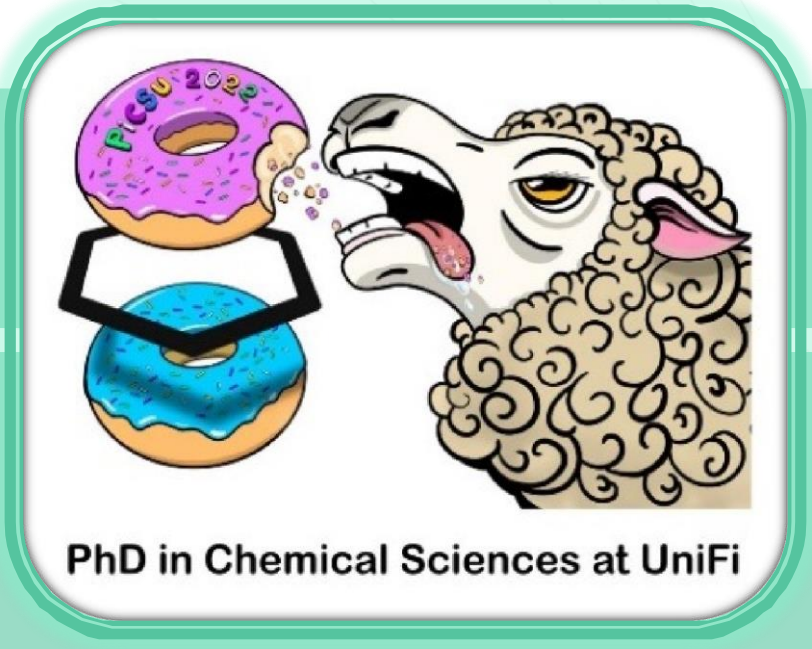
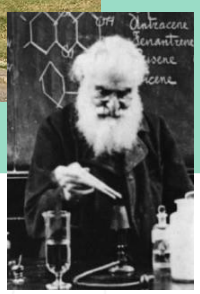
1° PiCSU Symposium



Book of Abstracts

19-21 January 2022



UNIVERSITÀ DEGLI STUDI FIRENZE
UGO SCHIFF
DIPARTIMENTO DI CHIMICA

PhD in Chemical Sciences at UniFI

PiCSU2022

1st edition

Edited and ideated by: *Anna Maria Papini, Martina Vizza, Gina Elena Giacomazzo, Saul Santini, Marco Bonechi, Mert Acar, Davide Ranieri, Mariagrazia Lettieri, Debora Pratesi*

About the Symposium…

We are going through complicated times, because of the pandemic we are constrained to distance ourselves and often meet remotely. We still live in a context in which social distancing imposes us to isolate ourselves, slows down our productivity, and minimizes our social interactions.

Since the global pandemic made its appearance, PhD students of the Department of Chemistry “Ugo Schiff” were not able to meet except through digital platforms, with remote lessons and seminars followed individually. Those moments in which it was possible to confront ideas have been missing, creating a barrier between us, slowing down the scientific and cultural growth of young researchers, limiting the possibility of discussion, and limiting our knowledge of the research activities of our fellow PhD students including their educational progress.
All this, however, is in contrast with what research means and represents: the creation of a scientific network that promotes cultural and scientific enrichment, that rests its foundations on the sharing and elaboration of ideas, therefore improves the projects discussed and at the same time enriches the figure of the researcher who presents them.

The intention to experience the very meaning of research has kick-started the idea of organizing the first Symposium "PhD in Chemical Sciences at Unifi - PiCSU2022", entirely managed by the PhD students of the Department of Chemistry of the University of Florence, with the collaboration and help of the PhD Coordinator and the professors who have supported this initiative.

Like every “first time”, there might be things to improve, angles to smooth and shades to define but the roots on which this idea grew will not change. These roots are not based on competition, but on the exposure and sharing of the path that some PhD students have just started and that others have completed, a path that can be difficult and, in some cases, discouraging but must still pursue the goal of forming and growing new people of research, who will constitute the scientific community of the future.

PhD projects can change and transform, but to do so, it is also necessary to know those areas that might seem far from our skills, but in a multidisciplinary perspective can instead enrich one's research and in some cases can give concreteness or ideal solutions to dead ends.

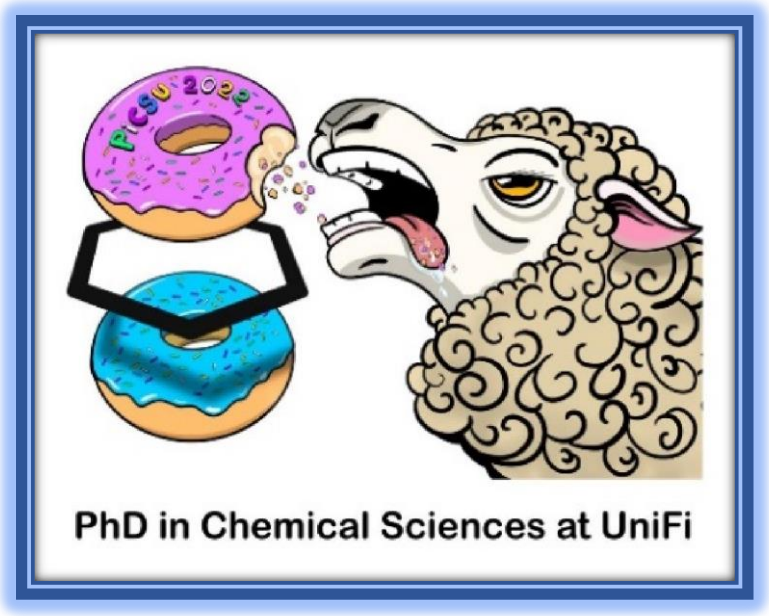
We hope that the basic principle of this Symposium, namely sharing and comparison of scientific experiences, can be accepted and conserved within our scientific community even in the years to come.

“Chemistry is something needed for everything. It serves to cultivate oneself; it serves to grow; it serves to insert oneself, in some way, into concrete things "

Primo Levi

“La chimica è una cosa che serve a tutto. Serve a coltivarsi, serve a crescere, serve a inserirsi in qualche modo nelle cose concrete”

Primo Levi



PhD Coordinator

Prof. Anna Maria Papini

Organizing Committee

Acar Mert

Bonechi Marco

Giacomazzo Elena Gina

Lettieri Mariagrazia

Pratesi Debora

Ranieri Davide

Santini Saul

Vizza Martina

Organizing Committee

Some of the students enrolled in the PhD program in Chemical Sciences volunteered to organize this symposium forming the organizing committee. The committee created this Symposium in its entirety and made it accessible to all students in order for all PhD students to share their research projects.

Acar Mert

Bonechi Marco

Giacomazzo Elena Gina

Lettieri Mariagrazia

Pratesi Debora

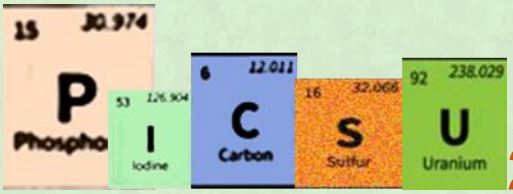
Ranieri Davide

Santini Saul

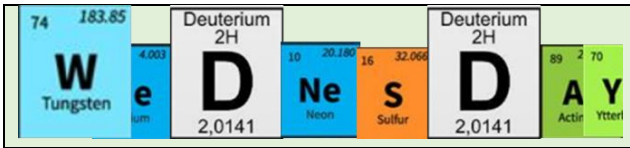
Vizza Martina

Participants at PiCSU 2022 Symposium

PhD in Chemical Science at Unifi



2022 Program

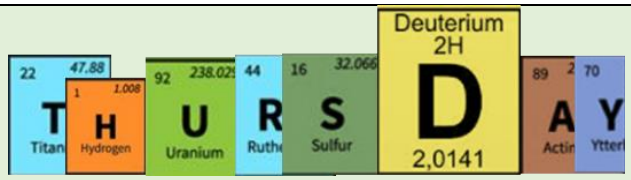


19 January 2022

14:00-14:15	***Institutional Greetings and Welcome Introduction***			
1st session ***Chair:*** *Davide Ranieri*; *Mariagrazia Lettieri*				
14:15-16:00	OC01	XXXIV	Vanessa Rosciardi	**"Green" Poly(vinyl alcohol)/Starch based cryogels for the cleaning of works of art: Application, characterization, and investigation of the Amylose/Amylopectin structural role**
	OC02	XXXV	Lapo Renai	**Comparison of chemometric workflows strategies for potential exposure markers discovery and false positive reduction in untargeted metabolomics: application to the serum analysis by LC-HRMS after intake of *Vaccinium* fruits supplements**
	OC03	XXXV	Debora Pratesi	**Glycomimetic azasugars for selective inhibition of Carbonic Anhydrases**
	OC04	XXXV	Martina Vizza	**Electrodeposition of poly(3,4-ethylenedioxythiophene), CdSe and MoS_2 on Silicon electrodes to obtain interesting technological and catalytic surfaces**
	OC05	XXXVI	Gavino Bassu	**Poly(ethylene glycol)-based hydrogels as transparent porous network for diffusivity studies**
	OC06	XXXVI	Lorenzo Baldini	**Synthesis and elaboration of novel heterocyclic scaffolds through C-H bond activation for application as peptidomimetics**
	OC07	XXXVI	Patrick Severin Sfragano	**Bicyclic Peptides as Bioreceptors towards the electrochemical detection of the Human Urokinase-Type Plasminogen Activator**
16:00-16:20 - Break				

2nd session **Chair:** *Mariagrazia Lettieri*; *Davide Ranieri*				
16:20-17:40	OC08	XXXIV (online)	Raffaello Nardin	**The link between past, and future: investigating climatic and environmental variability through Ice Records from East Antarctica**
	OC09	XXXV (online)	Lorenzo Briccolani Bandini	**Adsorption of Bio-Molecules on Metal Surfaces: a Computational Study**
	OC10	XXXVI (online)	Andrea Comparini	**Development of aluminum alloys plating processes via sustainable galvanic processes**
	OC11	XXXVII	Elena Merli	**Development of eco-friendly hydrogels with structures optimized for nano / micro filtration, selective absorption and prevention of biofouling**
	OC12	XXXVII	Alessandro Gerace	**Intelligent and sustainable synthesis and processing of innovative permanent magnets**
	OC13	XXXVII	Laura Vespignani	**Study of new materials with low environmental impact and their use in the conservation of Cultural Heritage**
	OC14	XXXVII	Michele Casoria	**From a bioinformatic approach to synthetic conformational peptide epitopes to disclose molecular mechanism of aberrant immune response in auto-immune diseases.**
	OC15	XXXVII (online)	Margherita Verrucchi	**Electrodeposition and surfaces analysis in galvanic for industry 4.0**

Evening session **Chairs:** *Gina Elena Giacomazzo; Marco Bonechi*				
20:00-20:55	OC16	XXXVII (online)	Sara Aquilia	**Development of macromolecular and cross-linked materials based on proteins/peptides from vegetable sources**
	OC17	XXXVI (online)	Giulia Guidelli	**New formulation approaches for the development of cleanser with high efficacy and gentle on the skin eco-friendly proven**
	OC18	XXXIV (online)	Andrea Ridolfi	**Probing the mechanical response of lipid membranes at the nanoscale**
	OC19	XXXV (online)	Arianna Balestri	**Smart amphiphilic block copolymers as stabilizers of lipid-based drug delivery systems**



20 January 2022

1st Session

Chair: *Mert Acar*, *Martina Vizza*

14:00-15:55	OC20	XXXIV	Francesca Torrini	**An enzyme-linked immunosorbent assay (BELISA) for the analysis of a small neuropeptide by using molecularly imprinted polymer-coated microplates**
	OC21	XXXIV	Fabio Santanni	**A Novel Series of Hydrogen-Free M^{II} (Cu^{II}, Ni^{II}) Complexes of 1,3,2-Dithiazole-4-thione-5-thiolate Ligand as Potential Molecular Spin Qubits on Surface**
	OC22	XXXV (online)	Giulia Mugnaini	**Photocross-linked gelatin methacrylate porous microparticles for drug release**
	OC23	XXXV	Gheorghe Melinte	**Electrochemical platforms for allergens detection**
	OC24	XXXV	Mariagrazia Lettieri	**Melanochrome-based colorimetric assay for quantitative detection of levodopa in Parkinson's drugs**
	OC25	XXXV	Agnieszka Staśkiewicz	**Design, synthesis, conformational studies, and biological activity of clicked oxytocin analogues**
	OC26	XXXVI	Sara Calandra	**Optimization of the binder selection protocol for radiocarbon dating of historical mortars**

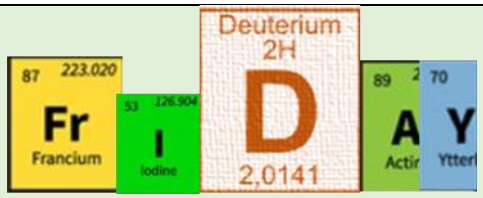
15:55-16:15 – Break

2nd session

Chair: *Martina Vizza*; *Mert Acar*

16:15-17:55	OC27	XXXIV (online)	Andrea Albino	**Structural and Vibrational Properties of Magnetic Systems from the Bulk Phase to the Adsorption on Surface**
	OC28	XXXV (online)	Gina Elena Giacomazzo	**Ruthenium (II) polypyridyl complexes: playing with structural parameters to design promising light-responsive therapeutic agents**
	OC29	XXXVI	Michela Lupi	**Molecular and macromolecular hetero[4]helicenes: synthesis, red-ox properties and applications**
	OC30	XXXVI	Kristian Vasa	**Design and synthesis of macromolecular and nanostructured carbonic anhydrases-based materials**

	OC31	XXXVI	Simi Maria Emilia Mangani	**Interdisciplinary study of Majolica of Montelupo: preliminary results**
	OC32	XXXVII	Michael Quagliata	**Peptides inhibitors of Protein-Protein Interactions: the COVID-19 case of study**
	OC33	XXXVII	Lorenzo Bracaglia	**Investigating the role of disorder in structurally heterogeneous proteins**
	OC34	XXXVII	Daniela Porcu	**New strategies for the monitoring and the inhibition of metals and alloys corrosion in Cultural Heritage**
	OC35	XXXVII	Michelangelo Fichera	**Production of carbonaceous materials from biomass of high environmental hazard, their characterization and application on water purification**



21 January 2022

1st Session

Chair: *Saul Santini*; *Chiara Sarti*

9:00-10:55	OC36	XXXIV	Lorenzo Fabbri	**Electrodeposition and characterization of industrial and technological interesting surfaces**
	OC37	XXXV	Gianmarco Maria Romano	**Polyamine receptors as fluorescent chemosensors for anti-inflammatory nonsteroidal drugs in aqueous media**
	OC38	XXXV (online)	Stefano Mauro Martinuzzi	**Measurement of metal coatings thickness by X-ray spectrometric method without the need for certified standards**
	OC39	XXXV	Giacomo Lucchesi	**A new neuroprotective bola-amphiphile: the trodusquemine**
	OC40	XXXVI	Valentina Vitali	**Enlarging the scenario of site direct ^{19}F labelling in NMR spectroscopy**
	OC41	XXXVI	Davide Ranieri	**Synthesis and magnetic studies of molecular spin qubits**
	OC42	XXXVII	Mert Acar	**Smart Autonomous Responsive Materials**
	OC43	XXXVII (online)	Andrea Dali	**Advanced spectroscopic study aiming to the understanding of the heme-biosynthesis pathway of gram-positive bacteria**
	OC44	XXXVII	Lucrezia Cosottini	**Ferritin-based anticancers**
	OC45	XXXVII	Lorenzo Pacini	**Greening peptide chemistry, a necessary step to the future**

10:55-11:15 - Break

2nd Session

Chair: *Debora Pratesi*; *Lapo Renai*

11:15-12:40	OC46	XXXIV (online)	Annunziata D'Ercole	**Development and scale-up of synthetic strategies for exotic macrocyclisation to increase druggability of peptides as active pharmaceutical ingredients of industrial and academic interest**

	OC47	XXXV	Jacopo Tricomi	**Drug-protein interactions: "from first to last" workflow in three different cases of studies**
	OC48	XXXV	Letizia Pontoriero	**NMR reveals specific tracts within the intrinsically disordered regions of the SARS-CoV-2 Nucleocapsid protein involved in RNA encountering**
	OC49	XXXVI	Saul Santini	**Development of analytical procedures for the determination of emerging organic compounds**
	OC50	XXXVII	Chiara Sarti	**Green Deal and Zero Pollution strategy: innovative solutions for emerging contaminants removal in wastewater and runoff water**
	OC51	XXXVII	Alice Cappitti	**Design and synthesis of high performance polymers**
	OC52	XXXVII	Marco Bonechi	**Modified surfaces of technological and industrial relevance**
12:40-14:00 – Lunch Break				
3rd Session ***Chair:*** *Francesca Torrini*; *Davide Ranieri*				
14:00-16:30	OC53	XXXIV	Andrea Casini	**Jin Shofu starch-based nano-sized hydrogel dispersions for the consolidation of modern and contemporary paintings**
	OC54	XXXIV (online)	Anna Ranzenigo	**Synthesis of hydroxylated indolizidines and diamino suberic acid derivatives: use of tartaric acid and other approaches**
	OC55	XXXV	Maria Giulia Davighi	**Stimuli-responsive pharmacological chaperones for Gaucher Disease**
	OC56	XXXV (online)	Jacopo Cardellini	**Membrane Phase Drives the Assembly of Gold Nanoparticles on Biomimetic Lipid Bilayers**
	OC57	XXXVI	Francesca Porpora	**Development of a multi-analytical protocol to study the “vinegar syndrome” on films made of cellulose triacetate**
	OC58	XXXVII	Serena Cabigliera	**Environmental impact of microfibers (MFs) pollution and the developing of efficient and sustainable mitigation strategies**
	OC59	XXXVII	Alessandro Veneri	**Development of flexible molecular and inorganic hybrid solar cells for the design of self-powered greenhouses**
	OC60	XXXVII	Francesca Buco	**Gold nanoparticles coated with D-(+)-galactose as potential therapeutics for lysosomal storage disorders**

	OC61	XXXVII (online)	Yschtar Tecla Simonini Steiner	**Recognition of emerging pollutants (Eps) with artificial fluorescence chemical sensors: a supramolecular approach**
	OC62	XXXIV	Irene Vettori	**Monomeric 2-hydroxyethyl methacrylate (HEMA) and acrylic acid (AA): structural influences on solute-solvent interactions and spectroscopic properties**
	OC63	XXXVII (online)	Fernando Soto-Bustamante	**Optimizing the structure of sustainable hydrogels for nano/microfiltration, selective absorption, and anti-biofouling behavior**
16:30-16:50	***Conclusions:*** *Prof.ssa Anna Maria Papini; Martina Vizza*			

Index

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OC01

"Green" Poly(vinyl alcohol)/Starch based cryogels for the cleaning of works of art: Application, characterization, and investigation of the Amylose/Amylopectin structural role

Vanessa Rosciardi [a,b], David Chelazzi [a,b] and Piero Baglioni [a,b]

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Cultural Heritage assets are crucial to mankind, as they are drivers of welfare and economic improvement. Unfortunately, degradation processes inevitably threaten works of art. Material science has been providing effective solutions to preserve works of art in the last decades. As regards the cleaning of painted artworks, excellent results have been obtained using gels based on synthetic polymers. However, there is still large room for the formulation of polymer networks that retain optimal cleaning ability but have higher eco-compatibility. Hence, we have developed different biocomposite hydrogels based on poly(vinyl alcohol) (PVA) and rice starch (RS) obtained via freeze-thawing, with water as the only used solvent. The PVA/RS hydrogels have been characterized from a morphological, rheological, and structural point of view and have been tested as cleaning tools on painted mock-ups, showing performances comparable to their state-of-the-art synthetic counterparts: the introduction of a biopolymer in the synthetic path improved the sustainability of the formulations while maintaining optimal mechanical behavior. Furthermore, the reduction of usage of synthetic polymers is a transversal need, and PVA/starch-based systems meet the requirements that different applications demand. Nevertheless, starch as a raw product comes with a variety of compositions regarding its polymeric portion (i.e., the amylose to amylopectin ratio), which is cardinal in determining the properties of the biocomposite systems. The investigation of the interactions between PVA, amylose, and amylopectin is therefore necessary. Said interactions have been investigated by means of direct laser imaging of fluorescently labeled systems, thermal analysis, and Small-Angle X-ray Scattering, coupling the results with rheological measurements and gel fraction trends to provide a theoretical framework, aim of which is to support future developments of highly performing eco - sustainable materials.

PhD in Chemical Sciences at UniFi - PiCSU 2022
OC02

Comparison of chemometric workflows strategies for potential exposure markers discovery and false positive reduction in untargeted metabolomics: application to the serum analysis by LC-HRMS after intake of *Vaccinium* fruits supplements

Lapo Renai [a], Marynka Ulaszewska [b] and Massimo Del Bubba[a]

[a] *Department of Chemistry, University of Florence, Via della Lastruccia 3, 50019, Sesto Fiorentino, Italy.*
[b] *IRCCS San Raffaele Scientific Institute, Center for Omics Sciences, Proteomics and Metabolomics Facility - ProMeFa, Milan, Italy.*
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Untargeted liquid chromatographic-high resolution mass spectrometric (LC-HRMS) metabolomics for potential exposure markers (PEMs) discovery in nutrikinetic studies generates complex outputs. The correct selection of statistically significant PEMs is a crucial analytical step for understanding nutrition-health interactions [1]. Hence, as a part of the PhD project focused on LC-MS based nutrimetabolomics and chemometrics, in this paper different chemometric selection workflows for PEMs discovery, using multivariate or univariate parametric or non-parametric data analyses were tested. The PEMs selection protocols were applied to a small sample size untargeted LC-HRMS study of a longitudinal set of serum samples from 20 volunteers after a single intake of (poly)phenolic-rich *Vaccinium myrtillus* and *Vaccinium corymbosum* supplements [2]. The non-parametric Games-Howell test identified a restricted group of significant features, thus minimizing the risk of false positive results. Among the 47 PEMs exhibiting a statistically significant postprandial kinetics, 12 were successfully annotated as purine pathway metabolites, benzoic and benzodiol metabolites, indole alkaloids, and organic and fatty acids, and 5 were associated to Vaccinium berry consumption for the first time. The AUC analysis of the longitudinal dataset highlighted 13 statistically significant PEMs discriminating the two interventions, including 4 inter-intervention relevant metabolites (i.e. abscisic acid, catechol sulphate, methyl-catechol sulphate, and α-hydroxy-hippuric acid). Principal component analysis and samples classification through linear discriminant analysis performed on PEMs Tmax intensity confirmed the discriminating role of these PEMs.

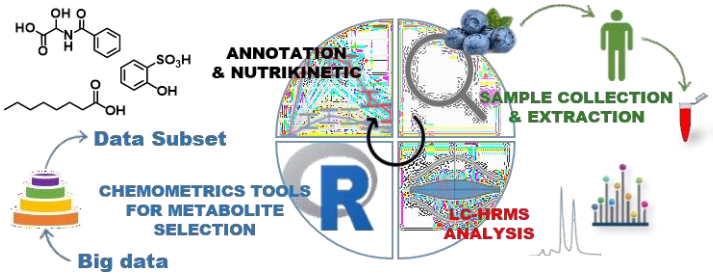

Figure 1: Graphical workflow of the experimental steps followed in this study.

[1] M. Ulaszewska, C. H. Weinert, *Genes & Nutrition.* **2019**, 63, 1800384.
[2] C. Ancillotti, L. Ciofi, *Food Chem.* **2016**, 204, 176-184.

OC03

Glycomimetic azasugars for selective inhibition of Carbonic Anhydrases

Debora Pratesi,[a] Camilla Matassini,[a] Francesca Cardona,[a] Andrea Angeli,[b] Claudiu T. Supuran,[b] and Andrea Goti[a]

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[b] *Dipartimento Neurofarba, Sezione di Scienze Farmaceutiche e Nutraceutiche, Università degli Studi di Firenze, Via U. Schiff 6, Sesto Fiorentino (FI) 50019, Italy.*
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Carbonic Anhydrases (CAs; EC 4.2.1.1) are zinc metalloenzymes which play a fundamental role both in physiological and pathological processes in humans (h). Therefore, modulation of the activity of hCAs represents an important target for drug development and requires the discovery of selective inhibitors towards one specific isozymes. By following the "sugar approach"[1] and considering our recent disclosure of two selective hCAs inhibitors based on glycomimetic-sulfonamide conjugates[2], new compounds have been synthesized[3] by conjugating several benzenesulfonamides to a triazole-armed azasugar with different linkers (such as thioureido, ureido, amido and amine groups). These compounds were found to be potent selective inhibitors; some of them showed interesting data towards the therapeutically relevant hCAs II and VII isoforms.

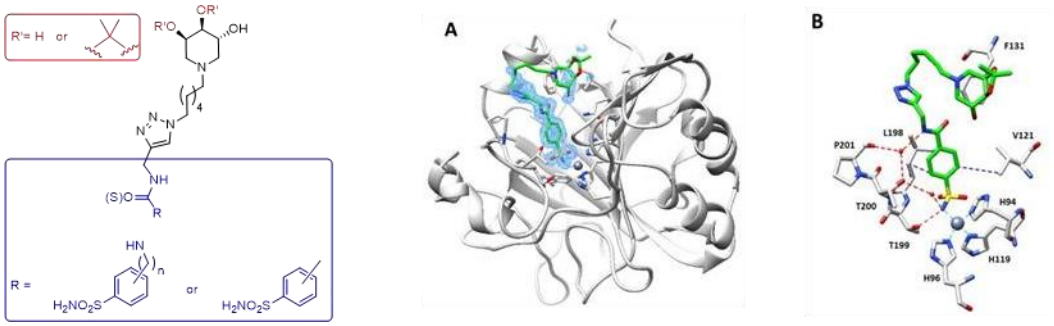

Figure 1: New azasugar-sulfonamide compounds and X-ray studies (A and B).

Based on the X-ray studies of the inhibitor-enzyme complexes, new analogues lacking the triazole linker were synthesized in order to evaluate the influence of the heterocycle moiety on the enzymatic inhibition. Furthermore, a reference compound with the commercial piperidine skeleton instead of the azasugar moiety was synthesized and tested to verify "the azasugar approach".

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OC04

Electrodeposition of poly(3,4-ethylenedioxythiophene), CdSe and MoS_2 on Silicon electrodes to obtain interesting technological and catalytic 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 operating at room temperature and pressure. Secondly, electrochemical processes can be scaled to industrial level still obtaining a fine control on the growth conditions, with considerable financial gains [1]. 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/Si electronic solid-state device, which showed high conductivity and an ohmic behavior over a wide range of frequencies. This further expands the range of possible uses of PEDOT, especially regarding systems prone to be used as electrodes in stacked devices [2,3]. Then, the investigation of the electrodeposition of II-IV compounds was performed on Silicon, which is the pillar of modern technology, in order to obtain surfaces with interesting photo-emissive and catalytic features [1,4]. In particular, both CdSe nanoparticles and thin films were electrodeposited on n-Si (100) and characterized by means of microscopic and spectroscopic techniques. Then, annealing techniques were optimized to obtain photo-emissive CdSe/n-Si (100) surfaces [1]. In addition to it, the possibility of electrodepositing MoS_2 on n-Si (100) was confirmed by means of X-Rays Photoelectron Spectroscopy (XPS). The morphological characteristics of MoS_2 deposits were analyzed by microscopic techniques, which allowed detecting the presence of MoS_2 nanoparticles on n-Si (100). The catalytic features of the electrodeposited MoS_2 are under current evaluation.

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OC05

Poly(ethylene glycol)-based hydrogels as transparent porous network for diffusivity studies

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Although hydrogels are widely studied for their controlled-release properties, their use as model porous media to investigate diffusion in three-dimensional confinement has been limited. The strong opacity usually associated to micron-scale porous networks does not allows the direct visualization of diffusing objects. A better understanding of how micrometric objects move within confined systems would enable huge improvements in the understanding and control of migration processes in disordered, porous media, such as bioremediation, biofertilization, and microbial therapy.

Here we present a facile synthesis of transparent porous poly(ethylene glycol)-based (PEG) hydrogels that allows the study of mobility and migration properties of microscopic objects in confined systems. Through polymerization of acrylated-polymeric unit, we synthetized biocompatible hydrogels with high transparency.[1] By freeze-drying we induced the desired porosity without significant effects on the transparency. Thanks to its low opacity, confocal microscopy analysis allowed a deep visualization of the hydrogels' structure, and the structural characterization of the porous media by morphological image analysis revealing interconnected networks with tunable pore size at the micron-scale.

The diffusion properties of thermo-responsive pNIPAM microgels (1.8μm in diameter) through the PEG gels were studied, providing a reference for the investigation of more complex living systems (i.e. bacteria). Positions, trajectories and mean squared displacements of the pNIPAM particles were determined by particle tracking system. Consistent with the structural features, a transition from diffusive to subdiffusive motion was observed when the pore size approaches the particles size.

The presented system can be easily modified in terms of the final architecture and interface reactivity allowing to study the effect of the microscopic, internal structure of the gels on bacterial diffusion.

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OC06

Synthesis and elaboration of novel heterocyclic scaffolds through C-H bond activation for application as peptidomimetics

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Exploiting the use of the Diversity-Oriented Synthesis (DOS) approach and Late-Stage Functionalization (LSF) techniques, we aim to synthesize new small molecules inhibitors. We focus on natural product-inspired molecules, with regard to compounds derived from amino acids, for the discovery of novel peptidomimetics. We dealt with the synthesis and functionalization of 2-oxo pyrrolidine and piperidine scaffolds, using the Castagnoli-Cushman Reaction and a Pd-catalyzed β-C(sp^3)-H bond activation reaction, thanks to the use of the 8-aminoquinoline (8-AQ) Directing Group (DG). We obtained variously arylated constrained heterocyclic compounds, which will be further processed to generate non-natural amino acids for the application in peptidomimetic chemistry. We tried to exploit the thioamide Functional Group (FG) as a DG in C(sp^3)-H bond activation reactions, to avoid the drawbacks of synthetic steps for DG insertion and removal, as well as to apply an LSF approach on compounds related to previously synthesized inhibitors of BACE-1, containing the thioamide FG [1]. Taking inspiration by reported works of Yu and collaborators, on exocyclic thioamides employed as DG [2], we tried to apply that chemistry on endocyclic thioamides with a 2-thioxo piperidine scaffold. Anyhow, no product was isolated and further studies are ongoing, to rationalize the critical aspects encountered in the synthetic procedure. We are now synthesizing the necessary building blocks to produce chiral heterocyclic amino acids, which we aim to obtain by using the established procedure for β-C(sp^3)-H bond activation reaction using 8-AQ as DG. These amino acids will be then used for the synthesis of peptidomimetics and foldamers.

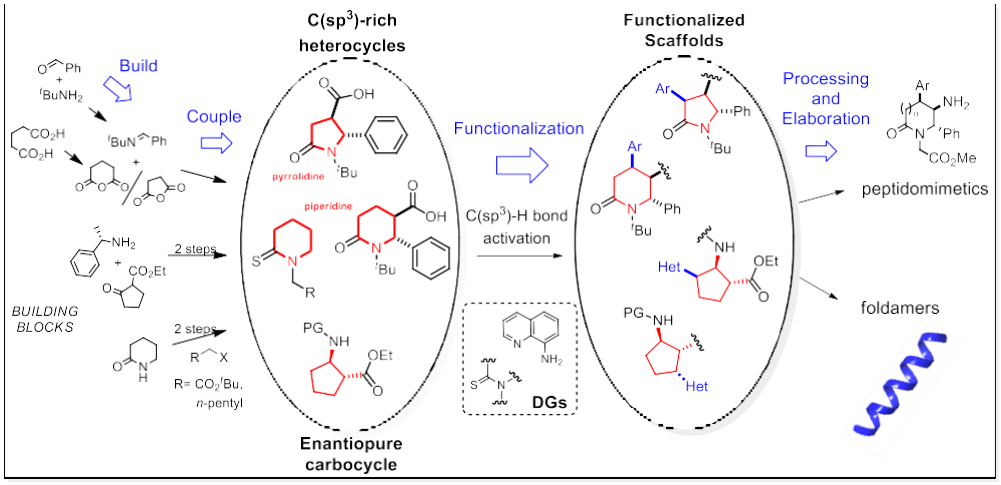

Figure 1: Synthesis and elaboration of heterocyclic scaffolds

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OC07

Bicyclic Peptides as Bioreceptors towards the electrochemical detection of the Human Urokinase-Type Plasminogen Activator

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Amidst human diseases, cancer represents one of the main causes of mortality and is often treated with late-stage invasive diagnostic solutions. To this end, we focused on the human Urokinase-type Plasminogen Activator (h-uPA), a serine protease capable of converting plasminogen into the proteolytic enzyme plasmin, therefore promoting cancer diffusion [1]. Recent clinical research identified a correlation between metastasis growth in cancer patients and high levels of h-uPA in biological fluids. Bicyclic peptides, which show several advantages over linear and cyclic peptides, were found to be a burgeoning class of biorecognition elements in the last decade [2]. In this proof-of-concept study, the performances of two similar bicyclic peptides with a large interaction surface for h-uPA, were assessed in a sandwich-type affinity assay interfaced to an electrochemical readout. Superparamagnetic microbeads, functionalised with such chemically constrained bicyclic peptides, managed to capture h-uPA in spiked buffered or diluted-serum samples, hence simplifying isolation procedures of the analyte. An incubation step with a primary antibody that selectively binds to h-uPA followed. A secondary Anti-Rabbit antibody conjugated with alkaline phosphatase provided signal amplification. By introducing the substrate of this latter enzyme, the oxidation current of the electroactive product of the enzymatic reaction was correlated with the concentration of h-uPA in the sample. Following sundry optimisation steps of the assay conditions (i.e., concerning antibodies concentrations and specificity, and incubation times), calibration plots were obtained for both bicyclic peptides. These preliminary results highlight that, despite showing similar peptide sequences and kinetics in the recognition event, major discrepancies in the overall performance of the biosensing platform can be observed by using slightly different bioreceptors.

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OC08

The link between past, and future: investigating climatic and environmental variability through Ice Records from East Antarctica

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Despite the huge efforts of internationals programs (e.g. ITASE, EAIIST), a large part of the Antarctic sheet is still unexplored and further studies are needed to understand the role of the continent in the Earth's climate. Furthermore, due to the lack of anthropogenic pollution and its remoteness, Antarctica provides a unique opportunity to investigate the past climate via environmental proxies fixed in the snow and therefore in ice core retrieved from the ice sheet. Main focus is given here to the East Antarctic plateau, where two deep ice cores (GV7(B) and DC3D) and multiple shallow snow pits were retrieved with the aim of understanding the chemical/environmental variability in the last millennium. The dating of the records was accomplished using well known volcanoes whose signature are superimposed in the sulphate stratigraphy of the records [1] and the seasonal pattern of the d18O ratio and the marine sulphate [2,3], evaluation on the snow accumulation on the sites were made. Interest was then shifted to investigate the correlation between chemical signatures in the core and environmental parameters and satellite data of the sea ice extent. In particular, the correlation between Nitrate and TSI [4], the one between MSA and SIE and the ENSO phenomena [5] and the atmospheric circulation over Antarctica were investigated. Both yearly and multi-year period correlation were considered here, with the aim of finding a potential candidate for extending SIE data beyond the satellite era.

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OC09

Adsorption of Bio-Molecules on Metal Surfaces: a Computational Study

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The adsorption processes of biological molecules on nanostructured surfaces of noble metals are of particular importance for possible applications regarding medical, biological, and technological sectors. For the correct development of systems based on molecules interacting with surfaces a detailed knowledge of the interactions between adsorbate and metal surface is required. This problem is particularly complex in the case of biomolecules because different interacting sites can exist in the molecular structure. Adenine, a fundamental constituent of nucleic acids, represents a particularly interesting system to assess the correct application of computational methods and experimental measurements to state the interactions with metal surfaces. The chemical adsorption of adenine on silver and gold surfaces has been investigated by means of surface-enhanced Raman scattering (SERS). The interpretation of the SERS spectra has been carried out through density functional theory (DFT) approach, which is able to characterize the interactions with the metal substrate by considering complexes constituted by molecules bound to the explicit surface. These interactions are basic for the chemical mechanism of the SERS effect and, consequently, for the SERS profile concerning band frequencies and relative intensities. The Raman frequencies and intensities are obtained with an ab initio molecular dynamics (AIMD) approach, where the computation of Raman spectra occurs via time correlation functions of the polarizability tensor, calculated by adopting the generalized variational density functional perturbation theory. [1,2] The initial guess for the AIMD simulation into the NVE ensamble are obtained through the characterization of the potential energy surface of the adsorbate. The configurations of selected minima will be isolated and DFT calculations will be performed to obtain the optimized molecular structures. The complexity of the potential energy surface, given by the several possible orientation and distance of the adenine respect to the surface, requires accelerated sampling techniques such as the metadynamics approach to quickly recognise the different relative minima.[3] However, the computational cost given by the necessity to explore several minima and the need to perform AIMD for each selected configuration make requires HPC resources. This computational procedure, once validated, would provide a useful tool to simulate the absorption of the large family of bio-molecules and this will also allow to correlate the orientation of the molecule to the chemical and physical properties of the system.

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PhD in Chemical Sciences at UniFi - PiCSU 2022
OC10

Development of aluminum alloys plating processes via sustainable galvanic processes

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The depletion of metals and the rising willingness of the industry sector to finding alternatives with respect to technologies that either still make use of old-fashioned methods or have detrimental impact on the eco-system push the major R&D players towards the continuous research of technologies that allow for a more sustainable approach.
Among other sectors, the fashion industry in particular has to face a tough challenge in substituting metals that have been so far extensively used.
Aluminum, being largely available as well as countless times recyclable, address the sustainability criterion and thereby shed a light on its making use across a wide variety of industrial applications [1]. Concerning the fashion industry, when it comes to plating processes, aluminum is known to be a difficult metal to be galvanized, mostly due to other metal impurities within the alloy [2].
The present work aimed to characterizing a Al6082 series (largely available on the market) sample surface and to getting an understanding of how the pretreatment affects the quality of the deposits. At first, thin rectangular shaped samples were cut out of an Al plate: AFM technique was used to characterizing the surface roughness prior to the plating process. SEM technique was used both to figure out what kind of elements might have been present within the alloy and in what quantity. First experiments focused on validating a pretreatment for the activation of the aluminum surface towards the electroplating to assess whether the adhesion criterion was fulfilled or not. It turned out that the surface roughness plays a key role in the plating process.

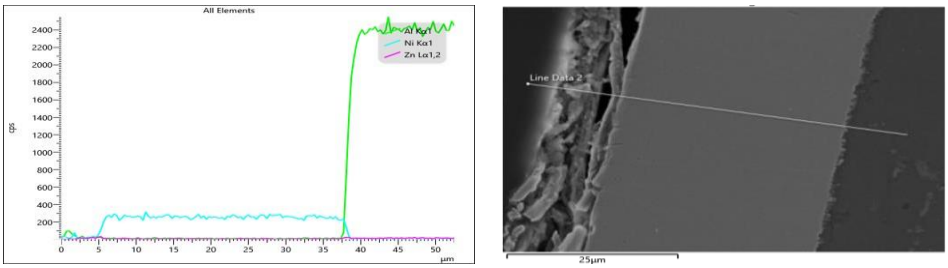

Figure 1: SEM line-scan function – Low roughness nikel-plated aluminum.

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OC11

Development of eco-friendly hydrogels with structures optimized for nano / micro filtration, selective absorption and prevention of biofouling

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The depletion of water resources obliges to recycle wastewater. Water purification finds in hydrogels an interesting material for apply in the water purification process, such as membrane bioreactor (MBR). But the membrane bioreactors are hit by the biofouling: process of accumulation and development on an interface of a complex biological community belonging to the animal or plant kingdom. Biofouling stops the membrane operation, so there are increases in the cost due to more/frequently membrane cleaning and replacement [1].
In the water the main contaminants are: heavy metals, dyes, microplastics and bacteria. The hydrogels, thanks to various compositions and structures, are able to selectively absorb organic and inorganic contaminants (Fig. 1) [2].
Chitosan or other natural polysaccharides-based hydrogels will be synthesized and we are going to study which functional groups and which superficial morphology optimize the nano / micro filtration and the selective absorption of the contaminants and the prevention of biofouling [3].
In particular, Fluorescence correlation spectroscopy and particle-tracking are two innovative techniques will be use to define the geometry and dimensions of porosity, mechanical properties of the gel and gel-particle interactions. These techniques are therefore necessary to optimize the transport properties in processes of filtration, absorption and formation of biological deposits [4][5].

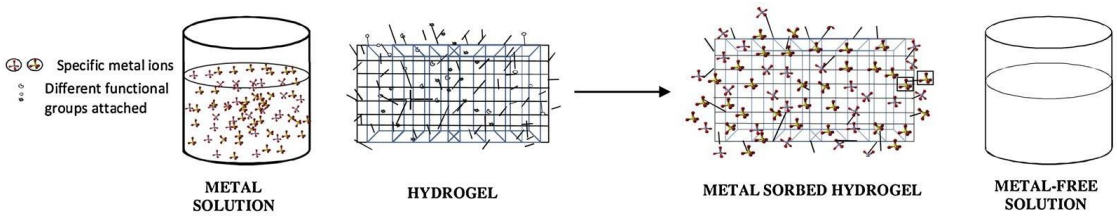

Figure 1: Absorption of metals by a hydrogel for water purification [2].

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OC12

Intelligent and sustainable synthesis and processing of innovative permanent magnets

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The project proposed aims at developing a new class of materials to produce Permanent Magnets which could substitute those based on Rare Earths [1], alongside their recycling rate upgrading to encourage a sustainable and circular economy. To this aim, we propose to realize exchange coupled nanocomposites comprising hard (hexagonal ferrite) and soft (Fe or spinel ferrite) moieties [2]. The two components will be synthesized by colloidal chemistry technique and solid-state reactions, which are economic processes, with low environmental impact and scalable to the industrial scale [3]. The use of recycled hard magnetic powders from recycled ferrite and NdFeB permanent magnets will be also investigated [4]. Finally, the best nanocomposites will be tested as elements for the realization of bonded or sintered permanent magnets.

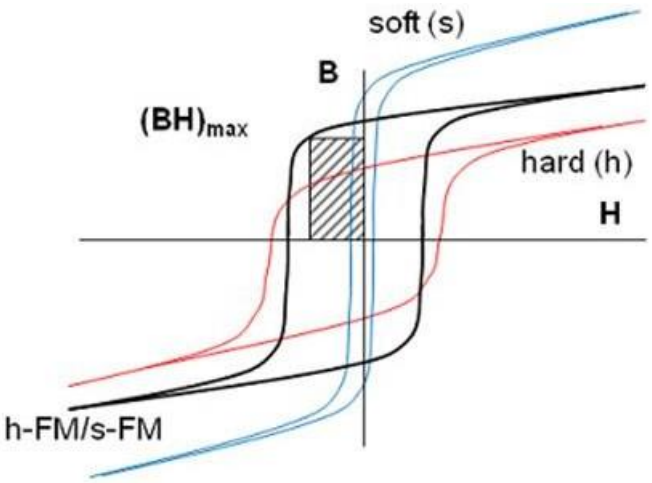

Figure 1: Exemplification of enhanced *maximum energy product* of permanent magnets through exchange-coupling.

[1] Permanent Magnets Market Size, Share & Trends Analysis Report By Material (Ferrite, NdFeB, Alnico, SmCo), By Application (Medical, Consumer Goods & Electronics), By Region, And Segment Forecasts, 2020 - 2027
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OC13

Study of new materials with low environmental impact and their use in the conservation of Cultural Heritage

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The purpose of this research project is the identification of new materials that can be used for the protection of manufacts of historical and artistic interest in place of long-chain perfluoroalkyl compounds (PFAS) [1], highly efficient products but with a high environmental impact, and, for this, currently subject to restrictions on use. The project will focus on the synthesis of oligomeric products with low fluorine content, soluble in organic solvents, non-film-forming, capable of giving, with small quantities of product, highly hydrophobic, transparent and photostable coatings. On the basis of the studies on perfluorinated compounds carried out in the last decade [2-4], recently, fluorinated derivatives have been synthesized at the Department of Chemistry of the University of Florence by reacting oligoamides with terminal -NH_2 groups with a fluorinated short-chain epoxide (C6) and tested as protectives on stone and wood with very promising results. Starting from the fluorinated oligoamides already studied, new formulations will be designed, favoring the use of substances of natural origin and/or from industrial waste, and accurately characterized in terms of chemical structure, interactions with the substrate and protective abilities, using ATR-FTIR spectroscopy, ^{1}H, ^{13}C, ^{19}F NMR, colorimetry and ^{1}H MRI. Particular attention will be given to the study of their behavior after aging in terms of mobility and bioaccumulation. An analysis of risk and effective applicability in the real world will be carried out on the materials of greatest interest, and a possible industrial scale up will be designed.

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OC14

From a bioinformatic approach to synthetic conformational peptide epitopes to disclose molecular mechanism of aberrant immune response in auto-immune diseases.

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Autoantibodies are relevant in many autoimmune diseases and may be the direct cause of lesions. Therefore, serum antibodies circulation in blood, can be used as biomarker for an early diagnosis. [1].
To this end, a 'chemical reverse approach' based on the use of patient' sera to screen focused libraries of synthetic modified peptides can lead to the identification of specific probes able to characterize specific and high affinity autoantibodies.
A structure-based designed type I' β turn glucopeptide structure, was the first antigenic probe in which an aberrant glucosylated asparagine (N-Glc) recognized the presence of specific IgM autoAbs in the sera of a Multiple Sclerosis (MS) patient population [2]. The N-glucosylation post-translational modification is virtually absent in eukaryotes, but is a modification found in bacterial Adhesin of non-typeable H. Influenzae on at least twelve beta-turns. Adhesin represents the first example of an N-glucosylated native antigen that can be considered a relevant candidate for triggering pathogenic antibodies in MS cross reacting with the original N- glucosylated structure [3]. Moreover, tentacle-like polymers decorated with multivalent presentation of the di-glucosylated Adhesin peptide antigen HMW1(Glc)(1346-1354) was demonstrated the ability to capture circulating antibodies in MS patient sera [4].
With these considerations, we plan to adopt computational chemistry approaches, in particular molecular dynamics simulations to obtain specific structural aspect of probes optimally exposing the minimal epitope. This information and results will be compared with available experimental data.
Moreover, these computational chemistry results could provide insights useful to search structural homologies, through bioinformatic approaches, with different bacterial proteins (putatively glucosylated) with the aim to identify, design and synthesize new peptide sequences. This will give a focus on molecular mechanisms of autoimmune diseases.

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OC15

Electrodeposition and surfaces analysis in galvanic for industry 4.0

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Galvanic electrodeposition is, to date, the most used technique to create metal coatings for different applications, from technological to decorative ones, because of strengths like exact layer thickness control, high quality morphology and well-controlled composition and uniformity [1]. However, the galvanic field is now facing increasingly complex challenges to respond to the growing interest towards environmental sustainability and new market demands. This PhD project aims to seek innovative solutions in the field of electroplating in the “fashion jewelry & fashion accessory” sector. Particular attention will be paid to the reduction of the load of precious metals and to the development of innovative electrodeposition sequences, by focusing on nickel-free sequences and on cheap and recyclable substrates, such as aluminum. These aspects are particularly important in order to reduce the total costs of galvanic processes and to increase their sustainability, at an environmental level, too. The project also aims to limit the use of cyanide baths, investigating the industrial applicability of laboratory-tested alternative baths [2]. In order to maintain the high-quality standards required by the market, especially by luxury brands, suitable surface analysis techniques will be used for the characterization of metal alloys and corrosion tests will be conducted on galvanized pieces, using both traditional and innovative electrochemical techniques (such as EIS) [3]. Finally, novel control systems will be designed for effective and eco-friendly process water management, with a view to industry 4.0. In this way, it will be possible to establish an active collaboration between the University of Florence and Valmet Plating s.r.l., allowing scientific research to present application and extensibility in the industrial field.

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OC16

Development of macromolecular and cross-linked materials based on proteins/peptides from vegetable sources

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Recently, proteins have attracted much attention in the search for new eco-sustainable polymeric materials, particularly for packaging. Despite their favourable properties that would make them suitable for these applications, proteins present some limitations, such as their very slow biodegradability which only happens under composting conditions, scarce mechanical properties, and excessive hydrophilicity. This project intends to address these issues evaluating the possible development of biocompatible and renewable polymeric materials based on vegetal proteins, by integrating the experience Spin-PET acquired so far in the field with the consolidated competences of the PeptLab at the University of Florence on peptide and protein molecules.
The activity will concern the study and preparation of molecules of natural origin, primarily peptides, that will be used as additives for industrially produced proteins, in order to develop prototypes of protein-rich materials showing desirable structural and functional properties. The project will enable the establishment of sustainable processes and the production of recyclable compounds that will contribute to the green transition.

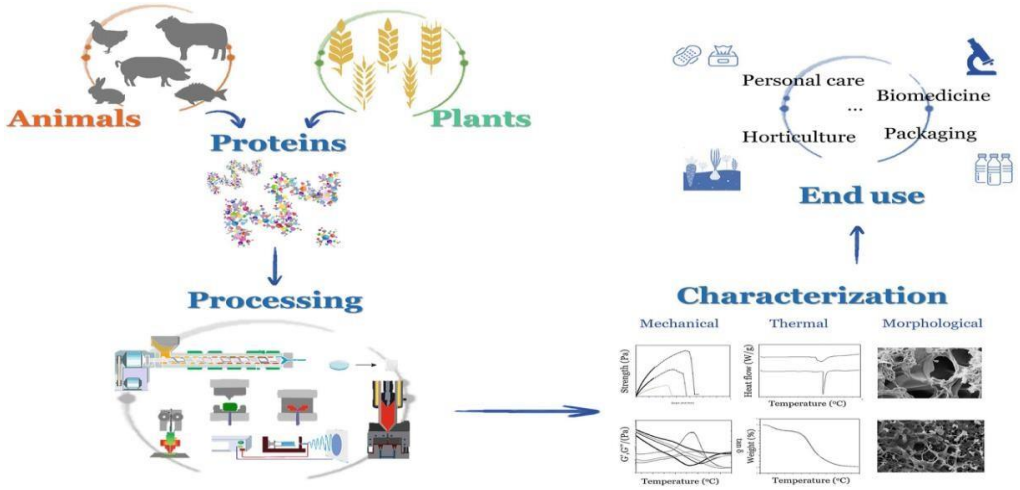

Figure 1: *Overview for the manufacture, characterization and lifetime of protein-based bioplastics. Figure from [4].*

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OC17

New formulation approaches for the development of cleanser with high efficacy and gentle on the skin eco-friendly proven

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The cosmetic industry is an important economic sector worldwide and therefore a lot impressively involved in the field of eco-sustainability in terms of raw materials, packaging, and also production by limiting the use of water and energy resources, all these aspects can have a significant impact on the environment and consequently on human health. Principally, consumers continue to demand environmentally sustainable products from non-toxic and environmentally friendly raw materials, including for the sea, a primary biological environment. This study aims to the development of cosmetics containing eco-friendly conditioning agent, surfactant, other ingredients (chelators, antioxidants, preservatives, etc.) and also the packaging. In this view, a new generation of surfactants (glycolipid or sulfate-free surfactant) is desirable having also a low or deficient ability to irritate the skin or hair [1]. Accordingly, the developed formulation is based on glycolipids (RHEANCE®One), which are biosurfactants are synthesized by yeasts, bacteria and other microorganisms [2]. In addiction, Sodium Cocoyl Isethionate and Sodium Lauroyl Methyl Isethionate we are also selected for the formulation of detergens in solid form, which contain a very low water content in order to reduce waste during the production cycle and facilitate transport with reduction of energy waste. These ingredients have excellent washing and foaming properties and are highly biodegradable [3]. The formulation were studied when dissolved in pure aqueous solution and in seawater solution. The surface tension, size and shape of the micelles and other relevant parameters were investigated. Finally, aminopolycarboxylates (Dissolvine®), were selected as chelator, alternative to EDTA which is the most used chelator for cosmetics but is much more toxic to environmet [4].

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PhD in Chemical Sciences at UniFi - PiCSU 2022
OC18

Probing the mechanical response of lipid membranes at the nanoscale

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Lipid membranes represent one of the most important building blocks of life; mainly consisting of a ~5 nm thick lipid bilayer, they can be found in viruses, bacteria, cells and cell-derived vesicles. Although most membranes are visualized as planar sheets or closely isolated compartments, studies performed on starving or virally infected cells found that membranes may fold into nonlamellar architectures presenting 3D periodicity. When involved in biological processes, lipid membranes undergo stresses and deformations of different type and extent, hence making the study of their mechanical properties a fundamental step towards a thorough understanding of numerous biological interactions. We herein report our latest findings on the nanomechanics of lipid membranes and nanosized membrane delimited compartments. With respect to lamellar lipid membranes, our Atomic Force Microscopy (AFM)-based studies focused on the stiffness of lipid nanovesicles [1], i.e. their mechanical response to an applied force. Results lead to the development of high-throughput mechanical characterizations which were subsequently applied to Extracellular vesicles [2,3], biogenic lipid nanoparticles actively involved in intercellular communications. We then report on an equally intriguing yet unaddressed topic, that is the mechanical response of bicontinuous cubic phase membranes, nonlamellar lipid architectures that feature a huge potential for drug delivery applications. In this case, our AFM-Force Spectroscopy characterization represents the first nanomechanical investigation of these membranes and revealed a length scale independent mechanical response, strictly related to membrane topology [4]. Taken together, the herein reported results, provide new insights into the mechanical response of different lipid systems, hence enriching the current understanding of membrane nanomechanics.

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OC19

Smart amphiphilic block copolymers as stabilizers of lipid-based drug delivery systems

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In the last years, the design of drug delivery systems (DDS) for the solubilisation of the therapeutic and the successive release in a controlled way to the target site of the disease, is one of the main goals in pharmaceutical applications. Lipid assemblies, although addressed in many studies over the years, are still considered the most promising candidates as DDS for their biocompatibility and similarity with plasma membranes. Particularly, complex lipid assemblies, denominated cubosomes, are considered one of the most promising drug delivery vectors given the fascinating characteristics of these systems, like the high internal organization and large specific surface area. Cubosomes are, so far, the emerging platform for the in-vivo delivery of molecules of pharmaceutical and imaging interest, like drugs, bioactive and contrast agents for disease treatment and theragnostic [1], [2]. In this view, a novel class of stimuli-responsive drug delivery systems using body temperature as a non-invasive stimulus has been designed. The new class of drug delivery systems, consisting of the lipid glycerol-monooleate (GMO), has been engineered by replacing the conventional stabilizer Pluronic F127 (PEOx-PPOy-PEOx), with a recently synthesized thermo-responsive polymer poly(N,N-dimethylacrylamide)-b-poly(N-isopropylacrylamide) (PDMA-b-PNIPAM). Indeed, this copolymer changes its polarity from hydrophilic to hydrophobic in water, when the temperature increases over the lower critical solution temperature (LCST) [3] of the thermo-responsive block, the PNIPAM, at a temperature close to physiological conditions. Cubic dispersions stabilized by two block copolymers DMA-b-NIPAM, the polymer B10K (M_w = 10.000 g/mol) and B20K (M_w = 20.000 g/mol), were realized, physicochemical investigated and compared to the standard dispersions stabilized by the polymer Pluronic F-127.

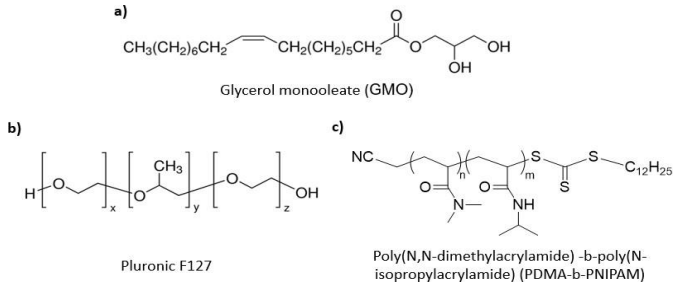

Figure 1: Chemical structures of the lipid GMO (a) and of the stabilizers Pluronic F127 (b) and PDMA-b-PNIPAM (c).

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OC20

An enzyme-linked immunosorbent assay (BELISA) for the analysis of a small neuropeptide by using molecularly imprinted polymer-coated microplates

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Molecularly imprinted polymers (MIPs), named "plastic antibodies", are synthetic affinity reagents with tailor-made binding sites mimicking the ability of natural receptors to bind a target molecule. The latest decade has witnessed a great advance in MIPs and nowadays soft and biocompatible polymers, e.g., polycatecholamines, represent a powerful tool to detect biomolecules such as proteins, peptides, glycoproteins, etc. Facile one-step synthesis, low cost, stability, and reusability are some features that make them very attractive. We recently started to investigate the potential application of polynorepinephrine (PNE) [1,2], in the biosensing field, which displays a markedly more hydrophilic and smoother surface compared to PDA. Here we report the development of an original biomimetic enzyme-linked immunoassay (BELISA) to target the small peptide hormone gonadorelin (MW = 1182.33 Da). This peptide has been recently listed among the substances banned in sports by the World Antidoping Agency (WADA) since its misuse by male athletes triggers testosterone increase. Hence, in response to this emerging issue in anti-doping controls, we proposed a BELISA assay which involves the growth of a polynorepinephrine (PNE)-based molecularly imprinted polymer (MIP) directly on microwells. PNE, a polydopamine (PDA) analogue, has recently displayed impressive performances when it was exploited for MIPs preparation, giving even better results than PDA. Gonadorelin quantification was accomplished via a colorimetric indirect competitive bioassay involving the competition between biotinylated gonadorelin linked to the signal reporter and the unlabeled analyte. These compete for the same MIP binding sites resulting in an inverse correlation between gonadorelin concentration and the output color signal (λ = 450 nm). A detection limit of 277 pmol L^{-1} was achieved with very good reproducibility in standard solutions ($_{av}$CV% = 4.07%) and urine samples ($_{av}$CV% = 5.24%). The selectivity of the assay resulted adequate for biological specimens and non-specific control peptides. In addition, the analytical figures of merit were successfully validated by mass-spectrometry, the reference anti-doping benchtop platform for the analyte. This BELISA assay was aimed to open real perspectives for PNE-based MIPs as alternatives to antibodies, especially when the target analyte is a poorly or non-immunogenic small molecule, such as gonadorelin.

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OC21

A Novel Series of Hydrogen-Free M^{II} (Cu^{II}, Ni^{II}) Complexes of 1,3,2-Dithiazole-4-thione-5-thiolate Ligand as Potential Molecular Spin Qubits on Surface

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The coherence time (T_m) of a quantum bit (*i.e.* the *qubit*) is the time in which the information, stored in this fundamental unit of quantum computers. In general, the longer the T_m of a potential qubit, the better the qubit. Nowadays, it has been observed that magnetic molecules containing paramagnetic centers can be employed as qubits since they are characterized by long coherence times up to tenths of milliseconds when specific requirements are fulfilled [1]. In this work, we present a novel set of metal complexes of the 1,3,2-Dithiazole-4-thione-5-thiolate ($dttt^-$) ligand with Cu^{II} or Ni^{II} ions intending to contemporarily satisfy the nuclear spin economy principles proposed so far [2, 3] and the necessity of deposable systems for hardware's realization (Fig.1).

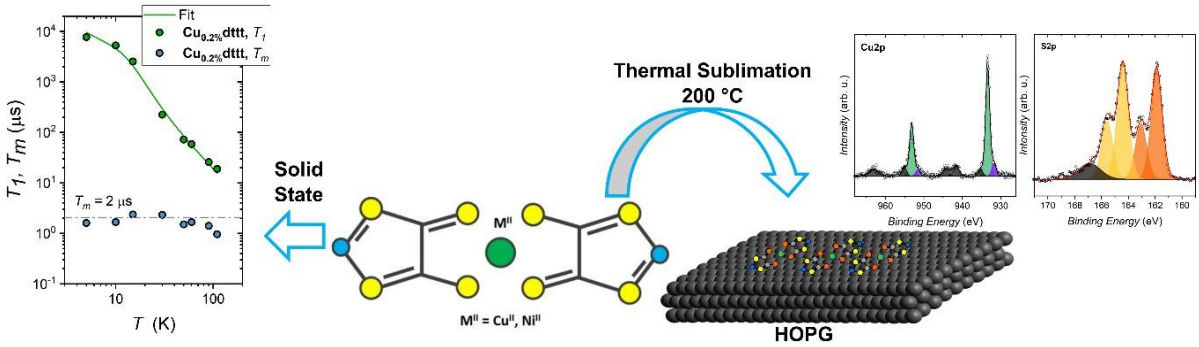

Figure 1. i) Plot of spin-lattice (T_1) and T_m values extracted from Q-band pulsed EPR measurements on a 0.2% doped sample of $[Cu(dttt)_2]$; ii) sketch of the molecular structure of $[M(dttt)_2]$ complexes. Color code: S = yellow, N = blue, C = grey, M^{II} = green; iii) representative sketch of molecules on HOPG substrate and experimental XPS spectra of Cu2p and S2p regions.

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Photocross-linked gelatin methacrylate porous microparticles for drug release

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Gelatin has been commonly used for the preparation of drug delivery system, like porous microparticles [1], due to its simple fabrication methods, excellent biocompatibility, and versatility. Compared to traditional chemical cross-linking methods, such as glutaraldehyde or glyceraldehyde, methacrylation is a great alternative method to reduce cytotoxicity of the final material [2], especially combined with a photo-polymerization process [3]. Here we reported the preparation of gelatin methacrylate porous microparticles (GMA) from oil-in-water-in-oil emulsion method cross-linked with photo-polymerization treatment. Different degrees of substitution (DS) ranging from 20% to 90% were achieved varying the amount of methacrylic anhydride used in the synthesis step. The effect of degrees of substitution on structural properties, including external size and surface porosity, was assessed by optical and electron microscopy techniques. Microparticle dimensions and pores were slightly influenced by degrees of substitution, whereas photo-treatment enhanced the stability in water up to several days without affecting the structural features. The swelling properties of crosslinked GMA were strictly dependent on the substitution degree: the swelling ratio sharply decreases as the substitution entity increases. Release properties in water at 37 °C of crosslinked GMA were evaluated by UV spectroscopy, choosing methylene blue as model drug. The methacrylation degree strongly affected the kinetic releases: as the amount of methacrylate units increases, the release passes from a combination of Fick and Case II diffusion to a Fick diffusion mechanism. This study demonstrates that methacrylate gelatin-based microparticles, obtained by double emulsion approach, can be cross-linked with photo-treatment, which results in less toxicity than traditional cross-linking. The direct control of the substitution degrees enables tailoring the release properties of the microparticles.

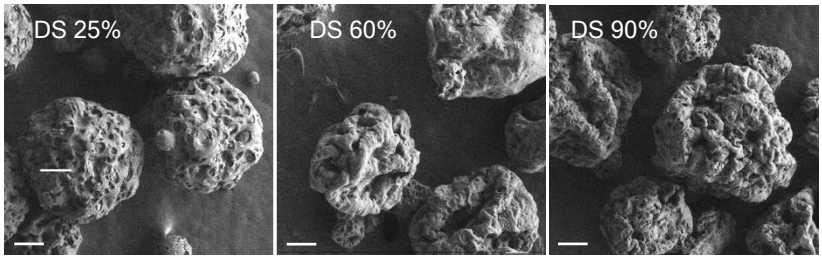

Figure 1: FE-SEM micrographs of the porous gelatin methacrylate microparticles. The scale bar is 100 µm.

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Electrochemical platforms for allergens detection

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Lysozyme is an enzyme present in multiple organisms where it plays various vital roles. One of the most important relies on its antibacterial activity, being also called the body's own antibiotic. Despite its proven utility, lysozyme can potentially trigger allergic reactions in sensitive individuals, even in trace amounts, thus the need of continue monitoring of lysozyme in products rich in lysozyme like wine or egg white is of high importance.

In this work, an electrochemical aptasensor was designed for the flow analysis of lysozyme. First, poly-L-lysine was electrodeposited at screen printed carbon electrodes (SPCE) in order to obtain a more structured platform with higher electroactive area. The best architecture was further chosen for sensor development. Next, gold nanostructures were electrodeposited from a mixture of HAuCl4 and PEG 10000 solution for enhanced electrocatalytic effect and to serve as immobilization platform for a thiolated aptamer.

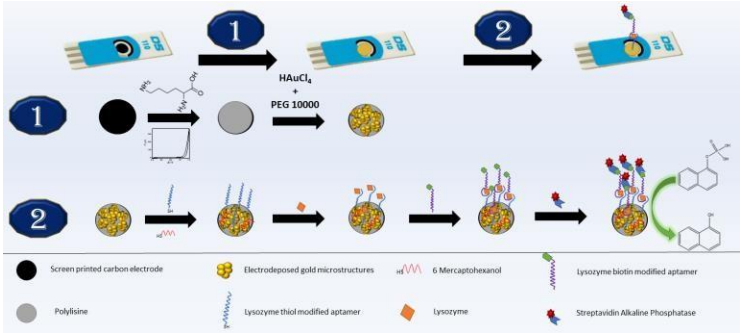

Figure 1: Graphical representation of the lysozyme specific aptasensor

For lysozyme detection, a thiolated aptamer was immobilized at its 3'-end at the gold nanostructures surface, followed by a blocking step of the remaining free sites with 6-mercaptohexanol. Next, the affinity reaction with lysozyme was realised at the electrode surface and a second aptamer, labelled with biotin, was put in contact with lysozyme to obtain a sandwich assay. Further, streptavidin-alkaline phosphatase (ALP) reacted with the biotin bound to the second aptamer. The enymatic product, 1-naphtol, was subsequently triggered using differential pulse voltammetry to realise the lysozyme quantification. The aptasensor was succesfully applied in real samples, using different types of wine with very good recoveries.

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OC24

Melanochrome-based colorimetric assay for quantitative detection of levodopa in Parkinson's drugs

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Levodopa is the mainstay in the pharmacological therapy applied to treat patients who suffer of Parkinson's diseases [1]. The diagnosis of Parkinson's disease is confirmed by a concrete response to levodopa treatment. A single oral dose of drug, containing levodopa, is able to improve drastically motor difficulties providing remarkable benefit in the patients. Levodopa is a pro-drug able to pass through the blood brain barrier and to be enzymatically converted in dopamine which acts directly on the degenerated dopaminergic neurons. Here, selective detection strategy for levodopa quantification in co-presence of carbidopa, was developed. The method took advantage of the spontaneous oxidation and color development of levodopa at basic pH here driven by alkaline earth cations and co-solvent in solution. We have shown for the first time the generation and stabilization of the purple melanochrome from levodopa, by using magnesium acetate and dimethyl sulfoxide, which was here exploited for the development of a quantitative colorimetric assay for the active principle ingredient in commercial drugs for the treatment of Parkinson's disease. The calibration curves of levodopa in the two tablet formulations, containing carbidopa as decarboxylase inhibitor, showed a common linear trend between 10 mg L^{-1} and 40 mg L^{-1} with levodopa alone or in combination with carbidopa in standard solutions, with very good reproducibility (CV_{av}%, 3.3% for both brand and generic drug) and very good sensitivity, with limit of quantification about 0.6 mg L^{-1} in any case. The colorimetric method here developed is very simple and effective, appearing as a rapid and low-cost alternative to other methodologies [2], involving large and expensive instrumentations, for drug estimation and quality control of pharmaceutical formulations.

Figure 1. Schematic representation of melanochrome-based colorimetric assay.

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OC25

Design, synthesis, conformational studies, and biological activity of clicked oxytocin analogues

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Oxytocin (OT) is an endogenous nonapeptide hormone, produced in the hypothalamus, involved in a variety of physiological functions. The clinical use of OT neuropeptide is limited by its short half-life *in vivo*. The OT sequence is characterized by a disulfide bridge between Cys^1 and Cys^6 and by a β-turn secondary structure. Introduction of the 1,2,3-triazole moiety into a peptide backbone is a known approach to achieve stabilization of specific conformations, such as α-helices and β-turns, and a recognized strategy to improve resistance toward proteolytic degradation, thus increasing the metabolic stability *in vitro* and *in vivo* [1-3]. Macrocyclization mediated by Cu(I)-catalysed azide alkyne cycloaddition (CuAAC) has been extensively applied by our group to explore the relationship among structural diversity of triazolyl-bridged cyclopeptides, biological activity and conformational analysis demonstrating the capacity to stabilize secondary structures such as β-turns [4,5]. With this idea in mind, the aim of the present study is to develop OT analogues in which the disulfide bridge has been replaced by a triazolyl bridge to increase selectivity and stability. Considering all the possible permutations at positions *i* and *i*+5 of the azide and alkyne modified amino acid residues in the OT peptide chain, we synthesized by CuAAC a series of triazolyl-bridged OT analogues, differing in the size, location, and orientation of the 1,2,3-triazolyl moiety. Furthermore, in this project conformational and biological analysis of all peptidomimetics were performed. Preliminary biological results demonstrate that some OT analogues displayed oxytocin receptor antagonist activity.

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OC26

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

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The possibility to date an aerial mortar by radiocarbon relies on the feasibility to precisely separate the binder from carbonate aggregates of geological origin, i.e geogenic calcite. The datable component is represented by calcite that results from the reaction of calcium hydroxide with the atmospheric CO_2 during the hardening of the material, i.e. anthropogenic calcite [1,2]. Considering the critical aspects encountered in ^{14}C dating of ancient mortars and the importance of sample selection, great attention is paid on how to estimate whether the selected samples can be good candidates for dating [2,3]. My PhD project aims at optimization of the binder selection protocol for ^{14}C dating of historical mortars, using non-destructive methods. The use of Fourier transform infrared spectroscopy (FTIR) in transmission on KBr pellet to distinguish the origin of calcite was proposed in [4]. However, assuming we can typically recover very small samples of datable material from the entire collected mortar, it is worth to select a non-destructive spectroscopic technique, as e.g. FTIR in attenuated total reflectance mode (ATR) to preserve the material for further analyses. In my research, ancient mortars, from archaeological sites and historical buildings, fresh plasters, modern binder samples factory-made and geological samples were collected to perform a complete chemical and minero-petrographic characterization and to evaluate whether the ATR mode could lead to the same results as the FTIR on KBr pellet. ATR method was employed to select samples to dating for two case studies, to evaluate whether samples selected are consisting of anthropogenic calcite. In addition, the project has included the possibility to date difficult contexts such as painted plasters rich of carbonate contaminants by collecting organic residues (straw fragments) and measuring the ^{14}C concentration there. Since low mass selected of samples, Lilliput graphitization line at INFN-LABEC [5], was used.

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PhD in Chemical Sciences at UniFi - PiCSU 2022

OC27

Structural and Vibrational Properties of Magnetic Systems from the Bulk Phase to the Adsorption on Surface

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Today, a steadily growing community of scientists is developing the tools of a new science that merges quantum physics and theoretical computer science, called quantum information science. Its basic constituent is the quantum analogue of the classical bit, say the qubit. In the development of spin-based quantum technologies it has become clear that molecules carrying a paramagnetic center represent particularly versatile building blocks as they can offer a high degree of tunability. The microscopic description of time dependent spin phenomena represents an aspect of paramount importance due to its broad impact in magnetism. A tailored computational protocol is proposed, able to reproduce magnetic, structural, and vibrational properties of transition metal complexes. The importance of several factors influencing the vibrational degree of freedom is highlighted [1]. Intrinsic effects are due to the chemical nature of the first coordination shell, and extrinsic effects are related to interaction with the lattice environment. The results of these studies represent further pieces of the puzzle of the role played by vibrations in determining the relaxation properties of potential molecular qubits at the quantitative level.

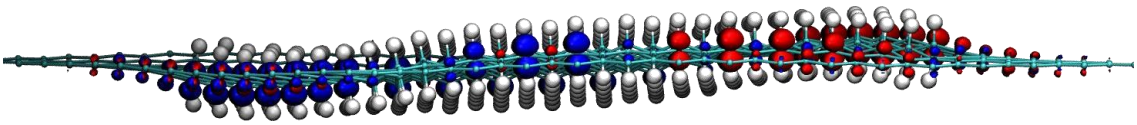

Figure 1: Side view of a hydrogenated island of graphene highlighting ripples.

A further investigation [2] regarded the implantation of magnetic moments in graphene for spintronics applications (Fig. 1). This computational study aims at systematic and comprehensive understanding of structural and magnetic properties of graphene across its chemical space when covalently functionalized with hydrogen or fluorine atoms in different stoichiometries. The hydrogenated systems are then adsorbed on Au(111) crystal face or on a graphene buffer layer. A new strategy, based on non homogeneous graphene hydrogenation, is rationalized to build stable magnetic structures and maximize the magnetic moment per unit area.

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OC28

Ruthenium (II) polypyridyl complexes: playing with structural parameters to design promising light-responsive therapeutic agents

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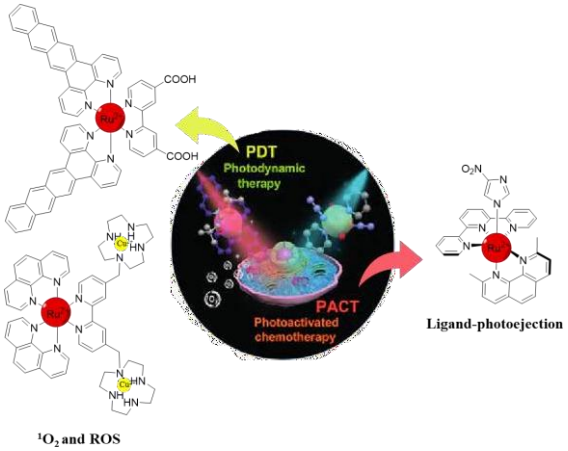
The widely known drawbacks associated to the use of commonly employed antitumoral drugs, along with the increasing multidrug resistance of bacterial pathogens [1] make it urgent to develop new and effective antitumoral as well as antimicrobial agents, which should be based on a new class of compounds, rather than on analogues of known scaffolds.

In this scenario, ruthenium (II) polypyridyl complexes represent an attractive class of compounds due to their unique chemical-physical repertoires, structural diversity and redox properties which provide a unique opportunity for designing effective antitumoral and antibacterial agents. [2] Furthermore, modulation of ancillary ligands on ruthenium (II) complexes allows to obtain both photostable sensitizers, whose activation promotes the production of reactive oxygen species, and photoactivable complexes capable to release bioactive molecules following irradiation with low-energy visible light. The two approaches, named respectively photodynamic therapy (PDT) and photoactivated chemotherapy (PACT), are compared presenting different classes of ruthenium (II) polypyridyl complexes with a broad spectrum of biological application. [3] [4]

The aim of this contribute is to highlight the versatility of ruthenium (II) polypyridyl complexes in the development of effective therapeutic agents with widespread biological application.



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OC29

Molecular and macromolecular hetero[4]helicenes: synthesis, red-ox properties and applications

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Helicenes are inherently chiral molecules with several valuable applications in medicinal chemistry, asymmetric synthesis and, above all, in material science. Here we report the preparation of enantiomerically stable [4]helicenes obtained from a triarylamine or a *N*-aryl phenothiazine scaffold *via* consecutive electrophilic sulfur insertions [1]. These peculiar systems can be oxidized to exceptionally stable radical cations *via* multiple pathways [2, 3]. The radicals obtained, thanks to their chemical and geometric stability, can be assembled on Au (111) surface preserving their handedness and paramagnetism, paving the way for the rational design of new spintronics devices [4]. Additionally, new polynorbornene-based polymers with pending helicene units were prepared and their electrochromic behavior was investigated [5].

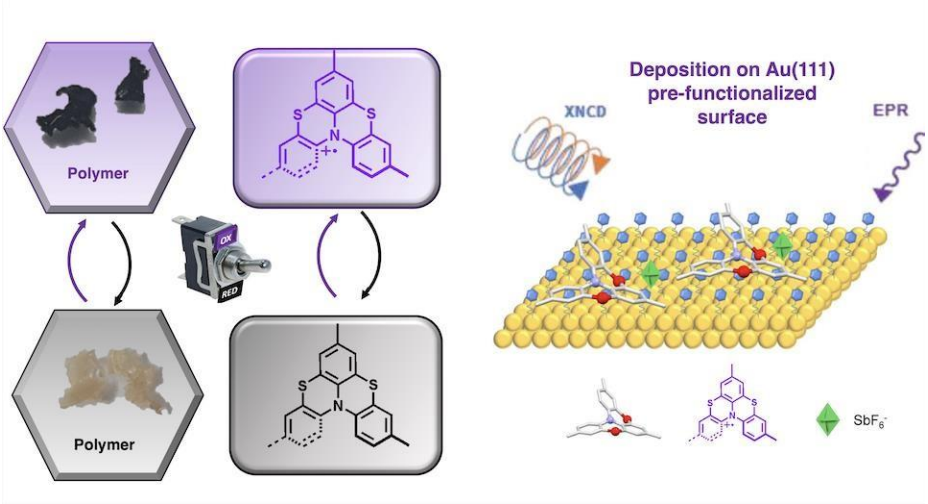

Figure 1

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OC30

Design and synthesis of macromolecular and nanostructured carbonic anhydrases-based materials

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We report the synthesis of new macromolecular and nanostructured Carbonic Anhydrases (CA)-based functional materials which combine the exceptionally kinetic performances of such enzymes with the feature of mesoporous spherical silica nanoparticles, or polyolefins. The goal of this study is transforming these materials in valid devices for CO_2 capture thus inducing or controlling pH variations. We performed and compared several methods for the encapsulation of bovine b-CA within mesoporous silica nanoparticles generated by controlled biomimetic silica precipitation induced with silaffin peptides (Cys_R5) [1]. Furthermore, the b-CA was covalently conjugated to polypropylene-graft-maleic anhydride (PP-*g*-MA) via a ball-milling green synthetic procedure effecting chemical reactions by mechanical energy [2]. The enzymatic activity, structural, physical and chemical characteristics of the obtained materials are currently investigated with the purpose to further evolve our findings to diverse CA isoforms.

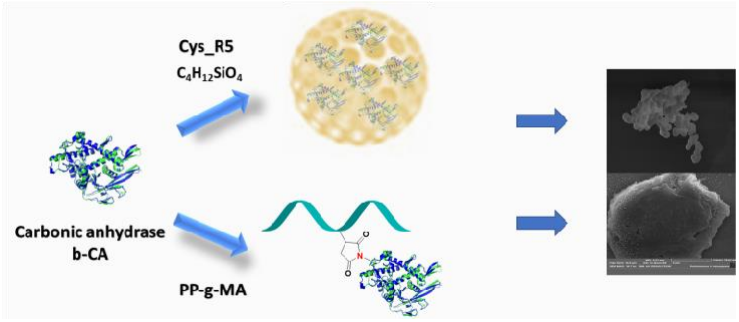

Figure 1: General representation of Carbonic Anhydrase immobilization.

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Interdisciplinary study of Majolica of Montelupo: preliminary results

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The project aims to define a multi-analytical approach suitable for the study of complex artefacts such as Montelupo majolica, to deepen the knowledge about materials, techniques and production context. In collaboration with the Museum of Ceramics of Montelupo Fiorentino and the Superintendence of Florence, a sufficiently numerous set of samples was selected to cover the entire production span (XIV-XVIII Century) [1].
A non-destructive and non-invasive approach was initially preferred, in total respect of the conservation status of samples. The focus was therefore placed on the most superficial layers of the majolicas: the white/opaque glaze applied on ceramic body, the coloured decorative apparatus and the transparent glazed coatings. MA-XRF scans and Raman analyses (Renishaw inVia confocal microscope) were firstly exploited to get an overview of main characteristic elements, their distribution and chemical nature [2][3]; a first attempt to determine the polymerization index of glazes, fallowing Colomban's works, was also done [4]. Interesting results were achieved for the glazes, while additional analysis will be necessary for the decorative apparatus. Semi-quantitative IBA analyses, which were carried out on a small group of samples, revealed compositions consistent with ones hypothesized by XRF-Raman results but also highlighted limitations of the non-invasive chosen approach that detects average concentration on the entire thickness, not allowing to highlight composition differences in the single layers; hence the need to perform a differential PIXE [5]. A series of sampling from a few selected majolicas were accorded by the Superintendence, in order to directly measure the layers thicknesses and compositions (with a SEM analysis campaign): it will allow evaluating the ability of non-invasive techniques to extract the same information in a non-invasive way for all the other samples as well as making the interpretation of Raman spectra easier and more straightforward.

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OC32

Peptides inhibitors of Protein-Protein Interactions: the COVID-19 case of study

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Protein-Protein Interactions (PPIs) modulate a wide range of biological processes, including cell-cell interaction and metabolic and developmental control[1] This that PPIs are extremely important to regulate the cell biological activity can be exploited by xenobiotics in the host infection. This project is focused on the case of COVID-19. In the SARS-CoV-2 infection there are two PPIs which can be therapeutically relevant targets. The first involves the interaction of the RBD (*Receptor Binding Domain*) with its receptor ACE2 (*Angiotensin-Converting Enzyme 2*). Blocking this interaction prevents the virus from entering the cell and starting its replication pathway. Sadremomtaz et *al*.[2] have designed and synthesized ACE2-based peptides able to antagonize the RBD-ACE2 interaction with strong binding affinity to RBD. The second PPI involves the HR1 (*Heptad Repeat 1*) and HR2 (*Heptad Repeat 2*), which are domains of the Spike protein, and is essential for membrane fusion. Therefore, blocking this interaction may lead to the development of fusion inhibitors. Xia et *al.*[3] have designed a lipopeptide which inhibited SARS-CoV-2 protein-mediated membrane fusion. Therefore, the aim of this project is to design, synthesize and characterize peptides able to inhibit the RBD-ACE2 and/or HR1-HR2 interactions to prevent a SARS-CoV-2 infection. Since the structure-activity relationship is very important in proteins, a synthetic analog must be conformationally constrain to perform its activity. The introduction of specific N-CAAs (*Non-Coded Amino Acids*) together with macrocyclization force the peptide to assume specific conformation by forming stable secondary structures and furthermore could improve the "druggability"[4]. Finally, the peptides will be tested with SPR (*Surface Plasmon Resonance*) to measure their affinity to the target and the efficacy in inhibiting the interaction. Moreover, exploiting collaborations with microbiologists, the peptides will be tested also *in vitro*[5].

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OC33

Investigating the role of disorder in structurally heterogeneous proteins

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In recent decades evidences that a large part of eukaryotic proteomes comprises proteins with natively unfolded regions has highlighted the importance of studying the role of disordered systems [1]. During the years it has been observed that misfunction of intrinsically disordered proteins (IDPs) is linked to many pathologies, e.g. cancer, neurodegenerative and cardiovascular diseases [2].
Nuclear Magnetic Resonance (NMR) spectroscopy has emerged as a leading technique for the characterization at atomic resolution of structural and dynamic features of intrinsically disordered regions (IDRs). The application of NMR on disordered proteins is challenging [3], nevertheless it is possible to exploit the resonances of heteronuclei (particularly ^{13}C and ^{15}N) to overcome the limits associated with ^{1}H-based experiments. Thanks to their greater chemical shift dispersion they are the most suitable for the characterization of IDPs, and in recent years many exclusively heteronuclear NMR approaches have been developed [4].
My Ph.D. project will aim to exploit and further develop NMR methods to study structurally heterogeneous proteins (i.e., proteins with folded and disordered domains) and carry out a biophysical characterization of these systems at atomic resolution. To investigate the role of IDRs in the proteins, intra-molecular interactions between different domains will be studied, as well as inter-molecular interactions with other partners (e.g. proteins, nucleic acids, peptides, and small molecules). The project will focus on human proteins with high biological and medical interest that present a heterogeneous structure (e.g. transcription regulatory proteins), to expand our knowledge on the role of disorder in cellular pathways.

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OC34

New strategies for the monitoring and the inhibition of metals and alloys corrosion in Cultural Heritage

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One of the main problems in the preservation of outdoor metallic artworks is corrosion, which causes severe impairment of all the artifacts' properties. On bronzes, corrosion may occur as a particularly aggressive cyclic phenomenon, known as bronze disease [1].

The purpose of this project is to develop new methodologies and materials to detect and inhibit metal corrosion, especially on copper alloys.

An innovative approach for the diagnosis and monitoring of metallic corrosion will be applied, based on Optical Coherence Tomography (OCT) [2] and Thermal Quasi-Reflectography (TQR) [3]. OCT will be used to acquire tomocubes (sets of cross-sectional images) to study both the morphology of metallic surfaces at the micrometric scale to differentiate metal, corroded material, and old protective coatings [4] and possibly to measure the thickness of the latter. The use of TQR, developed to detect sulfation in wall paintings, will be extended with the needed modifications to the diagnostics of metallic artworks. Basing on the different emissivity of the various substances, standard thermography will be performed as well.

Another aim of the project is the development of new materials and methods to inhibit the corrosive phenomena in a view of preventive conservation. In particular, the bronze disease is caused by the combined action of oxygen and chlorides. The research strategy to contrast this kind of degradation could be the setup of a system based on functionalized nanomaterials [5] with the aim to slow down the kinetic of the process and/or to stabilize the active mineral phases. Electrochemical strategies will also be studied to inhibit the cyclic phenomenon.

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OC35

Production of carbonaceous materials from biomass of high environmental hazard, their characterization and application on water purification

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The research aims to produce carbonaceous materials by thermal conversion of biological sludge from wastewater treatment plants (WWTPs) in domestic or mixed domestic-industrial contexts, which represent a waste of high environmental concern. To this aim, conventional and innovative energy delivery techniques (i.e. microwaves) will be adopted. The carbonaceous materials will undergo to chemical and/or thermal activation processes to increase their adsorption capacity towards target molecules of particular environmental importance. The materials will be characterized from both product (e.g. surface area, porosity distribution, etc.) and environmental viewpoints (evaluation of the release of polycyclic aromatic hydrocarbons, metals, etc.), and compared with the characteristics of reference materials, such as commercial activated carbon [1]. The most promising materials will be used in removal studies of molecules of environmental interest, such as pharmaceutical, perfluorinated and polyfluorinated compounds, both by adsorption isotherms, and in column studies on real wastewaters fortified with these compounds, monitoring the removal by liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS). The best materials from the chemical release and composition (e.g. higher graphitic crystalline portion) viewpoints will also be tested as sorbents for clean-up of organic extracts, such as in the case of dispersive solid phase extraction (d-SPE) of QuEChERS extracts.

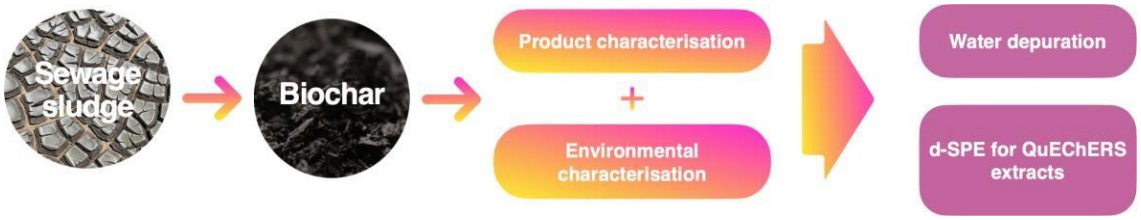

Figure 1. Graphical abstract

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OC36

Electrodeposition and characterization of industrial and technological interesting surfaces

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The work sought to explore the role of applied electrochemistry in the industrial and technological research for renewable energies. In the photovoltaic field the goal of the work was the obtainment of a Cu-Sn alloy with 2:1 atomic ratio of the two metals able to be considered a starting point in the obtainment of the semiconducting compound Cu2ZnSnS4 called kesterite via the electrodeposition technique[1]. The electrodeposition of kesterite compounds represents a sustainable and scalable process from an industrial point of view. In this context, was developed a cyanide-free bronze plating bath (Cu-Sn alloy). Bronze deposition process was characterized in dept showing good performance in terms of bath stability, alloy structure, and composition. A copper plating bath was used as model-bath, to study from an electrochemical point of view the effect of thiourea (organic additive) on the structure and morphology of electrodeposited films[2] and to tailor the metal structure to develop kesterite compounds.
In the fuel cells field, I studied sustainable electrodeposited catalysts. In the case of non-noble-metals catalytic surfaces, was studied the enrichment of powders derived from the pyrolysis of waste tyres[3] by the electrodeposition of cobalt. The enrichment strategy resulted in samples with very good catalytic performances and optimal stability over work time. In the case of noble metals-based catalytic surfaces, was developed a combined electroless process to produce thin palladium coatings on copper substrates and thus to minimize the amount precious metal needed[4]. Exploiting electroless plating was managed to produce nanometres-range and micrometres-range continuous palladium films able to be implemented as catalytic surfaces.

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OC37

Polyamine receptors as fluorescent chemosensors for anti-inflammatory nonsteroidal drugs in aqueous media

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In the last few years, the interest in the development of new sensing systems for certain consumer drugs, such as non-steroidal anti-inflammatories drugs (NSAIDs), has progressively increased. Their wide use and release in the environment, which is still poorly regulated, can lead to a continuous uptake from living beings, with possible long term toxic effects [1,2]. In the course of our PhD activity, we have reported four fluorescent receptors, L1-L4, constituted by a triamine chain linked to anthracene (L1 and L2) or pyrene signaling units (L3 and L4), as optical probes for NSAIDs. As first example of substrate, we have chosen ketoprofen, one of the most used NSAIDs. Binding and sensing properties of the receptors and their Zn(II) complexes have been studied in aqueous media by coupling potentiometric, ^{1}H NMR, UV-Vis spectrophotometric and fluorescent emission measurements. The receptors can interact with the substrate to form 1:1 or 1:2 receptor to substrate adducts in aqueous matrices, stabilized by charge-charge and hydrogen bonding interactions between the protonated triamine chain of the receptors and the carboxylate group of ketoprofen. At pH 7 the interaction gives rise to an increase fluorescence emission of L1-L4. Indeed, binding of ketoprofen induces a translation of the acidic proton from the central nitrogen of the monoprotonated triamine chain to a benzylic amine group, inhibiting the quenching effect of the PET process from the amine lone pairs to the excited fluorophores.

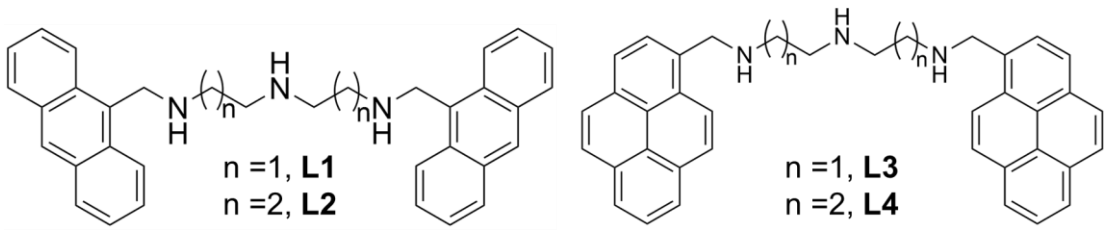

Figure 1: Structure of the receptors

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OC38

Measurement of metal coatings thickness by X-ray spectrometric method without the need for certified standards

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The XRF analysis is the most widespread in the industry setting to determine the thickness of metallic coatings, thanks to its ease of use, robustness, and non-destructive nature [1-3]. However, accurate measurement requires primary standards that are expensive, not always available, and must be periodically replaced due to a limited shelf-life [4,5].
In this context, we developed a versatile and cost-effective way to measure metallic coatings' thickness based on self-produced calibration standards. Specifically, we start conducting a feasibility assessment by primary current distribution simulations to determine cathode sizes needed to attain adequate thickness homogeneity. Uniformity maps were then constructed by measuring Ni Ka x-ray line net counts inside a matrix of points on the surface of the electroplated brass plates. Results have shown a thickness variation within 5% for the central portion of the samples, consistent with certified standards specifications. Then we have evaluated the galvanic deposition manufacturing process by comparing the thickness of coatings of correspondent plating times, proving that electroplating has, at least, in this case, excellent reproducibility.
Cross-sections obtained from a predetermined series of samples were analyzed in their central portion by reflected-light microscopy and SEM-EDS to determine thicknesses to be taken as a reference for the XRF calibration curve. The results obtained with the two techniques were in good agreement. However, since it is well known that electron microscopy has a higher lateral resolution, its data were chosen to build a 5-point second-order calibration curve. Next, another calibration curve was built using a certified thickness standard in a semi-fundamental parameter approach. Then, the results obtained with standardless fundamental parameter (FP), FP with one-point empirical correction, and self-produced standards were compared. Data showed how the thicknesses obtained from the methods with calibration curves agree with each other for all the samples. Conversely, the standardless FP method was much less precise, revealing differences in thickness estimation that grew as thickness increased.
Since the cheapness of the galvanic process, it is possible to realize numerous standards with variable thickness, composition, and succession of layers. Therefore, this protocol reduces costs associated with XRF instrument calibration without major drawbacks in measurement accuracy.

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OC39

A new neuroprotective bola-amphiphile: the trodusquemine

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Trodusquemine is an amphipathic membrane active aminosterol that has shown therapeutic benefit in both τ and β amyloid mouse models of Alzheimer's disease. We studied the interactions between trodusquemine (Trod) and a model of the outer layer of the plasma membrane to understand how Trod affects the structure, using surface pressure-area isotherms combined with Brewster Angle Microscopy (BAM) to obtain structural, thermodynamic and morphological informations. We selected two different compositions of lipid mixture mimicking either a lipid-raft containing membrane (L_d-S_o) or a single-phase disordered membrane (L_d).

We demonstrated that Trod can form stable and fluid Langmuir monolayers at the air-phosphate buffer interface. Studying the lipid monolayers in the presence of increasing concentrations of Trod, we found that Trod interacts and penetrates in the lipid layer for both the selected lipid compositions. The maximum Trod uptake in the rafts-containing monolayer is observed for a Lipid/TRO molar ratio equal to 3:2. BAM images confirmed the presence of condensed raft domains for the L_d-S_o mixture whereas only dark homogeneous fluid domains were observed for the single L_d phase. Statistical analysis of the condensed domains revealed that Trod preferentially adsorbs at the border of the lipid rafts inducing a decrease in size of the raft domains without affecting significantly the thickness mismatch.

Removal of G_{M1} from the lipid L_d-S_o mixture resulted in an even greater reduction of the size of the lipid rafts suggesting that the presence of G_{M1} hinders the localization of Trod at the lipid rafts boundaries. Taken together these observations suggest that Trod can potentially influence the organization of lipid raft domains within the neuronal membrane, domains in which many signaling receptors are localized.

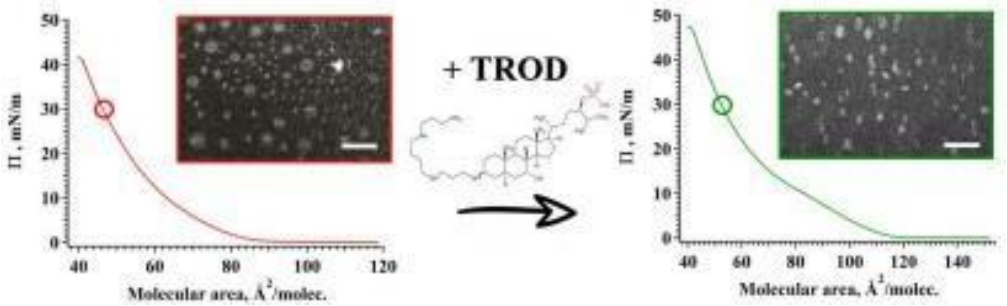

Figure 1: Langmuir isotherms and typical BAM images taken at 30 mN/m of lipids monolayer without (red curve) and with (green curve) TRO. Scale bar is 50 µm. In the center the chemical structure of TRO.

OC40

Enlarging the scenario of site direct ^{19}F labelling in NMR spectroscopy

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The possibility to use selectively incorporated ^{19}F nuclei has retrieved increasing interest in recent years. The high gyromagnetic ratio, the ½ nuclear magnetic spin, and its absence in native biomolecular systems make this nucleus an interesting alternative to the standard ^{1}H NMR spectroscopy [1]. Mainly two kinds of approaches dominate the scenario of ^{19}F nuclei incorporation in biomolecular systems: the direct expression of ^{19}F labelled proteins, or the chemical incorporation of specific molecules/labels containing fluorine nuclei [2]. Several works showed how the incorporation of specific fluorinated amino acids can be relatively easily achieved in E.coli cells using a modified minimal medium [3]. On the other hand, site directed labeling (SDL) represents an attractive and potentially low-cost alternative to the direct expression, especially in cases where the expression in minimal media is not feasible. Here is presented a systematic investigation on the post expression attachment of p-fluoroaniline to tyrosine residues, conjugating this ^{19}F label using the specific three component Mannich type reaction [4]. One of the features that makes tyrosine an appealing labeling site is its average low occurrence (just above 3%), making it one of the rarest amino acids in protein sequences. Moreover, being a partially hydrophobic residue, it prefers to be buried inside the hydrophobic core of proteins, leaving only few reactive residues on the surface. Therefore, choosing the right reaction conditions, it could be possible to target in a selective way exclusively or primarily a tyrosine residue among all the others. To confirm the success of the bioconjugation reaction and to validate the specificity towards multiple tyrosine biomolecular systems, several proteins have been investigated through ^{19}F NMR, Circular Dichroism and Mass Spectrometry analysis.

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OC41

Synthesis and magnetic studies of molecular spin qubits

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Quantum technologies are recently developing very fast and new computers, so called quantum computers, will probably change the world of science drastically. The fundamental unit of a quantum computer is the qubit, which could be any quantum mechanical system having two distinguishable quantum states like the electron or nuclear spin. Unpaired electron spins are found in V^{IV} and Cu^{II} metal-complexes. These kinds of qubits are called molecular spin qubits [1]. Molecular spin qubits have received many attentions in the quantum computational world, due to their manifoldness. A chemist can modify and vary chemical bonds e.g., in a metal complex in a way that it is possible to "combine" multiple unpaired electrons or nuclear spins, that act as qubits, altogether in one single molecule and create a multi-qubit system. These two spins could "communicate" through space (dipolar) or through the bond (exchange) creating a universal quantum logic gate like the controlled not (CNOT)-gate [2].
In this three years of PhD studies, the aim is to synthesize and study the magnetic properties of potential molecular spin qubits capable to perform these complex operations. Monometallic metal-complexes like Cu(II)-mercaptopyridinthione ($Cu(mpo)_2$) and bimetallic complexes like bis-VO(IV)-triphenylporphyrin ($[VO(TrPP)]_2$) were already synthesized and studied with dynamic (pulsed EPR spectroscopy, AC-magnetic measurements) and static magnetic measurements (cw-EPR, DC-magnetic measurements). The results show that the coherence time (lifetime of the qubit) and exchange parameters (interaction of qubit pairs) are in the right order of magnitude for logic gates implementations.

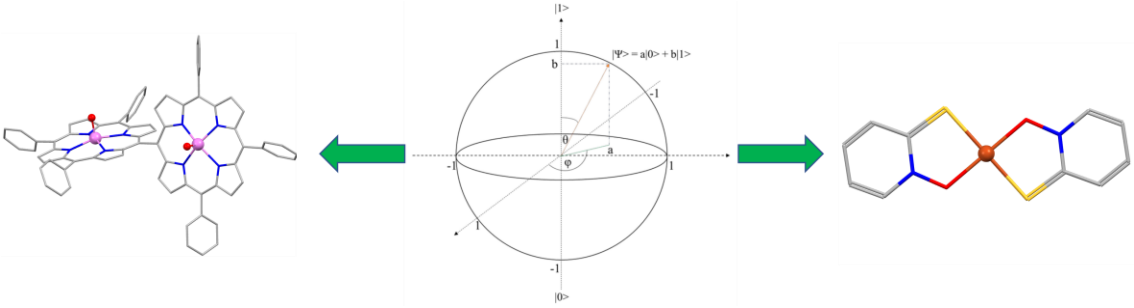

Figure 1: The representation of a single qubit in a Hilbert space (center), and two potential molecular spin qubits $[VO(TrPP)]_2$ (left) and $Cu(mpo)_2$ (right).

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OC42

Smart Autonomous Responsive Materials

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This project aims to design a smart "autonomous" material capable of tuning its response with respect to the surrounding environment, without the need for external triggers. In nature many processes are energetically uphill in far-from-equilibrium conditions, and they can self-regulate by a continuous consumption of chemical energy sources [1]. Incorporation of these tools into soft matter materials will allow a significant advance in the design of innovative "autonomous" materials for diverse applications [2].

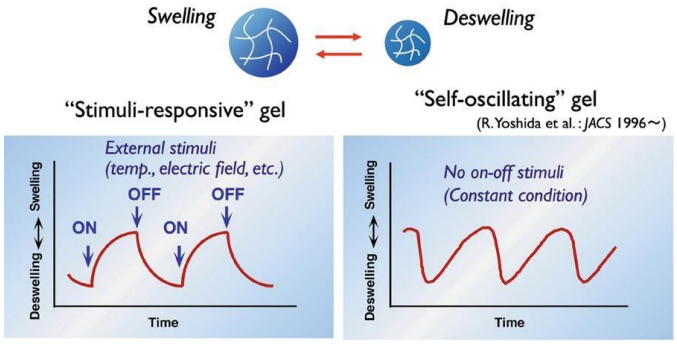

Figure 1: Autonomous responsive materials don't need on/off stimuli. Reprinted by permission from Springer Nature: Colloid Polym. Sci. 2011 [3].

The use of enzymatic autocatalytic reactions represents a biocompatible option that requires mild chemical conditions. The most promising options are based on the so called “pH clocks” that exploit a pH feedback-driven mechanism [4]. Urea-urease system is a solid candidate for the design of biocompatible pH-based feedback processes for bioinspired applications. Inclusion of an acid-producing enzyme in the reaction environment as negative feedback mechanism will give the possibility to obtain oscillatory dynamics in the urea-urease system. This system in a suitable formulation can lead to the setup of a molecular machine where a reversible shrinking and swelling activity in response to pH fuels the engine [5].
These sustained pH-oscillators will be capable of performing (bio)chemo-mechanical work, paving the way to applications as chronopharmacotheraphy, periodic drug release mechanisms, design of micro-swimmers, and the fabrication of actuators in soft robotics.

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OC43

Advanced spectroscopic study aiming to the understanding of the heme-biosynthesis pathway of gram-positive bacteria

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The coproporphyrin-dependent heme biosynthesis (CPD) pathway, utilized by monoderm bacteria to produce heme *b*, has been discovered in 2015 [1]. The coproporphyrin III (cpIII) is the substrate of coproporphyrin ferrochelatases (CpfCs) which catalyze the insertion of ferrous iron into the porphyrin ring, producing the iron coproporphyrin III (coproheme). This is the penultimate step within the CPD pathway. In the next 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 [2,3], to allow the decarboxylation of p4 to form heme *b*.
During my master thesis, I studied the wild-type and several variants of CpfC from Firmicute *Listeria monocytogenes* (*Lm*) complexed with the product (coproheme) using UV-Vis electronic absorption and resonance Raman spectroscopies (carried out at different temperatures and by using polarized light). I selectively assigned the vibrations of the four propionates, and I found that some hydrogen bonds observed in the crystal are not present in solution [4].
As PhD student, I started the spectroscopic characterization of the wild-type *Lm*CpfC complexed with the substrate (cpIII). These studies are fundamental to follow *in vitro* the synthesis of coproheme, starting from the CpfC-cpIII complex, upon addition of a solution of Fe(II), under anaerobic conditions. I found that the propionate vibrations of the cpIII-complex are at different frequencies as compared to those of the coproheme complex, and therefore, can be used to follow the titration. Interestingly, the preliminary data suggest that at the beginning of the titration, upon addition of 0.1-0.3 equivalents of a Fe(II) solution, an intermediate species is formed.

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OC44

Ferritin-based anticancers

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Ferritin is a natural iron storage protein, characterized by a unique hollow globular structure of about 480 kDa, which self-assembles providing a 24-mer nanocage, with an outer diameter of 12 nm and an inner cavity of 8 nm.
In vivo animal cytoplasmic ferritins are found as heteropolymers of two different subunits: the heavy (H) and light (L) chains that are recognized by two different cellular receptors, overexpressed on cancer cells, which allow the endocytosis of ferritins.
Human ferritin could be produced as a recombinant homopolymer in *E. coli* cells with high yields; it is biocompatible, and it is stable at high temperature and extreme pH. Furthermore, the 8 nm cavity can host small molecules and even small proteins via passive diffusion or pH assisted disassembly-reassembly methods, and the surface can be easily modified through chemical reactions or genetic modifications [1].
For my doctoral program, I propose the use of recombinant homopolymeric human H-ferritin for the development of: i) a tumor vaccine platform, through the exposure of antigens on the external surface of the protein, for the triggering of immune cells; ii) anticancer nanocarriers for the targeted delivery of drugs against cancer cells.
Here, I show an example of anticancer encapsulation: Ru-based photosensitizers were internalized into the ferritin cage and selective delivered to cancer cells for photodynamic therapy. We demonstrate the successful internalization of the complexes and the maintenance of the physical and chemical properties of the Ru-ferritin nanocomposites. Furthermore, we observed the cytotoxicity of the systems upon illumination, against two different tumor cell lines [2].

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Greening peptide chemistry, a necessary step to the future

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In the last decades the global market of therapeutic peptides has progressively grown. This has gone hand in hand with a remarkable increase in investments in research and technology development for the synthesis of peptides. Moreover, the cGMP production of peptide active pharmaceutical ingredients is becoming progressively attractive at the industrial level.
In this context, solid-phase strategies are considered methods of election for the synthesis of medium-length peptides, not only at the research scale but also for large-scale production.
Since large quantities of harmful and pollutant solvents, such as DMF, NMP, and/or CH_2Cl_2, are traditionally required to perform reactions and washings in this multi-steps process, in the last years many studies about greening SPPS have been conducted. In particular research has been focused on greener solvents and more efficient procedures and technologies [1-3].
The primary goal of this project is to give a positive contribution in identifying and testing new greener solvents and procedures, starting from state-of-the-art results. Moreover, the employment of cutting-edge technology with a wink to technology transfer and GMP scale-up studies will promote a fruitful direct link between academia and industry [4].

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OC46

Development and scale-up of synthetic strategies for exotic macrocyclisation to increase druggability of peptides as active pharmaceutical ingredients of industrial and academic interest

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A pilot production methodology of the API Eptifibatide acetate was optimized and scaled from 5 to 70 mmol leading to a high purity (99.6%) and good yield (22.1%) final product, decreasing reaction times, quantity of solvents and waste, therefore minimizing environmental and economic impact, in compliance with the quality specification imposed by regulatory agencies (FDA, EMA), in collaboration with Fabbrica Italiana Sintetici-FIS S.p.A. (VI)[1]. Moreover, to overcome patent limitations, 4 different solid-phase disulfide bond formation procedures (Strategies A÷D), characterized by the possibility to perform both MW-SPS and cyclization in the same reactor, were investigated on a 5 mmol scale[2].

On the other hand, a challenging conformational stabilization of H1-relaxin single B-chain minimized analogs was performed, to investigate the biological activity of the native hormone, still unknown. An innovative, efficient and reproducible MW-assisted Copper-Catalyzed Azide-Alkyne Cycloaddition (SP MW-CuAAC) performed on solid phase to prepare side-chain-to-side-chain clicked analogs was developed, overcoming aggregation tendency and poor solubility[3]. Two generations of analogs with different length and different position and orientation of the triazolyl ring were designed and synthesized with the aim to stabilize the α-helix conformation. H1-relaxin analogs were biologically tested, to verify binding to cells expressing the receptor RXFP1 and activity through cAMP signaling pathway in HEK-293T cells stably expressing the RXFP1 receptor.

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OC47

Drug-protein interactions: "from first to last" workflow in three different cases of studies

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95% of commercially available drugs target a protein (about 600 different target proteins). However recent data suggest that the druggable human proteome is much more extensive, indeed, the number of possible target proteins is estimated around 4.5 thousand [1]. Target proteins are quite heterogeneous from each other in terms of both activity and cell localization. In this wide and heterogeneous field of drug discovery, during my PhD, I focused on three different families of proteins.

The main objective of my PhD is 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. 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]. Therefore, the identification of selectivity and high affinity ligands able to control the activity of these receptors is a sought-after goal.

Then, sphingosine kinases (SKs) are cytosolic enzyme that catalyzes the production of sphingosine-1-phosphate (S1P) in an ATP-dependent manner. Solid experimental evidence implicates the S1P axis in different pathological conditions (*i.e.*, cancer, inflammatory diseases, fibrosis) and aberrant S1P levels and/or SKs expression have been associated with diseases progression. Our contribution in this field consists in the identification of monosaccharide bearing able to inhibit SK1. [3]

Finally, fucosyltransferase (FTs) are enzymes that transfer a L-fucose from a GDP-fucose donor substrate to an acceptor substrate on cell surface. Among the family of FTs, α-1,3-FTs specifically modify terminal lactosaminyl glycans, which is the last step in biosynthesis of Lewis X antigens (Lewis X, Le^X, and sialyl Lewis X, sLe^X). An upregulated α-1,3-FTs activity, resulting in the overexpression of Le^X and sLe^X antigens, is etiologic in several human diseases, including cancer and autoimmune conditions (*i.e.*, rheumatoid arthritis, Crohn's disease, diabetes). Our contribution in this field consists in the identification of selective inhibitors of FTVI and FTVII that consist on glycomimetic compounds. [4]

In this communication, I report the workflow we followed during the design, synthesis and finally the biological study of the selective ligands for the different proteins studied.

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OC48

NMR reveals specific tracts within the intrinsically disordered regions of the SARS-CoV-2 Nucleocapsid protein involved in RNA encountering

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The SARS-CoV-2 Nucleocapsid protein (N) is one of the four structural proteins of the virus and the most expressed one upon viral infection [1]. It is organized in an RNA binding N-terminal domain (NTD), a dimerization C-terminal domain (CTD) and three intrinsically disordered regions (namely IDR1, IDR2, and IDR3) that comprise almost 40% of the protein primary sequence. Thanks to its structural heterogeneous nature, N is involved in many crucial mechanisms for the infection cycle [2]. In this context, the interaction between N and several RNA constructs has been studied with various techniques. However, these studies focused on the N's structured domains due to the challenges posed by the absence of structure and the repetitive nature of the primary sequence of the disordered segments.

To obtain atomic resolution information on N disordered regions during RNA encountering, we exploited ^{13}C direct detected NMR experiments in combination with Multiple Receivers hardware [3].

The experiments were conducted on a 248 residue construct we designed comprising the folded N-terminal domain NTD and the flanking intrinsically disordered regions (IDR1 and IDR2) [4] and on a construct encompassing the NTD only, to identify the priming events of N binding to a structured regulatory SARS-CoV-2 5'-UTR RNA element. This also allowed us to unveil the behavior of the NTD, the domain responsible to bind genomic RNA, when connected to the disordered regions and to define the differences between the longer construct (referred to as NTR) and the NTD in isolation.

This is the first step to unravel the detailed molecular determinants of the N protein for its specificity for RNA interaction and to obtain topological information along the primary sequence of the IDRs, useful for the identification of any possible target site for the development of binding competitors for antiviral drug design.

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OC49

Development of analytical procedures for the determination of emerging organic compounds

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The project focused the attention to develop new analytical method for simultaneous determination of several persistent, bioaccumulative and toxic chemicals in biota matrices, overcoming the matrix effect that usually causes serious problems with the quantification analysis. Two different methods were developed for two different matrix and compounds: first method for fish and second one for tawny owl. In order to develop an effective method for fish matrix, traditional and new analytical methods to determine polychlorinated biphenyls, phthalate esters, polybrominated diphenyl ethers and novel brominated flame retardants were compared [1,2]. These chemicals are endocrine disruptors, cancerogenic and cause adverse effects on human health. Three different methods (A, B, C) were compared: Method A (traditional extraction method) consists of a Soxhlet extraction followed by purification in silica gel column; in Method B, Soxhlet followed by dispersive solid-phase extraction (d-SPE); method C, the "new" method, using ultrasound extraction (UAE) and d-SPE.
Moreover, to tawny owl matrix the aim was developed a fast, effective, easily applicable analytical method for determining second-generation anticoagulant rodenticides (SGARs). SGARs show high toxicity, accumulation and persistence, lethal to animals in a single feed [3]. The extraction was a fast UAE and the clean-up was not done.
Generally, to develop an analytical method, particular attention should be paid to the very low concentrations, the complexity of the matrix and the high amount of lipid content. Therefore, in both methods, to maximizing the recovery and minimizing the matrix effect, the extraction and clean-up/preconcentration have been the most critical steps of the analytical process. All procedures were validated by replicate analysis and using reference material when available. The linearity, matrix effect and precision of the methods were evaluated by internal standards, RSD, recovery and other parameters.

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OC50

Green Deal and Zero Pollution strategy: innovative solutions for emerging contaminants removal in wastewater and runoff water

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It is well known that many emerging pollutants (i.e., persistent organic contaminants, microplastics) are not, to date, efficiently removed by wastewater treatment plants, widely discharging into watersheds, and dangerously threatening aquatic ecosystems [1]. For this reason, there is a need for a thorough understanding of their behavior along the water purification process, as well as the development of complementary solutions to traditional treatment systems to remove them efficiently. However, the most critical environmental issues concern not only the contaminant, but also the complex degradation mechanisms in which it can be released and the resulting metabolites, that can sometimes be even more toxic than the native compound. This PhD project therefore aims to develop specific adsorbent materials for target organic pollutants and filtration systems for microplastics to be integrated into tertiary treatment in water treatment plants. The research will also include the evaluation of target biodegradation pathways, during all stages of the purification process, using both traditional analytical techniques and optimized methodologies, from sampling to final quantification of the analytes.
In a holistic view of the protection of the hydrosphere, in line with the latest European Green Deal principles, it is not enough to improve the removal efficiency of emerging pollutants at the level of sewage treatment plants, but it is essential to reduce their upstream load. In this respect, rainwater runoff is a well-known route for the mobilization and transport of contaminants from terrestrial environments to different aquatic ecosystems [2]. Therefore, the project aims also to develop specific Nature Based Solutions, in particular Sustainable Urban Drainage techniques, which will allow proper stormwater conveyance, avoiding hydraulic problems (i.e., overloading of sewers and overflow of water bodies), but also the entrainment of different classes of pollutants.

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OC51

Design and synthesis of high performance polymers

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The aim of the project is the development of new polymers designed for their use in several research fields such as biological application, packaging, adhesives and cultural heritage conservation. In order to obtain compounds with high performances, the monomers must be selected appropriately to obtain structure with chemical-physical characteristics modulated for each application field. In particular, starting from the results obtained in recent years at the chemistry department [1], several saccharides, obtainable from lignocellulosic biomasses, will be used as starting material and versatile building block to produce innovative biopolymers with a structure containing polar and reactive groups capable of influencing the application behavior. The use of derivatives of natural substances can allow obtaining products that are biocompatible, biodegradable, cheap and with high stability, which can be applied in the conservation of cellulosic artefacts or in biomedical field as potential cell scaffolds or multivalent systems.
Some of these monomers will be properly modified to expand the use towards artificial muscles development. Specifically, we would like to implement intelligent polymeric materials, such as elastomeric liquid crystals, materials able to respond to external stimuli in a reversible manner to generate movement or tension [2]. The possibility of preparing mixed polymeric supports, homo and copolymers, will be also evaluated, in order to implement the biocompatibility and mechanical efficiency of the material. Furthermore, in recent years, thanks to the growing attention of public opinion towards the environment, the exploitation of biomass for the production of fuels and chemicals has assumed a central role in the modern chemical industry. In this scenario, results of extreme interest also the exploitation of saccharide derivatives suitable for new polymer adhesive formulations. These biopolymers will be performed in accordance with the requirements of low environmental impact.

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OC52

Modified surfaces of technological and industrial relevance

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Fuel cells and solar cells are promising candidates for a sustainable future. Water Splitting (WS) and Oxygen Reduction Reaction (ORR) are regarded as an highly strategic reactions, but the use of a catalyst is mandatory to achieve a satisfying conversion rate. In general catalysts rely on the use of noble metals (Pd, Pt, Rh) which are both expensive and "strategic" materials. For this reason, the search for alternative catalysts based on surface-modified electrodes is a hot-topic [1]. Modified surfaces are also of interest in the industrial sector. Electroplating is still nowadays the main technology for the preparation of objects with metallic coatings, for both the technical and decorative purposes [2]. In the case of precious metals, the use of thin films deposited on a substrate decreases the quantity of precious metal which are needed.
The aim of this project is the development of novel modified surfaces of technological and industrial interest. The study will be focused on coatings for potential use in renewable energy applications and innovative systems for electroplating industries.
Electrochemical techniques will be used to carry out the surface modification with a focus on the electrodeposition of metals and the electropolymerisation of organic and chiral compounds [3]. Surface modifications will also include the induction of chirality of inorganic electrodes with enantiomer codeposition.
A combination of electrochemical and spectroscopic techniques will be exploited to investigate surfaces properties. Experimental results will be compared with physical quantities calculated by using *ab-initio* quantum mechanical based methods.

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OC53

Jin Shofu starch-based nano-sized hydrogel dispersions for the consolidation of modern and contemporary paintings

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The preservation of brittle and fragile paint surfaces is undoubtedly one of the most significant issues in contemporary and modern art, both for their technical and optical properties, as well as their aesthetic values. Artists' unfettered experimentation with painting techniques and additive-rich paint formulations have led to artworks with weak powdering surfaces, exacerbated by severe climatic conditions and outdoor pollution. Furthermore, current conservation practice lacks suitable consolidation procedures, and traditional consolidant can result detrimental as optical properties and water permeability of the treated surfaces are dramatically altered [1].
In order to enhance penetration into porous paint layers, while avoiding optical modifications, we developed a novel starch-based nanostructured consolidant; the high surface area of the starch nanoparticles (SNPs) is rich with -OH groups, boosting pigment adhesion [2].
Dispersions of nano-sized starch hydrogels were obtained by precipitating gelatinized gluten-removed wheat starch (Jin Shofu) in a nonsolvent [2], and then re-dispersing the SNPs in water or water-ethanol blends. Their consolidating efficacy was satisfactorily tested on aged painted mock-ups that resemble modern painting surfaces, and followed by means of 2D (FTIR-VIS) Imaging and Visible light (VIS) photography. Pigment cohesiveness was improved while the painted layer's original optical properties were preserved.
Overall, SNPs represent a valid example where the formulation of colloidal systems from biopolymers and renewable sources can improve the resiliency of Cultural Heritage to degradation processes, favoring the transfer of works of art to future generations.

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OC54

Synthesis of hydroxylated indolizidines and diamino suberic acid derivatives: use of tartaric acid and other approaches

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Tartaric acid enantiomers are very versatile and useful chiral pool compounds. Part of this research project was devoted to the study of these molecules as starting materials for the synthesis of biologically active natural products and analogs such as iminosugars and bis-α-amino acids. Bis-α-amino acids are a class of structurally interesting compounds. Among them, diaminosuberic acid is an appealing stable mimic of cystine [1]. Object of this work was to synthetize different derivatives of diamino suberic acid using various strategies, including the tartaric acid approach, in order to get new interesting polyfunctionalized small molecules and to assess a stereoselective synthetic approach to the challenging structure of the aglycone of ascaulitoxin.

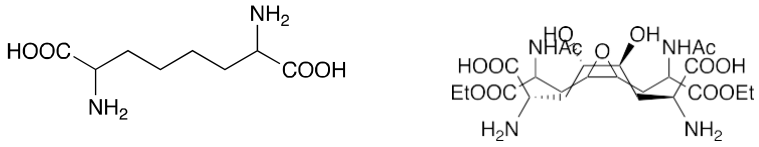
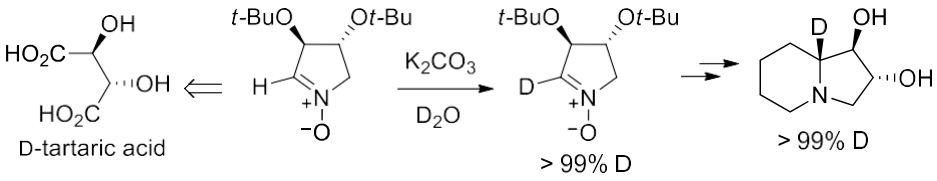


Figure 1: Diaminosuberic acid and new synthesized derivatives.

Iminosugars are another class highly studied compounds. Lentiginosine is a natural iminosugar whose synthesis can be achieved by 1,3-dipolar cycloaddition of an enantiopure dialkoxypyrroline *N*-oxide, in turn derived from tartaric acid. The highly versatility of cyclic nitrones as precursors of azaheterocycles motivated the labeling a dialkoxypyrroline *N*-oxide with deuterium and its application to the synthesis of 8a-*d*-lentiginosine [2].



Scheme 1: Synthesis and deuterium labeling of 3,4-di-*tert*-butoxypyrroline *N*-oxide and its use for the synthesis of C-8a deuterated lentiginosine.

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OC55

Stimuli-responsive pharmacological chaperones for Gaucher Disease

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Pharmacological Chaperones therapy (PCT) is emerging as promising therapeutic approach for the treatment of lysosomal storage disorders (LSD). Gaucher Disease (GD), the most prevalent LSD, is due to deficiencies in the activity of β-glucocerebrosidase (GCase), the enzyme which hydrolyses glucosylceramide to ceramide and glucose. The consequent progressive accumulation of glucosylceramide in the lysosomes ultimately leads to severe organ dysfunctions [1]. Pharmacological Chaperones (PCs) for GD are small molecules able to rescue GCase activity when used at sub-inhibitory concentration, thereby improving its trafficking to the lysosome. PCs behave as reversible inhibitors of the enzyme and they are replaced by glucosylceramide once in the lysosomes [2]. Nitrogenated glycomimetics, such as aza- and iminosugars, are the most investigated PCs for Gaucher disease. The aim of this project is the development of a series of stimuli-responsive azasugars, connecting a trihydroxypiperidine to pH- [3] or light-sensitive [4] functionalities. Both the approaches aim at a time dependent structural change of the PC induced by a stimulus which may modulate its binding affinity inside the lysosomes, thus helping the replacement of the PC by glucosylceramide (Figure 1). Several pH- and light-sensitive compounds have been investigated. The stability of pH-sensitive moieties has been studied at neutral and acidic pH via ^{1}H-NMR while the half-life of the light sensitive compounds has been examined by UV-Vis and ^{1}H-NMR spectroscopy. Moreover, some reference compounds have been synthesized to highlight the role of azasugar skeleton in the inhibitory activity.

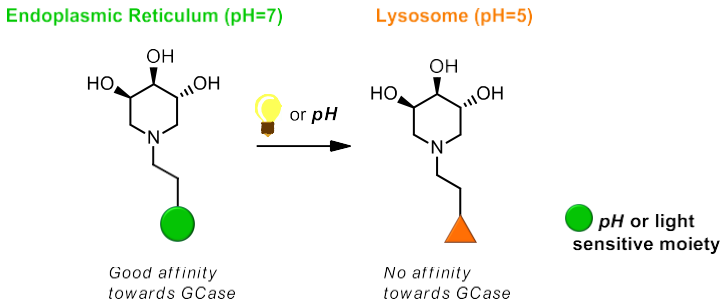

Figure 1: Structure of pH and light sensitive chaperones

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OC56

Membrane Phase Drives the Assembly of Gold Nanoparticles on Biomimetic Lipid Bilayers

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In recent years many efforts have been devoted to investigate the interaction of nanoparticles with lipid biomimetic interfaces, both from a fundamental perspective, aimed at understanding relevant phenomena occurring at the nano-bio interface, and from an applicative standpoint, for the design of novel lipid-nanoparticles hybrid materials [1]. In this area, recent reports have revealed that citrate-capped gold nanoparticles (AuNPs) spontaneously associate with synthetic phospholipid liposomes, and, in some cases, self-assemble on the lipid bilayer [2,3]. However, the mechanistic aspects of this phenomenon are not yet completely understood. In my PhD project, we address the kinetics of the interaction of citrate-capped AuNP with lipid vesicles of different rigidities (gel phase rigid membranes on one side, liquid crystalline phase-soft membranes on the other). The formation of AuNPs-lipid vesicles hybrids was monitored over different time and length scales. Our results highlight that the physical state of the membrane initiates a series of events at the colloidal length scale, which regulate the morphology of the AuNPs-lipid vesicles adducts. For lipid vesicles with soft membranes, the hybrids appear as single vesicles decorated by AuNPs, while more rigid membranes lead to flocculation, with AuNPs acting as bridges between vesicles. Moreover, exploiting the optical response of AuNPs to the aggregation and challenging synthetic liposomes of different rigidities with the AuNPs dispersion, we developed a simple and cost-effective colorimetric assay to determine the stiffness of synthetic and natural vesicles [4].
Overall, our results contribute to the mechanistic understanding of AuNPs self-assembly onto biomimetic membranes, provide design principles to control the morphology of lipid vesicles-inorganic NPs hybrids and allowed us to develop a plasmonic assay for the determination of the stiffness of unknown sample by tracking the surface plasmon resonance variations of AuNPs.

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PhD in Chemical Sciences at UniFi - PiCSU 2022
OC57

Development of a multi-analytical protocol to study the "vinegar syndrome" on films made of cellulose triacetate

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Motion picture films made of cellulose triacetate (a material widely used as support since the late eighties to the early 20th century) are subjected to degradation mainly due to the "vinegar syndrome" [1,2]. This phenomenon concerns the side chain scission through ester hydrolysis induced by moisture, with the formation of hydroxyl groups and the release of acetic acid. Above a critical concentration, acetic acid induces an autocatalytic process causing the progressive degradation of the CTA support. In addition to the smell, the deformation and the embrittlement of the support and the detachment of the emulsion layer are macroscopic symptoms of the vinegar syndrome that can strictly compromise the usability of the films (Figure 1). On these bases, it is mandatory to reduce environmental moisture and remove alteration by-products from the storing environment to limit this phenomenon.
The most important novelty of this project is the set up of an innovative protocol to inhibit the vinegar syndrome, based on the use of nanomaterials of alkaline character that can constitute a sort of alkaline reserve able to stop the acetic acid production.
The main aims of the first phase of this project are to develop an accelerating aging method to stress CTA in order to artificially induce the vinegar syndrome and to set up a multi-analytical protocol to monitor the evolution of this process. Fourier Transform Infrared – Attenuated Total Reflectance (FTIR-ATR) Spectroscopy was performed on samples before and after the aging to detect the decrease of the acetyl content in a non-invasive way [3,4]. To confirm the validity of this method, titration tests [5] and gravimetric analysis were also carried out. In addition, the variation of the properties due to the artificial aging protocol was detected through Derivative Thermogravimetry (DTG) and Dynamic Mechanical Analysis (DMA).

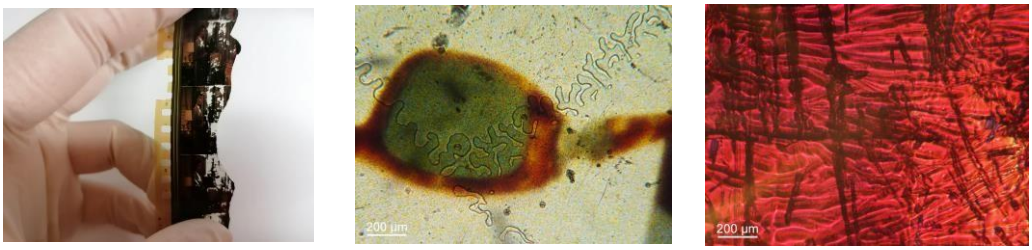

Figure 1: Optical micrographs showing the effects of the vinegar syndrome on real motion picture films made of cellulose triacetate.

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OC58

Environmental impact of microfibers (MFs) pollution and the developing of efficient and sustainable mitigation strategies

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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 recent decades, the persistence and slow environmental degradation of plastics, especially microplastics (MPs), has favoured their presence and accumulation in ecosystems [1]. In aquatic environments, the final destination of various anthropogenic pollutants, among the identified MPs, fibers are one of the most abundant types [2]. MFs are any natural or man-made fibrous material of filiform structure with a diameter of less than 50µm [3], length between 1µm and 5mm, and length-to-diameter ratio greater than 3 [4]. In the past, cellulosic fibers have often been included in the synthetic fiber count, generating increased quantitative estimates in both environmental matrices and organisms. In the initial (screening) phase, MPs and MFs from textile washings will be characterised and quantified. µ-FTIR is the technique of choice for investigation supported by fluorescence microscopy, and both are useful for the evaluation of further methods aimed at the quali-quantification of nanoplastics (NPs) and their direct impact on aquatic ecosystems and meiofauna. This phase will be followed by the study of mitigation systems aimed at reducing the release of MFs during washing and wastewater treatment. The results will make it possible to implement current filtration and washing technologies, develop environmentally friendly models, bring technological, industrial and environmental benefits in terms of safeguarding ecosystems and conduct ecotoxicity studies on meiofauna. The systems may be subject to patenting and both the activities carried out and the objectives achieved will be disseminated through scientific publications and the creation of social channels to illustrate the impacts of pollution by MFs and the good practices to be adopted to reduce the effects on ecosystems.

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Development of flexible molecular and inorganic hybrid solar cells for the design of self-powered greenhouses

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Nowadays silicon solar cells account for more than 90% of global PV energy production, however, even if high efficiencies can be obtained, their production requires big economic efforts [1]. In order to reduce fabrication costs, thin film PV technologies were developed, nevertheless, their efficiencies cannot match silicon-based solar cells, so it is necessary to find an implementation where thin-film specific properties (lightweight, flexibility, semitransparency [2]) offer clear advantages over any other technology in the market. In this framework, one of the most promising applications is the fabrication of self-powered greenhouses, which require the facility to maintain good agricultural activities and the use of non-toxic and cheap constituents, along with sustainable production approaches.

Kesterite $Cu_2ZnSn(S,Se)_4$ (CZTS) materials have earned a lot of attention in the last years, since they are based on Earth-abundant and poorly hazardous components, and show a high absorption coefficient (over 10^4 cm^{-1}), a tunable bandgap between 1.0 and 1.5 eV, and the highest efficiency (12.6%) among all emerging candidates for the fabrication of low-cost inorganic thin film PV [3]. Moreover, CZTS layers can be easily obtained from nanoparticle solution, making CZTS solar cells one of the most promising candidates for the fabrication of self-powered greenhouses. The final goal of this project is the realization of a functioning downscaled prototype hybrid PV system for greenhouse self-powering. The PV device will be based on a heterojunction architecture, blending CZTS (p-type inorganic semiconductor) with fullerene (n-type organic semiconductor), and will be fabricated in a layered structure in which the active layer, the interlayers (MnO_3 and ZnO) and the back-contact (Ag nanowires) will be sequentially deposited on a flexible polyethylene terephthalate/ fluorine-doped tin oxide (PEN/FTO) substrate (Figure 1).

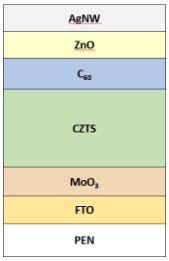

Figure 1: Scheme of the final PV device

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OC60

Gold nanoparticles coated with D-(+)-galactose as potential therapeutics for lysosomal storage disorders

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The overall aim of my PhD project is to design, synthesise and characterise nanoparticles (NPs) coated with carbohydrates (glyco-NPs) as universal and multifunctional platforms to incorporate bioactive molecules in a modular way towards the next generation of nanotherapeutics.
In these first months of my PhD work, I synthesised a carbohydrate derivative bearing a short thiol-ending linker, *i.e.* 5-mercaptopent-1-yl β-D-galactopyranoside, and I anchored it to gold nanoparticles (AuNPs) by means of a Brust and Schiffrin-like methodology in water [1]. The resulting βGal-AuNPs (Figure 1, left) were purified by dialysis against water and characterized by NMR, UV-Vis, IR, TEM and SAXS.
It has been reported that βGlc-AuNPs are multivalent inhibitors of the lysosomal enzyme *N*-acetylgalactosamine-6-sulfatase (GALNS), whose deficiency is related to the lysosomal storage disease Morquio A [2]. Thus, the aim of this work is to investigate whether the replacement of glucose with galactose at AuNPs surface influences the inhibition properties of the nanoparticles.
Regarding SAXS, in November I participated in the experimental campaign at Elettra synchrotron (Trieste) to study the βGal-AuNPs and their association with GALNS (Figure 1, right) and better understand the molecular basis of the multivalent interaction which is behind the strong inhibition found *in vitro* for GALNS by glyco-gold NPs.

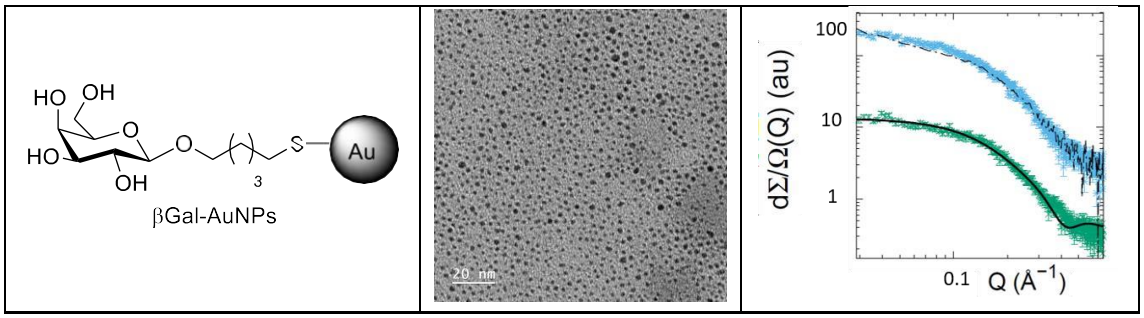

Figure 1: βGal-AuNPs (left), TEM (middle) and SAXS of these NPs in the absence (green points, bottom curve) and presence (cyan points, upper curve) of GALNS.

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OC61

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

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Introduction

The term 'emerging pollutants' (EPs) is used for chemical compounds currently not included in routine monitoring programs, but which could pose a significant risk requiring regulation, relating to their potential eco-toxicological and toxicological effects in the environment. EPs include mainly chemicals found in pharmaceuticals, industrial and household products.[1,2,3] The development of new chemical sensors able to detect these compounds at nanomolar concentration is a current challenge of environmental chemistry The purpose of his PhD work is the synthesis of new chemical sensors for EPs and characterization of their sensing/detecting ability.

Statement of purpose

PhD project aims to demonstrate the opportunity to develop fluorescence chemical sensors, targeting different model analytes chosen to be representative of different classes of emerging pollutants, in particular **antibiotics, plasticizers and perfluorinated hydrocarbons**. Fluorescent probes, composed by a binding unit and one or more fluorescent moieties can be able to signal and detect their presence in the environment at very low concentrations, making them appealing chemical sensors for these substances.

Project outline

In the earlier part of our project the main goal will be the synthesis of fluorescent conjugated chemosensors for the detection of the analytes. According to the receptor-spacer-fluorophore supramolecular-modular scheme[4], fluorescent conjugated chemosensors consist of a receptor unit and of a signalling unit, generally separated by a spacer. The interaction between the guest and the receptor unit causes some changes on the physical properties of the signalling unit, the luminescence emission in the case of fluorescent chemosensors, which can be easily monitored. The latter part of this project will concern the analysis of the emission properties of the adducts with the probe and clarification of mechanisms of signal transduction, which can potentially occur *via* electron, energy or proton transfer processes, and the analysis of the ability of the probes to detect the targets in pure water and/or in presence of interfering agents.

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OC62

Monomeric 2-hydroxyethyl methacrylate (HEMA) and acrylic acid (AA): structural influences on solute-solvent interactions and spectroscopic properties

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2-hydroxyethyl methacrylate (HEMA) and acrylic acid (AA) are widely used co-monomers for building polymeric hydrogels applied in various fields [1-3]. Because of poor literature data supporting the existence of different stable HEMA conformers in solution [4] [5], this work is focused on (i) the study of the structural and spectroscopic properties of monomers through Density Functional Theory (DFT) calculations; (ii) the investigation of the hydrogen bond interactions of solute in water by performing molecular dynamics (MD) simulations at different temperatures and with four water models (TIP3P, SPC/E, TIP3P-FB, TIP4P-FB); (iii) the comparison the spectroscopic properties of selected model to experimental UV-Vis and IR data. The main outcomes of these investigations were that: (a) the co-existence of two stable HEMA conformers was confirmed, even if switching temperature from 230 K to 360 K; (b) the solute-solvent interactions are not affected by the monomer conformation, and hydrogen bonds with water mainly involve the carbonyl and hydroxyl oxygens; (c) the first solvation shell of both HEMA and AA is characterized by hydrogen bond interaction with solvent; (d) the vibrational spectra allow to discriminate between the HEMA conformers, while no appreciable differences have been observed in UV-vis spectra. The asymmetric shape of the carbonyl stretching band observed in IR spectrum of HEMA in water has been rationalized by considering both the computed IR spectra and the dipole moments of two conformers; these results allow a differentiation and estimation of the conformers ratio, which results to be HEMA trans : cis equal to 56.5 : 43.5 at ambient conditions. Current results are the starting point to extend the investigation to more complex polymeric chains so to simulate the structure and dynamics in real hydrogels.

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

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The focus of this project is the development of sustainable hydrogels with internal structures that optimize transport in micro and nanofiltration processes, selective absorption, and anti-biofouling behavior. The study of three-dimensional transport of bacteria and molecules in the interior of highly transparent hydrogels presenting porous structures with a large variety of pore sizes and geometries, different mechanical properties, and distinct tracer-hydrogel interactions, will guide the structural optimization. Transport will be characterized by means of novel particle-tracking and optical correlation techniques. Sustainable hydrogels obtained from natural resources (polysaccharides) will be produced by designing green synthesis processes. The project is in collaboration with bioMérieux Italy, with the goal of developing hybrid hydrogels to be used in diagnostics.