldehyde and glyceraldehyde effect on structural, diffusional, and mechanical properties

Giulia Mugnaini, Rita Gelli, Leonardo Mori, and Massimo Bonini

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Hydrogels have received great attention owing to their high-water content, tunable properties, and similarity to natural tissues, which make them suitable for being used as tissue engineering scaffolds [1] or drug delivery systems [2]. The possibility to customize solute diffusion, mechanical and degradation properties modulating the cross-lining degree is of utmost importance for hydrogels applicability. Gelatin is a protein-based natural polymer, derived from the hydrolysis of collagen. Owing to its biological origin, it represents an excellent candidate for the preparation of biocompatible hydrogels, even if a cross-linking treatment is required to prevent its dissolution at physiological temperature. To overcome cytotoxicity problems raised by the use of glutaraldehyde, a conventional gelatin cross-linker, glutaraldehyde has been proposed as a more biocompatible alternative [3]. In this work, we investigated the effect of different cross-linking reaction conditions on the physicochemical properties of gelatin hydrogels. Samples were cross-linked with glutaraldehyde and glyceraldehyde systematically varying the concentration of cross-linkers, acetone, and water. The cross-linking degree, estimated from TNBSA assay, and the dissolution behavior at physiological temperature were investigated, showing that the reaction conditions strongly affect hydrogels stability against dissolution at 37 °C. The morphology and porosity were analyzed by means of scanning electron microscopy, whereas X-rays scattering was used to clarify the cross-linking effect on the gel network at the nanoscale. The mechanical and diffusional properties of gelatin cross-linked hydrogels were correlated with the cross-linking degree: compressive strength of gelatin hydrogels is strongly dependent on the cross-linking degree and on the type of cross-linker, whereas the diffusion coefficient of a model drug, namely methylene blue, thought the hydrogel is not affected by the chemical modifications.

[1] G.D. Nicodemus et al., *Tissue Eng. Part B Rev.* **2008**, *14*, 149-165.
[2] J. Li et al., *Nat. Rev. Mater* **2016**, *1*, 1-17.
[3] M. A. Vandelli et al., *Int. J. Pharm.* **2001**, *215*, 175-184.

OR02

Disentangling the complexity of modular proteins through advanced NMR spectroscopy: preliminary characterization of the full-length Nucleocapsid protein from SARS-CoV 2

Letizia Pontoriero, Marco Schiavina, Tessa Bolognesi, Isabella C. Felli, and Roberta Pierattelli

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Many of the proteins deputed to accomplish multifunctional roles present a modular organization of their structure [1]. In particular, the tethering of folded and disordered domains allows the compartmentalization of specific functions into dedicated portions along the primary sequence. This biological strategy is also adopted by viruses and the Nucleocapsid protein (N) from SARS CoV-2 is a clear example of the versatility given by the modular arrangements of several domains. It is composed of 419 residues, organized in two folded domains (NTD and CTD) and three intrinsically disordered regions (IDR1, IDR2 and IDR3) that constitute almost 45% of the primary sequence. Many studies were carried out on N but a complete high-resolution characterization is not yet achieved because of the challenges imposed by the dynamic and heterogeneous nature of the structure. In this context, heteronuclear NMR spectroscopy is unique to obtain atomic details, particularly for the flexible portions which usually limit canonic NMR investigations [2]. The technique proved to be fundamental to extrapolate pivotal information on N’ constructs that involve IDRs (such as the 1-248, namely NTR) [3]. Here we present the information obtained with the application of tailored multidimensional ^{13}C direct detected experiments and the use of high-field instrumentation, such as the 1200 MHz instrument with a probe tailored for ^{13}C direct detection. A protocol for protein sample production is also provided. The proposed experimental set-up allowed us to delineate the chemo-physical properties of N, even in challenging experimental conditions, and it constitutes a useful starting point for detailed studies. The strategy could be optimal to approach the study of complex protein machineries.

[1] B. M. Lunde et al., *Nat Rev Mol Cell Biol.* **2007**, *8*, 479–490.
[2] I. C. Felli, R. Pierattelli, *Chem Rev.* **2022**, *122*, 9468–9496.
[3] L. Pontoriero et al., *Biomolecules* **2022**,*12,* 929.

OR03

The nano-bio interface as a platform for technological applications

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Despite the revolutionary impact of the use of nanomaterials in medical applications, the number of nanoparticles (NPs) approved for clinical trials is still very limited. A vast research area focuses on disentangling the intricate nature of the nano-bio interface, i.e., the interface between NPs and biological systems, to predict the NPs' biological impact and potential cytotoxicity [1]. With this purpose, synthetic lipid membranes rapidly emerged as biomimics to study the nano-bio interface in simplified and controlled conditions, providing a simplistic yet comprehensive understanding of membrane-related phenomena. In this field, recent reports showed that citrate-capped gold nanoparticles (AuNPs) spontaneously aggregate on synthetic zwitterionic membranes with a membrane-templated process dependent on the rigidity of the membranes and the surface functionalization of the inorganic NPs. Despite the potential relevance of this peculiar aggregative phenomenon, its mechanistic and kinetic aspects were not completely understood. In the present work, the interaction between citrated inorganic nanoparticles and synthetic and natural membranes was thoroughly investigated, aiming at: i) contributing to improving the fundamental knowledge on the nano-bio interface [2]; ii) designing straightforward approaches for the synthesis of novel engineered hybrid nanomaterials; iii) demonstrating that the NPs-membrane interaction can be exploited for the characterization of free-standing vesicles and inorganic NPs-vesicles hybrids [3]. In conclusion, the presented results provide an overall description of the association of citrated NPs with lipid structures, shedding light on the main energetic contributions that drive the interaction and demonstrating its technological relevance, paving the way for the development of novel strategies for the production and characterization of nanomaterials.

[1] AE Nel et al., *Nat Mater*. **2009**, *8*(7), 543-557.
[2] J. Cardellini et al., *J Phys Chem C*. **2022**, *126*(9), 4483-4494.
[3] L. Caselli et al., *Nanoscale Horizons* **2021**, *6*(7), 543-550.

OR04

Optimization of the binder selection protocol for radiocarbon dating of historical mortars

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[c] Institute of Heritage Science - National Research Council of Italy, Via Madonna del Piano 10, 50019-Florence, Italy
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A complete characterization of the mortar before radiocarbon dating is mandatory to identify the type of mortar and to develop an efficient analytical approach that allows to select the most suitable component of mortar for absolute dating [1]. We optimized a characterization protocol of mortar to identify the datable fraction (or anthropogenic calcite), thank to multidisciplinary collaboration between INFN-LABEC, and ISPC-CNR and DST-UNIFI. The procedure includes a preliminary in-depth characterization of mortars, by means of different analyses such as OM, XRD, TGA, SEM-EDS, OM-CL and further ATR-FTIR, OM-CL, XRD on selected portions of sample. The analyses are non-destructive and allow to completely characterize the material truly used for dating [2]. From the datable isolated fraction CO_2 is extracted through acidification, thanks to a new set-up that permits to select different aliquots of CO_2 while the acidification reaction takes place. The characterization protocol was applied on Florentine mortar to assess the feasibility of radiocarbon dating.

In the last year, I evaluated high-resolution micro-Raman technique, non-destructive, to measure the order of crystal calcite [3], analyzing “standard” samples of geogenic and anthropogenic calcite. A wide range of different carbonate rock (geogenic calcite) and lime binder of mortar (anthropogenic calcite), obtained, respectively, by different geological and archaeological/historical contexts were selected. Frequencies, heights, and area of typical vibrations of carbonate groups in calcite samples were collected. A Key Influences Analysis (KI) and Principal Component Analysis (PCA) were used for visual inspection and reducing dimensionality of dataset from different calcite types.

[1] R. Hayen, et al., *Radiocarbon*. **2017,** *59*(6), 1859–1871.
[2] S. Calandra et al., *JPCS* **2022**, *2204*(1), 012048.
[3] E. Zolotoyabko, et al., *Cryst. Growth Des*. **2010**, *10*(3), 1207-1214.

OR05

Fast and Bacterious: motility drift from super to sub-diffusion behavior

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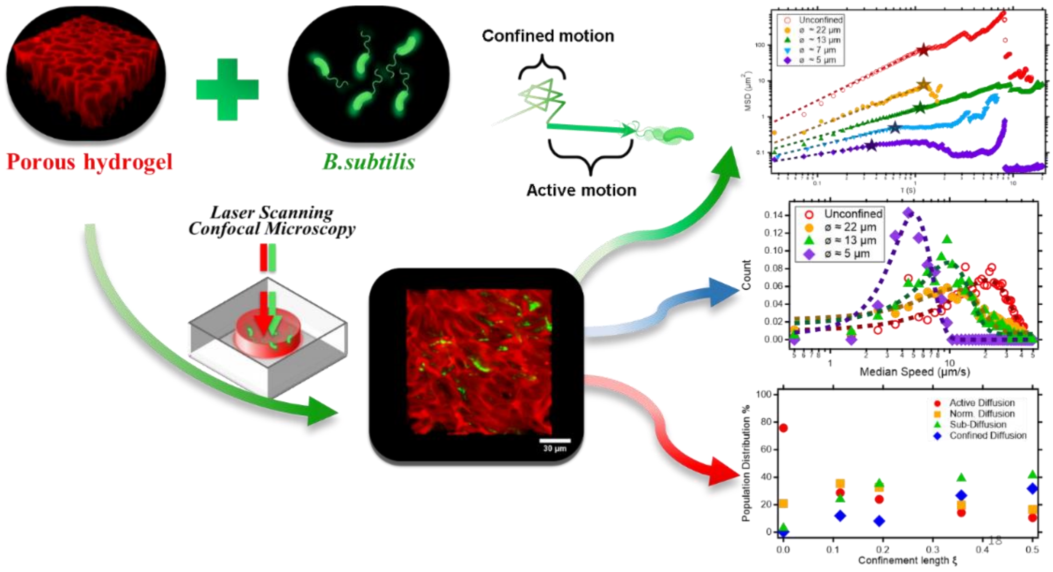
The ubiquitous presence of motile bacteria in micro-environments characterizes many interesting phenomena, from everyday life to technology; infection diseases, pharmaceuticals, nutrition, and agricultures are just few examples of the multitude of fields where the bacterial activity can represent a serious threat or an invaluable resource. Although bacterial motility has been extensively studied in aqueous dispersions or smooth surfaces, the characterization of these properties in realistic disordered three-dimensional porous matrices not been investigated principally due to the high opacity associated to these materials. Here we applied disordered 3D transparent hydrogels of polyethylene glycol with porosities in the micron scale [1] to investigate the confined motion of *B.subtilis.* Through single-cell tracking by laser scanning confocal microscopy, we found that the characteristic run-and-tumble motion of the bacteria is strongly affected by the porosity of the network, with cells being transiently trapped in the cavities of the network. The single-trajectory analysis has given a direct observation of the bacterial motility transition induced by the confining network. Our work provides an interesting insight into bacterial motility in complex disordered media, laying the principles for a better understanding and prediction of bioactive motions.



Graphical abstract: The direct observation of diffusing bacteria in porous 3D network highlights the motility transition confinement-induced

[1] G. Bassu et al., *Colloid Surf. B.* **2023**, *221*, 112938.

OR06

Divergent synthesis and chemoinformatic studies of natural product-derived small molecules for biomedical application

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The Diversity-Oriented Synthesis (DOS) approach aims to obtain a bouquet of complex and structurally diverse molecules, through a divergent synthetic strategy, to enhance the survey of the chemical space, and to increase the probability of discovering NMEs of biomedical relevance [1]. Particularly, we are interested in the amino acid chiral pool, due to their great applicability in such a field.

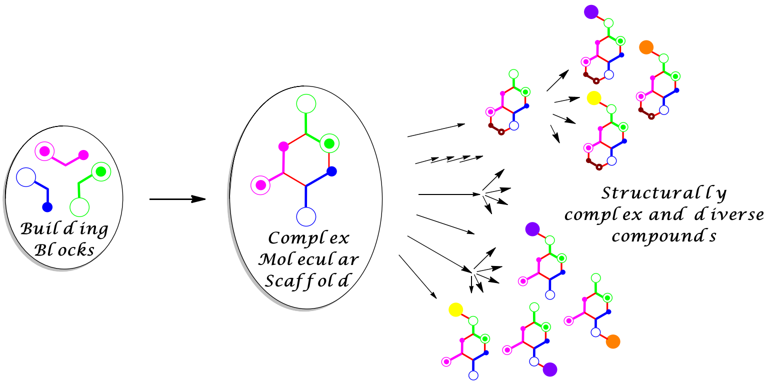

Figure 1: The DOS approach

Indeed, we identified *L*-tyrosine-derived dual integrin/gelatinase inhibitors [2], synthesizing a group of structurally diverse compounds through a divergent approach. Then, we synthesized the enantiopure β-amino acid *trans*-ACPC to functionalize it through two different strategies for the directed C(sp^3)-H bond activation, depending on the FG that we aim to exploit, the amino or the carboxylic acid FG. Complexity-generating reactions, like MCRs e.g., are of great importance in DOS, so we exploited and combined a DOS-compatible reaction such as the CCR, with a β-C(sp^3)-H bond activation reaction directed by the 8-AQ DG to obtain complex and diverse γ- and δ-lactams, among which we identified μM BACE-1 inhibitors. With the same reaction, the CCR, we simply obtained complex and diverse morpholinones that were designed to be applied as central scaffolds for the synthesis of a DEL [3], thanks to the collaboration with the research group of Dr. Brünschweiger at TU Dortmund. Thanks to which we also set up a MCR such as the Ugi multi-component reaction in an on-DNA fashion, to obtain structurally complex structures and scaffolds of biomedical relevance as lactams

[1] A. Trabocchi, (*John Wiley & Sons, Inc.*) **2013**. ISBN:9781118618110..
[2] L. Baldini, et al., *Molecules* **2022**, 27(4), 1249.
[3] (a) A.L. Satz et al., *Nat Rev Methods Primers* 2, *3* (**2022**).
(b) E. Lenci et al., *Bioorg. & Med. Chem.* **2021**, *41*, 11621

OR07

Glucopeptides derived from myelin-relevant proteins and hyperglucosylated non-typeable *Haemophilus influenzae* bacterial adhesin cross-react with multiple sclerosis specific antibodies

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[c] Department of Pharmacy, University of Naples "Federico II", Via Domenico Montesano 49, 80131-Naples, Italy
[d] Department of NeuroFarBa, University of Florence, Via Ugo Schiff 6, 50019-Sesto Fiorentino, Italy
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Multiple sclerosis (MS) is an inflammatory and autoimmune disorder, in which an antibody-mediated demyelination mechanism is accepted to play a role. We prepared two glucosylated peptides derived from the human myelin proteins, i.e., Oligodendrocyte-Myelin Glycoprotein (OMGp) and Reticulon-4 receptor (RTN4R), selected by a bioinformatic approach for their conformational homology with CSF114(Glc), a designed β-turn antigenic probe derived from myelin oligodendrocyte glycoprotein (MOG), a glycoprotein present in the central nervous system. This synthetic antigen is specifically recognized by antibodies in MS patient sera. We report herein the antigenic properties of these peptides, showing on one hand that MS patient antibodies recognize the two glucosylated peptides, and on the other hand that these antibodies cross-react with CSF114(Glc) and with the previously described hyper-glucosylated non-typeable *H. influenzae* bacterial adhesin protein HMW1ct(Glc) [1]. These observations point to an immunological association between human and bacterial protein antigens, underpinning the hypothesis that molecular mimicry triggers breakdown of self-tolerance in MS and suggesting that RTN4R and OMGp can be considered as autoantigens [2]. Moreover, we have developed an accelerated solid-phase synthesis of glycopeptides containing multiple N-glycosylated sites using the prototype of an efficient High-Temperature Fast Stirring Peptide Synthesizer (HTFS-PS), utilizing heating and stirring in combination with low-loading solid supports and equimolar concentrations of the precious *N*-glucosylated building-blocks [3].

[1] M.T.C. Walvoort et al., *Scientific Reports* **2016**, 6, 39430
[2] M. Quagliata et al., *J.Pep.Sci.* **2023,** e3475. DOI: 10.1002/psc.3475
[3] P. Strauss et al., *Org.Biomol.Chem.,* **2022**, DOI: 10.1039/D2OB01886A

OR08

Gold Nanoparticles as Scaffolds for the Multimerization of Iminosugars: New Multivalent Modulators of the Enzyme GCase

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The enzyme β-glucocerebrosidase (GCase) is a lysosomal glycosidase whose misfolding and dysfunction is involved in many pathological disorders, such as Gaucher Disease (a lysosomal storage disorder). A therapeutic strategy for restoring the GCase activity is based on the use of Pharmacological Chaperones (PCs), molecules able of binding and stabilizing the tertiary structure of the enzyme [1].

Recent studies showed that *N*-alkylated 3,4,5-trihydroxypiperidines (red moiety **1** in Figure 1) are promising PCs for GCase (1.25-fold recovery GCase activity at 100 µM) [2]. Moreover, the multimerization of **1** in a trimeric dendron has shown a significant enhancement in the PCs activity (1.25-fold recovery GCase activity at 10 µM) [2].

Gold nanoparticles (AuNPs) have already been used as scaffolds for the multimerization of iminosugars and sugars, leading to biocompatible and water dispersible systems and guaranteeing the possibility of the simultaneous grafting of different thiol-ending ligands in a controlled manner [3].

In my project, I employed for the first time AuNPs as scaffolds for the multimerization of dendronic *N*-alkylated 3,4,5-trihydroxypiperidine. After the synthesis and characterization, I performed preliminary *in vitro* tests demonstrating the binding affinity of the AuNPs towards GCase and their ability of stabilizing the tertiary structure of GCase against thermal denaturation.

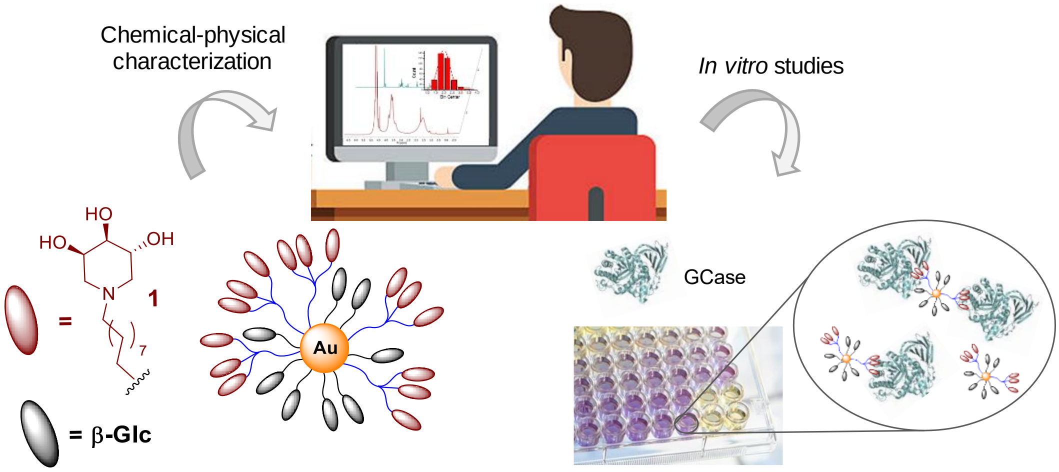

Figure 1: Graphical abstract.

[1] D. M. Pereira et al., *Chem. Sci.* **2018**, *9*, 1740-1752
[2] M. Martìnez-Bailén et al., *Pharmaceuticals* **2022**, *15*, 823
[3] M. Marradi et al., *Chem. Soc. Rev.* **2013**, *42*, 4728-4745.

OR09

Optimizing the structure of sustainable hydrogels for nano/microfiltration, selective absorption, and anti-biofouling behavior

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Hydrogels (HG) are porous polymeric networks that can find application in a wide variety of fields including antimicrobial protection. The focus of this project is the development of sustainable HGs obtained by green synthesis processes having internal structures that optimize transport in micro and nanofiltration processes, selective absorption, and anti-biofouling behavior. The HGs were fabricated using sustainable components as Chitosan (Ct) and Poly-vinyl alcohol (PVA), and freeze-thawing (F/T) to avoid inclusion of crosslinking agents [1,2]. HGs prepared with different CT-PVA compositions and F/T times were characterized by Confocal Microscopy, Small Angle X-Ray Scattering and Rheology. We found that the composition and F/T process result in different structures, porosity, morphology, and mechanical response that can be controlled and tuned for applications.

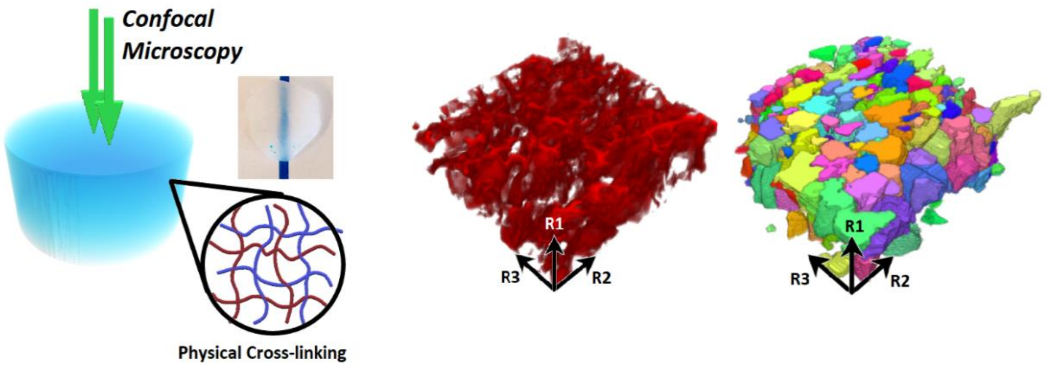

Figure 1: Hydrogel obtained using freeze-thawing as physical crosslinker, confocal image and porous reconstruction of the sample.

[1] Figueroa-Pizano et al., *Carbohydrate polymers*. **2018**, *195*, 476-485.
[2] Koosha et al., *Journal of Functional Biomaterials*, **2021**, *12*(4), 61.

OR10

Wastewater as a source of emerging micropollutants: occurrence, removal, and future perspectives

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The high presence of persistent organic microcontaminants, such as microplastics (MPs), is a key environmental concern due to their potential impact on water bodies and related ecosystems. MPs are not properly retained by wastewater treatment plants (WWTPs), which often represent a major source of release into rivers and seas [1].

In this context, the present study aims to investigate the effectiveness of treatment processes for the removal of MPs from wastewater by both different conventional WWTPs and Nature Based Systems (i.e., Combined Sewer Overflow-Constructed Wetlands, CSO-CWs), located in central-northern Italy, and to optimize a specific analytical protocol for the extraction and analysis of MPs in wastewater samples.

Indeed, since there is no standardized analytical methodology and the extremely complexity matrix of these samples [2], rich in particulate organic matter and possible interferents, the extraction of MPs is the main challenging step. In this regard, different H_2O_2 digestion conditions of the samples were tested, varying the concentration of hydrogen peroxide, digestion time and temperature. The effectiveness of a following density separation with NaCl-saturated solution was also evaluated to maximizing the removal of suspended organic solids without degrading the plastic polymers. The optimized sample pre-treatment developed allowed both a quantitative analysis, carried out with a stereomicroscope, and an accurate chemical characterization using micro-FTIR-FPA.

The experimental data led to a classification of the microparticles detected, based on their colors, shapes, and materials, as well as an initial assessment of the removal efficiency of the analytes by the different wastewater treatment systems under investigation. Despite the high removal rates, due to the large water volumes treated every day by the plants, even small quantities released per liter can result in a considerable number of MPs being discharged into the receiving water bodies, posing a threat to aquatic ecosystems. In general, the samples showed a prevalence of fibers, both polymeric and cellulosic, of various sizes and colors (predominantly blue and transparent), although the extent and characteristics of contamination is linked to the type of influent and fluctuates according to the seasons of the year.

[1] P. Kay et al., *Environ. Sci. Pollut. Res*. **2018**, *25*, 20264–20267.
[2] M. Simon et al., *Water Research* **2018**, *142*, 1-9.

OR11

Amphiphilic block copolymers as versatile tools for the design of smart lipid assemblies

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Lipids are amphiphilic molecules constituting the primary build blocks of cell membranes, which are ubiquitous biological motifs with a crucial role in cell functions. Given these peculiarities, they have inspired, over the years, the development of many different bilayer architectures for biomedical applications. Amphiphilicity is particularly common in biomacromolecules, but amphiphilic proprieties may be also found in synthetic molecules, like amphiphilic copolymers. They spontaneously self-assemble into similar lipid aggregates, introducing new properties to all the systems. In recent years, innovative systems combining both amphiphilic scaffolds have attracted considerable interest in the development of new smart materials [1]. Here, hybrid lipid-polymer systems in lamellar or non-lamellar assemblies were designed and characterized for two main purposes: i) the development of novel biomimetic platforms and ii) the design of smart stimuli-responsive lipid nanoparticles (NPs). Innovative biomimetic platforms consisting of the phospholipid 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC) and the block copolymer poly(butadiene-b-ethyleneoxide) (PBD-b-PEO) assembled in lamellar structures revealed the formation of lateral phase-separated bio-membranes [2]. Then, a novel class of thermo-responsive drug delivery systems has been addressed by the assembly and stabilization of not-lamellar lipid glycerol monooleate (GMO) nanoparticles by a new thermo-responsive dimethyl acrylamide (DMA) and N-isopropylacrylamide (NIPAM) copolymers [3], unveiling highly lipophilicity towards synthetic and natural membranes.

In conclusion, these results pave the way for the development of new smart devices by the combination of lipid bilayers with amphiphilic block copolymers for several bio-applications.

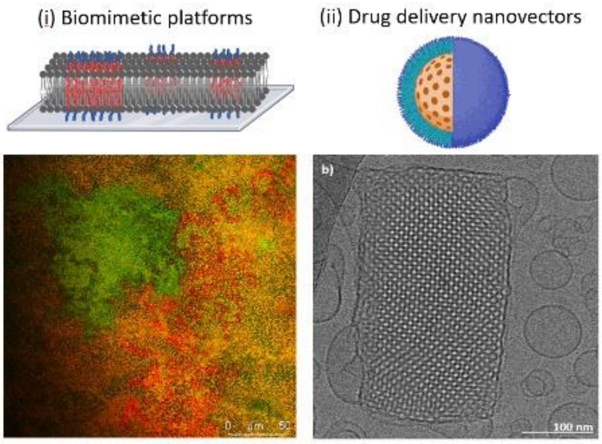

Figure 1: **(i)** illustration and CLSM image of hybrid biomimetic platforms; **(ii)** illustration and Cryo-TEM image of hybrid drug delivery nanovectors.

[1] M. Kang et al., *Adv. Funct. Mater.* **2018**, *28*, 1704356-1704376.
[2] A. Balestri et al., *Langmuir* **2020**, *36*, 10941-10951.
[3] A. Balestri et al., *Colloids Surf. B Biointerfaces* **2022**, *220*, 112884-112893.

OR12

Rational design, synthesis, and pharmacological evaluation of a new generation of β-adrenergic receptors (β-ARs) ligands

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The main objective of my PhD was the design of selective ligands for β-adrenergic receptors (β-ARs). β-ARs include three subtypes (β1/β2/β3-ARs) that belong to G-protein-coupled receptors (GPCRs), transmembrane receptors that mediate a wide range of catecholamine-induced physiological responses [1]. Thus, biomedical applications of molecules able to modulate β-adrenergic signaling have become increasingly attractive over the last decade, revealing that β-ARs are key targets for a plethora of therapeutic interventions. Moreover, recent reports proved that β-ARs, mainly β2- and β3-ARs, are significantly overexpressed in multiple tumor types, where their signaling is involved in boosting many important aspects of malignant phenotype, thus, opening a new area of oncological research called 'Neurobiology of cancer' [2].

Despite successes in β2-AR drug discovery, identification of β-AR ligands that are useful as selective tools in pharmacological studies of the three β-AR subtypes, or lead compounds for drug development is still a highly challenging task. This is mainly due to the intrinsic plasticity of β-ARs along with the need of molecules with a receptor subtype selectivity profile, tissue specificity and minimal off-target effects. In particular, a comprehensive understanding of the structure-activity relationships for the three β-AR subtypes is still incomplete and this significantly limits drug discovery.

In this thesis, we have addressed this challenge and we present a comparative study including all the three receptor subtypes, which provided an in-depth exploration of the 3 β-AR structure-activity relationships. We have synthesized and obtained the pharmacological profile of a series of structurally diverse compounds that were designed based on the aryloxy-propanolamine scaffold of **SR59230A** [3]. Comparative analysis of their predicted binding mode within the active and inactive states of the receptors in combination with their pharmacological profile revealed key structural elements that control their activity as agonists or antagonists.

[1] B.K. Velmurugan, *et. al.*, *Biomed. Pharmacother.*, **2019,** *117*, 109039
[2] B. Mravec, *et. al., Int. J. Mol. Sci.*, **2020**, *21*, 7958.
[3] J. Tricomi, *et. al.*, *Eur. J. Med. Chem.*, **2023**, *246*, 11496

OR13

Ruthenium (II) polypyridyl complexes: versatile tools in the design of light-responsive therapeutic agents

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The widely known side effects associated with the use of commonly employed antitumoral drugs, along with the increasing multidrug resistance of bacterial pathogens, make it urgent to develop new and effective antitumoral as well as antimicrobial agents, which should be based on a new class of compounds, rather than on analogues of known scaffolds. In this scenario, ruthenium (II) polypyridyl complexes (RPCs) are an appealing family of compounds due to their unique chemical-physical repertoires, which include light-triggered singlet oxygen sensitizing properties, a good ability to interact with key biological targets, and structural diversity that allows access to various therapeutic modes of action by a careful selection of the spectator ligands. In each case, the main advantage is the spatial and temporal control of the drug activation using a light source, allowing for improved discrimination between malignant and healthy tissues [1]. The efforts in this work were focused on the precise design of RPCs to enable their adaptability to various therapeutic circumstances. In this regard, both photostable sensitizers for photodynamic therapy (PDT), and photoactivable complexes, capable of releasing bioactive molecules, for photoactivated chemotherapy (PACT) were developed [2]. Additionally, considerable efforts were also expended to improve the selectivity of the developed Ru(II)-drugs through encapsulation in biocompatible nanostructures such as proteins and lipidic nanoparticles [3]. The aim of this communication is to highlight the versatility of RPCs in the development of effective therapeutic agents with widespread application.

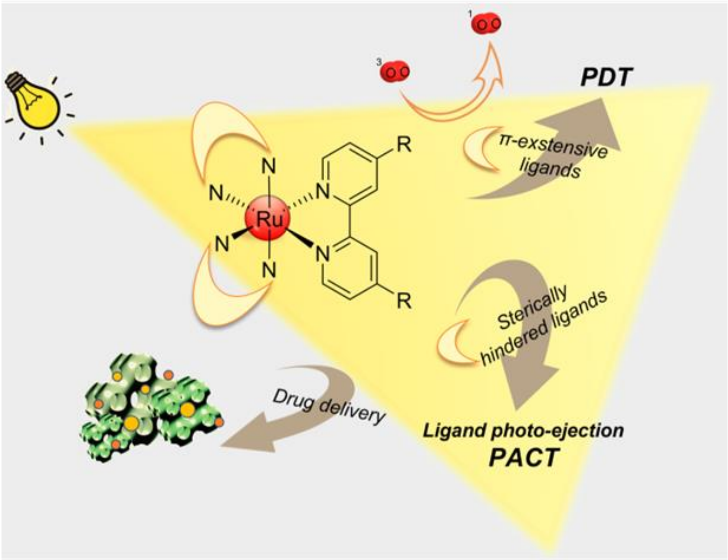

Figure 1: RPCs as versatile light-triggered tools for widespread therapeutic application.

[1] L. Conti et al., *Coord. Chem. Rev.* **2022**, *469*, 214656-214709.
[2] G. E. Giacomazzo et al., *Inorg. Chem.* **2021**, *61*,18, 6689-6694.
[3] L. Conti et al., *Inorg. Chem. Front.* ***2022**, 9*, 1070-1081.

OR14

Synthesis of enantioenriched hetero[4] and [5]helicenes through Lewis Base catalysis

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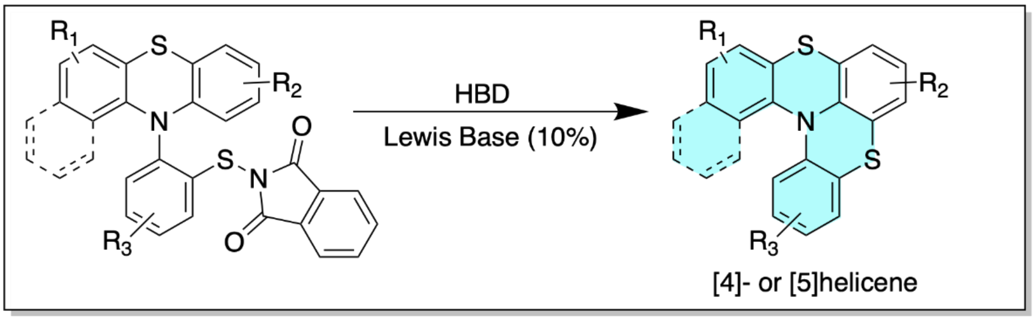
Helicenes are polycyclic aromatic compounds with screw shaped skeletons formed by ortho- fused aromatic rings. From just a chemical curiosity related with their inherent chirality, these compounds have stimulated manifold studies in several fields, owing to their unique structural features and physicochemical properties [1]. Most of these applications strongly requires the use of these molecules in their enantiomerically pure form. The resolution of these compounds is achievable by chiral HPLC or by the temporary insertion of chiral auxiliaries [2]. Efforts towards enantioselective syntheses of helicenes have also been reported [3] and represent a challenging goal. In this communication, a new promising strategy for the regio-, stereo- and enantioselective synthesis of configurationally stable aza-thia[4]- and [5]helicenes exploiting a Hydrogen Bond Donor - Lewis Base (HBD-LB) catalytic system will be described (Scheme 1). The scope and limitation of this new methodology as well as the applications of the enantiopure heterohelicenes prepared will be discussed in this communication.



Scheme 1

[1] Y. Shen et al., *Chem. Soc. Rev.* **2012**, *112*, 3, 1463–1535.
[2] M. Lupi et al., *Molecules* **2021**, *27(4)*, 1160.
[3] V. Pellicciolі et al., *Angew. Chem. Int. Ed.* **2022**, *61*, e202114577.

OR15

Electroplating on Al6082 aluminum: a new green and sustainable approach

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Recently, major fashion market players are aiming to introducing sustainable materials within their value chain. Among a vast variety of metals and materials in general, aluminum alloys, besides being unlimitedly recyclable, are also interesting because of their technical characteristics (as in being light and cheap).[1] Despite being a promising base material for the fashion-jewelry sector, its tendency to form a passivating film makes them difficult to be galvanized, even more when impurities of refractory elements are present. In this work we focused on the pre-treatments and electroplating on Al6082 aluminum which is largely used for fashion-jewelry applications. The objective of the present study was to assess whether Al6082 series aluminum is suitable as base material for the fashion market by means of assessing plating pre-treatments and cyanide-free zincations steps effectiveness.[2] After the electroplating, adhesion between the deposited layers was evaluated both with cross-sectional SEM analysis as well as with an adhesion evaluation test (ISO2819:2018): no detachments confirmed the positive test outcomes and thereby highlighted that Al6082 can be exploited as base material in the fashion-jewelry market.

[1] L. Xu et al., *Energies* **2021**, *14*, 1560
[2] J. Burgess, *Transactions of the IMF* **2019**, *97*, 285–288

OR16

Electrodeposition and modification of interesting catalytic and technogical surfaces

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In the last few decades, electrodeposition has gained great attention both scientifically and technologically. In particular, the deposition performed by means of electrochemical methods presents several advantages if compared to the vacuum-based techniques (e.g., Physical Vapor Deposition). Firstly, electrodeposition is more environmentally sustainable, since it allows to operate at room temperature and pressure. Secondly, electrochemical processes can be scaled to the industrial level still obtaining a fine control on the growth conditions, with considerable financial gains. For these reasons, the possibility to obtain interesting technologically and catalytic surfaces was studied, by means of electrochemical methods only. Firstly, the electrodeposition of the conductive polymer poly(3,4-ethylenedioxythiophene) (PEDOT) was evaluated to fabricate a hybrid PEDOT/Cu/Au electronic solid-state device, which showed high conductivity and ohmic behaviour over a wide range of frequencies. This further expanded the range of possible uses of PEDOT, especially regarding systems prone to be used as electrodes in stacked devices [1]. Then, the electrodeposition of II-IV compounds was investigated on Silicon, which is the pillar of modern technology, in order to obtain surfaces with interesting photo-emissive and catalytic features. In particular, CdSe nanoparticles and thin films were electrodeposited on n-Si (100). Microscopic and spectroscopic techniques. were used to characterize the obtained deposits. Then, annealing treatments were optimized to obtain photo-emissive CdSe/n-Si (100) surfaces [2,3]. MoS_2 nanoparticles were electrodeposited on n-Si (100) and characterized by X-Rays Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). Preliminary measurements of the MoS_2 activity towards HER confirmed the catalytic properties of the electrodeposited compound [4]. Finally, Magneto-Electrochemistry (MEC) experiments were performed during the electrodeposition of a ferromagnetic Heusler alloy. The potential occurrence of a Chiral Induced Spin Selectivity (CISS) effect during the deposit formation was hypothesized [5].

[1] M. Vizza et al., *Surfaces* **2021**, *4* (2), 157-168.
[2] W. Giurlani et al., *Nanomaterials* **2019**, *9* (10), 1504.
[3] W. Giurlani et. al., *Nanomaterials* **2022**, *12*, 1–11.
[4] M. Vizza et al., *Molecules* **2022**, *27*, 5416.
[5] W. Giurlani et. al., *Appl. Sci*. **2022**,*12.*

OR17

Biomass valorization towards new high-performance biopolymers

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In this research several saccharides have been used as starting material to produce innovative biopolymers for applications ranging from cultural heritage preservation, packaging, adhesives and biomedical use. In order to obtain compounds with high performances, the monomers must be selected appropriately to obtain specific structure with chemical-physical characteristics modulated for each application field. However, an important aspect in their design is also the attention towards the environment and their preparation calls for technological solutions with reduced environmental impact. Indeed, it is currently mandatory to reduce the use of petroleum and to implement renewable sources as starting materials, favoring even biodegradability and composting. With this aim, different monomers were synthesized by introducing polymerizable reactive groups on α,α'-trehalose, α-D-glucose, and methyl D-glucopyranoside. Allyl saccharide monomers, obtained using a substitution reaction, were selected for the synthesis of the vinyl alcohol copolymers by radical copolymerization reaction, to obtain water soluble products suitable to be used in the treatment of wood and paper [1].
Starting from the results obtained with allyl monomers, to increase the reactivity, the introduction of acrylic groups through transesterification reaction was also investigated. Such monomers were used for the synthesis of both, vinyl acetate and ethyl methacrylate copolymers, always through radical copolymerization reactions. These biopolymers will be evaluated for cultural heritage conservation but also for the preparation of artificial muscles or new adhesive formulations.

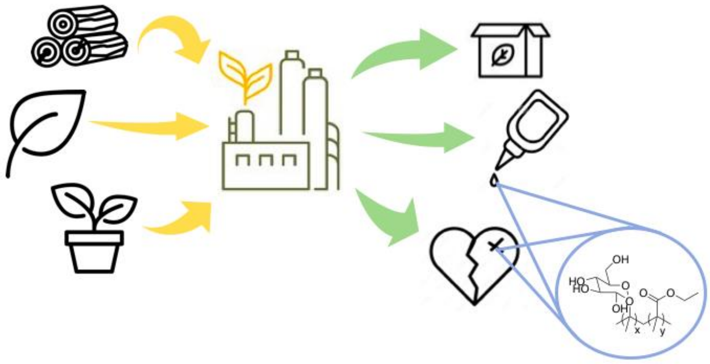

Figure 1: Development of new biopolymers from biomass valorization for different applications.

[1] G. Poggi et al., *J Appl Polym Sci.* **2022**, *139*

OR18

Study of new materials with low environmental impact and their use in the protection of wooden artifacts

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In recent years it has become increasingly essential to identify new materials that can be used in the protection of Cultural Heritage in place of long-chain perfluoroalkyl compounds (PFAS), highly efficient products but with a high environmental impact, and therefore currently under restriction in UE.

In order to develop specific products for the conservation and protection of degraded, non-varnishable wooden artifacts, in the last decade new materials have been designed, characterized by a chemical structure that is as similar as possible to the main components of the wood, so as not to alter its aesthetic appearance and chemical-physical characteristics but improve their mechanical properties [1,2].

Now, starting from the compounds studied as consolidating agents, new fluorinated oligoamides have been synthesized and studied for waterproofing wood surfaces.

The new oligoamides were designed to achieve the best performance and the lowest environmental impact. In order to minimize the risk of bioaccumulation, short perfluoroalkyl side chains were reacted with various oligoamides and an amine (diethylenetriamine). Different combinations of monomers have been tested and the reaction conditions have been optimized to obtain low molecular weight compounds characterized by non-film-forming properties and solubility or dispersibility in environmentally friendly organic solvents. In particular, a new PFA with a lower fluorine content (C4) and its derivatives have been compared with the corresponding C6 products [3] in terms of reactivity and performance. Their behavior in terms of modification of the wood surface characteristics, such as wettability and color, was analyzed using a specific diagnostic protocol to rapidly obtain preliminary, but reliable, results for optimizing a future synthesis of new and tailored protectives. The influence of different monomer units on the reactivity, solubility, and hydrophobic properties of different oligoamides was compared showing promising results.

The results obtained allow us to better understand the properties of the new protective agents in order to design formulations suitable for meeting the ever-changing regulations in the future. In particular, the estimation of the mobility and the actual risk to the environment of these new compounds will allow us to design products with a lower (or zero) fluorine content.

[1] G. Cipriani et al., *J. Appl. Polym. Sci.* **2013**, 420-431.
[2] A. Papacchini et al., *J. Cult. Herit.* **2019**, 49-58.
[3] Y. Zhang et al., *Coatings* **2022**, *927*, 1-25.

OR19

Development of renewable materials based on proteins and peptides from vegetable sources

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Petrol-based polymers are widely used in the production of both common and high added value products, thanks to their exceptional properties, versatility, and low price. However, their uncontrolled disposal and extremely low degradability, have resulted in one of the most serious environmental problems of the last two centuries. Therefore, in recent years, there has been a rising interest in the development of polymeric materials based on natural biopolymers as a renewable alternative to petrol-based plastics [1]. Due to the increased availability of proteins from agricultural by-products and their favorable properties, a renewed interest in protein-based materials has fueled research in innovative technologies for the preparation of bioplastics [2]. Proteins from rapeseed meal have been chosen as first candidates for our bioplastics main ingredient. Rapeseed meal samples were collected as a by-product from the crude oil production after the oil pressing and subsequent hexane extraction process [3]. After extraction and characterization of these proteins, we applied polymer traditional technology and chemical reactions to modulate their thermo-mechanical properties. The obtained bio-based material combines the processability properties typical of petrol-based plastics and the eco-sustainability of the proteins. To develop a fully sustainable bioplastic, we designed and prepared peptides, derived from protein lysates. Because of their high compatibility with the protein based matrix, these peptides will be employed as additives in protein-rich materials. The obtained results will contribute to the *green transition* achieving the goals of the *European Green Deal*.

[1] R. Hatti-Kaul et al., *Trends Biotechnol.* **2020**, *38* (1), 50–67.
[2] K.G. DeFrates et al., *Nanomaterials* **2018**, *8* (7), 457.
[3] W.R. Newson et al., *Industrial Oil Crops* **2012**, *59*

OR20

Spectroscopic and morphologic investigation of Bronze Disease in Cultural Heritage

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Bronze artworks can be subjected to chloride attack, which may trigger the cyclic and self-sustaining degradation known as "bronze disease". The presence of atacamite and its polymorphs (e. g. clinoatacamite and paratacamite) on the artifacts is indicative that bronze disease is underway, therefore their early detection is essential [1,2].

In the last decades, several studies tried to provide solutions against copper alloys corrosion in order to replace the use of benzotriazole (toxic and dangerous for the environment) [2]. Conversely, there are not many studies related to the early diagnosis of bronze disease using non-invasive and portable methods.

In this study, a laboratory protocol was developed to simulate the corrosion process on different kinds of copper alloys: samples were aged in sealed glass containers at controlled temperature and humidity (50°C, 100% RH) in the presence of HCl vapors [3]. Several tests were performed, varying the aging time, the HCl concentration and the setup inside the glass containers [3]. Confocal micro-Raman spectroscopy showed the actual formation of the clinoatacamite, proving the effectiveness of the artificial aging. Then, the aged samples were characterized by an innovative approach, using non-invasive and transportable techniques. Typically employed for the study of frescoes, pigments, easel paintings, Fiber Optics Reflectance Spectroscopy (FORS) and Optical Coherence Tomography (OCT) have provided good results for the early and non-invasive detection of the bronze disease [1,3]. FORS efficacy in detecting bronze disease and discerning clinoatacamite from other non-injurious green compounds was confirmed [3]. The possibility to study the surface morphology and acquire cross-sectional images of bronze corrosion patinas using OCT was demonstrated for the first time [3].

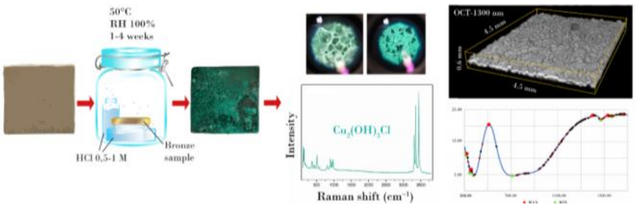

Figure 1: Graphical abstract.

[1] W. Liu et al., J. *Cult. Herit*., **2021**, *49*, 19-27.
[2] A. Artesani et al., *Coatings*., **2020**, *10*, 217-252.
[3] D. Porcu et al., *Heritage***.** **2022**, *5*, 4, 3548-3561.

OR21

Optimization of critical parameters to obtain difficult peptide sequences using induction-heat energy on solid phase peptide synthesizer PurePep$^{®}$ Chorus

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Peptides are assuming a relevant role over the years not only as active pharmaceutical ingredients (APIs) but also as innovative materials and for cosmeceutical industry.

In the synthetic production landscape, much effort has been focused on solid-phase peptide synthesis (SPPS). This strategy, available both at lab and pilot/large scale, leads to good quality crude products with reasonably low costs and execution time. In addition, it can be automated. We set up the machine provided by the company we collaborate with: PurePep Chorus by Gyros Protein Technologies, to optimize protocols and reagents for a panel of peptides selected for different applications. Peptide synthesis were conducted both at r.t. and with induction heating (up to 100°C) and taking advantage of up to 8 different reagent lines that allow a remarkable customization in terms of coupling reagents. We selected ten peptide sequences whose syntheses are prone to by-products such as deletion sequences and aspartimide formation due to their own primary structure and/or the steric hindrance of their building blocks. The performance of the synthetic procedure and, therefore, of the synthesizer, was evaluated in terms of peptide crude chromatographic purity together with the characterization/quantification of byproducts. Another important feature tested on the machine was the acetylation of unreacted -NH_2 group along the repetitive steps of solid-phase peptide synthesis. A final crude containing acetylated sequences as impurities is more easily purifiable. Moreover, all the fragments deriving from incomplete couplings belonging to a specific protein sequence is a fundamental requirement for the development of peptide antigens in the field of antibody diagnostics and vaccinology [1,2]. We demonstrated that the significant synthesis customization offered by PurePep Chorus (Gyros PT, Tucson, AZ, USA) is pivotal for reaching a high purity output for solid-phase peptide synthesis. Moreover, the use of different conditions in terms of coupling procedures and reagents, allowed to optimize protocols sewn on a specific sequence with a view to time and reagent saving.

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[2] A. Traoré et al., *Front Immunol.* **2022**, *13*, 856033.

OR22

Development of flexible molecular and inorganic hybrid solar cells: materials for a sustainable future

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The global demand for energy keeps rising since the 1960s, however, the limited availability of fossil fuels and their environmental impact will severely affect future generations. On the contrary, renewable resources replenish naturally and are more widespread. Among them, the most intriguing is solar energy, with almost 4 million exajoules of solar energy reaching Earth’s surface every year. Unfortunately, more than 90% of the global PV energy market is held by silicon solar cells whose production and disposal require big economic efforts, despite high efficiencies [1]. To reduce fabrication costs, different materials and architecture were investigated, resulting in the development of second, third and fourth-generation photovoltaic (PV) technologies. Nevertheless, these innovative solutions do not match the efficiencies of silicon solar cells, so more gumption is required to exploit the specific properties of the newest generation (*i.e.* lightweight, flexibility, semitransparency) to gain clear advantages over any other technology in the market. Recently, fourth-generation PV has earned a lot of attention, since they combine the economic flexibility of thin molecular or polymeric films with the stability of inorganic nanostructures, improving charge carriers’ separation and transport with the use of nanomaterials. Nowadays, the attention of the PV community is drawn to an emerging class of highly promising materials, inorganic chalcogenides. These compounds can be produced both as thin films and nanocrystals, are made by environmental-friendly elements and shows a high absorption coefficient (over 10^4 cm^{-1}) [2]. Despite this, device efficiency is still limited by low values of open-circuit voltage because of the formation of defect states at the surface/interface. To limit this issue, organic semiconductors can be employed to passivate nanoparticle surfaces. In this work, kesterite Cu_2ZnSnS_4 nanoparticles were produced through an innovative methodology and characterized with various techniques. At the same time, the sublimation in ultra-high vacuum of two different n-type organic semiconductors, C_{60} and $Cu(dtt)_2$, was investigated as suitable counterparts in the fabrication p-n heterojunction. Promising results were obtained and highlighted the possibility to use these compounds as active materials for the fabrication of hybrid solar cells.

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[2] G. A. Armin, *Thin Solid Films* **2009**, *517*, 4706-4710

OR23

The role of the propionate interactions in the *Listeria monocytogenes* coproporphyrin ferrochelatase bound to its physiological substrate

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The coproporphyrin-dependent heme biosynthesis (CPD) pathway has been discovered in 2015 and it is used by monoderm Gram-positive bacteria to produce heme *b* [1]. In the penultimate step, the coproporphyrin ferrochelatases (CpfCs) catalyzes the insertion of ferrous iron into the coproporphyrin III (cpIII) substrate, producing the iron coproporphyrin III (coproheme). In the final step, the coproheme decarboxylases (ChdCs) generate heme *b* by a two-step decarboxylation of the propionate groups of coproheme at positions 2 (p2) and 4 (p4), forming vinyl groups. After the cleavage of p2, the transiently formed monovinyl monopropionyl intermediate rotates by 90 degrees inside the protein pocket to bring p4 near the catalytic tyrosine, to allow the decarboxylation of p4 to form heme *b*.

Spectroscopic studies of wild-type (WT) CpfC and several variants, from *Listeria monocytogenes* (*Lm*CpfC) complexed with the product (coproheme), allowed us to conclude that the hydrogen bonding interactions to the propionate groups are fundamental for the stabilization and orientation of porphyrin ring inside the active site [2].

During my first year, the substrate (cpIII) free and complexed with *Lm*CpfC (WT protein and several variants) have been studied using UV-Vis electronic absorption and resonance Raman (RR) spectroscopies [3]. The results show that: i) the four propionate groups of cpIII form H-bonds with the protein matrix, and, as observed in the crystal, the H-bonds are characterized by different strengths; ii) unlike the coproheme complex, which is flat, cpIII shows a dome-like distortion when bound to the protein, as a consequence of the protein interaction with all four propionate groups. The differences between the RR spectra of the substrate and the product allowed us to highlight the differences in the H-bonds interactions established between the propionates and the conserved polar amino acids of the protein pocket. These differences will be used to follow *in vitro* the iron insertion process, upon addition of a solution of Fe (II), under anaerobic conditions, starting from the WT *Lm*CpfC - cpIII complex.

[1] H.A. Dailey et al., *Proc Natl Acad Sci USA.* **2015**, *112*, 2210-2215.
[2] T. Gabler et al., *Febs J.* **2022**, *289*, 1680-1699.
[3] A. Dali et al., *Protein Science*, **2022**, online (doi: 10.1002/pro.4534)

OR24

Synthesis and characterization of a new lead-free perovskite solar cell

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In the present work we realized a non-toxic lead-free perovskite solar cell (PSC) with low environmental impact. Perovskites are organic-inorganic materials with a ABX_3 structure (where A = monovalent organic cation, B = divalent metal, and X = halide) suitable for various fields of application such as solar cells and light emitting diodes [1].

The chemical composition of the new PSC active layer was chosen according to DFT/LDA calculations [2] substituting the more commonly used lead with magnesium to obtain a $CH_3NH_3MgI_3$ perovskite structure. The construction of the PSC device was realized in a multistep process: deposition of the electron transport layer, synthesis of the perovskite active layer, deposition of the hole transport layer and of the counter electrode. The synthesis of the photoactive layer was optimized changing the relative volume of the precursor (40 µL – 80 µL) and the annealing temperature.

The XRD characterization of the Mg-PSC active layer confirms the presence of the perovskite structure, the morphology of the active layer obtained both from SEM/EDX and CLSM images shows the presence of a uniform distribution of the perovskite layer and confirming the chemical composition.

The photophysical characterization allowed to evaluate the properties of photoluminescence and the band gap of the device as a function of the preparation procedure. The efficiency and stability of the solar cells were estimated from I-V curves as a function of irradiation and storage time.

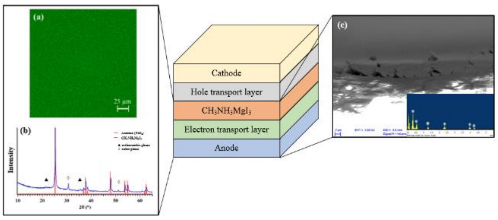

Figure 1: Schematic representation of the architecture of the Mg-perovskite. **(a)** CLSM image and **(b)** XRD pattern of the photoactive layer, **(c)** SEM and EDX of the device cross section.

[1] N. F. Atta et al., Perovskite Materials-Synthesis, Characterization, Properties, and Applications, **2016**, Chap 4, IntechOpen, London, United Kingdom
[2] M. R. Filip et al., *J. Phys. Chem.* **2016**, *120*, 166

OR25

Stimuli responsive inhibitors and pharmacological chaperones for Gaucher disease

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Gaucher disease (GD), the most common lysosomal storage disorder (LSD), is due to deficiencies in the activity of lysosomal β-glucocerebrosidase (GCase), the enzyme which hydrolyzes glucosylceramide (GlcCer) to ceramide and glucose. GCase malfunctioning results in the accumulation of GlcCer into the lysosome, ultimately leading to organ disfunction. Pharmacological Chaperones (PCs) are small compounds able to rescue the enzymatic activity when used at sub-inhibitory concentration [1]. Nitrogenated glycomimetics, such as aza- and iminosugars, are the most investigated PCs for LSDs. In this work we focused on the development of a novel collection of stimuli responsive azasugars connecting a trihydroxypiperidine to pH- or light-sensitive functionalities [2,3]. The synthetized pH sensitive compounds (e.g., orthoesters, nitrones, acetals) were designed to be stable at the neutral pH of the ER helping the mutated GCase to fold correctly and translocate to the lysosomes (pH 4.5-5.8) where they will be degraded to compounds poorly interacting with the enzyme, thus assuring to be displaced by glucosylceramide. The incorporation of a photoswitchable linker (azobenzene moiety) to an azasugar aims at a structural change of the PCs within time and therefore at modulating its binding affinity after it has entered the lysosome and helping the replacement of the PCs by glucosylceramide. The stability of pH sensitive molecules has been studied at neutral and acidic pH via 1H-NMR using acidic deuterated buffers while the half-life of the light sensitive compounds has been investigated by UV-Vis and NMR spectroscopy.

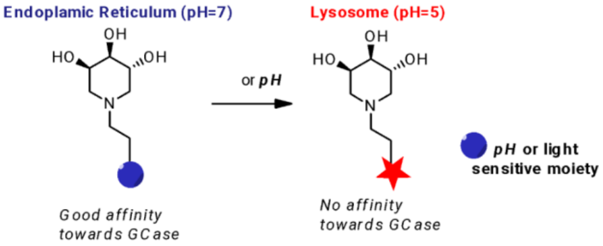

Figure 1: General structure of pH or light sensitive molecules.

[1] F. M. Platt et al., *Nat. Rev. Dis. Prim.* **2018**, *4*, 27-52.
[2] T. Mena-Barragán et al., *Angew. Chem. Int. Ed.* **2015**, *54*, 11696-11700.
[3] W. Szymanski et al., *Chem. Rev.* **2013**, *113*, 6114-6178.

OR26

Synthesis of *N*-glycomimetics from low cost and recycled saccharides

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Glycosylamine derivatives are biologically relevant compounds widespread in Nature [1], but the synthesis of this motif has been little addressed and its access with control of configuration at the anomeric carbon is challenging. Glycals substituted at C-3 with a carbamate group undergo, upon dehydration, a prompt allyl cyanate to isocyanate rearrangement to the isomeric *N*-glycosyl isocyanates, which can be conveniently trapped by a one-pot nucleophilic addition with alcohols or amines to afford *N*-glycosyl carbamates and ureas, respectively. The *N*-glycosyl derivatives were obtained with complete anomeric selectivity, affording α- or β-linked amines depending on the configuration at C-3 of the carbohydrate. Thus, glucal and galactal gave β-*N*-glycosides **1** and **2** exclusively while allal furnished α-*N*-glycosides **3**. *cis*-Dihydroxylation of the resulting unsaturated *N*-glycosides afford different 1-aminosugars with good selectivity [2]. The sigmatropic cyanate to isocyanate rearrangement has also been applied to levoglucosenone-derived carbamate **4**. Levoglucosenone (**5**) is a small molecule obtained from urban and industrial residual cellulose containing materials (such as waste paper) [3]. The rearrangement installs a nitrogen functionality at C-4 as shown in derivatives **6**. After dihydroxylation of the double bond and opening of the 1,6-bridge new precursors of 4-aminosugars were obtained in a stereocontrolled manner.

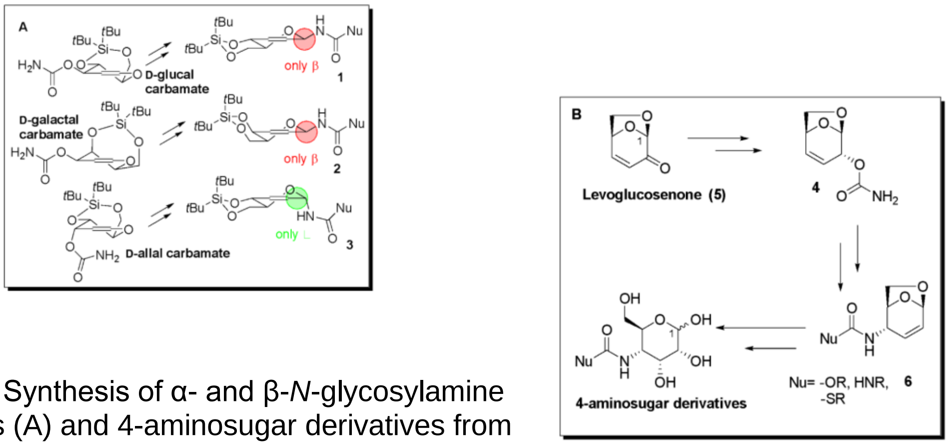

Figure 1: Synthesis of α- and β-*N*-glycosylamine derivatives (A) and 4-aminosugar derivatives from levoglucosenone (B).

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[2] D. Pratesi et al., *Eur. J. Org. Chem*. **2022**, e202200804.
[3] A. M. Sarotti et al., *Green Chem*. **2007**, *9*, 1137–1140.

OR27

Development and application of instrumental LC-MS/MS analytical platforms and chemometric data treatment for the study of complex matrices in the environmental and nutritional fields

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Liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) represents a fundamental analytical tool for the in-depth characterization of complex matrices, such as environmental samples, foods, and biological fluids. In fact, reliable targeted and untargeted LC-MS/MS platforms are of paramount importance in the aforementioned fields for the identification and quantification of micropollutants and their transformation products in environmental samples, as well as food constituents and human metabolites in metabolomics studies [1]. Also, the use of proper chemometrics and data analysis tools is crucial in both method development and data exploration/interpretation, the latter especially in untargeted studies [2]. This PhD project has been carried out to develop high throughput LC-MS/MS platforms exploiting both targeted and untargeted approaches capable to untangle the intricate data information from complex samples of environmental and nutritional interest. To this extent, the latest advanced wet (e.g., on-line SPE, LC×LC) and dry (e.g., molecular networking) lab platforms have been employed in the development of LC-MS/MS methods to investigate different types of (analytically challenging) samples, including fruit extracts, wastewaters, technical mixtures, and human biofluids (i.e., urine and serum) [3]. The LC systems used for the development of untargeted and targeted platforms were configured to perform: (i) low- (tens μL) and large-volume direct injection (hundreds μL), (ii) on-line SPE pre-treatment, and (iii) LC×LC analyses. Targeted experiments are performed using a hybrid triple quadrupole analyzer operating in MRM mode, capable to provide high sensitivity, accuracy and robustness required in quantitative protocols. The untargeted studies were conducted using two different high-resolution MS/MS analyzers, based on TOF (separation "in space") and Orbitrap (separation "in time") technologies, allowing for performing accurate mass determination (<1-10 ppm), isotopic profiling for molecular formula assignment, and tandem mass experiments for structural elucidation of unknow compounds. The development and/or application of (i) LC-MS/MS wet lab methods and (ii) dry lab chemometric workflows presented in this PhD thesis generated highly informative and accurate data that could help to increase the knowledge on the chemical space of the investigated samples.

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[3] M. Roca et al., *Anal. Chim. Acta* **2021**, *1147*, 38-55.

OR28

Archaeometric study of Montelupo Maiolica: a critical analysis of the non-invasive approach chosen.

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The main scope of this PhD project is to define a proper multi-analytical approach to study complex artefacts such as Montelupo maiolica in terms of materials, production techniques and development over the centuries. In dealing with cultural heritage samples, a non-invasive and non-destructive approach is preferable. Although, evidence emerged so far led to questioning this choice:

- Even if a three-layer stratigraphy (transparent glaze, coloured glaze and white glaze) is commonly reported for maiolicas in both historical and contemporary bibliography, Pb distribution inhomogeneities emerged in the XRF maps seem to contrast this information [1].
- Secondly, semi-quantitative IBA analysis carried out yields elemental concentrations averaged over the entire penetration thickness of proton incident beam (all three glaze layers) [2], not allowing to discriminate composition of each individual layer.

With permission granted by Cultural Heritage Superintendence, sampling was carried out on a limited, but significant, number of sherds. Polished sections, so obtained, were observed with the reflected light microscope (at LAM-DST laboratory) and analysed with SEM-EDS (at MEMA laboratory) [3].

Even if the optical microscope observations gave unclear results, they were valuable guidelines for planning SEM-EDS analysis: Transparent Glaze was confirmed only in few samples but an additional layer (a reaction layer between the White Glaze e the Ceramic body) was observed in two cases.

SEM-EDS allowed, furthermore, to discriminate the elemental composition of each individual layer (and its thickness).

Comparison between semiquantitative data obtained on White Glazes (by SEM-EDS) and White Areas (by IBA) showed confrontable concentrations for major elements (SiO_2, Al_2O_3, K_2O, PbO, SnO_2), especially for samples with no Transparent Glaze; presence of micrometric-submicrometric Cassiterite crystals (SnO_2) in all White Glazes was confirmed by SEM-EDS backscattered electron maps.

Finally, the SEM-EDS elemental distribution maps made distinguishable two types of colours in decorations: yellow-red-brown pigments and blue-green dyes. Semi-quantitative analysis allowed also to confirm some of the already hypothesized chromophores and obtain more detailed information about others (yellows and red especially).

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OR29

Development of a methodology for characterization and treatment of triacetate cellulose media of historical and artistic interest with a focus on those affected by «vinegar syndrome»

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Motion picture films made of cellulose triacetate (CTA) are subjected to degradation mainly due to the "vinegar syndrome". This phenomenon concerns the side chain scission through ester hydrolysis induced by moisture. The emitted acetic acid acts as a catalyst for the reaction and induces the hydrolysis of the glycosidic bonds between the units constituting the polymeric chain [1,2]. In addition to the smell, the deformation of the support and the detachment of the emulsion are macroscopic symptoms of this process and can strictly compromise the usability of the films (Figure 1). On these bases, reducing environmental moisture and removing alteration by-products from the storing environment is mandatory to limit the vinegar syndrome. The most important novelty of this project is the set-up of an innovative protocol to inhibit and/or prevent vinegar syndrome. We gave a first proof of concept of the neutralization action of various kinds of inorganic nanoparticles [3], applied in direct or not-direct contact with the surface of the samples. In order to evaluate the efficacy of these systems, we developed a method to artificially induce the vinegar syndrome on both CTA-based samples and real motion picture films and set up an analytical protocol to monitor the evolution of this process, based on gravimetry tests, FTIR-ATR Spectroscopy (validated by titration and free acidity tests), Tensile and Thermogravimetry Tests.

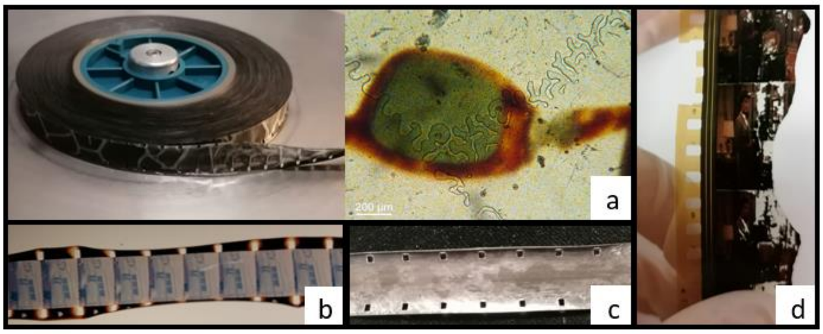

Figure 1: Typical degradation phenomena of CTA motion picture films: a) channeling, b) deformation and shrinkage, c) exudation of plasticizer, d) embrittlement.

[1] M. McGath, S. Jordan-Mowery et al., *Restaur*, **2015**, *36*, 333-365.
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OR30

Microfibers (MFs): the key to framing the problem and developing systems for their mitigation.

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Plastics are considered a persistent and ubiquitous pollutant and have therefore been proposed as a new stratigraphic indicator of the Anthropocene. In aquatic environments, which represent the final destination of various anthropogenic pollutants, fibres are one of the most abundant types of microplastics (MPs) identified. MFs are natural or man-made fibrous materials with a diameter of less than 50 μm, a length between 1 μm and 5 mm and length-to-diameter ratio greater than 3 [1]. In aquatic environments, MFs are highly persistent and tend to accumulate in various river and marine ecosystems. Recent studies have shown that 4.8 million tonnes of synthetic MFs (e.g. polyester and nylon) have entered water bodies and terrestrial environments since 1950 [2]. MFs size is such that they cannot be retained by conventional sewage treatment plants and thus become a threat to aquatic organisms. These types of emerging pollutants are also ingested by epibenthic meiofauna, posing a potential risk to humans as well [3]. In the initial steps of this study we collected samples from our partner company wastewater and analysed them both qualitatively and quantitatively through mainly μFTIR and optical microscopy. As expected, a huge abundance of fibres was detected. The problem of MFs release from industrial washing is proving to be more serious than expected and to mitigate its effects a more direct collaboration between research institutes and the involved companies is required. Since the textile sector in Italy is highly developed, strict regulation is required in order to reduce the impact deriving from these kinds of pollutants. The scientific community's efforts to harmonise the analytical protocols are pointing us in a common direction to develop a mitigation system that contains the spread of MFs.

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[2] J. Gavigan et al., *PLoS One*. **2020**, *15*, e0237839
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OR31

Electrochemical characterization of molecular properties and modified surfaces for energy and technological applications

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Electrochemistry is a useful tool to study organic reactivity for the characterization of molecular properties. Indeed, electrochemistry is a multidisciplinary science that can be useful in solving multiple challenges of our days. Using electrochemical techniques, surface coatings by oxidation and reduction of benzoderivatives can be obtained. Within this field we studied the electrochemical behaviour of two organic compounds: resorcinol and 1-bromo-2-methylnaphthalene. The electrochemical oxidation of resorcinol was studied using cyclic voltammetry as a function of the scan rate, resorcinol concentration and pH. Upon electrochemical oxidation, a polymer film can be easily grown. The polymer film morphology was characterized by recording SEM and AFM micrographs [1]. The dissociative electroreduction in 1-bromo-2-methylnaphthalene was disassembled at a molecular level and theoretically studied, exploiting the DFT ab initio analysis. A stepwise mechanism for the electroreduction dissociation of the C-Br bond was proposed [2]. Electrochemistry is useful also in the development of novel modified surfaces to be exploited in renewable energy applications. In this context, fuel cells are promising candidates for a sustainable future. Oxygen Reduction Reaction (ORR) is the bottle-neck strategic reaction ruling the fuel cell efficiency process. This reaction allows the release of chemical energy stored in the vector molecule O_2 in the form of electricity. It is well known that best available ORR catalysts, belong to the so-called platinum group metals (PGM) that are very expensive. Single-atom catalysts are used to reduce the amount of noble metal within the catalyst. In this work we studied Single-Ion catalysts formed by carbon nanotubes functionalized with palladium(II) complexes. Catalysts were treated by preparing dispersions and tested with electroanalytical techniques. ORR performance are evaluated via rotating ring-disk electrode (RRDE). Although carbon nanotubes have strong catalytic activity due to their high surface area but show increased production of H_2O_2, functionalisation with Pd(II) complexes makes it possible to reduce the amount of hydrogen peroxide formed. These results provide the basis for further developments to improve the efficiency of future low-cost catalysts for use in renewable energy technologies.

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OR32

Polyamine-based fluorescent receptors for Emerging Pollutants

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Emerging Pollutants (EPs) are chemical substances whose environmental concern is recently emerged and often not yet regulated by the Italian or European rules. EPs include several substances, among which largely used pharmaceuticals, such as non-steroidal anti-inflammatories drugs (NSAIDs), waterproofing agents, some herbicides, and plasticizers. Indeed, their wide, but poorly regulated, use and release in the environment can lead to a continuous intake from living beings, with possible long-term toxic effects [1]. Here we report some fluorescent polyamine-based systems, containing a metal cation or H-bonding donor groups and hydrophobic moieties, able to sense some representative targets, such as the NSAID ketoprofen (KP), the water proofing agent perfluoroctanoic acid (PFOA), the herbicides glyphosate (Gly) and its main metabolite, aminomethylphosphonic acid (AMPA) and glufosinate (Glu) and bisphenol A (BPA, a known plasticizers), in aqueous media [2,3]. Polyamines can protonate in neutral aqueous solution to give polyammonium receptors able to interact with the anionic substrates *via* hydrogen bonding and/or electrostatic interactions. The fluorogenic units not only stabilize the adducts *via* hydrophobic interactions, but also generate an optical signal thanks to changes in their fluorescence emission. In addition, these receptors afford stable Zn(II) complexes in aqueous media, which can also be used for binding and sensing of the substrates, exploiting the ability of the metal ion to expand its coordination sphere, acting as anchoring point for these analytes. The receptors and their coordination abilities have been studied by coupling UV-Vis absorption, fluorescence emission and NMR spectroscopies and potentiometric titrations in aqueous solution, and single-crystal X-ray diffraction in the solid state.

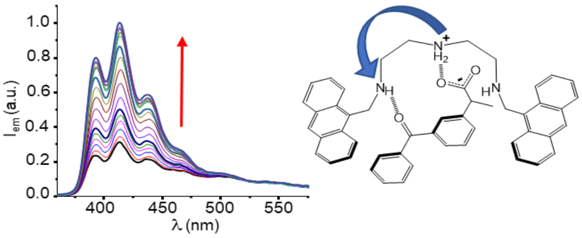

Figure 1: Triamine-based receptor containing two anthracene units is able to signals KP in aqueous solution via fluorescence emission enhancement, exploiting a proton transfer process upon substrate coordination.

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OR33

Effects of xc-functional choice on the characterization of a reaction mechanism

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In theoretical and computational chemistry, Koh-Sham density functional theory has become one of the most extensively utilized tools for describing the electronic structure. KS-DFT assumes that the ground state density of the original interacting system is equal to that of a set of non-interacting systems. This leads to independent particle equations for non-interacting systems that are exactly soluble with all of the problematic many-body terms included into an exchange-correlation functional of the density. However the exchange correlation in terms of density is unknown and it is necessary to use approximations, such as the use of semi-empirical parameters. The purpose of this study is to contribute to the topic of the arbitrariness of xc-functional choice within a given theoretical framework. To highlight any potential differences between the adopted xc-functionals, a model reaction involving proton transfer between highly conjugated systems in which the accuracy of the xc-functional is particularly important was required. All these requirement are satisfied by the tautomerization of [2,2'-bipyridyl]-3,3'-diol which involves a double proton transfer between a nitrogen and carbonyl moiety on conjugated bipyridyl rings. This reaction has been investigated in the ground state using both static and dynamic approaches, detailing the reaction process and estimating the free energy surface to highlight any potential differences between functionals that, according to the methodology, ought to be equivalent. Contrary to expectations, both static and dynamic simulations show that the characterization of the reaction mechanism is dependent on the delocalization error of the xc-functional adopted: functionals with a high delocalization error define a stepwise reaction mechanism, whereas xc-functionals with a lower delocalization error define a concerted reaction mechanism with different degrees of synchronicity.

OR34

The role of helical structure in a series of Myelin Basic Protein peptides for antibody recognition in Multiple Sclerosis

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Multiple Sclerosis (MS) is a chronic, inflammatory, and demyelinating disease of the central nervous system [1]. Herein, the attention was focused on a series of myelin basic protein (MBP) peptides characterized by the α-helix motif. This disordered protein contains a conformational epitope that may be involved in the triggering of antibodies in MS [2]. We studied the role of the helical structure in antibody recognition by a series of synthetic MBP peptides. Firstly, we observed that the peptide MBP(81-106) was characterized by a helical motif, but the longer analog MBP(76-116) increased IgM antibody recognition in MS patient sera in the condition of SP-ELISA. Interestingly, both peptides were able to inhibit anti-MBP(76-116) IgM antibodies. Moreover, conformational studies of a series of MBP peptides were prepared *via* CD and NMR experiments. The CD experiment, in stabilizing agent, showed that MBP(81-106) displays a high tendency to adopt a helical structure, which may be considered the bioactive conformation of the epitope recognized by IgMs. However, the peptide MBP(76-116) appears to be more suitable for being efficiently coated on the plate to capture IgM in the conditions of SP-ELISA [3].

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OR35

Synthesis of Peptide and Protein Drug-Conjugates for Targeted Therapy

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Drug conjugates are chemotherapeutic or cytotoxic agents covalently linked to targeting ligands such as proteins or peptides *via* a linker. While antibody-drug conjugates (ADCs) are now clinically established for cancer therapy, peptide-drug conjugates (PDCs) are gaining recognition as a valuable opportunity for targeted drug delivery with improved efficacy and reduced side effects. The linker in a drug conjugate plays a key role in the pharmacodynamics of the conjugate and in the release efficiency of the drug for full activity at the target site [1]. PDCs, designed to selectively deliver cytotoxic agents to the tumor cells, are poised to become an important class of cancer therapeutics. In this communication we report the design and preparation of different PDCs [2]. In particular, different linkers with a modulable cleavability, *i.e*. spontaneous or bio-promoted, were covalently linked to a tetrameric neurotensin peptide (NT4) used as carrier. On the other hand, when as carrier used was transthyretin protein (TTR) the linkers were instead armed with a Tafamidis unit since to exploit the hight TTR/Tafamidis association constant [3] for the targeting of the cytotoxic drugs (payloads). In both cases Paclitaxel and Monomethyl Auristatin E (MMA-E) were used as payloads (**Figure 1**). The new synthesized PDCs were tested in vitro on PANC-1 human tumour cell line. The in vitro testing pointed out the cytotoxic effect of the conjugates on tumour cells. Further testing will be done in vivo to investigate the cytotoxic selectivity of the conjugate for the tumour cells.

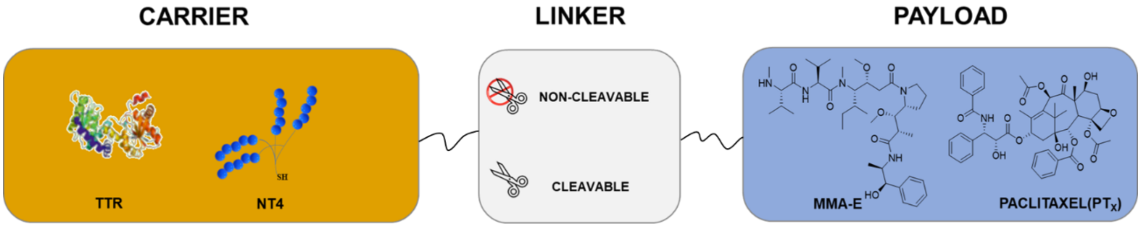

Figure 1: Peptide-Drug conjugates (PDC) structure

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OR36

Effects of protonated and deuterated environment: towards a detailed distance distribution analysis

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During the last decades the use of in cell approaches has retrieved an increasing interest. In this branch of approaches NMR and EPR spectroscopy are playing a central role for the biomolecular structural and functional characterization inside the cellular context. Double electron-electron resonance (DEER) coupled with Site Direct Spin Labelling (SDSL) is a powerful technique to gain insights both on structure and interactions of the investigated systems. However, short relaxation times impose a limit on the sensitivity and size of distances that can be measured using this technique [1]. Even if these measurements are usually carried out in frozen solution at low temperature (50K if a nitroxide is involved, even lower if the system contains metals), sometimes this is not sufficient to obtain a long enough electron spin echo dephasing time (T_m). Recent works have shown that while using deuterated solvents can moderately increase the T_m, total deuteration of a protein can extend it dramatically [2], since protein spin diffusion is a more effective mechanism of dephasing electron spins than deuterium. However, these improvements had yet to be applied to the in-cell approach. Herein we presented a systematical analysis of the influences of deuteriation, towards the final distance distribution analysis. Using both cells (prokaryotic and eukaryotic) and protein (doubly mutated Ubiquitin s20g35c labelled with maleimide-Proxyl) fully deuterated and the same cells and protein protonated, a methodical investigation of the effect of deuteration was carried out. The delivery of the protein inside the cells was carried out performing heat shock treatment, a powerful, simple, and recent developed approach which allows to internalize substantial amount of protein in short time [3]. At the end, we showed how, using the same experimental conditions, the full deuteration of both cells and the investigated protein, leads to a longer phase memory time and therefore a better DEER echo signal, respect to the ones obtained with protonated cells and protein.

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OR37

Development of analytical procedures for the determination of emerging organic compounds in environmental matrices

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The main objectives of my PhD are the optimization/validation of analytical methods for the determination of organic and inorganic contaminants that are toxic to humans and development of analytical methods able to simultaneously determine persistent, bioaccumulative and toxic (PBT) chemicals. The first step was to develop a simple and unique analytical method to detect polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), novel brominated flame retardants (NBFRs), phthalate esters (PAEs), all known for their toxic properties, in edible fish samples [1]. To this aim, three methods (named A, B, C) were compared. Method A involved traditional Soxhlet extraction with purification on silica gel column; method B consisted of a Soxhlet extraction followed by a dispersive solid-phase extraction (d-SPE); method C coupled ultrasound-assisted extraction (UAE) and clean-up by d-SPE. The choice of a method is not only based on statistical aspects, but on an analytical trade-off between efficiency and the sustainability of the process, therefore method C met this analytical compromise. To verify the versatility of the method, it was applied to more complex matrices: oily supplements of animal origin (fish and krill) and in *Talitrus Saltator*. To apply the method to oily supplements, it was optimized by the extraction with different solvent mixtures, trying to obtain the most optimal one. Also, in this method all necessary analytical parameters had to be evaluated; this step is still nearing completion. As far as *T. Saltator is concerned*, the method only was applied to detect concentration of PAEs. This analysis is a part of a larger project, whichaims to determine the variation of PAEs concentration in bioplastic-fed *T. Saltator* samples and to assess their effects on *T. Saltator* health. In collaboration with *Analytical Food*, a multi-residue analytical method was validated for commonly used and polar pesticides in edible vegetables. pesticides contamination of food is a human health concern worldwide, as pesticide residues can cause both short- and long-term toxic effects to humans and wildlife [2]. 461 pesticides were analysed by LC-MS in tomatoe samples. Pesticide contamination was detected in 34 samples from Tuscany and the estimated daily intake (EDI) values were calculated to determine the risk assessment. In addition, Analytical Food provided data on pesticides content in tomato samples from 2017 to 2021 in order to carry out a statistical analysis of a large dataset in order to understand the influence of agronomic, zoning and soil parameters on contaminant concentrations, identify potential traceability parameters and carry out risk assessment estimates

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OR38

^{13}C detected NMR spectroscopy applications for the study of multidomain proteins

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Intrinsically disordered regions (IDRs) are portions of proteins that lack a stable tertiary structure. IDRs often alternate with globular domains to form structurally heterogeneous multidomain proteins (e.g. human CREB-binding protein or SARS-CoV-2 nucleocapsid protein). Nuclear magnetic resonance (NMR) spectroscopy is a leading technique for the characterization of the structure and dynamics of these systems at atomic resolution [1]. However, the simultaneous presence of globular and disordered domains is challenging because of the different features of disordered and globular regions. Direct detection of heteronuclei was shown to provide clean information about highly flexible disordered regions also when part of complex multidomain proteins [2]. The availability of ultra-high field NMR instruments, in conjunction with ^{13}C detected experiments, holds promise to extend even further our capability to investigate complex systems. However, the experiments should be tailored to face the challenges posed by the advances provided by technological innovations. Here we focus on the optimization of ^{13}C-detected NMR experiments using a cryoprobe optimized for ^{13}C direct detection at 1.2 GHz. Different pulse sequences to measure the reference 2D NMR spectra (CACO, CON) were tested to assess their performance with different IDPs characterized by different molecular mass as well as structural and dynamic properties. In addition, we tested the performance of ^{13}C detection 2D experiments to determine the solvent paramagnetic relaxation enhancement (solvent PRE). Indeed, adding a small paramagnetic compound to the protein solution causes the PRE effect that can be experimentally determined to obtain information about the solvent accessibility of the protein surface [1],[3]. This alternative approach exploits carbon detection to avoid chemical exchange with the solvent and improve the resolution of NMR spectra.

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OR39

Electrochemical methods to quantify the content of organic additives in complex metrices of copper plating baths

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Commercial plating baths may contain a large number of organic additives that play an important role in ensuring good-quality deposits. During electrodeposition process these compounds tend to wear out and degrade, so they must be frequently monitored and dosed to keep constant their concentration. Plating baths are complex matrices in which organic additives are present in minimal quantities compared to the other components, electrochemical methods, therefore, represent a reliable alternative to conventional chromatographic techniques because they allow quantitative analyses to be carried out considering the effects of additives on the electrodeposition rate regardless of their chemical composition and provide, at the same time, useful information about the condition of the bath. Different electrochemical methods were tested in order to quantify the organic content of an acid copper commercial plating bath. These baths are widespread in different industrial sectors, such as fashion and electronic. At first, cyclic Voltammetric Stripping (CVS) experiments were carried out. Different analytical methods, such as dilution titration and standard additions were selected depending on the additive under investigation. However, such procedures have proven to be time and reagents-consuming and do not always provide accurate results. Electrochemical Impedance Spectroscopy (EIS) can represent a reliable alternative because it allows to achieve a detailed knowledge of the function of each additive and the interactions between them and to study the aging of plating baths [1]. Therefore, EIS measurements were performed in a three-electrodes cell, at 30 °C, by using a $10^5 - 10^{-2}$ Hz frequency range. Some screening experiments were carried out to find the right procedures on 8 different samples, testing two different concentrations for each additive and finding the right equivalent circuit to fit the data [2]. Then, a larger number of samples were investigated for a statistical treatment of the results that allowed us to find correlations between the concentration of each additive and some of the components of the equivalent circuit. The authors acknowledge MUR and EU-FSE for financial support of the PhD fellowship PON Research and Innovation 2014-2020 (D.M 1061/2021) XXXVII Cycle in Chemical Sciences.

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OR40

HuHf-Gold(I) compounds bioconjugates

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Human-heavy chain ferritin (HuHf) is a valuable nanocarrier for the selective delivery of drugs against cancer cells. It is a recombinant protein composed by 24 H-subunits that self-assemble to form a nano-cage with a hollow globular structure. H-chain subunits are known to be recognized by the transferrin receptor-1 (TfR1) that is overexpressed in many cancer cell lines.

Gold compounds emerged as potential anticancers with antiproliferative and proapoptotic properties [1].

Here I show the successful conjugation of three gold(I) compounds: Auranofin, Aurothiomalate (AuTm) and Au(NHC)Cl, with the ferritin cage.

Au(I) is known to selectively bind to Cysteines and Seleno-Cysteines; HuHf presents 3 Cys residues in each subunit. The formation of the adducts is performed with an incubation of the protein in the presence of different molar excesses of gold-compounds with respect to ferritin subunit (HuHf-AF 1:10; HuHf-AuTm 1:30 and HuHf-Au(NHC)Cl 1:3). All the samples were analyzed with ESI-MS to observe the different species formed between protein subunits and drug-derived species while with ICP-OES we quantified the amount of Au per cage of ferritin.

The ferritin conjugated with Auranofin (HuHf@AF hereafter) has been deeply characterized [2]. Site directed mutagenesis combined with ESI-MS and ICP experiments revealed the gold binding sites. C130A and C90AC102A mutants have been produced and their adducts have been analyzed. The results showed unambiguously that AF binds to the two spatially close Cys90 and Cys102. ^{1}H NMR metabolomic analysis on cell lysates demonstrated a superimposable mechanism of action of HuHf@AF with respect to the drug alone against A2780 tumor cells [3]. Competition binding of HuHf@AF conjugates with glutathione (GSH), serum albumin (HSA) and the C-terminal dodecapeptide of thioredoxin reductase (TrxR) bearing the thiol-selenol active site has been studied via ESI-MS. Interestingly the adduct is able to metalate the peptide derived from TrxR, which is considered the main intracellular protein target of AF, but not GSH and HSA. Preliminary data on the two mutants conjugated with AuTm and Au(NHC)Cl show different gold binding behaviors to ferritin subunits.

Lastly, labeled ^{19}F-HuHf has been produced as a probe to monitor the HuHf TfR1-guided entrance into A2780 cells via NMR. Preliminary data of ESI-MS and NMR experiments confirmed the efficient labeling of ferritin with ^{19}F.

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OR41

Smart Autonomous Responsive Materials

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In nature, many processes are energetically uphill in far-from-equilibrium conditions, and they can self-regulate by continuous consumption of chemical energy sources. The incorporation of far-from-equilibrium reactions, such as chemical oscillators, into soft matter materials allows a significant advance in the design of innovative materials. Urea-urease system is a candidate for the design of biocompatible pH-based feedback processes for bioinspired applications. This system can be exploited to set up a molecular machine capable of performing (bio)chemo-mechanical work.

Chemistry and biology are strongly ion specific. The presence of electrolytes for proteins and enzymes is extremely important and determines changes in protein folding, stability, solubility, aggregation, fibrillation, and action kinetics. The role of polarizability, one of the most crucial descriptors of the Hofmeister phenomena, was revisited in the case of halates XO_3^- (X=Cl, Br, I) [1]. The effects of anions and cations on the enzymatic activity of urease were studied in non-buffered solutions by potentiometric measurements.

The removal of dissolved gases from liquids brings about significant changes in their bulk and interfacial properties. Ionochromism, solvatochromism, and the effects of the dissolved gasses on the spectral properties of bromothymol blue (BTB) solutions were studied by UV-VIS spectroscopy [2].

For oscillation studies, giant vesicles of 1-palmitoyl-2-oleoyl phosphatidylcholine (POPC) were prepared by the droplet-transfer method to obtain differential urea and H^+ transportation, a prerequisite to attain oscillations. The vesicles were loaded with urease and fluorescent probe pyranine and were monitored by epifluorescence microscopy.

Formulation studies were conducted investigating a low-volatile organic solvent, GC, that has excellent applications in formulations, thanks to its biodegradability and low toxicity. Its hydrodynamic radius and the mutual diffusion coefficient were determined [3]. Also, the gels of ACP(65-74) peptide were studied in the function of concentration, pH, temperature, and in different solvents. These gels are temperature and pH-responsive and have thixotropic properties. The pH responsiveness can be exploited in the urea-urease system.

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OR42

Production of carbonaceous materials through thermoconversion of sewage sludge, their activation and characterization for application in wastewater depuration

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Biological sludge is a widely available waste material of high environmental concern, the disposal of which involves a high cost, whereas its reuse is in line with the modern approach to the waste management and the circular economy. Furthermore, thermal conversion of biological sludge for biochar production allows inhibiting the intrinsic toxicity related to the presence in this matrix of poorly biodegradable organic micropollutants, heavy metals, and potentially pathogenic organisms (i.e., viruses and bacteria). Thus, conversion of biological sludge into biochar as a sorbent for wastewater treatment seems to be a "win-win" solution for both improving sludge management and protecting the environment.

Based on the aforementioned considerations, production of biochars from biological sludge was carried out, along with the assessment of their environmental compatibility towards European Standard [1], their in-depth characterization and evaluation of applicability for the removal of organic micropollutants, as elsewhere described [2]. The best biochar in terms of environmental compatibility and most promising properties as adsorbent medium underwent different chemical and/or thermal treatments in order to improve its physicochemical properties. Removal of selected dyes was preliminarily assessed by kinetic studies on real wastewaters fortified with these target analytes, spectrophotometrically monitoring their removal. Results obtained have been compared with the performance of a commercially available activated carbon (AC), the latter considered as a reference material.

Figure 1. Schematic representation of possible application of sludge-based biochar

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OR43

Recognition of emerging pollutants (EPs) with artificial fluorescence chemical sensors: a supramolecular approach

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‘Emerging Pollutants’ (EPs) are chemicals currently not included in routine monitoring programs, but which could pose a significant risk for their potential toxicological effects towards humans and environment. EPs include mainly chemicals found in pharmaceuticals, industrial and household products [1]. The development of new chemical sensors able to detect these compounds at nanomolar concentration is a current challenge of environmental chemistry. This PhD project aims to develop fluorescent chemical sensors, targeting different model analytes representative of emerging pollutants, in particular fluoroquinolone and anthracycline antibiotics, the bis-phenol A plasticizer, and perfluoralkyl sulphonic and carboxylic acids, used in waterproofing fabric industry. These EPs contain an easily ionizable polar function, such as a carboxylic group, and a hydrophobic portion. Our aim has been design and synthesis of fluorescent conjugated chemosensors consisting of a receptor and a signaling unit, generally linked by spacers, accordingly to the receptor-spacer-fluorophore modular approach [2]. Therefore, we have synthesized receptors units able to bind the polar head of the targeted analytes, taking advantage from the combination of specific intermolecular interactions, such as charge-charge contacts and hydrogen bonds, linked to hydrophobic fluorescent moieties, able to signal substrate binding *via* change in their emission properties. During the first year of PhD, we addressed, with promising results, the design and trial synthesis of new fluorescence chemosensors containing cyanine, coumarin and pyrene fluorescent units linked to binding units containing amine and amide functions. While the amine groups can protonate in aqueous solution affording ammonium cations able to form salt bridges with the carboxylate group of the analytes, the amide moieties can interact *via* H-bonding with the substrates. The first tests for optical recognition of selected EPs are in due course.

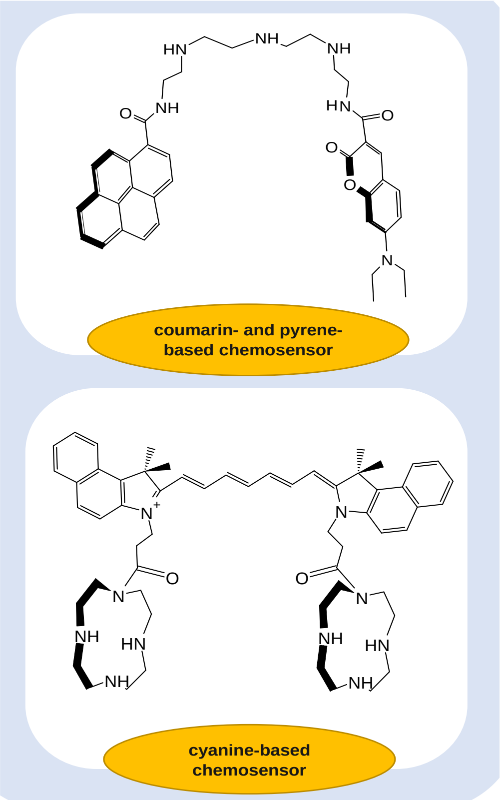

Figure 1: designed and synthetized chemosensors

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OR44

Improved Fluorinated Alcohol Force Fields for Molecular Dynamics Simulations of Peptide and Proteins in Biomimetic Media

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Fluorinated alcohols/water mixtures allow to study structural and dynamic properties of proteins and peptides in their bioactive state. Among the different fluorinated alcohols those most employed are trifluoroethanol (TFE), hexafluoroisopropanol (HFIP) and hexafluoroacetone (HFA).

The availability of accurate force fields for molecular dynamics simulations is an essential requisite for a reliable reproduction of experimental data. To improve the parametrization of the fluorinated force fields, DFT calculations have been performed to determine the low-energy conformer, which has been adopted as reference structures in subsequent steps.

General Amber Force Field (GAFF2) has initially obtained by using PrimaDORAC web interface [1]. The atomic charges have been refined by employing both ESP and Mulliken population analyses.

To assess the accuracy of the force fields [2], different thermodynamic property on pure and mixed solution were calculated and compared with experimental data. Furthermore, melittin (MLT), a component of the venom of Apis mellifica, has been adopted to verify properties of the solvents since this protein is unstructured in water at low pH but adopts an α-helical conformation when alcohols are present. Molecular dynamics simulations in biomimetic media show that the organic cosolvent aggregates around the peptide with a concentration two times higher than in the bulk. Although GAFF2 allows a correct description of some properties of the system in agreement with experiments, the new FFs provide more accurate and reliable results.

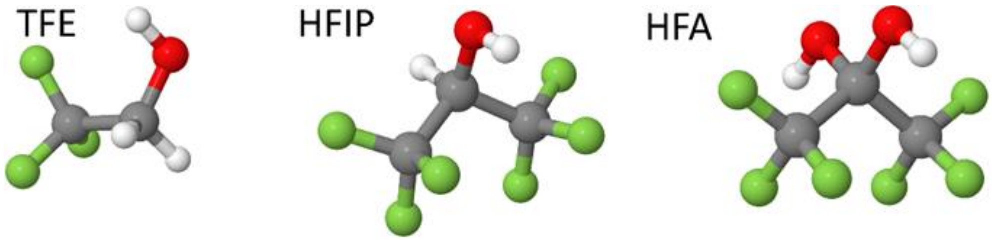

Figure 1: Molecular structure of TFE, HFIP, and HFA biomimetic solvents.

[1] P. Procacci, *J. Chem. Inf. Model*. **2017**, *57*, 1240–1245
[2] J. W. Ponder, *Adv. Protein. Chem.* **2003**, *66* 27–85

OR45

A Comparative Research on Corrosion Behavior of Electroplated and PVD Chromium Coatings

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Due to chromium’s multiple desired properties, thin metal layers have been widely used to improve surface quality from both functional and aesthetical points of view. Hardness, high corrosion and high wear resistance, low friction, and an attractive lustrous appearance, to say a few, can be imparted to most various items by the traditional hexavalent chromium plating process [1,2]. However, hexavalent chromium has been proven toxic, mutagenic, and cancerogenic. As a result, many regulatory agencies worldwide have banned or strictly regulated its use. For these reasons, many manufacturers and metal finishing companies have been looking for environmentally friendly alternatives, and physical vapor deposition (PVD) techniques represent one of the most promising ones [3].

In this context, we have investigated the effect of deposition methods on coatings’ corrosion performance. The study has been carried out by comparing chromium coatings obtained by direct current electrodeposition and PVD Magnetron Sputtering. We present results of functional and aesthetical properties characterization for both types of coatings deposited onto copper substrates. Looking at electroplated samples as the benchmark, we found that Magnetron Sputtering preserves the eye-catching mirror-like finish imparted by metallic chromium, although exhibiting darker shades of grey. Along this, Scanning Electron Microscopy (SEM) investigations evidenced that magnetron-sputtered coatings have superior thickness homogeneity and better surface morphology, lacking in submicrometer defects (voids and macrocracks) peculiar to electroplated samples. Regarding the anticorrosion performances, electrochemical and neutral salt spray tests carried out at room temperature in 3.5% NaCl solution evidenced similar or even better results for the magnetron-sputtered coatings. Our findings support PVD Magnetron Sputtering as an industrially scalable technology for aesthetic and functional finishing processes.

[1] D.P. Weston et al., *Wear* **2009**, *267*, 934-943.
[2] T. Ohmi et al., *Vac. Sci. Technol. A Vacuum, Surfaces, Film*. **1998**, *14*, 2505.
[3] R. Bandinelli et al., *Sustain.* **2021**, *13*, 4453.

OR46

Optical-based bioanalytical assays for drugs quality control and diagnostic applications

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Driven by the interest in the design of easy-to-use, low-cost and fast-response diagnostic devices that ensure continuous monitoring of the patient's health, this work aims to the development of innovative and alternative optical-based bioanalytical assays. The easiness to use, the non-destructive features, as well as the possibility of label-free approaches for direct optical detection, render optical methods a powerful tool for bioanalytical investigations. In these last, more frequently is necessary to determine small quantities of the analyte. For this purpose, photoluminescence properties of a class of nanomaterials (copper nanoclusters) and of a novel fluorophore, derived from serotonin self-oxidation, were respectively applied for the sensitive detection of human serum albumin [1] and Cu(II) in human samples. These optical-based bioanalytical approaches could represent a valid alternative for an early diagnosis of albumin [1] and copper-dependent diseases.

Optical-bioanalytical detection strategies were also applied for drugs active principles estimation. The design of methods for pharmaceutical analysis for the drugs quality control, that is the unambiguous detection of a drug in a pharmaceutical product, is as crucial as its determination in complex matrices, since the pharmaceutical product quality is directly related to the patient's health. Colorimetric methods, here, were applied for the determination of two active principles in commercial Parkinson's drugs, levodopa, and carbidopa. Levodopa was quantified by exploiting a colorimetric reaction that leads to the purple melanochrome formation, here isolated and stabilized for the first time [2]. The designed melanochrome-based colorimetric assay was effectively applied to levodopa and dopamine detection in human urinary samples, paving the way for future application in the monitoring of pharmacological therapy in Parkinson's patients. Carbidopa content was also determined in pharmaceutical formulation by using an alternative colorimetric approach based on the selective condensation reaction between the hydrazine group of carbidopa and the formyl functional group of vanillin leading to the formation of yellow 4-hydroxy-3-methoxybenzaldazine [3].

The novel optical-based bioanalytical approaches designed in this research work could have a significant impact on analytical diagnostic tools commonly employed in clinical practice and pharmaceutical analysis improving their availability and applicability.

[1] M. Lettieri et al., *Mikrochim. Acta.* **2021**, *188* , 116.
[2] M. Lettieri et al., *Anal. Bioanal. Chem.* **2022**, *414*,1713–1722.
[3] M. Lettieri et al., *Anal. Bioanal. Chem*. **2022**, *414*, 6911–6918.

OR47

Electrochemical platforms for allergens aptasensing

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Ara H1 is one of the major peanut allergens. It is considered one of the most life-threatening food allergens since it triggers the highest frequency of severe and fatal reactions, even in trace amounts. Thus, it is crucial to develop fast, accurate and easy-to-use analytical methods for the determination of Ara H1 allergen from food products to aid diet compliance within sensitive subjects [1].

Lysozyme is an enzyme found in multiple organisms that plays various roles. One of the most important relies on its intrinsic antibacterial activity, also called the body's natural antibiotic. Despite its proven utility, lysozyme can potentially trigger allergic reactions in sensitive individuals; thus the need for continuous monitoring of lysozyme in products like wine or egg white is of high importance [2].

Electrochemical aptasensors have a high specificity thanks to the affinity reaction between the ssDNA receptor and the analyte, even in complex matrices. However, key steps in their development are represented by the immobilisation of the ssDNA probe and the signal generation [3]. Therefore, platforms with overall improved electrochemical features that can immobilise the ssDNA probes in a tailored manner to enable the optimum signal generation are of high demand.

Two different platforms for the electrochemical sensitive aptasensing of Ara H1 and Lysozyme allergens will be presented. For Ara H1 detection, a platform based on graphene oxide as carboxylic groups donors and metallic nanoparticles was developed. Further, the conjugation of a polymer matrix (poly-L-lysine) with gold nanostructures was exploited for the ultra-sensitive detection of lysozyme. Both platforms were developed at disposable screen-printed carbon electrodes (SPCE) to obtain effective biosensors that could be potentially applied for on-site analysis. The two developed platforms were functionalized with the specific ssDNA strands and optimized for the detection and quantification of Ara H1 and lysozyme, respectively. Applications on food/drinks samples will be presented.

Acknowledgements

This research was funded by the European Union's Horizon 2020 Research and Innovation Program under grant agreement No 883484, PathoCERT, Italian Government in the framework of PRIN 2017, Prot. 2017YER72 K_005 and the Romanian Ministry of Education and Research, CNCS-UEFISCDI, project number PN-III-P1-1.1-PD-2019-0631, within PNCDI III.

[1] D.T. Tran et al., *Biosensors and Bioelectronics* **2013**, *43*, 245–251
[2] G. Melinte et al., *Talanta,* **2021,** 226, 122169
[3] B. Piro et al., *Biosensors* **2016**, *6*.

OR48

Paramagnetic Porphyrin Dimers: New Building Blocks for the Development of two Qubit Quantum Gates

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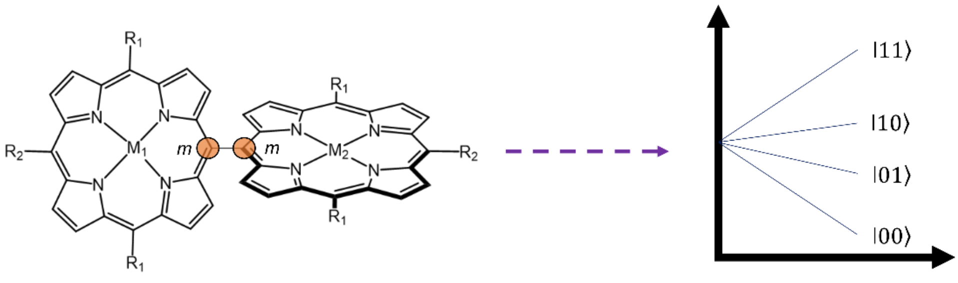
In the last two decades, vanadyl(IV) and copper(II) based paramagnetic metal complexes were considered to be attractive candidates for molecular spin qubits [1]. Qubits are the quantum mechanical counterpart of the classical bit and serve as the core unit in the quantum computer [2]. In a molecular spin qubit, the two states of the unpaired electron spin in the transition metal complex can act as a qubit, when put into an external magnetic field, creating the two computational basis states $|0\rangle$ and $|1\rangle$ necessary for quantum information processing. However, for reaching the goal of quantum supremacy [2] at least four computation basis states (namely, $|00\rangle$, $|01\rangle$, $|10\rangle$, and $|11\rangle$, **Figure 1**) are necessary. We think that intrigues candidates are porphyrinic systems, since they can be functionalized, are neutral, and it is possible to sublimate them on various surfaces [3]. This PhD thesis focus mostly on the synthesis and magnetic characterization of porphyrinic two qubit systems. The two novel porphyrin dimers synthesized during the PhD Thesis (**[VO(TrPP)]$_2$** and **VOCu(DPP)$_2$**, **Figure 1**) showed, according to EPR measurements, that meso-meso linked homometallic VO(IV)-VO(IV) and heterometallic (VO(IV)-Cu(II)) dimers are indeed weak exchange coupled and therefore have four computational basis states available, that can be used to create quantum logic gates such as the CNOT or SWAP-gate [2].



[VO(TrPP)]$_2$: $M_1 = M_2 = VO(IV)$; $R_1 = R_2 = Ph$; **[VOCu(DPP)$_2$]:** $M_1 = VO(IV)$; $M_2 = Cu(II)$; $R_1 = Ph$; $R_2 = H$

Figure 1: Porphyrin dimers that were synthesized and magnetically studied. The weak exchange coupled systems contain the four computational basis states necessary for the quantum logic gates.

[1] M. Atzori et al., *J. Am. Chem. Soc.* **2019**, *141*, 11339–11352.
[2] J. P. Dowling et al., *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.* **2003**, *361*, 1655–1674.
[3] S. Hiroto et al., *Chem. Rev.* **2017**, *117*, 2910–3043.

OR49

Sewage sludge-derived biochar to design more sustainable electrochemical sensors

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Within the context of a circular economy and environmental consciousness, the scientific community is continuously seeking more sustainable analytical approaches. The design of electrochemical (bio)sensors could benefit from the utilisation of recycled carbonaceous materials as a promising "greener" alternative to other virgin carbon-based materials [1]. In this study, we tested biochar, a recycled carbon-rich material derived by controlled pyrolysis or gasification of waste biomass, to obtain carbon paste electrodes that are more environmentally friendly [2]. Notably, 90% of the carbonaceous paste used was produced by recycling a mixture of waste woody biomass and sewage sludge originating from municipal and industrial wastewater treatment plants, which usually require expensive procedures for their disposal (Figure 1a). The electrodes' surface was characterised by analysing the electrochemical behaviour of widely used redox indicators and phenol compounds. Three berry fruits, namely *Vaccinium myrtillus*, *Vaccinium uliginosum* subsp. *gaultherioides*, and *Fragaria* × *ananassa*, were then chosen to characterise the phenolic fingerprints associated with their anthocyanin fractions. Through a rapid electrochemical screening, standard anthocyanin mixtures that mimic the natural composition of such berries, as well as fruit extracts (Figure 1b-c), were evaluated and compared [3]. This work supports the applicability of biochar-based electrodes as an eco-friendlier solution for the electroanalysis of real agri-food samples.

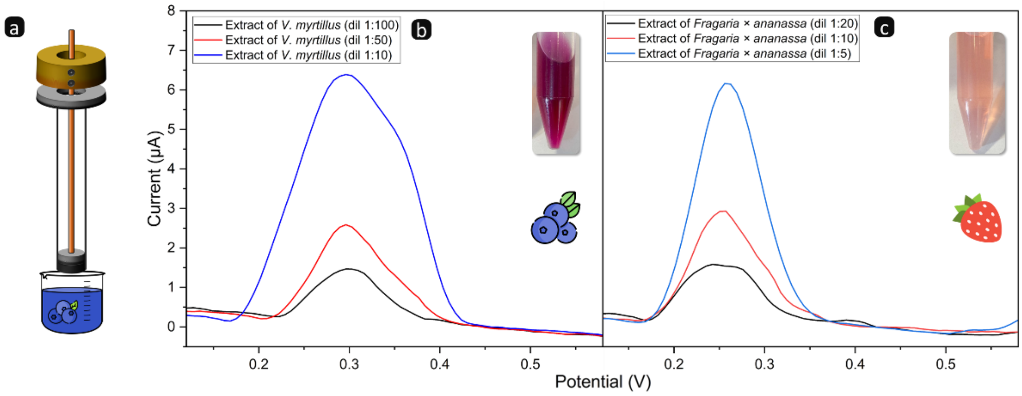

Figure 1: **(a)** biochar-based carbon-paste electrode; differential pulse voltammograms of real extracts of **(b)** *Vaccinium myrtillus* and **(c)** *Fragaria* × *ananassa*.

[1] P.S. Sfragano et al., *Front. Chem*. **2020**, *8*, 644
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[3] P.S. Sfragano et al., *Anal. Bioanal. Chem*. **2022**, *414*, 6295-6307.

OR50

Synthesis of new materials to develop innovative permanent magnets: hard/soft coupling

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Permanent magnets (PMs) are classified according to their capacity of storing energy, expressed by the maximum energy product (BH_{max}). The BH_{max} value is obtained from the analysis of the magnetic hysteresis loop, that is a characteristic magnetization behavior of ferromagnetic materials in the presence of an external magnetic field. A particular shape of the hysteresis loop defines two different kinds of materials, named “hard” and “soft” materials. By merging the large coercivity of a “hard” phase and the high saturation magnetization of a “soft” one, BH_{max} could be increased: a valuable strategy is through the coupling (exchange or dipolar) of nano-sized grains of the two components [1]. In this framework, the synthesis process of the two chosen components is presented: strontium hexaferrite as hard phase, and metallic iron as the soft one. The aim is to obtain coupled hard/soft nanocomposites with enhanced energy products with respect to standard ferrite (at least 10%), for the partial replacement of PMs based on Rare Earth Elements (REEs) [2].

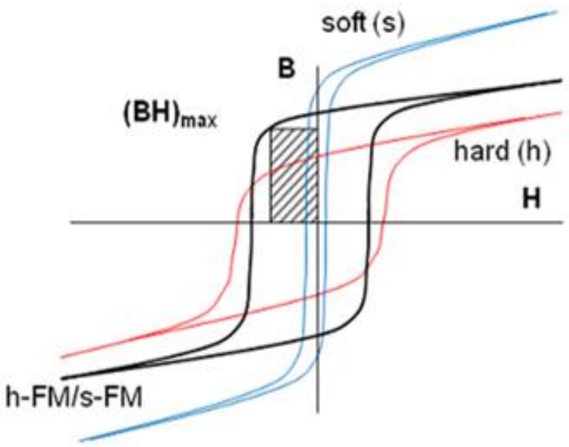

Figure 1: Exemplification of enhanced BH_{max} through hard/soft coupling.

[1] F. Liu et al., *Chem Soc Rev* **2014**, *43*, 8098–8113.
[2] J. M. D. Coey, *Engineering* **2020**, *6*, 119–131.

OR51

Design and fabrication of micro- and milli- fluidic chip for the development of green industrial formulations

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In recent years, there has been increasing interest in the substitution of current components of consumer products with new eco-compatible chemicals and in the development of more sustainable industrial processes. In particular, current industrial formulations for the care of fabrics contain encapsulating agents, generally core-shell capsules, characterized by poor biodegradability and high environmental impact. However, their replacement with "greener" formulations would require the application of efficient screening methodologies, to characterize the performances of the different capsules, which are currently lacking. In this framework, micro-,milli-fluidic tools [2] can be instrumental both to provide new analytical tools to boost the development of novel formulations, and to substitute common methodologies to "greener" ones. Three types of studies can be of interest in the characterization of encapsulating agents: (i) their behavior in the pipeline, that is, their processability (ii) their interaction with fabrics, (iii) the kinetics and/or mechanism of release of the encapsulated active principle.

With the aim to develop a washing machine on a chip, suitable for different studies, two main microfluidic devices have been designed and built-up, to directly investigate the interaction of encapsulating agents with fabrics of different compositions, included inside the devices. The devices are characterized by different geometries, with the flow of the encapsulating agents being orthogonal or tangential to the fabrics fibers.

Preliminary experiments were performed by confocal laser scanning microscopy to monitor the adhesion/detachment of fluorescently-labeled capsules to fabrics fibers; a MATLAB code was then applied to analyze the image and achieve quantitative evaluation of the interaction between the capsules and the fabrics.

Overall, the obtained results indicate the ability of the device to discriminate the interaction of a single type of capsules with different fabrics, suggesting this system as a promising alternative to the classical methods.

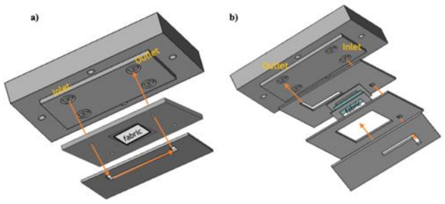

Figure 2: Representation of the two configurations of the chip for the analysis in case of (a) tangential and (b) orthogonal flows

[1] T. Pirzada et al., *Current Opinion in Colloid & Interface Science* **2020**, *48*, 121-136
[2] L. Chen et al., *Materials Today Nano* **2021**, *16*, 100136

Abstracts of the Poster Presentations

POS01	Angela Sofia Tino
POS02	Elena Mariani
POS03	Andrea Geri
POS04	Chiara Cianci
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POS07	Ilaria De Santis
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POS26	Chiara Mangini
POS27	Neri Fuochi
POS28	Laura Conti
POS29	Francesca Milano
POS30	Prem Prakash Sahu
POS31	Shagufta Sajjad

POS01

NMR-based investigation of intrinsically disordered regions of modular proteins for tailored design of peptides

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Several RNA-binding proteins (RBPs) are characterized by modular structures encompassing folded domains and intrinsically disordered regions (IDRs). Understanding the mode of interaction of these different domains may stimulate the development of innovative strategies to interfere with modular proteins, such as viral proteins. The Nucleocapsid protein (N) of SARS-CoV-2 is a pivotal example of RBPs representing the first subject of this research project. N is one of the most important proteins encoded by the virus involved into the packaging of the viral genome and facilitating its replication inside the host cell. Moreover, the N protein has recently been proposed as an alternative drug target because it is characterized by a low rate of mutations. Its complex structure encompasses two folded domains and three IDRs. In particular, the globular N-terminal domain (NTD) is responsible for the interaction with the viral RNA and the two flanking IDRs are demonstrated to play an important and synergic role in the interaction [1]. The objective of my PhD research project is to investigate the whole structure of the N protein by exploiting the power of solution NMR spectroscopy and to design and synthesize peptides able to interfere with its function. The research is organized into three major work packages: 1) the design and solid phase synthesis of peptides; 2) the expression in *E. coli* of N protein constructs; 3) the evaluation of the interaction between synthetic peptides and the N protein by solution NMR titration experiments. The preliminary results obtained during my master thesis constitutes the basis of the present study. In particular, the lead synthetic peptide **1** was demonstrated to interact with the NTD of the N protein, miming the interactions established by the RNA with the protein. Since the beginning of my PhD, three peptide sequences have been synthesized with slight modifications with respect to peptide **1** to understand the residues and/or conformational motifs essential for the interaction with the protein target. A collection of different peptide sequences has been designed and will be synthesized possibly to enhance the affinity with the NTD of N protein. The final aim is to discover the ideal peptide displacing the nucleic acid from the protein with an antiviral activity. Therefore, some novel synthetic strategies, such as the click reaction, will be used to increase the stability of the peptide molecule *in vivo* [2]. Finally, Nucleocapsid constructs encompassing IDRs will be expressed and their interaction with the synthetic peptides will be evaluated to understand the role of the disordered domains.

[1] L. Pontoriero et al., *Biomolecules* **2022**, *12*, 1.
[2] A. D'Ercole et al., *Peptide Science* **2020**, *112*, 24159.

POS02

Electrodeposition with modulated currents in optics of a Circular Economy

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Recent problems with the availability of raw materials and the consequent volatility of metal prices has highlighted the need for innovation that correlates the chemical sector and the environment, with the aim of bringing renewal to the galvanic sector. Innovation can only be achieved through the reduction of metal quantities and subsequent treatment of process water with waste recovery and reuse in view of a circular and sustainable economy. The entire research project revolves around the use of pulsed current and its manifold potentiality. The application of this particular type of current is able to intimately modify the chemical-physical phenomena that occur in solution and determine the goodness of the deposition: simply by adjusting the amplitude and length of the pulses, it is possible to control not only the composition and thickness of deposits, but improve their characteristics such as grain size, porosity and homogeneity [1,2].

New and innovative electrodeposition processes can find application not only in the galvanic sector but also in the energy field.

The project proposal includes a systematic study of modulated currents applied to the palladium bath, with a focus on improving the performance properties of the deposit.

Being able to produce layers characterised by a uniform thickness over the entire surface, regardless of the shape of the object, would mean savings in terms of the amount of precious (and non-precious) material to be deposited, and would also guarantee good homogeneity for subsequent deposits.

The electroplating process will inevitably produce processing waste, and it is here that a further process innovation comes into play, that of galvanic waste treatment. The electro-recovery of metals from washing solutions is the system that allows the greatest control from a qualitative and quantitative point of view. The limitations of a DC electro-recoverer emerge in the treatment of metal alloy solutions, while, the use of pulsed currents could be crucial, since, by appropriately adjusting the pulse parameters, it is possible to selectively depose certain metals rather than others.

The energy aspect of palladium electrodeposition is its application in the production, storage and use of hydrogen in catalytic fuel cells. Pd-Ni alloys, in addition, have ferromagnetic characteristics that are considered very important in water splitting reactions [3], where the major drawback is the formation of hydrogen peroxide, which reduces the efficiency of the entire process. Ferromagnetic electrode surfaces lead to the production of hydroxyl radicals with the same spin state, which prevents them from aggregating to form H_2O_2. Modulated currents would allow extremely homogeneous catalytic surfaces achievable at a reduced cost.

[1] N. V. Mandich, *Met. Finish.* **2002**, *97*, 382–387.
[2] M. S. Chandrasekar et al., *Electrochim. Acta* **2008**, *53*, 3313–3322.
[3] A. R. Usgaocar et al., *J. Electroanal. Chem.* **2011**, *655*, 87–9

POS03

Mechanistic studies on antitumor gold compounds

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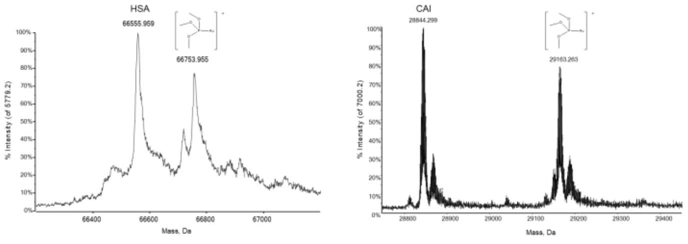
Owing to the great success of Pt-based drugs in anticancer chemotherapy, the study of metal complexes has gained a lot of interest in the view of the discovery of innovative antitumor agents. Gold compounds form a promising class of anticancer drug candidates, endowed with prominent cytotoxic properties [1]. The interactions of gold compounds with nucleic acids are relatively weak; currently, it is believed that the main targets of anticancer Au(I) complexes are proteins. However, the precise modes of action of gold compounds remain largely unexplored.

The aim of this project is to investigate the mechanism of action of a panel of Gold-based drugs, to identify the targets and the affected pathways and to characterize the interactions taking place between proteins and specific gold complexes. The panel is highly representative and includes gold(I) and gold (III) compounds such as Auranofin and its analogues, Au(NHC)Cl, Aubipyc and Aurothiomalate.

The ESI MS technique bears a few unique features that make it well-suitable for this kind of investigation. The Electrospray Ionization (ESI) is a soft ionization technique extensively used for the production of gas phase ions without fragmentation of thermally labile large supramolecules, allowing to preserve and characterize metal-protein adducts at the molecular level. Systematic MS measurements will allow us to define the general patterns of interaction between gold compounds and the model proteins [2].

The analysis of the obtained mass spectra, represented in the Figure 1, permits to reveal the formation of adducts between gold complexes and proteins and to characterize the occurring interactions.



a) *b)*

Figure 1: Deconvoluted mass spectra of the formed adduct between $AuP(OCH_3)_3Br$ and a) Human Serum Albumin (HSA); b) Carbonic Anhydrase (CAI).

Furthermore, to gain deeper insight into protein binding of these gold compounds, the project has the aim to develop a new protocol, that combines protein digestion with Liquid Chromatography ESI-MS. The analysis of the fragments produced by trypsin, or another proteolytic enzyme, may lead to identify unambiguously the specific sites of metal binding.

[1] S. Nobili et al., *Med Res Rev*. **2010**, *30*, 550-80.
[2] L. Massai et al., *Front Chem*. **2020**, *8*, 581648

POS04

Preliminary studies on the formulation of nanostructured composites for the consolidation and protection of Street Art

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Street Art, like graffiti, can be considered the new kind of artistic expression of the current century. The constant exposure of outdoor murals to environmental conditions makes graffiti conservation difficult. Furthermore, biological agents play a non-negligible role in the degradation of urban art [1]. The materials involved in street art are commonly both organic (polymeric paints) and inorganic (concrete, mortar, etc.). For this reason, their physicochemical properties must be considered for the development of effective products for their conservation. This research will focus on the formulation of hybrid solutions with both a macromolecular component, which overcomes the limits of the traditional synthetic polymers used in conservation and an inorganic component, which is compatible to the inorganic matrix of the masonry. The study will initially concentrate on evaluating the applicability of chitosan. It is an abundant, green, inexpensive, non-toxic biopolymer that exhibits antimicrobial properties [2]. Recent studies have demonstrated that chitosan also has a key role in inhibiting the dangerous crystallization of salts in porous stone matrices [3]. Our hypothesis is to exploit the properties of chitosan as a protective agent against salts and microbial agents. Chitosan is studied for various applications in Cultural heritage, both for the consolidation and the protection of different substrates such as stone, metal alloys, wood, and paper. However, a thorough investigation into its long-term stability needs to be carried out. Therefore, the first part of this project will assess the chemical stability of chitosan coatings applied to concrete prototypes. Photochemical and hydrothermal accelerated aging tests are performed. The preliminary results will be useful to evaluate the further processing of chitosan through the addition of inorganic nanoparticles to provide a consolidating action to the concrete.

[1] E. G. Gayo, *SAUC - Journal*, **2015**, *1*, 99-100
[2] M. Rinaudo, *Prog. Polym. Sci*. **2006**, *31*, 603-632
[3] M. Bassi et al., *Front. Mater*. **2021**, *8*, 583112

POS05

Electric fields in molecular quantum technologies: a systematic approach to study the spin-electric effect

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In the last two decades, data generated yearly from humanity have increased exponentially. The quick development of new technologies able to handle this amount of data is then mandatory. Including magnetic molecular systems in information technology is highly appealing for several reasons. The usage of molecules would miniaturize devices (therefore favoring a more considerate use of resources) and would unlock the fascinating possibility to simulate reality using bits that obey the law of quantum physics (i.e. qubits). However, conventional methods to write, store and process informations (i.e. applying magnetic fields) are non-local, and cannot reach the required spatial resolution. On the contrary, electric fields can be applied with very high control even on single atoms [1]. Therefore, a better comprehension of how electric fields interact with the spins of molecules, a phenomenon known as Spin-Electric (SE) effect, is fundamental for pursuing this technological strategy.

The SE effect can only occur in molecules that meet some specific symmetry requirements. Therefore, coordination chemistry has a crucial role, and can be exploited to design specific synthetic routes that lead to the desired symmetry. During my PhD, several molecules will be characterized experimentally using a combination of spectroscopic and magnetic techniques, while the SE effect will be determined using a novel spectroscopic method [2]. Experimental data will be combined with *ab initio* calculations in *ad-hoc* homemade programs to obtain models that describe the observed SE effect.

Preliminary studies have been performed on chiral lanthanides complexes of formula $Na_5[Ln(C_4O_5H_4)_3](BF_4)_2(H_2O)_6$ to understand the role of different metal ions in tuning the SE effect.

[1] Eigler et al., *Nature* **1990**, *344*, 524-526.
[2] Fittipaldi et al., *Nature Materials* **2019**, *18*, 329-334.

POS06

Study of electroplating processes and production sustainability of an electroplating plant

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The need to obtain surface-functionalised artefacts from thin and ultra-thin films of metallic (but also polymeric) material has increased drastically in recent years. This is because they allow obtaining goods with, at least, the same functionality of the bulk material and, in particular the electrodeposited ones, they allow to create new materials too [1]. This increase in demand is due to a multiplicity of factors, but two of the most prominent are the scarcity of strategic elements for the 4.0 industrial revolution and the uprising need for the energy transition from an oil-based to a hydrogen-based economy. Within these changes, electroplating industries are on the front line to become more efficient and provide better products to satisfy the increasing demand and reduce the usage of strategic metals like Nickel, Gold and Palladium. Electrodeposition is one of the most used, scalable and tuneable methods to obtain thin and ultra-thin films on substrate of various geometries. The purposes of this research project are multiple but all synergistic to achieve the goals set before: studying intermetallic diffusion and, in general, non-equilibrium multilayer systems and an in-depth theoretical study of charge transfer processes. Intermetallic diffusion is a thermodynamic driven phenomenon [2]. It brings changes in crucial chemical-physical parameters such as conductivity, colour and corrosion resistance, limiting the lifetime of artefacts, increasing their embodied energy and environmental impact. To kinetically stop the intermetallic diffusion, barrier layers are used. The main problem is that those barrier layers are, in majority, alloys of strategic metals such as Palladium or Nickel or deposited with cyanide baths (like bronzes). A study of the performances of classic and innovative barrier layers is going on and it’s performed with a novel methodology based on Monte Carlo simulations, Energy Dispersive Spectroscopy assisted by X-ray Diffraction and Atomic Force Microscopy. Then, to fully optimize an electroplating plant, it’s necessary to understand all theoretical aspects of charge transfer process (CTP) and the kinetic of diffusion-controlled CTP. To perfectly tune an electroplating factory, computational chemistry methods are really promising and innovative, with first principle calculations we could better understand how additives such as levellers and brighteners act during deposition, and, in general, we could better understand and foresee the results of a deposition. Ab-initio calculations are fundamental to open electrodeposition plants to other markets such as catalyst or semiconductor production, then we are studying CTP of molecular crystals [3] with Density Functional Theory calculations coupled with plane wave basis sets to characterize those promising materials.

[1] Innocenti et al., *J Power Sources***. 2013**, *241*, 80-86
[2] P.M. Hall et al., *Thin Solid Films***. 1977**, *41*, 341-361
[3] Solano et al., *Phys. Chem. Chem. Phys***. 2022**, *31*, 18816-18823

POS07

Engineering biomimetic lipid interfaces to form smart materials

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In the past years, events occurring at the nano-bio interface, i.e. where engineered nanomaterials (ENMs) meet biological interfaces such as biomembranes, have been intensively investigated. However, probing these interfacial interactions and their underlying mechanisms remains extremely challenging due to their complex and dynamic nature [1,2]. This project will focus on the rational design and subsequent preparation of advanced biomimetic lipid interfaces, capable of acting as functional, stimuli-responsive and versatile building blocks to form hybrid (synthetic/biologic) and smart nanosystems. New synthetic strategies for these nanostructured membranes will be developed employing amphiphilic lipids whose self-assembly can lead to well-defined, thermodynamically stable structures in water, e.g. liposomes, cubosomes and hexosomes [3]. The use of photoswitchable lipids, ionizable lipids and/or targeting moieties within the lipid formulation could be of particular importance for possible applications, especially regarding medical and biological fields. These engineered biomimetic lipid interfaces will be then used to study physicochemical interactions with various materials, such as simple inorganic nanoparticles for diagnostic purposes and complex drug delivery systems. The overall aim of my PhD project is to contribute to the fundamental knowledge on the mechanisms underlying nano-bio interactions, build up novel synthetic smart hybrid materials combining lipid membranes of different compositions and structures and to predict their biological fate, hence enriching the current understanding of their behavior for biomedical applications.

[1] J. Cardellini et al., *J. Phys. Chem. C* **2022**, *126*, 4483-4494.
[2] J. Cardellini et al., *Front. Bioeng. Biotechnol.* **2022**, *10*, 848687.
[3] C. Tan et al., *J. Agric. Food Chem.* **2022**, *70*, 1423-1437.

POS08

Electrodeposition and modification of surfaces of technological interest with low environmental impact

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The proposed research project aims to synergistically exploit the advantages of semiconductors and Heusler alloys using electrodeposition as a synthesis method for spin-filtered photoelectrochemical water splitting and optimized hydrogen production directly from solar energy, with a focus on 4.0 industry applications, environmental sustainability, overcoming cyanides galvanic baths, antibacterial films, and metals recovery.

One of the biggest problems for contemporary society concerns the growing increase in energy demand. The intensive use of non-renewable energy sources has raised environmental problems and is not a long-term solution by its definition. Solar energy holds a prominent position among renewable sources, but the main limitation of this source, like other renewable sources, is the production discontinuity. For this reason, an efficient storage system is essential. Over the years it has been proposed several times to use hydrogen as an energy vector because it is easy to store and produce from water electrolysis and with a harmless oxidation product, returning to simple water.

The water splitting reaction is commonly carried out by an external current generator and immersed electrodes, but a photoelectrochemical (PEC) process allows, through specialized semiconductors, to exploit the photons to directly dissociate the water molecules, to convert the solar energy directly into chemical energy.

The use of electrodeposition enables to obtain thin and ordered films, to fabricate p-n junctions, to prepare nanoparticles and thin film materials at room temperature and pressure, still preserving a fine control on the morphology and thickness of the resulting material. The electrolysis reaction often brings the formation of peroxides and by-products of superoxide radicals that poison the catalyst. The peroxide formation reaction can be suppressed with the use of a filtered spin current: if the decoupled electrons of the radical species have a parallel spin the peroxide formation is prohibited [1]. In this area, Heusler alloys have shown important spin-selective properties, so it would be of great interest to include their use within the project to combine the spin-filtering selectivity with the PEC properties of the semiconductor [2].

Following this idea, it will be possible to produce the entire device through electrodeposition, even exploiting nanostructured deposition to maximize the absorption of light radiation and optimize the efficiency of hydrogen production lowering its price for the large-scale introduction of this low-impact energy vector [3].

[1] U. Gupta et al., *Nano Energy*. **2017**, *41*, 49-65.
[2] W. Mtangi et al., *J Am Chem Soc*. **2017**, *139*, 2794-2798.
[3] T. Graf et al., *Prog Solid State Chem*. **2011**, *39*, 1-50.

POS09

Preparation and characterization of functional alginate-based composites for wound healing, water/air purification and pressure-based sensors

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The development of functional composite materials is currently revolutionizing many applications, such as sensors, scaffolds for tissue engineering, filtration systems, etc. Thanks to its biocompatibility, biodegradability, sustainability and reactivity towards divalent cations, alginate is a very well-suited matrix for the preparation of composites. The combination with functional fillers paves the way towards devices with tunable chemistry, shape, responsiveness and actions. With these premises, my PhD project aims to prepare alginate wires crosslinked with copper ions and containing nanoparticles of the same element. The filiform structure of the products, important for a possible use in non-woven fabrics, can be easily imparted by extrusion and instant ionic crosslinking of the polymer. In order to prepare the desired nanoparticles, it is possible to exploit a reducing agent of natural origin such as ascorbic acid. The aforementioned composite material therefore aims to be attractive for its antimicrobial qualities in sectors that require high biocompatibility (*e.g.* wound healing and water/air purification) and sustainability. I am going to spend part of my PhD at the *Institut de Science et d’Ingeniérie Supramoléculaires* (ISIS, University of Strasbourg) with the aim to extend the use of alginate in the preparation of pressure-sensitive devices intended for biomedical applications, such as heart rate monitoring and bone/cartilage tissue engineering [1]. In this context, alginate will constitute the matrix of the device, as its sensitivity to the surrounding environment (chemical composition, temperature, humidity, ...) gives it considerable application potential. The other element chosen for the realization of the aforementioned devices will be graphene, capable of significantly influencing the electrical, mechanical and adsorption properties of a material. The optimization of the compatibilization process between the components will be studied at the Department of Chemistry "Ugo Schiff" of the University of Florence, exploiting the skills and instruments available in mechanical characterization, morphological and thermal properties of materials. The electrical properties will then be examined at ISIS in order to evaluate how composition, structure and environmental factors influence them. The evidence will thus make it possible to design reusable, highly sensitive devices capable of working in multiple environments.

[1] C. B. Huang, *Adv. Mater.* **2019**, *31*, 1804600.

POS10

Valorization of waste biomasses through thermochemical and chemical conversion

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The circular economy has received considerable attention in recent years as a solution to overcome current consumption and production requirements. Among the renewable resources, lignocellulosic biomass, available at low cost, plays a fundamental role in the biobased and circular economy. The three biopolymers (cellulose, hemicellulose, and lignin) that compose lignocellulosic biomasses can be the source of high value-added products. In this PhD project, waste biomass will be treated through thermochemical conversions such as pyrolysis, hydrothermal liquefaction, and hydrothermal carbonization. Thanks to the versatility of thermochemical processes, it will be possible to perform tests on different substrates, to give these wastes a new life in a circular economy perspective. Pyrolysis is a heat treatment performed at relatively high temperatures (greater than 673K) under anoxic conditions, with or without a catalyst [1]. Instead, hydrothermal liquefaction and carbonization processes use water as medium and reactant, avoiding the use of organic solvents that are harmful to humans and the environment [2]. The aim of this PhD project is to identify waste biomasses and lignocellulosic by-products of industrial processes and convert them using thermochemical and chemical reactions. Thermochemical conversion will be used as a pre-treatment to convert biomass into fractions with high application potential: a gaseous, a solid (char), and a liquid fraction (bio-oil) [3]. Thanks to these reactions it will be possible obtain chemicals and industrially relevant materials (catalyst supports, soils amendment). In particular, through bio-oil upgrading, the purpose is to identify and maximize the yield of high value-added chemicals to be employed in industrial productions.

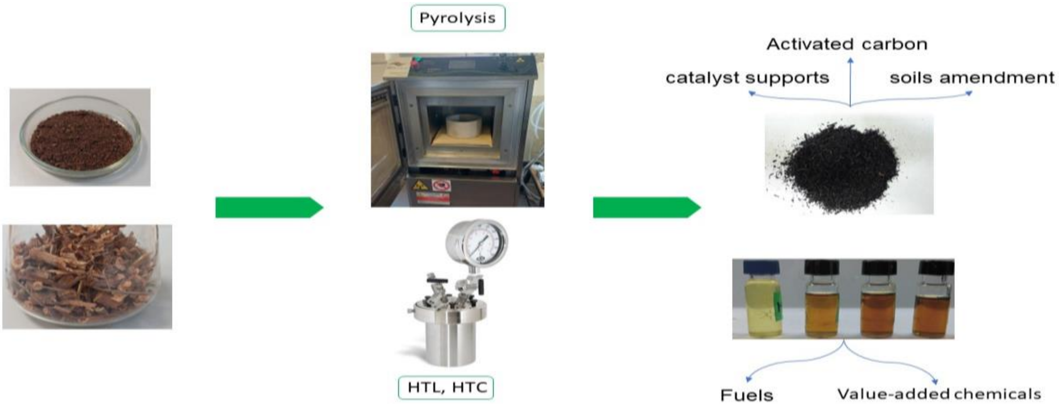

Figure 1: Valorization of waste biomasses through thermochemical conversion

[1] H. Lee et al., *Can. J. Chem. Eng.* **2022**.
[2] I. Agostini et al., *Molecules,* **2022,** *27*, 7112.
[3] R. Gallorini et al., *ACS Omega,* **2022,** *7*, 37757-37763

POS11

Innovative liquid chromatographic-mass spectrometric technologies to purify and identify glycated and glycosylated proteins in biological fluids.

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The aim of this PhD project is the development of innovative liquid chromatography-mass spectrometric technologies to efficiently fishing and identify glucose both in glycated and N-glucosylated peptides in proteins. In fact, both glycation and glucosylation in biological fluids have been already accepted to be relevant in specific disease conditions. In fact, this aberrant post-translational modifications, can be responsible of degenerative diseases. Glycation is a non enzymatic reaction that consists in the covalent bond of glucose to amino functions of proteins (N-terminus and/or Lys or Arg side-chains) and is often irreversible because of Amadori rearrangement, leading to advanced glycation endproducts involved in diabetes complications [1]. On the other hand, glycosylation is generally a covalent enzymatic modification of proteins. In the case of Multiple Sclerosis, our group has demonstrated that N-glucosylation is involved in antibody response possibly triggered by non-typeable haemophilus influenzae infection via hyperglucosylated bacterial adhesin [2].

Sera sample of patients affected by type I diabetes, multiple sclerosis, and controls will be used to set up affinity chromatography, SEC or IEX protocols to trap the glycated or N-glucosylated peptides. After enzymatic digestion of pretreated sera samples, in the case of glycated peptides the separation will be performed using an affinity chromatography based on ChemMatrix Rink resin functionalized with units of phenyl boronic acids [3]. In the case of N-glucosylated peptides, hyperglucosylated adhesin will be used in immunoaffinity columns to fish out specific anti-non typeable Haemophilus influenzae antibodies in Multìple Sclerosis patient sera. The specific antibodies will be used in immunoprecipitation experiments to identify potential native protein/peptide antigens in myelin mouse brain by high resolution mass spectrometry (MS) such as Q-TOF or Orbitrap MS/MS and taking advantage of innovative bioinformatic software. 3D LC-MS/MS is also proposed, with a first step of tandem analytic chromatography, such as SEC and CEX to identify the peaks after injection into reverse-phase columns and into high resolution MS instrumentation.The 3D LC-MS/MS technology developed for identification of both glycation and N-glucosylation in the complex serum matrix, will be proposed to food industries to monitor undesired formation of these modifications in proteins during the fundamental steps of food production due to the use of high glucose concentration as preservative. Our technology will have the impact not only to save time and materials but also to reach the most important goal of sustainability of the process in agreement with PNRR goals.

[1] A. Lapolla et al., *Mass Spectrometry Reviews*, **2018**, *9999,* 1-35
[2] A. M. Papini et al., *Sci Rep.,* **2016**, *6*, 39430
[3] A. M. Papini et al., *Molecules*, **2020**, *25*-75

POS12

Synthesis of agrochemicals against canker of kiwifruit

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Since 2008, the crops of kiwifruit in Italy were devasted by *Pseudomonas syringae* pv. actinidiae (Psa) that is the causative agent of canker disease of kiwifruit. In this bacterium the enzyme levansucrase is responsible for the synthesis of levan, a polymer investigated for its role in the early stages of the infections. Levan is involved in the mechanism of masking and protecting the pathogen from the detection and defence mechanisms of the host, as it has been proposed to be the case for *P. syringae* pv. Phaseolicola [1]. The aim of this project is the development of safe bactericides to be employed in crop protection. We would like to focus on natural compounds, non-toxic for humans and plants, but able to interact with specific targets for the bacterium. In particular, the first studies will be focused on the inhibition of the hydrolytic activity but also of polymerasic activity of the enzyme levansucrase. Monovalent and multivalent iminosugars have already shown good results because of their structural similarities to carbohydrates. The best result was obtained with a trimeric (**Figure 1**) polyhydroxypyrrolidine known as 1,4-deoxy-1,4-imine-D-arabinitol (DAB-1), which is derived from an inexpensive sugar (D-arabinose) [2].

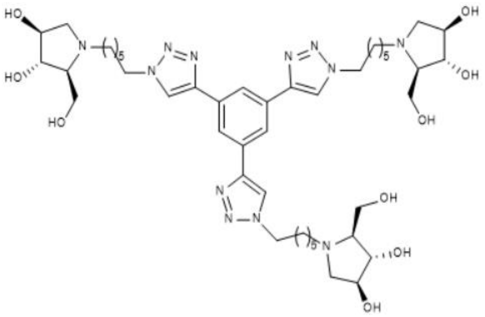

Figure 1: Trivalent iminosugar.

Because of the good results, we would like to synthesize analogues of this compound and study them in collaboration with Syngenta AG (Basilea, CH) as new antibacterial agents. These compounds will be also tested on different bacterial strains and the investigation of alternative control methods aimed at inducing host plant resistance to the pathogen will be performed, with the ultimate goal of implementing an approach of precision agriculture.

[1] S. Kasapis et al., *Carbohydr. Polym*. **1994**, *23*, 55-64
[2] A. Berto, Tesi di laurea triennale in chimica, Università di Firenze (**2022**), Relatore: F. Cardona, Correlatore: F. Clemente

POS13

Multivalent Glycosidic Vectors for the Modulation of the Immune System

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Among the different breast cancer types, the triple negative breast cancer (TNBC) is the most difficult to treat and to recover from [1]. Cancer immunotherapy is nowadays a consolidated strategy and Tumor-Associated Carbohydrate Antigens (TACAs) are used to develop therapeutic cancer vaccines (CVs). In designing a potential TACA-based CV it must be considered that saccharidic antigens suffer from a reduced metabolic stability *in vivo* and a poor T cells-dependent immunogenicity, which compromise a strong immune response, crucial for a promising CV. To overcome these issues, synthetic organic chemists offer may offer a solution by designing TACA analogues to mimic the native antigens and which are endowed with a better stability and immunogenicity [2]. Over the past two decades, saccharidic structures mimicking the well-established MUC-1 TACAs, were successfully developed at the University of Florence. To overcome their low immunogenicity TACAs are generally covalently linked to immunogenic proteins. Very recently, novel vectors have been exploited in vaccine assembling to deliver and efficiently present TACAs. This is the case of Outer Membrane Vesicles (OMVs) spontaneously released from Gram-negative bacteria [3] and containing the antigenic elements required to trigger an effective immune response. In the last years, OMVs have received an increasing attention in vaccines designing, because they are biocompatible and can be easily handled. The aim of this project is proposing a new, forefront, TNBC vaccine candidate which relies on structurally immunogenic TACAs mimetics and on OMVs as carrier-adjuvant. OMVs will be conjugated to multiple copies of MUC-1 mimetic, specifically Tn and STn mimetics (see **Figure 1**), always co-expressed in adenocarcinomas, and fully characterized.

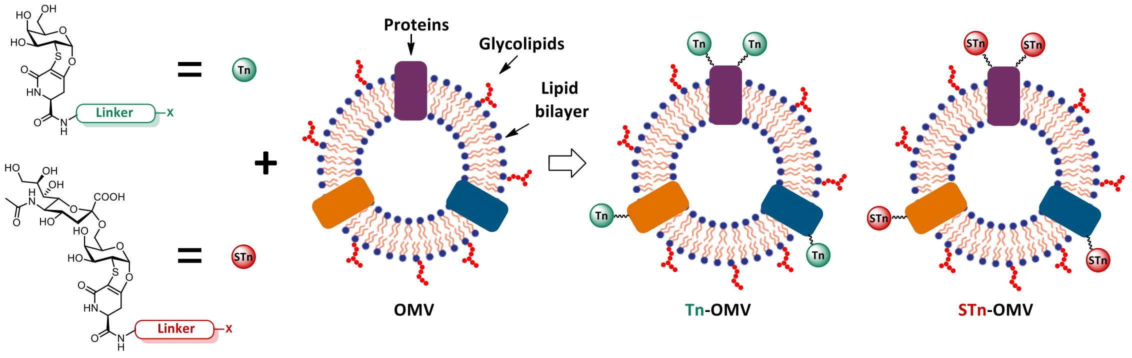

Figure 1: *OMVs conjugates with Tn and STn mimetics.*

[1] R. L. Siegel, et al., *CA. Cancer J. Clin*., **2020**, *70*, 7–30.
[2] R. M. Wilson, et al., *J. Am. Chem. Soc*., **2013**, *135*, 14462–14472.
[3] F. Micoli et al., *Semin. Immunol.,* **2020**, *50*, 101433–101445.

POS14

Development of an analytical platform for determining the concentration of Urea in wastewater

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Urea is one of the main waste products of protein catabolism in humans. High blood levels of urea can cause gout, kidney complications or other diseases. Humans and animals eliminate urea through urine (428.4 to 714 mmol/day in the case of humans). Furthermore, the production of urea in industries, and the use of urea as a nitrogen-release fertilizer in agriculture can lead to eutrophication phenomena [1] and to the generation of urea-containing wastewater. Different techniques are used to break down the concentration of urea in wastewater treatment plants. Some examples are electrochemical oxidation, carried out through Ni, NiO, Ni/C, NiCo/C–based electrodes, biotreatment through enzymes or bacteria, or adsorption on zeolites or nanostructured materials, and as the last methodology, hydrolysis through cascade combined hydrolysis/desorption processes [2]. The goal should be to valorize this waste by recovering components such as urea or phosphate. Currently, urea is produced from synthesized ammonium with high costs and environmental impact. The purpose of this doctoral project is the development of an electroanalytical platform for in-stream quantification of urea in sewage water through the use of enzymes, nanozymes and other catalysts. Several examples are reported in the literature where ion-selective electrodes for ammonia, CO_2-permeable gas membranes or ISE for ammonium are exploited. Furthermore, examples of nanostructured amperometric sensors are reported [3]. In this PhD project, innovative amperometric and potentiometric transducers will be assembled using suitable innovative “green” materials, in line with the concepts of the sustainable development and the circular economy. Recycled carbonaceous materials obtained from the pyrolysis or gasification of waste biomass as well as biocompatible metals or metal oxides will be tested. In order to increase the selectivity and stability of the transducer different functionalization processes will be optimized.

[1] L. Goeyens et al., Estuar. *Coast. Shelf Sci.* **1998**, *47*, 415–418.
[2] X. Wang et al., *Chem. Cat. Chem*. **2022**, *14*, 1-25.
[3] S. N. Botewad et al., *Biotechnol. Appl. Biochem.* **2021**.

POS15

Analytical platforms based on chromatographic techniques coupled with mass spectrometry for the high throughput identification and quantification of organic micropollutants in environmental matrices

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This research aims to develop high throughput analytical platforms for the identification and the quantification of organic micropollutants (OMPs) in environmental matrices, using chromatographic techniques coupled with mass spectrometry. In particular, the research will focus on three different aspects.

(i) Non-targeted/suspect screening approach. Liquid chromatography coupled with high-resolution mass spectrometry (LC-HRMS) is the technique of choice for the challenging task of identifying in environmental matrices, unknown organic micropollutants (OMPs), characterized by different chromatographic behaviours and ionization modes [1]. Thanks to *in silico* studies it is possible to simulate and identify potential transformation products (TPs) starting from OMPs. Non-targeted and/or suspect screening protocols make it possible to predict or identify and perhaps prioritize unknown molecules that are suspected to be present in water samples, drawing up lists of «candidate compounds» to be evaluated. Therefore, this approach will allow obtaining databases containing OMPs and their TPs, present in aqueous samples, allowing performing risk assessment analyses on drinking and irrigation water.

(ii) Targeted approach for the development of an automated method able to meet the requirements of the "white" chemistry criteria. The on-line solid phase extraction (on-line SPE) coupled to LC-MS/MS will be used for the quantification of OMPs in aqueous matrices. The target analytes are characterized by a wide range of physicochemical properties and the sorbent phase must make available different retention mechanisms ensuring good retention without breakthrough or over-retention effects, which are often present. To overcome the latter problem, the use of thermal desorption will be tested using a homemade system: it allows to increase the exposure temperature of the cartridge in order to perform the desorption step using only water, without using organic solvents and thus with good combination with RP chromatography.

(iii) Automatic extraction of solid matrices (e.g., soils, sediments, sludge, and biota). It is necessary to integrate the extraction apparatus with a system capable of enriching the analytes, often present in traces, and purifying the extract before the liquid chromatographic analysis. In the extraction step, "subcritical hot water extraction" may represent a technique suitable to achieve good recoveries of organic molecules from solid matrices. A prototype system for the extraction, on-line enrichment, and LC-MS/MS analysis will be tested, evaluating the influence of temperature, pressure, and ion exchange on OMPs recovery and matrix effect.

[1] B. González-Gaya et al., *Anal Methods* **2021**, *13*, 1876-1904.

POS16

A second life for waste: thermochemical and catalytic recycling

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According to Plastic The Facts [1], the world production of plastic material in 2021 reached 367 Mt, of which only 55 Mt were produced in Europe. These data are constantly growing every year and with them also the risks and environmental problems. As established in objective 12 of the 2030 Agenda for Sustainable Development, it is vital for the planet to identify efficient methods for the treatment of plastic waste and for their recycling. Based on these premises, the goal of this PhD project is to enhance highly complex waste with a high environmental impact, which today are destined only for landfills or only partially recycled, through thermal processes such as pyrolysis and hydrothermal liquefaction (HTL). Pyrolysis is a well-established thermal decomposition process for valorization of biomasses, performed at high temperatures in an inert atmosphere. Hydrothermal liquefaction takes place in the presence of water in its sub- or super-critical state ($T_c = 374.1$ ◦C, $P_c = 22.1$ MPa). In these conditions water acts at the same time as a reactant and solvent, taking part in the depolymerization reactions of plastics. The main advantages of the HTL process are: use of wet raw materials (eliminating the need of drying as pretreatment); opportunity to enhance heterogeneous wastes; use of water: a low-cost, available and non-hazardous solvent. Through pyrolysis and HTL it is possible to obtain products with high added value. Depending on their characteristics, these products can be used for the production of: energy sources (fuels), materials with applicative interest (chars) and chemicals [2]. In this PhD project in particular, the enhancement of the oil phases will be carried out in order to identify and maximize the yield of target molecules of high industrial interest.

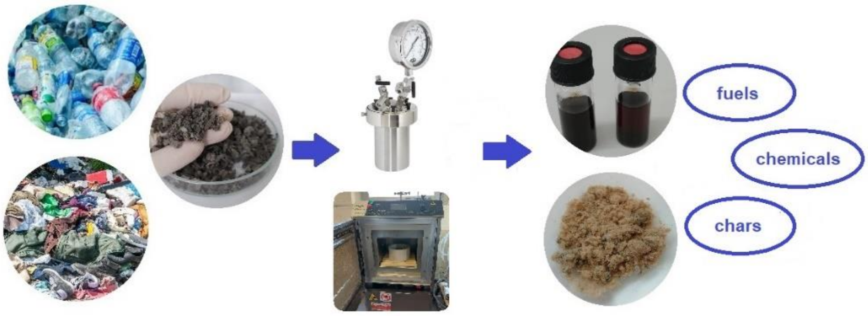

Figure 1: Conversion of different types of plastic materials through pyrolysis and HTL processes

[1] https://plasticseurope.org/knowledge-hub/plastics-the-facts-2021/
[2] I. Agostini et al., *Molecules*. **2022**, *27*, 7112.

POS17

Computational and theoretical study of structural and dynamic properties of molecular systems on solid surfaces

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The progress requires to develop smaller, faster, and less energy demanding devices for information processing and data storage. Research on these topics is particularly active, especially for the study and characterization of new magnetic materials. Therefore, the PhD project consists in a theoretical and computational study at different levels of theory of systems composed by molecular magnets (MMs) adsorbed on metal surfaces. In fact, MMs have gained considerable research importance in recent years because of their possible applications in fields such as spintronics, quantum computing and data storage.

The characterization of the magnetic properties of these materials is usually limited by the computational cost to a MM interacting with a surface. To overcome this limitation, semi-empirical methods can be employed, since these represent a good compromise between accuracy and computational cost. However, the semi-empirical methods have the downside of relying on force fields highly specific to the system for which they have been parametrized.

One of the objectives of the PhD project is to improve the accuracy in reproducing experimental results, developing new force fields for the study and characterization of the structural and dynamic properties of systems consisting of several MMs adsorbed on a metal surfaces.

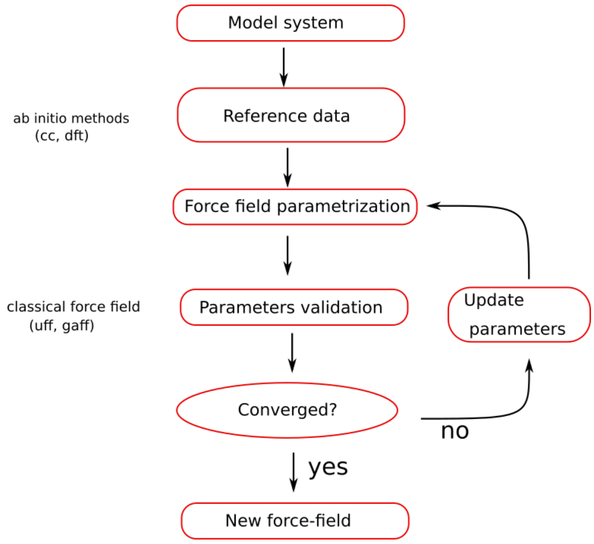

Figure 1: Flowchart illustrating the process of parametrization of a force field.

POS18

Development of materials for the selective coordination of critical metal ions present in brines

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The recovery of metal ions is a fundamental ecological goal, especially looking at the importance of reaching a circular economy. The selective coordination of metal ions, both alkali and alkaline-earth and transitional is affected by the type and number of donor atoms and the pre-organization of the ligands (polydentate chelators, macrocycles, cryptands). Exploiting these design elements, selective ligands for the coordination of metal ions of environmental and commercial interest, will be design and synthesized. These ligands will be bonded to an eco-compatible carbon-based materials (activated carbon, graphene, carbon nanotubes) or boehmite and used for the selective extraction of metal ions. The bond will be based on a on non-covalent π-π stacking interactions, between an electron-poor group and the electron-rich graphitic surfaces according to previously reported procedures [1, 2]. The reaction is spontaneous, irreversible and it can be generated in water without any protected atmosphere. The prepared materials will be regenerable and reusable. The advantage of this extraction method consists not only in the reusability of the materials used, but also in their high selectivity towards metal ions, in their simplicity of use (they can be packed in columns) and in their eco-friendliness.

[1] M. Savastano et al., *J. Catal.*, **2017**, *353*, 239–249.
[2] M. Passaponti et al., *Inorg. Chem.*, **2018**, *57*, 14484–14488.

POS19

Smart nanomaterials in diagnosis and therapy

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Interest in nanomaterials from sustainable and natural sources has grown enormously in recent years. The use of nanocellulose materials extracted from renewable biomass has proved promising in various applications: they are biocompatible, have good mechanical properties and are easy to functionalize [1]. Carbon-based nanomaterials, such as graphene oxide (GO), have also proved versatile in nanomedicine, due to their favorable characteristics and high surface area that can be exploited. Functionalization of these materials with molecules or nanoparticles with antimicrobial activity could attribute innovative properties to the materials, making it possible to obtain medical devices that are resistant to the development of microbial films which are considered a factor in bacterial resistance. Indeed, most chronic bacterial infections today are associated with the formation of biofilms. Specifically, biofilms are aggregations of bacteria wrapped in a self-produced matrix of extracellular polymeric substances that protects the microbial community from external environmental stresses, such as antibiotic use [2]. A biofilm-related infection of a medical device can usually only be treated by surgical replacement of the device, and recurrences of infection tend to be high. For these reasons, the discovery of effective anti-biofilm materials is now a healthcare priority [3].

[1] A. S. Finny et al., *Nanomaterials* **2021**, *11.*
[2] J. Tricomi et al., *Nanoscale* **2022**, *14*, 10190–10199.
[3] S. Gilbert-Girard et al., *Biofouling* **2021**, *37*, 791–807.

POS20

(Micro)-plastics and emerging contaminants in aquatic environments

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Microplastics (MPs) are currently included among emerging organic contaminants (EOCs) because they are ubiquitously present in the environment and their presence, especially in aquatic environment, could lead to ingestion by the biota and cause serious health issues [1]. Also, MPs could reach wastewater treatment plants from which they are never completely removed [2]. These kinds of pollutants threaten the ecological function of rivers as well as the coastal marine areas. This PhD project aims to quantify and qualify EOCs and MPs in freshwater and marine environments with a view to investigate the transfer of these pollutants from abiotic to biotic matrices and the effects on the organisms' health. The research also looks at the possibility to implement control strategies and technologies to prevent plastic from reaching the environment. Various kinds of samples will be collected among Arno River and its tributaries but also along coastal marine areas. For EOCs methods of extraction and purification will be optimized, while for MPs there will be evaluated the most suitable technics for chemical characterization among those currently available. Lastly, the influence of water column transport and sedimentation processes will be evaluated with modeling and statistical data treatment. This project fits in the framework of the PNR 2021-2027 as part of the intervention area about sustainable management of marine ecosystems, as it is increasing important the principle of water reuse and the biodiversity conservation.

[1] V. Rimondi et al., *Toxics* **2022**, *10*, 407.
[2] P. L. Ngo et al., *Environ. Poll.* **2019**, *255*, 113326.

POS21

Characterization of the mechanism of action of gold compounds

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The mechanisms of biological action of most therapeutic metal compounds are still not fully elucidated. In the case of anticancer metallodrugs, DNA is not always the primary target as it is for cisplatin [1]. In fact, many metal-containing chemotherapeutics show a rather high selectivity towards proteins, indicating that different modes of action occur depending on the specific type of metal complex. Among them, gold compounds form a promising class of anticancer drug candidates [2]. The interactions of gold compounds with nucleic acids are relatively weak; on the other hand, a variety of likely protein targets were proposed, such as thioredoxin reductase [3] and various proteases of the ubiquitin-proteasome system. It was determined that gold compounds can produce relevant alterations of the mitochondrial functions, trigger ROS production and affect glucose metabolism. Rather different mechanistic profiles were delineated, as they depend on the structure and reactivity of the specific compound.

This PhD project aims to develop a new effective workflow that can allow to determine the mechanisms of action of several gold compounds. To fulfill my goals, a research plan with an experimental workflow has been set up.

First, tumor cell lines will be treated in vitro with the previously synthetized/purchased compounds. Once this step is completed, culture media and cell lysates will be investigated throughout metabolomics analyses. NMR can be exploited to perform metabolomics studies, especially thanks to high resolution 1D ^{1}H spectra. The comparison between treated and untreated cells spectra enables the identification of the metabolites whose levels are mainly affected by drug treatment.

Metabolomics data will be analyzed and interpreted to identify a series of possible protein targets. Subsequently, it will be necessary to express and purify a panel of proteins using heterologous expression systems. To further characterize the drug-target binding mechanism and identify the binding sites, protein variants will be obtained via site directed mutagenesis.

Drug-target adducts will be obtained and structurally analyzed. ESI-MS will be exploited to evaluate the formation of metal-protein adducts and to clarify the binding selectivity via competition binding experiments. High resolution methods such as NMR, cryo-EM or X-ray crystallography will be then used on a selected panel of the most promising adducts to elucidate the binding site and the interaction mode of the two partners.

[1] N. Muhammad et al., *Current Opinion in Chemical Biology*, **2014**, *19*, 144–153.
[2] S. Nobili et al., *Med. Res. Rev.*, **2010**, *30*, 550–580.
[3] A. Bindoli et al., *Coordination Chemistry Reviews*, **2009**, *253*, 1692–1707.

POS22

Paramagnetic Nuclear Magnetic Resonance of Nitrogenase's Cofactor Maturating Bio-enzymes

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This PhD project is focused on the methodological development of NMR spectroscopy strategies for the structural study of high mass highly paramagnetic systems. The aim of the project is indeed double: i. to provide novel paramagnetic NMR experiments to investigate the structure of high mass highly paramagnetic proteins, ii. to characterize the exotic reaction mechanism of NifB enzyme, with the final goal of producing improved and stable versions of the protein and installing them in plant organisms, overcoming the use of polluting fertilizers that impar the ecosystem. Starting from the development of NMR experiments for small paramagnetic proteins (like the HIPIP PioC), this work will be further developed focusing on challenging proteins involved in the nitrogenase's maturation process [1]. Within the frame of an international collaboration with the Center for Plant Biotechnology and Genomics (CBGP, Madrid), the structure, functions and dynamics of the Radical SAM methyltransferase NifB will be investigated according to the already established NMR methodologies and applying innovative strategies mostly entailing the effects due to the presence of multiple paramagnets contained inside the protein, in particular paramagnetic relaxation enhancement (PRE) [2,3].

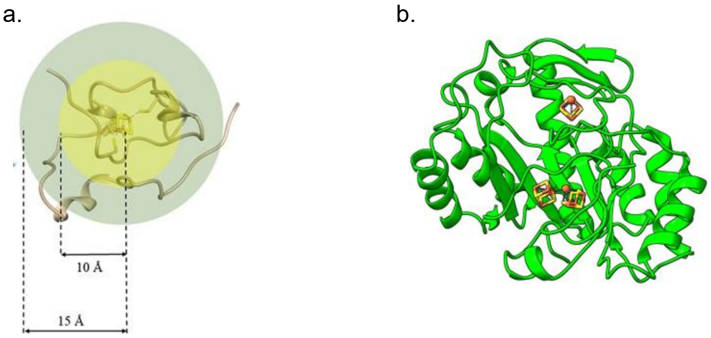

Figure 1: a. HiPIP PioC surrounded by the paramagnetic blind sphere. b. NifB complemented with three [Fe$_4$S$_4$] clusters

[1] I. Trindade et al., *Inorganica Chim. Acta* **2021**, 514, 119984.
[2] M. Mori et al., *J. Am. Chem. Soc.* **2010**, *132*, 3594–3600.
[3] Wilcoxen et al., *J. Am. Chem. Soc.* **2016**, *138*, 7468–7471.

POS23

Design, characterization and optimization of nanostructured vectors for the delivery of mi-RNA- Development and optimization of intelligent vector for RNA delivery.

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Immune-mediated disease (IMDs) are pathologies characterized by an altered response of the immune system, which leads to consequences such as chronic inflammation of the tissues, pain and a reduction in the quality of life of patients. Nowadays, there are no effective treatments for this group of diseases. This research work aims to develop a nose to brain (N2B) formulation composed of Lipid nanocarriers (LNPCs) [1] containing miRNA [2]. The first step of this work involves the screening and selection of the components necessary for the formulation of the LNCs [3], using an experimental design technique called MODDE, followed by the production of LNCs with different methods and the choice of the best one. The LNCs properties like surface charges, stability and encapsulation capacity of the mRNA will be characterized with HPLC-DAD-MS, Light scattering, DSC and Cryo-TEM techniques. The last step will be focused on the selection of the components for development of an N2B formulation and the study of mucus adhesion, in vitro release, permeation, stability and a test on cell cultures.

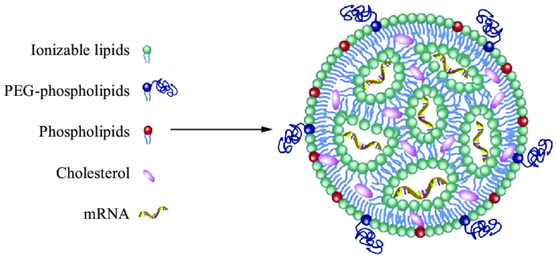

Figure 1: Hypothetical structure of mRNA-LNPs.

[1] Kiaie et al., *Journal of Nanobiotechnology* **2022**. 10.1186/s12951-022-01478-7
[2] Rinoldi et al., *small methods* **2021**. 10.1002/smtd.202100402
[3] Sargazi et al., *Cell Biology International* **2022**. 10.1016/B978-0-12-800148-6.00004-3

POS24

Design and development of wearable (bio)sensors based on advance materials for smart and non-invasive clinical parameters monitoring

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Neurodegenerative diseases represent a condition of irreversible deterioration of nerve cells, resulting in a loss of cognitive and motorial abilities [1]. Wearable sensors offer amazing potential for diagnosis or treating of neurodegenerative conditions. Thanks to the miniaturization it is possible to integrate these sensors into comfortable wearables (such as bracelet). This project focuses on the development of a sensitive wearable (bio)sensor to be embedded in a miniaturized smart device. The device will be able to monitor, with high selectivity, biomarkers or drugs, thanks to the use of stable biomimetics (e.g. aptamers and nanozyme). New biocompatible advanced materials will be used to design a controlled sweat collection system, in order to implant the collector in the same wearable tool leading to an integrated sensor [2].

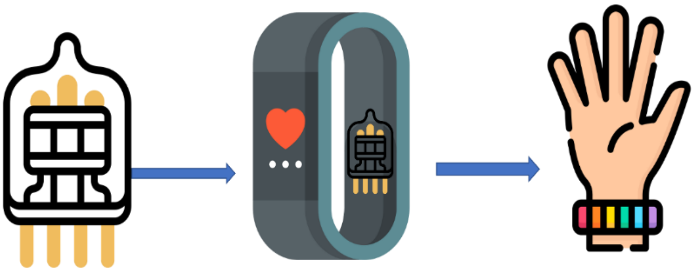

Figure 1: Development of sweat collector using new biocompatible stretchable materials combined with a selective platform for biomarkers detection. Implementation of the proposed system in a smart bracelet.

[1] O. Hansson, *Nat. Med.* **2021**, *27*, 954–963.
[2] L. Song, et al., ACS Nano **2021**, *15*(12), 18822-18847.

POS25

Structural characterization of enzyme complexes with new antitumor agents for the development of theranostics

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The development of effective anticancer therapies still represents a challenging issue; one possible way to approach this problem is by the rational design of drugs through the structural characterization of the enzyme-inhibitor complexes [1].

This project aims to improve the efficacy of dual-target inhibitors as anticancer agents by studying the X-ray crystallographic structures of the complexes obtained with cancer target enzymes. In particular, the analyses will focus on the human Carbonic Anhydrases (CAs) isoforms IX/XII, Histone deacetylases (HDACs) and fibroblast activation protein (FAP), which are strictly related to the development of cancer. The achievement of these studies could play an important role in providing new insight and information about the binding of the dual target inhibitors to the above-mentioned enzymes, leading to more specific inhibitors and effective anticancer treatment.

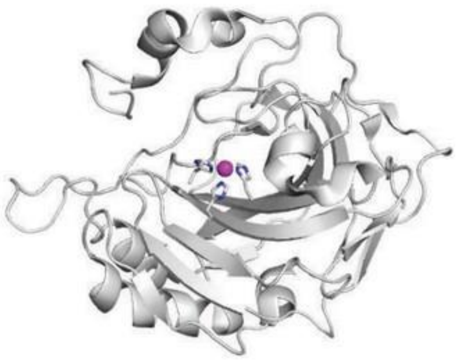

Figure 1: Structure of α-class Carbonic Anhydrase [2].

[1] R. R. Ramsay et al., *Clin. Transl. Med.* **2018**, *7*.
[2] C. L. Lomelino et al., *Int. J. Med. Chem.* **2018**.

POS26

Synthesis and surface engineering of a biocompatible nanomaterial for precision cancer therapy

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Despite the numerous anti-cancer therapies available today, there are still many challenges for the scientific community to overcome. Issues are mainly related to the side and cytotoxic effects associated with most cancer therapies. Therefore, in order to overcome these limitations, many research groups are trying to develop new precision cancer therapies: therapies that target specific molecular entities responsible for cancer development and progression and enable significant therapeutic benefits. During this PhD, we propose to synthesize and engineer the surface of a biocompatible nanomaterial, such as nanocrystalline cellulose to develop next generation of nanomaterials for precision cancer therapy applications. Cellulose nanocrystal (CNC) is a nanomaterial with interesting properties: it is biodegradable, biocompatible, and it has a large surface area characterized by several hydroxyl groups, which can be exploited for the functionalization of its surface [1]. The aim of this study is to find a simple methodology to easily access functionalized CNC with high batch-to-batch reproducibility. The CNC surface will be functionalized with sugar headgroups which target glycan-binding lectins and channels commonly overexpressed in cancer cells, to ensure the precision delivery of the nanomaterial into cancer cells (Figure 1) [2].

Figure 3: Functionalized nanocrystalline cellulose

Then, the functionalized CNC will be exploited for the development of new chemo- and radiotherapy therapies. In particular, we propose to prepare a bifunctional CNC including radioactive ions (e.g., lutetium 177), and EGFR receptor inhibitors in order to achieve high sensitivity to cancer therapy [3].

[1] I. Lugoloobi et al., *J Control Release*. **2021**, *336*, 207-232
[2] M. Martínez-Bailén et al., *Chem Soc Rev*. **2022** Dec
[3] S. Imlimthan et al., *Small*. **2021**, *17*, 2007705.

Funder: Project funded under the National Recovery and Resilience Plan (NRRP), Mission 4 Component 2 Investment 1.4 - Call for tender No. 3277 of 30 December 2021 of Italian Ministry of University and Research funded by the European Union – NextGenerationEU; Award Number: Project code ECS_00000017, Concession Decree No. 1055 of 23 June 2022 adopted by the Italian Ministry of University and Research, CUP B83C22003930001, project title “Tuscany Health Ecosystem – THE”.

POS27

Advanced sensors/materials – Development of innovative materials and advanced sensors for life sciences

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Recent advancements in the fields of flexible electronics, miniaturized systems, and smart materials are leading to the development of new kinds of sensors useful for applications related to healthcare, environment, energy harvesting, electronics, and food industry.

However, the realization of wearable multifunctional devices is still an open challenge, and liquid crystals (LC) and liquid crystalline elastomers (LCEs) represent valid options to realize sensitive, simple, effective, and portable systems in principle able to detect variation of physical and chemical parameters (temperature, pH, toxicants or (bio)molecules) [1]. Standard LC sensors are based on molecular orientation order changes due to the presence of specific chemicals at the LC-air (or water) interfaces detectable by polarized light. The development of LCE instead will open to wearable devices as colorimetric sensors, versatile supports for stretchable and wearable devices or coatings able to release and adsorb drugs or fluids in a controllable and reversible way, for the realization of multifunctional devices. The objective of this project is to develop new biocompatible LCs and LCEs materials, testing new chemistries and technologies to obtain advanced materials for the realization of sensors and for the controlled release of specific molecules towards the obtainment of wearable multifunctional devices.

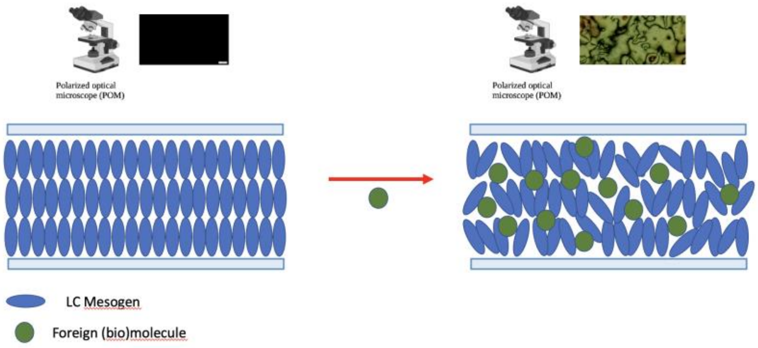

Figure 1: Liquid Crystal based sensoring

[1] H. K. Bisoyi, & Q. Li, *Chemical Reviews* **2021**, *122*, 4887–4926.

POS28

Design and characterization of lipid nanoparticles for RNA encapsulation and targeted delivery

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In the past years, RNA delivery demonstrated its unique advantages over traditional biopharmaceutical and vaccine technology. However, to promote its application, RNA's inherent limitations [1] must be overcome by designing delivery vectors able to protect the RNA cargo from the environment and to transport/release it in proximity to its biological target. Among such systems, lipid nanoparticles (LNPs) are particularly promising [2, 3]. They play a key role in protecting and efficiently transporting RNA into cells. To boost the clinical translation of such materials, it is crucial to obtain a deep physicochemical understanding of these systems. The proposed PhD project will have two main objectives: first, I will design and prepare different kinds of LNPs as RNA vectors, such as cubosomes and hexosomes, functionalized to achieve targeted delivery. Then, the carriers will be physiochemically and functionally characterized with various methodologies, to determine their physicochemical, structural, and colloidal properties and to test their potentiality as RNA carriers.

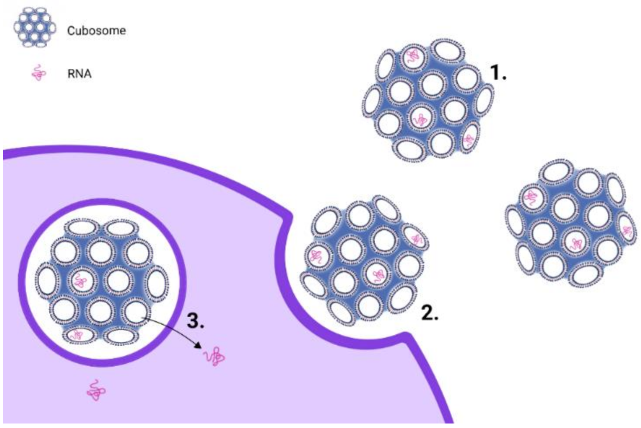

Figure 1: Schematic representation of (1.) free cubosome (2.) cubosome internalization (3.) RNA release.

[1] C. J. Knudson et al., *Mol. Ther.*, **2021**, 2769-81.
[2] D. Guimarães et al., *Int. J. Pharm.*, **2021**, *601*:120571.
[3] I. D. Azmi et al., *Ther Deliv.*, **2015**, *6*, 1347-64.

POS29

Theranostic Iminoglyco-NPs targeting the Blood Brain Barrier

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Gaucher's disease (GD) is a rare autosomal recessive disease caused by a deficiency in the activity of the glucocerebrosidase (GCase) enzyme due to mutations in the GBA gene. Studies show that GBA genetic mutations are also a risk factor for Parkinson's disease, suggesting that therapeutic approaches to modulate GCase activity could play an important role in treating both diseases [1]. An innovative therapeutic strategy for the treatment of GD is the use of pharmacological chaperones (PCs) to enhance natural enzymatic activity, although currently no PC has yet reached the market for this pathology. Iminosugars and other substrate analogues acting as competitive inhibitors of GCase are promising candidates as PCs [2]. As the blood brain barrier (BBB) represents an obstacle for the classical enzyme replacement treatment of neuronopathic forms of GD, in this PhD project the synthesis of novel iminosugars functionalized with specific ligands able to enhance the transport through the BBB will be investigated. In addition, since a greater affinity between enzyme and multivalent iminosugars has been demonstrated, the multimerization of the iminosugars onto nanoparticles (NPs) will be carried out to combine the properties of the inhibitors to the multivalency of the NPs, thus yielding smart systems with theranostic properties [3].

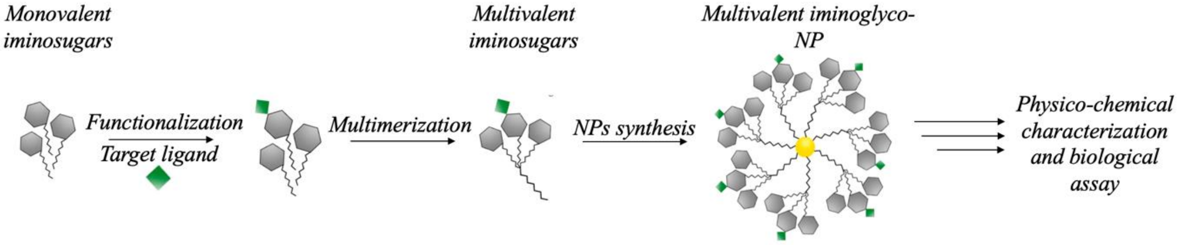

Figure 1: Schematic drawing of a strategy to obtain a representative type of iminoglyco-NPs.

[1] G. M Riboldi, et al. *Cells* **2019**, *8*, 364.
[2] E. M. Sánchez-Fernández, et al. *Chem Commun* **2016**, *52*, 5497.
[3] M. A. Malvindi, et al. *Nanoscale* **2011**, *3*, 5110.

We acknowledge the support of the European Union by the Next Generation EU project ECS00000017 'Ecosistema dell'Innovazione' Tuscany Health Ecosystem (THE, PNRR, Spoke 4: Nanotechnologies for diagnosis and therapy)

POS30

Computational characterization of dimeric transition metal molecular qubits from bulk to the adsorbed phase

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Over the past decade, transition metal complexes have become increasingly popular candidates for electron spin-based quantum bits (qubits) due to their synthetic tunability and long achievable coherence times [1]. The decoherence of magnetic quantum states limits their utility in quantum information technologies such as quantum computing, sensing, and communication [2]. Recently, an experimental cum DFT study on a unique singly linked vanadyl-porphyrin dimer, $[VO(TrPP)]_2$, that crystallized in two separate pseudo-polymorphs, with isotropic exchange interaction, J, of the order of 10^{-2} cm^{-1} illustrated by single crystal continuous-wave EPR was reported, where further pulsed EPR investigation revealed that the two vanadyl dimers retain the monomer's coherence time [3]. In the current work, we further aim to come up with similar dimeric analogs of the aforementioned complex, by applying first-principles calculations to open up new avenues for the rational design of multi-qubit architecture made of molecular dimeric units at the atomic scale in gas and bulk phases as also adsorbed on surfaces.

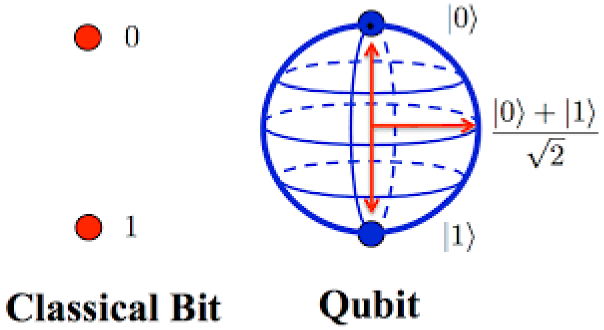

Figure 1: Schematic representation of two states available for a classical bit 0 and 1 (left) and those available for a quantum bit |Ψ⟩ (right).

[1] Graham et al., *J. Am. Chem. Soc.* **2014**, *136 (21)*, 7623–7626..
[2] Atzori et al., *J. Am. Chem. Soc*. **2019**, *141 (29)*, 11339–11352.
[3] Ranieri et al., *Chem. Sci.* **2023**,*14*, 61-69.

POS31

Development and characterization of theranostic nanosystems for targeted cancer therapy

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Naturally occurring polysaccharides have gained great attention in biomedical field due to their distinct features including biocompatibility and biodegradability as well as facile modification [1]. Recent efforts have been paid on synthesizing polysaccharide nanoparticles to seriously tackle and enhance immune response against tumours with minimal side effects. Polysaccharides morphology provide additional benefit in synthesizing nanoparticles with ability to be chemically modified to achieve maximum precision in delivering drug to tumour cells [2]. Although polysaccharides nanoparticles are long known and many techniques have been applied to target cancer cells from these molecules, much work remains to be done to completely understand and implement the mechanism that would effectively target tumour cells without disrupting of the internal balance of the human body. This project is focused on the study of the isolation, design and development of novel polysaccharides and modify their structure with different techniques and functional groups in order to discover a system that would be precise, less toxic, cost efficient and effective in terms of diagnostic imaging as well as carrying anticancer agents, such as fibroblast activation protein (FAP) inhibitors and carbonic anhydrase (CA IX / XII) inhibitors to specific tumour cells. Special attention will be paid on the synthesis and characterization of nanocomposites naturally and easily in bulk given that it is novel fundamental and feasible approach of treating cancer. In order to synthesize polysaccharide-based nanoparticles, biologically active compounds will be first isolated and then these compounds will be characterized by UV/VIS, IR and NMR spectroscopy in the proposed study. In addition, their chemical functionalization and facile modification will be achieved by crosslinking them with different chemical species in attempt to enhance their function [3]. Certain biochemical tests will be conducted to check the feasibility of synthesizing such compounds on large scale for successful designing and manufacturing of drugs to treat cancer cells with high precision and accuracy.

[1] J. Venkatesan et al., *Polym*. **2021**, *30*.
[2] Z. Yujun et al., *Bioactive Mat*. **2021**, *6*, 3358-3382.
[3] F. Lei et al., *Carb. Polym*. **2020**, *234*, 115930

Gentilissimi studenti,
con due versi, com'è d'uso,
qui vi faccio i complimenti
per l'evento ormai concluso.

Il simposio è un'occasione
di confronto di esperienze,
e di gran dissertazione
su progetti e conoscenze,

che potrete sviluppare
sino al termine del corso,
per dipoi delineare
qual sarà il vostro percorso.

Possa ancor più il Dottorato
arricchir la vostra mente,
e il ricordo maturato
vi accompagni dolcemente !!!

Dr. Roberto Di Camillo

PiCSU II ed.
Dottorato di Ricerca in Scienze Chimiche
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