



Book of Abstracts

3rd Edition of the Symposium PhD in Chemical Sciences at UniFi



23-26 January 2024

Tue the 23rd: 14:00-17:15

Wed the 24th: 09:00-16:30

Thu the 25th: 09:00-16:30

Fri the 26th: 09:30-17:00



Plesso aule "Enrica Calabresi"

Room C3

Scientific campus of Sesto F.no

Via Edoardo Detti 3, 50019 Sesto F.no (FI)



3rd Edition of the Symposium
PhD in Chemical Sciences at UniFi
PiCSU 2024

23-26 January 2024, Sesto Fiorentino (FI), Italy

BOOK OF ABSTRACTS

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Ideated and edited by:

Anna Maria Papini, Andrea Sodini, Chiara Sarti, Francesca Buco,
Leonardo Tacconi, Lorenzo Pacini, Marco Bonechi, Michael Quagliata,
Michele Casoria, Patrick Severin Sfragano, Serena Benedetta Cabigliera,
Yshtar Tecla Simonini Steiner



Organizing committee

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

Andrea **Sodini**, XXXVIII cycle

Chiara **Sarti**, XXXVII cycle

Francesca **Buco**, XXXVII cycle

Leonardo **Tacconi**, XXXVIII cycle

Lorenzo **Pacini**, XXXVII cycle

Marco **Bonechi**, XXXVII cycle

Michael **Quagliata**, XXXVII cycle

Michele **Casoria**, XXXVII cycle

Patrick Severin **Sfragano**, XXXVI cycle

Serena Benedetta **Cabigliera**, XXXVII cycle

Yshtar Tecla **Simonini Steiner**, XXXVII cycle



List of Participants

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

XXXVI cycle

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

XXXVII cycle

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



XXXVIII cycle

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

XXXIX cycle

Giulia Agnoloni
Marta Albanesi
Samuele Baldini
Alice Beni
Deborah Bonavolontà
Silvia Bracci
Luca Campagiorni
Valentina Ceccherini
Lapo Gabellini
Thomas Lulli
Amina Mumtaz
Matteo Orlandi
Valentina Pacciani
Lapo Querci
Matilde Rossi
Martina Tozzetti
Filippo Turchi
Simone Ventisette



Programme of the Symposium

Tuesday, 23/01/2024

14:00 14:45 **Opening Session** *Opening speech*

Chair: Lorenzo Pacini, Michelangelo Fichera

| | | | | |
|-------|-------|-----------------------|-------------------|--|
| 14.45 | 15.05 | OR01 | Valentina Vitali | Bioconjugation of proteins with 19F and nitroxide tags for in vitro and in cell characterization |
| 15.05 | 15.15 | OR02 | Margherita Marino | Innovative liquid chromatographic-mass spectrometric technologies to purify and identify glycosylated and glycosylated proteins in biological fluids |
| 15.15 | 15.30 | OR03 | Andrea Dali | The metalation process of coproporphyrin III by ferrochelatase from <i>Listeria monocytogenes</i> |
| 15.30 | 15.40 | OR04 | Fabio Biffoli | Sustainability in the electroplating industry: from barrier layers to new non-toxic additives |
| 15:40 | 16:10 | Coffee Break | | |
| 16.10 | 16.30 | OR05 | Kristian Vasa | Design and synthesis of molecular, macromolecular, and nano-supported bio-probes and biosensors |
| 16.30 | 16.40 | OR06 | Prem Prakash Sahu | Computation of magnetic exchange interaction on transition metal-based molecular spin Qubits using periodic DFT+U |
| 16.40 | 16.55 | OR07 | Alice Cappitti | Biopolymers: from saccharides to new high-performance materials |
| 16:55 | 17:10 | End of day one | | |

Wednesday, 24/01/2024

09.00 09.10 *Opening of day two*

Chair: Laura Sforzi, Lapo Renai, Serena Cabigliera

| | | | | |
|-------|-------|------|------------------|--|
| 09.10 | 09.30 | OR08 | Andrea Comparini | Development of aluminium alloys sustainable electroplating processes |
| 09.30 | 09.40 | OR09 | Leonardo Querci | NMR of Paramagnetic Proteins: New Routes for ¹³ C Direct Detection in Challenging Iron-Sulphur Proteins |



| | | | | |
|---|-------|--|--|---|
| 09.40 | 09.55 | OR10 | Michael Quagliata | Triazole stapled analogs of ACE2(24-42) and sequences derived from Internal Fusion Peptide (IFP) demonstrate antiviral efficacy against SARS-CoV-2 |
| 09.55 | 10.10 | OR11 | Riccardo Spena | Washing machine on a chip: design and fabrication of microfluidic devices for investigating industrial formulations |
| 10.10 | 10.20 | OR12 | Riccardo Gallorini | Valorization of residual biomasses through thermochemical conversion |
| 10.20 | 10.30 | OR13 | Pietro Tordi | A bioinspired and sustainable route for the preparation of Ag-crosslinked alginate fibers decorated with silver nanoparticles |
| 10:30 | 11:30 | Coffee Break & Poster Session | | |
| 11:30 | 13:00 | <i>Invited speakers</i> | <i>Benessere nei giovani ricercatori</i> | |
| 13:00 | 14:00 | Lunch Break | | |
| Chair: Andrea Sodini, Francesca Buco | | | | |
| 14.00 | 14.20 | OR14 | Gavino Bassu | Once upon a time motility: from active motion to bacteriostasis |
| 14.20 | 14.30 | OR15 | Sara Pavone | Synthesis of agrochemicals against canker of kiwifruit |
| 14.30 | 14.40 | OR16 | Giulia Bonaccorso | Pressurized hot water extraction coupled with liquid chromatography-tandem mass spectrometry for the automated determination of pharmaceuticals in soil samples |
| 14.40 | 14.50 | OR17 | Leonardo Tacconi | Reversible control of the magnetic anisotropy in a lanthanide molecular complex thin film |
| 14.50 | 15.05 | OR18 | Marco Bonechi | Electrochemical characterization of Polycyclic Aromatic Hydrocarbons and Metal-organic frameworks for coatings and energy applications |
| 15.05 | 15.15 | OR19 | Chiara Baroni | Structural characterization of Carbonic Anhydrase complexes with dual-target inhibitors |
| 15:15 | 15:35 | Coffee Break | | |
| 15.35 | 15.55 | OR20 | Francesca Porpora | A remediation proposal for the “vinegar syndrome” of cellulose acetate-based motion picture films |
| 15.55 | 16.10 | OR21 | Margherita Verrucchi | Electrodeposition of anti-corrosive and barrier layers by using Direct and Pulsed current |
| 16.10 | 16.25 | OR22 | Lorenzo Pacini | Green solvents on the PurePep® Chorus® taking advantage of induction heating: synthesis and HPLC-free purification of a 72mer deriving from COVID-19 Spike protein and β -amyloid(1-42) |
| 16:25 | 16:40 | End of day two | | |



Thursday, 25/01/2024

9:00 9:10 *Opening of day three*

Chair: Yshtar Tecla Simonini Steiner, Michele Casoria

| | | | | |
|-------|-------|------|--------------------------|--|
| 09.10 | 09.30 | OR23 | Patrick Severin Sfragano | An electrochemical magneto-assay: from a manual to an automatable microfluidic approach |
| 09.30 | 09.45 | OR24 | Lucrezia Cosottini | Ferritin-Au(I) bioconjugates as anticancer agents |
| 09.45 | 09.55 | OR25 | Andrea Sodini | Glycolipids synthesis and formulation in biocompatible nanovesicles |
| 09.55 | 10.10 | OR26 | Sara Aquilia | Protein-Based Biopolymer Material from Rapeseed Meal: Extraction, Modification, and Peptidomic Characterization for Environmental Sustainability |
| 10.10 | 10.20 | OR27 | Laura Conti | Design and characterization of lipid nanoparticles for RNA encapsulation and targeted delivery |
| 10.20 | 10.30 | OR28 | Chiara Mangini | An easily customizable glyconanomaterial with biomolecular recognition properties |

10:30 11:30

Coffee Break & Poster Session

| | | | | |
|-------|-------|------|------------------|--|
| 11.30 | 11.50 | OR29 | Davide Ranieri | Development of Porphyrin based two-Qubits Quantum Logic Gates |
| 11.50 | 12.00 | OR30 | Francesca Milano | Multivalent iminoglyco-NPs for theranostic applications |
| 12.00 | 12.15 | OR31 | Chiara Sarti | Challenges and technological approaches for tackling emerging microcontaminants in wastewater |
| 12.15 | 12.25 | OR32 | Ilaria Chiarugi | Development and optimization of nanocarriers for the delivery of Si-RNA |
| 12.25 | 12.35 | OR33 | Neri Fuochi | Bridging Smart Materials and Sensing Platforms: Advancements in Liquid Crystalline Elastomers and PDMS Microfluidic Supports |
| 12.35 | 12.50 | OR34 | Francesca Buco | Multivalent iminosugars as enhancers of the lysosomal enzyme GCCase activity |
| 12.50 | 13.00 | OR35 | Elena Mariani | Electrodeposition with modulated currents in optics of a Circular Economy |

13:00 14:00

Lunch Break

Chair: Chiara Sarti, Prem Prakash Sahu

| | | | | |
|-------|-------|------|--------------|---|
| 14.00 | 14.20 | OR36 | Michela Lupi | Thia-Bridged Heterohelicenes: synthesis, resolution, and applications |
|-------|-------|------|--------------|---|



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|-------|-------|------|-------------------|---|
| 14.20 | 14.35 | OR37 | Mert Acar | Unusual Behavior of Responsive Peptide Gels |
| 14.35 | 14.45 | OR38 | Andrea Geri | Mechanistic studies on antitumor gold compounds |
| 14.45 | 15.00 | OR39 | Laura Vespignani | Study of new materials with low environmental impact and their use in the protection of wooden artifacts |
| 15.00 | 15.15 | OR40 | Alessandro Veneri | New synthetic pathway to Kesterite nanoparticles with different tin content: an in-depth study of magnetic and optical properties |
| 15:15 | 15:35 | | | Coffee Break |
| 15.35 | 15.45 | OR41 | Laura Sforzi | Evidence of microplastics (MPs) in ground- and well- waters: from sampling to analysis |
| 15.45 | 16.00 | OR42 | Daniela Porcu | Bronze disease: synthesis and electrochemical characterization of a new recycled polystyrene-based coating |
| 16.00 | 16.15 | OR43 | Alessandro Gerace | Hard/soft magnetic nanocomposites for high energy product permanent magnet |
| 16:15 | 16:30 | | | End of day three |

Friday, 26/01/2024

09.30 09.40 *Opening of day four*

Chair: Patrick S. Sfragano, Andrea Dali

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|-------|-------|------|--------------------------|---|
| 09.40 | 10.00 | OR44 | Saul Santini | Advancing analytical methods for a comprehensive evaluation of emerging and legacy contaminants and their implications on human health following exposure |
| 10.00 | 10.10 | OR45 | Benedetta Ciuffi | Study of enzymatic recycling of end-of-life polymers |
| 10.10 | 10.25 | OR46 | Fernando Soto Bustamante | Mechanical Rupture of Polyethylene Glycol, Gelatin, Alginate Micro-capsules |
| 10.25 | 10.35 | OR47 | Angela Sofia Tino | NMR-based investigation of intrinsically disordered regions of modular proteins for tailored design of peptides |
| 10.35 | 10.50 | OR48 | Lorenzo Bracaglia | Characterization of structurally heterogeneous proteins with NMR |
| 10.50 | 11.00 | OR49 | Ilaria De Santis | Plasmonic properties of gold nanoparticles interacting with synthetic lipid bilayers |
| 11:00 | 11:30 | | | Coffee Break |
| 11.30 | 11.50 | OR50 | Lorenzo Baldini | Different auxiliary-promoted C(sp ³)-H bond activations on a challenging substrate, the trans-2-aminocyclopentanecarboxylic acid (ACPC) |



| | | | | |
|---|--|---------------------------------------|-------------------------------|---|
| 11.50 | 12.00 | OR51 | Mariano Riccardi | Adsorption of molecular magnets on metal surfaces |
| 12.00 | 12.15 | OR52 | Serena Cabigliera | Microbial Synergy: Exploring Bioremediation and Microplastic Dynamics in Environmental Resilience |
| 12.15 | 12.25 | OR53 | Pietro Gentilesca | Development of materials for the selective coordination of critical elements present in produced waters |
| 12.25 | 12.40 | OR54 | Michele Casoria | A Comprehensive Statistical Analysis of the Structural Properties Exhibited by Glycoproteins |
| 12.40 | 12.50 | OR55 | Chiara Cianci | Preliminary studies on the formulation of nanostructured composites for the consolidation and protection of Street Art |
| 12.50 | 13.00 | OR56 | Giulio Pappaianni | Electrodeposition and modification of surfaces of technological interest with low environmental impact |
| 13.00 | 14.00 | Lunch Break | | |
| <i>Chair: Leonardo Tacconi, Lapo Querci</i> | | | | |
| 14.00 | 14.20 | OR57 | Simi M.E. Mangani | Archaeometric study of Montelupo Maiolica |
| 14.20 | 14.30 | OR58 | Ilaria Antonia Vitale | Miniaturized Electrochemical Sensor For Dopamine Detection in Biological Fluids |
| 14.30 | 14.45 | OR59 | Yshtar Tecla Simonini Steiner | “Recognition of emerging pollutants (EPs) with artificial fluorescence chemical sensors: a supramolecular approach” |
| 14.45 | 14.55 | OR60 | Francesca Mancusi | Modified crystalline nanocellulose for the production of hybrid materials for biomedical applications |
| 14.55 | 15.10 | OR61 | Michelangelo Fichera | Sewage sludge-derived biochar for the adsorptive removal of antibiotics in wastewater |
| 15.10 | 15.20 | OR62 | Stefano Zineddu | Metal-based Antimicrobials to fight Antibiotic Resistance |
| 15:20 | 15:40 | Coffee Break | | |
| 15.40 | 15.55 | OR63 | Sara Calandra | Optimization of the sample selection procedure of historical mortars for radiocarbon dating |
| 15.55 | 16.05 | OR64 | Lorenzo Quadrini | Development of immersion and/or runoff measurement techniques for determining the concentration of Urea in water and organic liquids. |
| 16.05 | 17.00 | <i>Closing Session</i> | | |
| 16.05 | 17.00 | PhD Coordinator, Organizing Committee | | |
| 19.00 | Social event at <i>Cartabianca Cafè</i> in Firenze Rifredi Via Panciatichi 49 - 50127 Firenze (FI) | | | |



PhD in Chemical Sciences at UniFi

PiCSU 2024

Abstracts of the Oral Presentations



OR01

Bioconjugation of proteins with ^{19}F and nitroxide tags for in vitro and in cell characterization

Valentina Vitali and Lucia Banci

Department of Chemistry "Ugo Schiff", University of Florence, via della Lastruccia 3, 50019 Sesto Fiorentino, Italy
Magnetic Resonance Center (CERM), University of Florence, via Luigi Sacconi 6, 50019 Sesto Fiorentino, Italy
E-mail: valentina.vitali@unifi.it

Proteins are complex biomacromolecules that are at the basis of all physiological processes, such as respiration, metabolism, immunity, and signaling. To better understand their function, it is essential to elucidate their structures, dynamics, and interactions. Structural biology techniques, such as X-ray crystallography, Nuclear Magnetic Resonance (NMR) spectroscopy, cryo-electron microscopy (cryo-EM), Förster resonance energy transfer (FRET) and Electron Paramagnetic Resonance (EPR) are essential for this task. However, to effectively utilize some of these techniques, bioconjugation with small external molecules - often referred to as tags or probes - at specific sites is essential for the functionality of the technique itself. In this work, we explored the application of various tag topologies, from ^{19}F moieties to nitroxide spin labels. The former were investigated to explore novel alternatives for post-expression covalent modification of tyrosine residues [1], providing valuable approaches for preparing ^{19}F NMR samples. On the other hand, we compared four different nitroxide spin probes bound to cysteine residues to assess their different behaviour while attached on two different secondary structural elements (α -helix and the β -sheet) [2]. At the same time, we employed a Cu(II) chelate complex, attached to a double histidine motif. Retrieving the distances between the Cu(II)-nitroxide orthogonal spin labels, using pulse EPR techniques, while alternating both label types between the α -helix and the β -sheet allowed us to analyze in depth the nitroxides features. Lastly, one of the aforementioned nitroxide spin labels was also utilized for in-cell studies on both *Escherichia coli* and *Pichia pastoris*. We employed different combinations of deuterated protein and deuterated cells to assess the influence of deuteration on the transverse relaxation time T_2 .

[1] P. Szijj et al., *Org Biomol Chem*, **2020**, 18, 9018-9028.

[2] F. Torricella et al., *Biochim Biophys Acta Proteins Proteom*, **2021**, 1869, 140653.



OR02

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

Margherita Marino^a, Paolo Rovero^a, Hendrik Rusche^b, Michael Chorev^c,
and Anna Maria Papini^a

^a *Interdepartmental Research Unit of Peptide & Protein Chemistry & Biology, Departments of Chemistry "Ugo Schiff" and NeuroFarba, University of Florence, 50019-Sesto F.no, Italy*

^b *Fischer Analytics GmbH, Saarlandstrasse 377, 55411-Bingen, Germany*

^c *Mellitus, LLC. CIC Boston (USA), Professor Emeritus at the Hebrew University of Jerusalem(IL)*

E-mail: margherita.marino@unifi.it

Cancer is among the leading causes of death worldwide. It is important to understand that every cancer type and every tumor is unique and finding the right treatment for every patient is extremely challenging but crucial for positive outcomes [1]. Nowadays the researches of new chemotherapeutic agents are focused on two major aspects: selectivity and cytotoxicity. Most of these new treatments are focused on the concept of the "magic bullet" introduced by a German scientist Paul Ehrlich in the early 1900s, and currently the antibody-drug conjugates are the ones with better performance in targeting tumor cells with high precision and specificity [2].

The focus of this PhD project isn't the design of a new ADC but the optimization of a purification and characterization system. The liquid chromatography coupled to mass spectrometry is one of the most promising and advanced techniques generally used to identify and characterize small molecules, proteins and peptide in simple and complex biological matrix such as plasma, sera and urines. The power of LC-MS is in the possibility of combining the best qualities in separation of the liquid chromatography and the power of the ionization of mass systems for the recognition. Nowadays this technology is widely used in pharmaceutical and food industry as it is easy to find in literature. For these reasons this project is involved in development new optimized methodology to identify and purify not only ADCs but also bioactive peptides and proteins in autoimmune diseases. In particular the main focus is on the identification of aberrant glycated peptides in sera of patients affected by diabetes. The plan is to take advantage of the affinity of phenylboronate with cis-diols, fish out from complex matrix glycated peptides by performing an affinity chromatography and later identify them through high resolution LC-MS analysis [3]. The innovative technique proposed is a 3D LC-MS/MS technology. Our technology will have the impact not only to save time and materials but also to reach the most important goal of sustainability of the process in agreement with PNRR goals.

[1] W. Mier et al., *Drug Discovery Today*. **2022**, 27.

[2] R.C. Bates et al., *J. Natl. Cancer Inst.* **2019**, 111.

[3] A.M. Papini et al., *Molecules*. **2020**, 25, 755.



OR03

The metalation process of coproporphyrin III by ferrochelatase from *Listeria monocytogenes*.

Andrea Dali ^a, Federico Sebastiani ^a, Thomas Gabler ^b, Paul G. Furtmüller ^b,
Maurizio Becucci ^a, Stefan Hofbauer ^b, and Giulietta Smulevich ^a

^a Department of Chemistry “Ugo Schiff” (DICUS), University of Florence, Via della Lastruccia 3,
50019 Sesto Fiorentino, Italy

^b Department of Chemistry – Institute of Biochemistry, University of Natural Resources and Life
Sciences, Gregor-Mendel-Strasse 33, 1180 Wien, Austria

E-mail: andrea.dali@unifi.it

Unlike humans, monoderm Gram-positive bacteria use the coproporphyrin-dependent heme biosynthesis pathway (CPD) to produce heme *b* [1], an iron porphyrin essential to pathogens for surviving and infecting the host. In the penultimate step of CPD, the coproporphyrin ferrochelatase (CpfC) catalyses the insertion and oxidation of Fe²⁺ into the coproporphyrin III (cpIII), producing ferric coproporphyrin III (coproheme). The latter is eventually decarboxylated by the coproheme decarboxylase to form heme *b* through a two-step decarboxylation of the propionate groups at positions 2 and 4 forming vinyl groups. In CpfC from *Listeria monocytogenes* (*Lm*), both the porphyrin substrate (cpIII) and product (coproheme) are stabilized by several H-bond interactions of different strength, between the four propionate groups and the polar amino acids of the protein active site [2].

By following, in solution and under anaerobic conditions, the *in vitro* insertion of Fe²⁺ into cpIII by wild-type *LmCpfC* using UV-vis electronic absorption and resonance Raman spectroscopies, we proved that upon metalation of the native substrate, a stable and saddled-distorted catalytic intermediate is formed. The distortion is a consequence of the reorganization of the H-bonds interaction between the propionate groups and the protein matrix [3]. Therefore, the active site's environment controls the orientation and distortion of the porphyrin before and during metalation.

Moreover, preliminary data on the role of the His182 and Glu263 distal residues in the metalation process showed that, unlike what was suggested in the literature, these residues are not fundamental for iron insertion. Instead, Glu263 is involved in the iron oxidation of the product.

[1] H.A. Dailey et al., *Proc. Natl. Acad. Sci USA*, **2015**, 112, 2210-2215.

[2] A. Dali et al., *Protein Sci.*, **2023**, 32, e4534.

[3] T. Gabler et al., *Protein Sci.*, **2023**, 32, e4788.



OR04

Sustainability in the electroplating industry: from barrier layers to new non-toxic additives

Fabio Biffoli^{a,b}, Manuel Salvi^b, Marco Pagliai^a, and Massimo Innocenti^a

^a DICUS, University of Florence, Via della Lastruccia, 3, 50019 Sesto Fiorentino (FI), Italy

^b Materia Firenze Lab s.r.l., Gruppo Materia Firenze, Via delle Fonti 8/E, 50018 Scandicci (FI), Italy

E-mail: fabio.biffoli@unifi.it

The sustainability of an electroplating facility specialized in High Fashion is a wide and horizontal topic: from the social sustainability involving better conditions to employee to environmental sustainability reducing pollutants in wastewater. Two of the most important topics, from a chemist point of view, are the reduction of usage of strategic and/or toxic metals and the development of new non-toxic alternatives to state-of-the-art organic additives. Strategic metals such as Nickel and Palladium are often employed as barrier layers to stop Copper intermetallic diffusion into Gold matrices, little is known on the effectiveness of barrier layers especially at room temperature, and a standardized protocol to optimize them or test novel solutions is still lacking. Furthermore, to reduce the usage of Pd and substitute Ni in Ni-free cycles anticorrosion layers based on Tin-Oxide layers are employed as barrier layers too. A novel methodology [1] based on Energy Dispersive Spectroscopy and X-Ray Fluorescence was developed and tested to determine the diffusion coefficient (D) and later a routine involving it in conjunction with Atomic Force Microscopy and X-Ray Diffractometry (XRD) was proposed to test barrier layers. On the other hand, to fully replace Ni electroplating, Acid Copper (AC) baths are necessary to provide the good amount of shine and levelling of the deposit [2]. Commercial AC baths are formulated with a set of three organic additives (suppressor, brightener, and leveler) that are needed to obtain shiny and adherent deposits. Some of the most common additives in AC baths are PEG as suppressor, and thiourea (TU) as brightener. Despite the widespread use of those molecules in industrial processes, their mechanism of action during the deposition is not clear yet and theoretical studies are lacking. An in-depth understanding of this topic is essential to achieve the environmental sustainability goals of reducing organics in wastewater and replacing toxic additives like TU with eco-friendly alternatives such as cysteine (Cys). This work aims to characterize the whole electrodeposition process with a combined experimental-theoretical methodology. The effects on Cu morphology and crystalline structure of additives were investigated by SEM and XRD. Then, Classical Molecular Dynamics simulations (supported by ab-initio calculations, Raman and X-Ray Photoelectron Spectroscopy and electrochemical studies) were carried out to unveil the deposition mechanism.

[1] W. Giurlani et al., *Anal. Chim. Acta* **2023**, 1269, 341428.

[2] M. Vorobyova et al., *Materials (Basel)* **2023**, 16, 4919.



OR05

Design and synthesis of molecular, macromolecular, and nano-supported bio-probes and biosensors

Kristian Vasa, Stefano Menichetti, and Caterina Viglianisi

*Department of Chemistry 'Ugo Schiff', University of Florence, Via Della Lastruccia 3-13, 50019 Sesto Fiorentino, Italy
E-mail: kristian.vasa@unifi.it*

During the three years of the PhD, I was involved in different projects and collaborations with the common aim to design and synthesize bio-probes or biosensors. Precisely during the first year I worked on the synthesis of a polymer-based bio-probe where bovine carbonic anhydrase was immobilized over polypropylene to get a more stable enzyme and to exploit its industrial applications for carbon capture and utilization [1]. Carbonic anhydrase (CA) is a metalloenzyme ubiquitous in Nature. In fact, it is one of the most active enzymes with a turnover number up to 10^6 s^{-1} . Because its high activity, CA shows significant improvements in CO_2 absorption rate as this enzyme catalyzes the rate limiting step that is CO_2 hydration. Enzymes are highly unstable if used pure, immobilization improves enzyme recovery, stability, and reusability, decreasing enzyme overall cost. The second year I worked on the synthesis of chemical linkers either cleavable and/or non-cleavable. Then the linkers were functionalized with different cytotoxic molecules and carriers to obtain conjugates to be used as bio-probes for targeted drug delivery in tumor therapy [2]. To achieve a better selectivity of the cytotoxic agent for the tumor cells, two different linkers were designed and synthesized. The dipeptide VA was introduced in the linker structure being specifically hydrolyzed from cathepsin B; an enzyme overexpressed in many types of tumors. Monomethyl Auristatin E and paclitaxel were used as a chemotherapeutic agent. MMA-E and paclitaxel both can inhibit tubulin polymerization which causes cell apoptosis. Linkers have as a payload MMA-E or paclitaxel and, as carriers, has been used a NT-4 peptide or tafamidis. During the third year of the PhD the work was devoted to the synthesis of a receptor which was then inserted in QCM device to build a sensor capable of detecting nM quantities of FKBP12 protein. FKBP12 is a precursor protein formed during the first stages of disease such as Alzheimer and Parkinson and thus the development of a cheap sensor can be very useful for a point of care diagnosis of such disease.[3] FKBP12 assists as a chaperone the folding and isomerization of various proteins containing proline residues, is therefore involved in numerous metabolic pathways and in many physiological processes such as the folding of nascent polypeptide chains, protein transport. Meanwhile I also exploited semi-synthetic vitamin E derivatives as bio-probes and the data obtained are suitable for a patent application and thus weren't discussed in detail.

[1] R.E. Maria et al., *Appl. Microbiol. Biotechnol.* **2022**, *106*, 3419-3430.

[2] J. Brunetti et al., *Molecules*, **2020**, *25*, 1088.

[3] M.R. Maria et al., *J. Med. Chem.* **2013**, *56*, 1041-1051.

OR06

Computation of magnetic exchange interaction on transition metal-based molecular spin Qubits using periodic DFT+U

Prem Prakash Sahu, Fabio Santanni, Matteo Briganti, Roberta Sessoli,
and Federico Totti

Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia 3, 50019
Sesto Fiorentino, Italy

E-mail: premprakash.sahu@unifi.it

Over the past decade, transition metal complexes have become increasingly popular candidates for electron spin-based quantum bits (qubits) due to their synthetic tunability and long achievable coherence times. To thrive in quantum technologies such as computing, sensing, and communication, overcoming decoherence challenges and obtaining multi-qubit architectures suitable as quantum logical gates is pivotal. Recent research on molecular materials for quantum information processing unveiled two promising candidates, demonstrating prowess in encoding single-qubit and multi-qubit logical operations through EPR and magnetic measurements, driven by distinctive magnetic exchange interactions: (i) a sulfur-rich $[\text{Cu}(\text{dttt})_2]$ system, [(dttt) $^-$ = 1,3,2-dithiazole-4-thione-5-thiolate] exhibiting van der Waals-mediated strong antiferromagnetic exchange interactions, reaching an impressive value of 108 cm^{-1} [1] and (ii) a ferromagnetic exchange coupling of $J = -8 \times 10^{-3} \text{ cm}^{-1}$ was observed in a heteronuclear $\text{V}^{\text{IV}}\text{O}-\text{Cu}^{\text{II}}$ porphyrin-based complex $[\text{VOCu}(\text{TrPP})_2]$ (TrPP $^-$ = triphenyl porphyrinate) respectively [2]. In this work, we enhance the previously reported DFT gas-phase calculations by incorporating essential periodic boundary conditions for comprehensive intermolecular and packing interactions. We aim for accurate determination of the J value by correcting the intrinsic delocalization in the DFT by incorporating the Hubbard correction (DFT + U) computed through Linear Response Theory in the Quantum ESPRESSO software package. To closely align with experimental J values, our robust DFT+U computational technique overcomes the empirical U value derivation and the dimer approximations for the exchange parameters. Finally, we will explore how and if the J values vary as the scenario evolves from the bulk to hybrid systems (upon surface deposition).

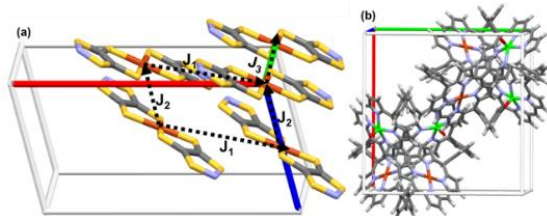


Figure 1: (a) Potential magnetic exchange pathways of relevance in $[\text{Cu}(\text{dttt})_2]$ system; (b) Primitive cell of the bulk $[\text{VOCu}(\text{TrPP})_2]$ system.

[1] F. Santanni et al., *JACS Au*, **2023**, 3, 1250-1262 .

[2] D. Ranieri et al., *Angew. Chem., Int. Ed.* **2023**, e202312936.

Biopolymers: from saccharides to new high-performance materials

Alice Cappitti, Camilla Parmeggiani, Marco Frediani, and Antonella Salvini

Department of Chemistry "Ugo Schiff" University of Florence, Via della Lastruccia 3-13, 50019 Sesto Fiorentino (Italy)

The exploitation of renewable materials coming from biomass is an interesting strategy to obtain new polymer formulations through the design of biomonomers and biopolymers. In particular, biopolymers obtained from saccharide sources with structures containing polar and reactive groups can influence both the properties of the final products and the sustainability and ease of recycling. These characteristics represent a fundamental step in eco-design strategies for different fields of manufacturing industry.

This work starts from the results obtained with allyl α,α' -trehalose¹, a biomonomer synthesized through sugar functionalization. Vinyl copolymers previously obtained with this biomonomer had shown interesting properties as consolidants for cultural heritage but had a low molecular weight² for applications in other production fields. In order to increase the reactivity of allyl monomer for industrial applications, new copolymers and terpolymers were synthesized using acrylic comonomers, as ethyl methacrylate, even in low amount and the presence of vinyl acetate as the prevalent comonomer. The synthetic methodology has been performed in accordance with the requirements of low environmental impact, green chemistry and industrial sustainability.

All the materials obtained were analyzed by SEC, for the determination of the molecular weight, FT-IR and NMR spectroscopy, for the evaluation of the molar ratio between the various monomeric components. Finally, DSC analysis was used to evaluate the thermal characteristics. Furthermore, to evaluate the role of biomonomers containing free hydroxyl groups in cross-linking phenomena, expected in high-performance formulations, a specific protocol has been developed and preliminary reactivity tests were carried out.

Based on the results, these biopolymers show particular interest for the preparation of new adhesives and other polymer formulations which represents a fundamental step in eco-design strategies.

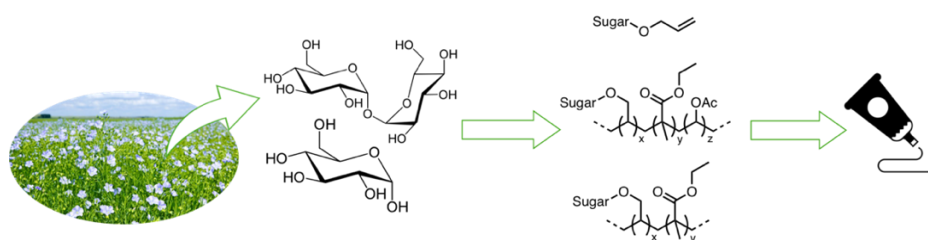


Figure 1: Development of new biopolymers from biomass valorization.

[1] A. Papacchini et al., *Royal Soc Open Sci.* **2018**, *5*, 171313

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

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OR08

Development of aluminium alloys sustainable electroplating processes

Andrea Comparini^{a,b}, Ivan Del Pace^a, Roberta Emanuele^a, Walter Giurlani^b,
Marco Bonechi^b, Margherita Verrucchi^b, and Massimo Innocenti^b

^a Valmet Plating Srl, Via Erbosa 5, 50041 Calenzano (FI), Italy

^b Dipartimento di Chimica, Università Degli Studi di Firenze, Via della Lastruccia 3, 50019 Sesto Fiorentino (FI), Italy.

E-mail: andrea.comparini@valmet.it

Recently, major fashion market players are aiming to introducing sustainable materials within their value chain. Among a vast variety of metals and materials in general, aluminum alloys, besides being unlimitedly recyclable, are also interesting because of their technical characteristics (as in being light), their market prices and their large availability [1]. Accordingly, aluminium alloys are promising feedstock for the fashion-jewelry but their tendency to form a passivating film makes it difficult to be galvanized, even more when impurities of refractory elements are present. Effective electroplating cycles do exist when it comes to aluminium-based materials and are nowadays being employed within the fashion-industry value chain. Despite that, the galvanic baths being employed contains cyanides and other toxic nickel compounds. The objective of the present study was to develop a cyanide and nickel-free galvanic cycle able to electroplate aluminium-based materials. In particular, in this work we focused on the pre-treatments and electroplating of Al6082, which is largely available in the market. The very first step of the three-year PhD was to set-up a pre-treatment cycle in order to remove undesired elements like silicon and compounds like alumina from the aluminium alloy's surface [2,3]. Afterwards, cyanide and nickel-free zincate step and alkaline copper were developed in order to substitute old-fashioned, toxic yet effective processes. After a whole electroplating cycle performed onto aluminium items, adhesion between the deposited layers was evaluated both with cross-sectional SEM analysis as well as with an adhesion evaluation test (ISO2819:2018). Furthermore, 24 h "synthetic sweat", 48 h "salt spray" and 96 h "dump heat with leather" which are -within the fashion market- the most used aging tests, were employed to evaluate the quality of the final products. Positive test outcomes highlighted that Al6082 can be galvanized with a green electroplating cycle and thereby can be used as sustainable base material in the fashion-jewelry market.

[1] L. Xu et al., *Energies*. **2021**, *14*, 1560 2021.

[2] J. Burgess et al., *Transactions of the IMF*. **2019**, *97*, 285–288.

[3] P. Ashtari et al., *Int. J. Cast Met. Res.* **2012**, *25*, 100–102.

OR09

NMR of Paramagnetic Proteins: New Routes for ^{13}C Direct Detection in Challenging Iron-Sulphur Proteins

Leonardo Querci^b, Ines B. Trindade^a, Deborah Grifagni^b, José Malanho Silva^b,
Francesca Cantini^b, Ricardo O. Louro^a, and Mario Piccioli^b

^a Instituto de Tecnologia Química e Biológica António Xavier (ITQB-NOVA), Universidade Nova de Lisboa, Av. da República (EAN), 2780-157 Oeiras, Portugal; E-mail: louro@itqb.unl.pt; phone: +351214469332

^b Magnetic Resonance Center and Department of Chemistry, University of Florence, Via L. Sacconi 6 50019 Sesto Fiorentino, Italy; E-mail: piccioli@cerm.unifi.it; phone: + 39 055 4574188
E-mail: leonardo.querci@unifi.it

For Iron-Sulfur Proteins, the robustness of NMR coherence transfer in proximity of the cluster depends on the relaxation properties of the nuclei involved, therefore recording the same experiment with different pulse schemes or different parameter sets provides often complementary results. The integrative effect of ^1H start and ^{13}C start CACO experiments will be discussed in practice attending a non-canonical sequence-specific assignment of revived Cisd3¹ $\text{C}^\alpha/\text{C}'$ correlations in the spectra². Additionally, in paramagnetic metalloproteins, longitudinal relaxation rates of $^{13}\text{C}'$ and $^{13}\text{C}^\alpha$ nuclei can be measured using ^{13}C detected experiments and converted into electron spin-nuclear spin distance restraints (Figure 1), also known as Paramagnetic Relaxation Enhancements Restraints (PRE). We will discuss the complementarity of ^{13}C PRE restraints with ^1H PRE restraints in the case of the High Potential Iron Sulfur Protein (HiPIP) PioC³ and how ^{13}C R_1 values can be measured also at very short distances from the paramagnetic center. The obtained set of ^{13}C based restraints can be added to ^1H PREs and to other classical and paramagnetism based NMR restraints.

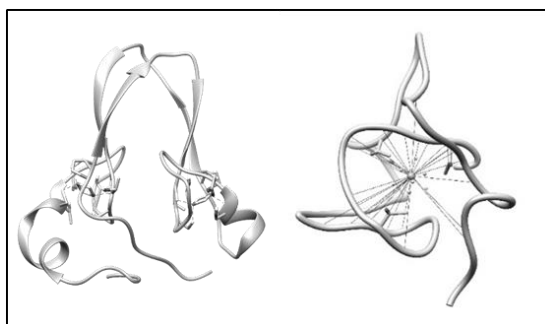


Figure 1: 3D structure of Cisd3 (right) and PioC (left). Lines in PioC structure represent $\text{C}'/\text{C}^\alpha$ -to-metal distances calculated from longitudinal relaxation rates, R_1

[1] L. Querci et al., *J Biomol NMR*. **2023**.

[2] D. Grifagni et al., *JBC* (Submitted).

[3] L. Querci et al., *Magnetochemistry*. **2023**, 9(3), 66.



OR10

Triazole stapled analogs of ACE2(24-42) and sequences derived from Internal Fusion Peptide (IFP) demonstrate antiviral efficacy against SARS-CoV-2

Michael Quagliata^a, Maria Alfreda Stincarelli^b, Andrea Di Santo^c, Lorenzo Pacini^a, Feliciano Real Fernandez^d, Rosaria Arvia^b, Silvia Rinaldi^d, Simone Giannecchini^b, Paolo Rovero^c, and Anna Maria Papini^a

^a Department of Chemistry "Ugo Schiff", University of Florence, Sesto Fiorentino 50019, Italy

^b Department of Experimental and Clinical Medicine, University of Florence, Viale Morgagni 48, Florence 50134, Italy

^c Department of NeuroFarBa, University of Florence, Sesto Fiorentino 50019, Italy

^d CNR - Istituto di Chimica dei Composti Organometallici (CNR-ICCOM), Via Madonna del Piano 10, Sesto Fiorentino I-50019, Italy
E-mail: michael.quagliata@unifi.it

Despite the availability of vaccines, COVID-19 continues to be aggressive, especially in immunocompromised individuals. Therefore, the development of a specific therapeutic agent with antiviral activity against SARS-CoV-2 is necessary. The mechanism of SARS-CoV-2 entry into cells is complex, being based on molecular events that can be targeted to block cell infection, whose key player is the viral spike glycoprotein, located on the surface of the viral membrane envelop. The infection pathway starts when the receptor binding domain (RBD) of the viral spike protein interacts with the angiotensin converting enzyme 2 (ACE2), which acts as a host receptor for the RBD expressed on the host cell surface. In particular, the key residue for this interaction are located in the helix $\alpha 1$, namely ACE2(24-42). In order to stabilize the important secondary structure, we synthesised different triazolyl bridged ACE2(24-42) analogs exploiting the copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC). The analog bearing the triazole-containing bridge in the positions 36-40, showed promising antiviral activity at micromolar concentrations assessed by plaque reduction assay. On the other hand, the double-stapled analog lost the activity, showing that excessive rigidity disfavours the interaction with the RBD [1,2]. Another fundamental step concerning SARS-CoV-2 cell entry is membrane fusion. In this scenario a key role is played by the interaction between the Internal Fusion Peptide (IFP) and the Membrane Proximity External Region (MPER) located in the S2 subunit of Spike. The peptide Spike (888-906), contained in the IFP sequence, is shown to have a significant antiviral activity *in vitro* (IC_{50} : $0.20 \pm 1.11 \mu M$). Surface Plasmon Resonance (SPR) demonstrated a high affinity of this peptide to the MPER fragment (K_d = 9.44 nM). Finally, Ala-scan revealed the key role of the aromatic residues in antiviral activity [3].

[1] Quagliata M, et al. *ACS Omega*, **2023**, 8, 25, 22665–22672.

[2] Quagliata M, et al. *J Pept Sci*. **2023**, e3541.

[3] Stincarelli M.A, et al. *Virus Research*, **2023**, 334, 199170.

OR11

Washing machine on a chip: design and fabrication of microfluidic devices for investigating industrial formulations

Riccardo Spena^a, Pierre Joseph^b, and Costanza Montis^a

^a Department of Chemistry “Ugo Schiff” (DICUS), University of Florence, via della Lastruccia 13, 50019 Sesto Fiorentino (FI), Italy

^b LAAS-CNRS: Laboratory, Laboratory for Analysis and Architecture of Systems, 7 Av. Du colonel Roche, 31400 Toulouse, France

E-mail: riccardo.spena@unifi.it

Encapsulation is a key strategy for efficient delivery in various nanotechnological applications, including nanomedicine and fabric care products. Fabric care items, in particular, use capsules to encase active ingredients, ensuring their adherence to fabric fibers. Current industrial methods to assess capsule efficiency in fabric care products rely on washing machine tests. However, these tests involve substantial water, chemical, and energy consumption, offering limited insights into the capsules' specific interaction with fabric fibers.

The aim of this work is to develop alternative methods to evaluate capsules efficiency, based on micro- and millifluidics, reducing the environmental impact and providing in-depth information on capsules-fabrics interactions. Micro- and milli-fluidic based systems have been designed as “washing machine on a chip” to investigate qualitatively and quantitatively different aspects of the behavior of capsules at different time scales. Specifically, two main microfluidic devices [Fig.1 a,b] have been designed and built-up, to directly investigate the interactions with different fabrics, by integrating an entire piece of fabrics in the chip. Three prototypical capsules formulations (differing in terms of size or chemical composition) were investigated challenging two different prototypical fabrics type (flat cotton or polyester).

Qualitative and quantitative informations were achieved through live imaging of the fluorescently-labeled capsules adhering to the fabrics fibers and via image analysis. First results [Fig.1 c] indicate the ability of the developed devices to discriminate the interaction of a single type of capsule with different fabrics, in line with off-chip efficiency tests. Altogether, the results highlight the developed washing-machine-on-a-chip as a promising, eco-friendly, efficient and versatile alternative to conventional washing machine tests.

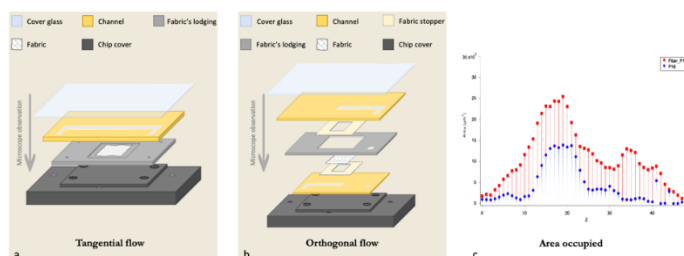


Figure 1: Microfluidic chip design, a) tangential design, b) orthogonal design, c) total area occupied by the particles vs the one occupied by the fibers, after the image analysis.



OR12

Valorization of residual biomasses through thermochemical conversion

Riccardo Gallorini^a, Luca Rosi^a, Anna Maria Papini^{a,b},
and Anna Maria Raspolli Galletti^c

^a Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia 13, I-50019 Sesto Fiorentino, Italy.

^b Interdepartmental Research Unit of Peptide and Protein Chemistry and Biology, University of Florence, Via della Lastruccia 13, I-50019 Sesto Fiorentino, Italy

^c I Department of Chemistry and Industrial Chemistry, University of Pisa, Via G. Moruzzi 13, 56124 Pisa, Italy

E-mail: riccardo.gallorini@unifi.it

The pressing environmental concerns related to fossil fuel consumption and the growing global demand for energy, chemicals and materials greatly encourage the development of technologies to replace oil with renewable carbon sources [1]. In this context, lignocellulosic biomass (i.e., plant-derived feedstock, particularly from non-edible sources) stands out as a promising alternative carbon source due to its high availability and versatility. Residual biomass not competing with the food industry has been converted, in accordance with the RED II Directive, which sets a target for 2030 to produce 3.5 percent of energy consumed in the transportation sector from advanced biofuels. [2]. Two different types of biomasses as feedstock were processed: a waste biomass from the agri-food industry (spent rapeseed meal) and a biomass that is naturally accumulated (Posidonia balls). The work was focused on studying the performance of different waste biomasses during the pyrolysis reaction. Pyrolysis was carried out employing a multi-mode microwave oven, placing the microwave absorbent outside the reaction flask and varying the operating parameters (MW power, temperature, time, heating rate) to identify the optimal conditions [3]. Characterization of the collected liquid fractions revealed various chemical compositions related to the use of different feedstocks. The collected bio-oils are rich in value-added chemicals, such as aromatic hydrocarbons (mainly phenolic) and aromatic heterocyclic compounds, especially nitrogen chemicals such as pyrrole or pyrazine derivatives. The presence of hetero atoms requires upgrading prior to the use of these reaction products as biofuels, to increase their calorific value and chemical stability. The selected operating conditions provided a bio-char, avoiding contamination by absorbents normally used in microwave processes. Furthermore, bio-char shows the presence of residual functional groups on the surface, in particular C=O and C-O-C groups. In this study, pyrolysis is confirmed as a valuable and versatile method for biomass valorization, collecting fractions with different characteristics according to the feedstock used.

[1] J. Jacquet and D. Jamieson. *Nature Clim Change*. **2016**, 6, 643–646.

[2] C. Panoutsou, et al., *Energy Strategy Rev.* **2021**, 34, 100633.

[3] R. Gallorini, et al., *J Anal Appl Pyrolysis*. **2023**, 174, 106138-106146.

OR13

A bioinspired and sustainable route for the preparation of Ag-crosslinked alginate fibers decorated with silver nanoparticlesPietro Tordi^{a,b}, Rita Gelli^a, Francesca Ridi^a, and Massimo Bonini^a^a Department of Chemistry “Ugo Schiff” and CSGI, University of Florence,
via della Lastruccia 3, 50019 Sesto Fiorentino, Italy^b Institut de Science et d’Ingénierie Supramoléculaires (ISIS) - Université de Strasbourg and
CNRS, 8 Allée Gaspard Monge, F 67000 Strasbourg, FranceE-mail: pietro.tordi@unifi.it

Functional materials obtained through green and sustainable routes are attracting particular attention due to the need to reduce the environmental impact of the chemical industry. In this work we propose a bioinspired approach for the preparation of alginate fibers containing silver nanoparticles (AgNPs), to be used for antimicrobial purposes [1]. We demonstrate that filiform polymeric structures with length of a few meters can be easily obtained by extruding an alginate solution in an aqueous Ag⁺-containing bath (i.e. wet spinning) and that treating the fibers with freshly-squeezed lemon juice leads to the formation of AgNPs homogeneously distributed within the polymeric network. Using mixtures of ascorbic and citric acid to mimic lemon juice composition [2] we highlight the influence of the aforementioned molecules on the nanoparticles’ formation process as well as on the properties of the fibers. Varying the amount of citric and ascorbic acid used for the treatment allows to finely tune the thermal, morphological and water absorption properties of the fibers. This evidence, along with the possibility to easily monitor the preparation through FT-IR spectroscopy, endows the fibers with a high application potential in several fields such as wound healing, water/air purification and agriculture.

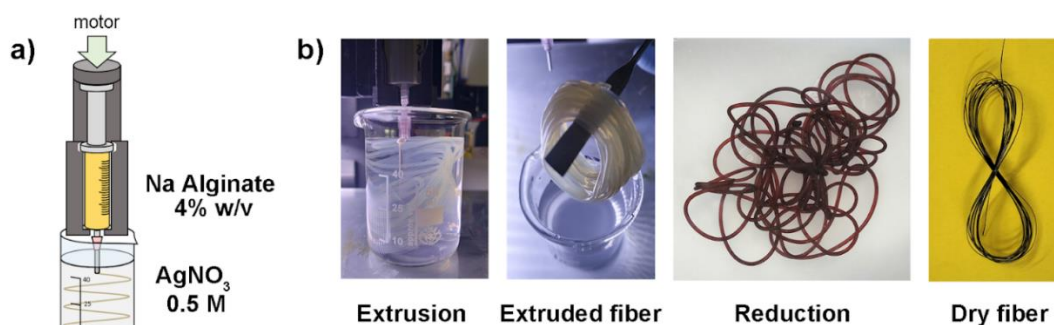


Figure 1: Preparation steps of Ag-crosslinked alginate fibers decorated with silver nanoparticles.

[1] Durán et al., *Nanomedicine Nanotechnol. Biol. Med.* **2016**, *12*(3), 789–799.

[2] Prathna et al., *Colloids and Surfaces B: Biointerfaces.* **2011**, *82*(1), 152–159.



OR14

Once upon a time motility: from active motion to bacteriostasis

Gavino Bassu, Marco Laurati, and Emiliano Fratini

*Department of Chemistry and CSGI, University of Florence, Address via della Lastruccia 3 –
50019 – Sesto Fiorentino (FI), Italy
E-mail: gavino.bassu@unifi.it*

Motile bacteria are ubiquitous and play a fundamental role from everyday life to medicine, environmental science, and industrial activities. For this reason, understanding how this class of active micro-swimmers interact with natural-like environment is important for optimizing particle transport in application relevant processes such as filtration, antibiofouling, and bioremediation. In this work, both the initial transient and steady behavior of *B. subtilis* into a heterogeneous porous media from bulk unconfined fluid are investigated. The motility behavior of *B. subtilis* was investigated under different confinement conditions induced by transparent porous hydrogels of poly (ethylene-glycol). The dynamical behavior of the bacteria at short times is related to the characteristic structural parameters of the confining network. The run-and-tumble dynamics of unconfined *B. subtilis* progressively turns into sub-diffusive motion with increasing confinement as a result of complex displacements, in which active, diffusive and sub-diffusive segments coexist. The alternation of sub-diffusion, diffusion and active motion along the same trajectory can be described as a hopping and trapping motion, in which hopping events correspond to displacements with an instantaneous velocity exceeding the corresponding mean value along a trajectory. Different from previous observations, we propose a quantitative relationship linking the median velocity of confined and unconfined bacteria through the characteristic confinement length of the hydrogel matrix. In order to have a complete overview on how micro-swimmers interact with porous natural-like environment, the dynamic behavior of the bacteria was investigated at the interface with hydrogels with different degree of porosity. As a result of the decreasing porosity the bacterial motility turns from run-and-tumble dynamic of unconfined swimmer to into sub-diffusive motion. Consistent with simulations performed by Kjeldbjerg et al [1], the steady-state concentration of *B. subtilis* in the confining network increases linearly with the imposed confinement highlighting the partitioning process resulting from the interaction with the porous network, and the threshold diameter below which the bacterial diffusion is not allowed due to steric exclusion. In order to explore the bacterial behavior in the presence of adverse species the motility suppression of metal-based nano antimicrobial agents was evaluated highlighting their consistent bacteriostatic effect.

Our work provides new insights for the bacterial motility in complex media that mimic natural environments and are relevant to important problems like sterilization, water purification, biofilm formation, membrane permeation and bacteria separation.

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OR15

Synthesis of agrochemicals against canker of kiwifruit

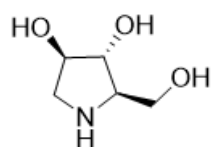
Sara Pavone^a, Stefano Rendine^b, Olivier Loiseleur^b, Francesca Clemente^a,
Camilla Matassini^a, and Francesca Cardona^a

^a Department of Chemistry "Ugo Schiff" (DICUS), University of Florence, Via della Lastruccia 13,
50019, Sesto Fiorentino (FI), Italy

^b Syngenta Crop Protection AG, Crop Protection Research, Schaffhauserstrasse, CH-4332
Stein, Switzerland, Switzerland
E-mail: sara.pavone@unifi.it

Since few years the Italian crops of kiwifruit are devastated by a bacterial canker disease caused by *Pseudomonas syringae* pv. *actinidiae* (Psa) with strong consequences for the environment [1]. The aim of this project is the development of safe molecules derived from natural compounds, non-toxic for humans and plants, but able to interact with specific targets for the bacterium. Recent studies have identified a polysaccharide, known as levan, which seems to be involved in the mechanism of masking and protecting the pathogen from the detection and defence mechanisms of the host, as it has been proposed to be the case for *P. syringae* pv. *Phaseolicola* [2]. The synthesis of levan is due to an enzyme, known as levansucrase, recently characterized from *Pseudomonas syringae* pv. *actinidiae* (Psa) [1], which is able to catalyse both sucrose hydrolysis and levan synthesis directly from sucrose, thus acting both as a glycosidase and a polymerase. For the putative multiple functions of levan as an energy storage and important structural component of bacterial biofilms, the identification of new compounds able to inhibit the levansucrases is an important goal. Since no levansucrase inhibitors have been yet reported, to the best of our knowledge, we envisaged that valuable candidates could be found among iminosugars, natural or synthetic carbohydrates analogues in which the endocyclic oxygen is replaced by a nitrogen atom. From a preliminary screening a trimeric and a tetrameric [3] polyhydroxypyrrolidine known as 1,4-deoxy-1,4-imine-D-arabinitol (**DAB-1**, **Figure 1**) emerged as the best inhibitors.

The last step of the synthesis of **DAB-1**, which is obtained from an inexpensive sugar (D-arabinose) in five steps, consists of a hydrogenation reaction that has showed reproducibility problems. So, in collaboration with Syngenta AG (Basilea, CH), we are performing some hydrogenation studies with the aim to optimize the synthesis of



DAB-1

Figure 1: Structure of **DAB-1**.

DAB-1 and then synthesize other multimeric polyhydroxypyrrolidine analogues to test them as levansucrase's inhibitors. We are also investigating the chemical space of iminosugars as inhibitors of bacterial growth of different bacterial strains, by coupling them to different scaffolds to figure out which structures are more promising.

We thank #NEXTGENERATIONEU (NGEU) and the Ministry of University and Research (MUR), National Recovery and Resilience Plan (NRRP), DM 352/2022, for a PhD fellowship.

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[2] S. Kasapis et al., *Carbohydr. Polym.* **1994**, 23, 55-64.

[3] C. Cicchi et al., in preparation.

OR16

Pressurized hot water extraction coupled with liquid chromatography-tandem mass spectrometry for the automated determination of pharmaceuticals in soil samples

Giulia Bonaccorso, Lapo Renai, Leonardo Checchini, and Massimo Del Bubba

Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia 3, 50019
Sesto Fiorentino, Florence, Italy
giulia.bonaccorso@unifi.it

In this study, an automated method based on pressurized hot water extraction (PHWE) directly coupled with liquid chromatography-tandem mass spectrometry, was developed for the analysis of 38 pharmaceutical compounds from soil samples. The principle of PHWE allows the development of an extraction system in which water is used as the most "environmentally friendly" extractant. As temperature increases, water behaves like a protic organic solvent, being its permittivity closer to that of certain alcohols at room temperature [1]. A self-assembled apparatus, employing a modified chromatographic equipment, permits hot water recirculation (i.e., dynamic mode [2]) through the sample cell. A frank soil (Soil A, Fig. 1A) was chosen to optimize the extraction process using a multivariate strategy based on design of experiment, studying temperature, pressure, and number of cycles on three levels. From the sweet spot plot, the optimized conditions were obtained, i.e. 7 cycles, 115°C, 165 bar. These conditions were tested on soil A and two others with distinct textural characteristics (soil B: silt loam, and soil C: silt clay loam, see Fig. 1A). Figure 1B shows that the optimized conditions allow recoveries ranging from 65 to 80% for all analytes in the three chosen soil. Consequently, it was possible to demonstrate that, regardless of the textural properties of the samples, the proposed system allows a good recovery for all analytes.

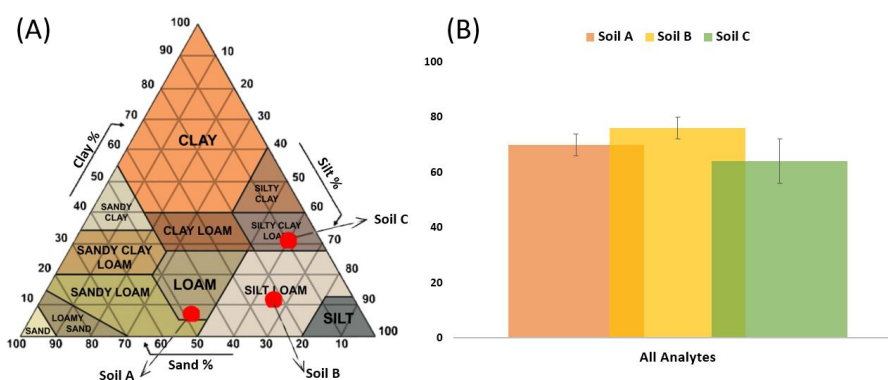


Figure 1: (A) Textural triangle reporting the three analyzed soils; (B) average recoveries for the three soils under the optimized conditions.

[1] M. Plaza et al., *Trends in Analytical Chemistry*. **2015**, 71, 39-54.

[2] E. Ong et al., *Journal of Chromatography A*. **2006**, 1112, 92-102.

OR17

Reversible control of the magnetic anisotropy in a lanthanide molecular complex thin film

 Leonardo Tacconi^a, Sofie Stampe Leiszner^b, Giuseppe Cucinotta^a,
 Edwige Otero^c, Matteo Mannini^a, and Mauro Perfetti^a
^a Department of Chemistry "Ugo Schiff", University of Florence, 50019 Sesto Fiorentino, Italy

^b Department of Chemistry, Aarhus University, DK 8000 Aarhus C, Denmark

^c Synchrotron SOLEIL, L'Orme des Merisiers, Gif-sur-Yvette, France

E-mail: leonardo.tacconi@unifi.it

Magnetic anisotropy is a critical characteristic of various materials [1]. Thus, it is imperative to achieve efficient and reversible control of magnetic anisotropy on a surface to develop molecular-based spintronic devices. In this study, we exhibit the potential to reversibly change the magnetic anisotropy of adsorbed molecules on a surface through temperature exploitation.

The present study was carried out on the trigonal lanthanide complex Nd(trensal). Torque magnetometry measurements on oriented single crystals revealed a transition from an easy-axis to an easy-plane magnetic anisotropy around 37 K (Figure 1a). The complex was then deposited on highly oriented pyrolytic graphite (HOPG) under HV conditions to obtain a film with a nominal thickness of 2 nm. Such film was then investigated with synchrotron radiation at the M_{4,5} edges of Nd at the SOLEIL facility. The XNLD spectrum (Figure 1b) confirmed an ordered deposition of the molecule analogue to the Er(trensal) complex [2,3]. The magnetic properties of the film were determined acquiring X-ray Magnetic Circular Dichroism (XMCD) spectra at several temperatures and orientations in a 6 T magnetic field. The maximum values of the acquired XMCD spectra at the M₄ edge of Nd are shown in Figure 1c. Reported trends demonstrate the retention of the solid state magnetic anisotropy switch behaviour in the deposited film.

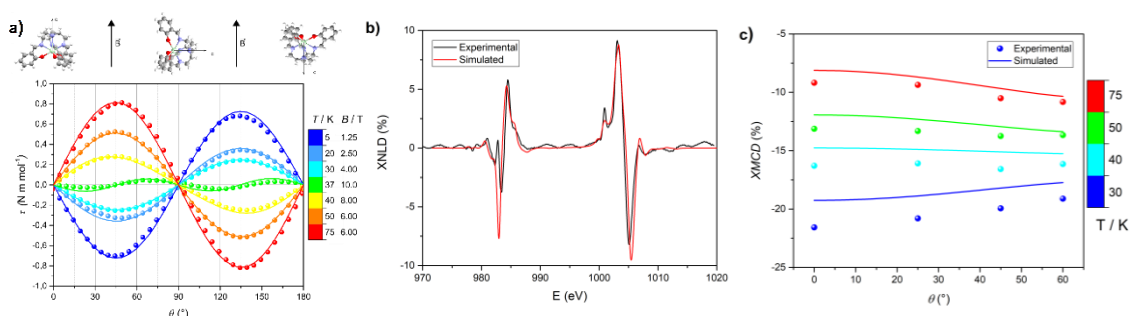


Figure 1: Torque magnetometry curves at various temperatures and magnetic fields (a); XNLD spectrum acquired at 4.3K and $\theta = 60^\circ$ (b); XMCD maximum values at M₄ edge of Nd at various temperatures and angles (c).

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OR18

Electrochemical characterization of Polycyclic Aromatic Hydrocarbons and Metal-organic frameworks for coatings and energy applications

Marco Bonechi^a, Walter Giurlani^a, Claudio Fontanesi^b, and Massimo Innocenti^a

^a Department of Chemistry "Ugo Schiff", University of Florence, via della Lastruccia 3 Sesto Fiorentino, 50019, Italy

^b Department of Engineering "Enzo Ferrari," University of Modena and Reggio Emilia, Via Vivarelli, 10 Modena, 41125, Italy
E-mail: marco.bonechi@unifi.it

Polycyclic Aromatic Hydrocarbons (PAH) feature extremely interesting properties leading to their use in organic electronics, sensors, and energy applications [1]. The classical approaches of bottom-up production of PHA are mostly based on chemical synthetic procedures but more recently many works have shown the advantages of new electrochemical PAH synthesis [2]. Electric current can be used as an oxidant to replace strong chemical oxidizing agents and promote an anodic electrochemical oligomerization. Our work focuses on a C₉₆ dendrimer PPD, to obtain a thin film of poly PPD on the electrode surface. Cyclic voltammetry CV results show a prominent oxidation peak and suggest an auto-acceleration effect in pPPD film growth, as is observed in the case of conductive polymers. UV-Vis spectra, Gel permeation chromatography (GPC) and MALDI-TOF spectrometry results suggest the formation of partially cyclodehydrogenated structures in which, following intramolecular reactions, new bonds are formed between the aromatic rings and it is also noticed the presence of PPD dimers and trimers.

About Energy application, we performed an electrochemical characterization of metal-organic frameworks (MOFs). MOFs have attracted increasing scientific interest in electronic applications, sensors, and catalysis [3]. In recent years, scientists have conducted intense research in the production of chiral MOFs. Remarkably, the effective use of chiral surfaces in the water-splitting process, has already been demonstrated in the recent past. Thus, chiral MOFs appear to be promising materials for use in the water-splitting process. In this work, we focused on MIL 53 Fe-based and Zn-based MOFs doped with chiral molecules (L-cysteine, R-camphorsulfonic acid, and S-camphorsulfonic acid). The CV of the MIL53 S-CSA MOF features two redox peaks that can be assigned to the Fe (III)/Fe(II) redox couple. In addition, MOFs supported on titania were used as working electrodes in the water-splitting process. Results of Chronoamperometry curves show that chiralized MIL53 S-CSA is characterized by a substantial increase in the photocurrent (light on) with respect to the achiral one.

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OR19

Structural characterization of Carbonic Anhydrase complexes with dual-target inhibitors

Chiara Baroni^a, Marta Ferraroni^a, Fabrizio Carta^b, Silvia Selleri^b,
Clemente Capasso^c, Viviana De Luca^c, and Claudiu T. Supuran^b

^a Department of Chemistry “Ugo Schiff”, University of Florence, Via Ugo Schiff 6, 50019 Sesto Fiorentino (FI), Italy.

^b NEUROFARBA Department, University of Florence, Via Ugo Schiff 6, 50019 Sesto Fiorentino (FI), Italy.

^c Department of Biology, Institute of Bioscience and Bioresources (IBBR)-CNR, via P. Castellino 111, 80131 Napoli (NA), Italy.

E-mail: chiara.baroni@unifi.it

The microenvironment of many types of tumors is often characterized by low oxygen concentration (hypoxia), which causes a shift from glucose metabolism to glycolysis leading to the acidification of the extracellular space. In these conditions, the overexpression of Carbonic Anhydrase (CA) isoforms IX and XII is a component of the complex response of cancer cells to preserve their survival and growth¹. CA IX and XII are hypoxia-regulated and tumor-specific proteins that maintain the physiological pH essential for cell function. Consequently, they are recognized as therapeutic antitumor targets and nowadays many studies aim at the development of new and more efficient CA inhibitors (CAIs). In this project, a series of dual-target compounds were designed and synthesized incorporating the zinc-binding sulfonamide moiety (specific CAIs) combined with an emerging anticancer drug: the biguanide metformin. Metformin is widely known as an antidiabetic drug, but numerous studies over the past few years have identified novel activities, including anticancer one². The metformin derivatives were found to be potent and selective (versus the cytosolic CA I and II isoforms) inhibitors of the tumor-associated CA isoforms. The structures of the CA IX and XII-dual-target inhibitor complexes were determined through the X-ray crystallography technique to rationally improve the efficacy of these promising compounds as anticancer agents. Different cryoprotectants have been tried for crystal freezing to avoid the interaction of the cryoprotectant molecules with the inhibitors within the active site of the protein that may interfere with the inhibitor binding mode. A new crystal form with unit cell dimension $a=157.96 \text{ \AA}$ in cubic space group $I 4 3 2$ has been found for the CA IX isoform, due to the presence of the His-tag residues at the enzyme N-terminal.

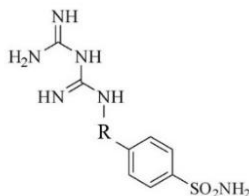


Figure 1. Structure of the metformin derivative dual-target CAIs.

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OR20

A remediation proposal for the “vinegar syndrome” of cellulose acetate-based motion picture films

Francesca Porpora^a, A. Maiano^a, C. Forcellini^a, C. D'Aleo^a, L. Lisi^a,
E. Carretti^{a,b}, L. Dei^a, R. Weiss^c, M. De Sanctis^d, and M. Pischedda^d

^a Department of Chemistry, University of Florence and CSGI, Via della Lastruccia 3-13, 50019, Italy

^b CNR-INO, Largo E. Fermi 6, 50125 Florence, Italy

^c Georgetown University, 37th and O Streets NW, Washington, DC 20057 – USA

^d L'Immagine ritrovata SRL, Via Riva di Reno, 72, 40122, Bologna, Italy

E-mail: francesca.porpora@unifi.it

Motion picture films made of cellulose acetate (CA) are subjected to chemical degradation mainly due to the “vinegar syndrome”, i.e. the deacetylation of the acetyl groups and the release of acetic acid. It is strictly influenced by temperature, moisture and acidity and the released acetic acid acts as a catalyst for the reaction. Also, by-products of deacetylation can promote the hydrolysis of the glycosidic bonds of the cellulosic backbone. In addition to the smell, the deformation of the support and the detachment of the emulsion layer are the main macroscopic symptoms of this phenomenon and can strictly compromise the usability of the films [1]. On these bases, reducing environmental moisture and removing alteration by-products from the storing environment is mandatory to limit this degradation process.

The most important goal of this project is to set up an innovative chemical approach to inhibit and/or prevent the vinegar syndrome through soft matter and nanotechnologies. The idea was to set up systems able to neutralize acetic acid and also act as an alkaline reserve to prevent further degradation. The efficacy of various treatments based on sponge-like systems and nanoparticles was evaluated by characterizing samples of CA-based motion picture films before and after the artificial and controlled induction of the vinegar syndrome, within and without the treatment. The decrease in the acetyl content was monitored by Fourier Transform Infrared - Attenuated Total Reflected Spectroscopy (FTIR-ATR) in a non-destructive and non-invasive way: the ratio between the intensity of a peak associated with the acetyl group and the intensity of a reference peak, assuming that it does not vary during the aging, was calculated [2]. These data are validated by titration and free acidity tests [3]. In addition, the variation in mechanical and thermal properties was evaluated by Tensile Tests and Thermogravimetric Analysis (TGA).

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OR21

Electrodeposition of anti-corrosive and barrier layers by using Direct and Pulsed current

Margherita Verrucchi^a, Ivan Del Pace^b, and Massimo Innocenti^a

^a Department of Chemistry Ugo Schiff, via della Lastruccia 3, 50015 Sesto Fiorentino, Italy

^b Valmet Plating s.r.l., via Erbosa 5, 50041 Calenzano, Italy

E-mail: margherita.verrucchi@unifi.it

Anti – corrosive layers are thin metal deposits used in the electroplating industry to protect the underlying layers from oxidizing agents. We studied an innovative tin-ruthenium electroplating bath provided by Valmet plating as a sustainable alternative to NiP and Pd. At first, we characterized the system with electrochemical measurements, then we performed direct current experiments to observe any differences in alloy composition as the deposition time changes. [1] Samples were then made using pulsed current (PC) and reverse pulsed current (PRC) to investigate the possibility of using these techniques to make deposits with specific characteristics. [2]

Therefore, energy-dispersive x-rays spectroscopy (EDS), X-rays Fluorescence (XRF) and colorimetric analysis were performed to observe any compositional or thickness differences in the deposited alloy while SEM images were acquired for a morphological characterization of the surfaces.

At the same time, a diffractometric study was carried out on deposits obtained with a pure palladium galvanic bath by varying thicknesses and current densities in order to identify the conditions of Pd- β hydride formation. Palladium is currently used, alone or alloyed with other metals either as a final or intermediate layer, primarily as a barrier to intermetallic diffusion. However, palladium deposits are often prone to microfractures formation due to hydrogen desorption and subsequent lattice contraction due to the transition from the β -PdH_x to the thermodynamically stable α -PdH_x that contains a smaller amount of hydrogen. [3] For this reason, it is of particular importance to identify the formation conditions of the two palladium hydrides during the electrodeposition process.

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OR22

Green solvents on the PurePep® Chorus® taking advantage of induction heating: synthesis and HPLC-free purification of a 72mer deriving from COVID-19 Spike protein and β -amyloid(1-42)

Lorenzo Pacini^{a,b}, Stephan Lüdtkke^c, Manoj Muthyala^c, Robert Zitterbart^c, Dominik Sarma^c, Paolo Rovero^{a,d}, and Anna Maria Papini^{a,b}

^a Interdepartmental Research Unit of Peptide and Protein Chemistry and Biology - Peptlab, MoD&LS Laboratory, University of Florence, Sesto Fiorentino 50019, Italy

^b Department of Chemistry "Ugo Schiff", University of Florence, Sesto Fiorentino 50019, Italy

^c Gyros Protein Technologies Inc., 4675 South Coach Drive, Tucson, Arizona 85714, USA

^d Department of Neurosciences, Psychology, Drug Research and Child Health Section of Pharmaceutical Sciences and Nutraceuticals, University of Florence, Sesto Fiorentino 50019, Italy

E-mail: L.pacini@unifi.it

Over the past few decades, environmental concerns have become increasingly urgent, particularly in the context of manufacturing processes involving chemicals. Traditionally, solvents such as DMF, NMP, and TFA have been used in solid-phase peptide synthesis (SPPS) despite their negative impact on the environment. However, the use of such solvents conflicts with the current trend toward green solvents [1].

In this study, we investigated the use of PurePep® Chorus taking advantage of magnetic induction heating to produce, at first, model peptides such as ACP and poly-Alanine while avoiding the use of DMF. We tested binary solvent mixtures that varied in polarity, viscosity, boiling points, safety, and sustainability having as goal to demonstrate the feasibility of a green synthesis using magnetic induction heating to speed the SPPS and to avoid by-products [2]. Then, we focused on longer difficult peptides to stress the green process performance comparing DMF and green mixture results in terms of crude peptide purity.

After succeeding in the synthesis, we applied a catch-and-release method to purify the product without using chromatography, probably the biggest bottleneck of a whole manufacturing process of a peptide [3].

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OR23

An electrochemical magneto-assay: from a manual to an automatable microfluidic approach

Patrick Severin Sfragano^a, Eduardo Canek Reynoso^{a,b},
Norma Elena Rojas-Ruíz^c, Serena Laschi^a, Giulia Rossi^a, Martin Buchinger^a,
Eduardo Torres^{b,d}, and Ilaria Palchetti^a

^a Department of Chemistry "Ugo Schiff", University of Florence, 50019 Sesto Fiorentino, Italy

^b Posgrado en Ciencias Ambientales, Instituto de Ciencias, Benemérita Universidad Autónoma de Puebla, 72570 Puebla, México

^c Centro de Investigaciones en Ciencias Microbiológicas, Instituto de Ciencias, Benemérita Universidad Autónoma de Puebla, 72000 Puebla, México

^d Centro de Química, Benemérita Universidad Autónoma de Puebla, 72570 Puebla, México

E-mail: patrickseverin.sfragano@unifi.it

Most analytical tools for biomarkers detection rely on complex and expensive methodologies. Electrochemical biosensors have emerged as cost-effective and versatile solutions with minimal requirements in terms of apparatus. This project was dedicated to the assessment of a versatile electrochemical magneto-assay that employed superparamagnetic microbeads (MBs) coated with biomimetic receptors to capture target analytes, followed by an enzyme-based signal generation and amplification strategy. The versatility of this methodology was challenged in the analysis of different analytes by choosing appropriate biorecognition elements capable of synergically working with MBs. However, such analytical protocol was characterised by repetitive and time-consuming steps that expert personnel must meticulously follow by manually pipetting reagents into/from plastic vials. Therefore, efforts were dedicated to transform this procedure into a more practical and automatable solution. Particularly, the goal was to run the assay inside a small card-based platform powered by microfluidic manipulation, requiring minimal human intervention and consumables. MBs functionalised with capture molecules were loaded inside the channel of a microfluidic card, while a magnet ensured their positioning. The various assay reagents were then injected into the channel using a peristaltic pump, in a continuous controlled microfluidic flow. Once that the hybridisation and labelling reactions occurred, the beads were placed on a screen-printed electrode for the electrochemical readout. As a proof-of-concept, this semi-automated system was tested on the analysis of genes responsible for antimicrobial resistance, a serious threat to public health mainly caused by the misuse of antibiotics. After multiple optimisations, the method was applied to the analysis of the *sul1* gene extracted from cells of *Escherichia coli* and amplified through an isothermal DNA amplification technique, achieving limits of detection in the picomolar range and detecting ≥ 500 -fold diluted amplification products. Efforts are now being directed towards achieving full automation of the entire system by using software-controlled mechanisms.

Acknowledgements: Regione Toscana (Bando Salute 2018, research project CUP n. D78D20000870002) is acknowledged for financial support.

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OR24

Ferritin-Au(I) bioconjugates as anticancer agents

Lucrezia Cosottini

Department of Chemistry "Ugo Schiff" & CSGI, University of Florence, Via della Lastruccia, 3-13, 50019 Sesto, Fiorentino (FI), Italy
E-mail: lucrezia.cosottini@unifi.it

Human heavy-chain ferritin (HuHf) is a recombinant protein composed of 24 H-subunits (21 kDa each), that self-assemble to form a nanocage with a hollow globular structure (inner cavity 8 nm, external diameter of 12 nm). The H-chain is known to be recognized by the transferrin receptor-1 (TfR1) that is overexpressed in many cancer cell lines. HuHf is considered a suitable nanocarrier due to its versatility, excellent safety profile, nano-range size and conformation [1]. Gold compounds emerged as potential anticancers with antiproliferative and proapoptotic properties [2]. Here I worked on the development of human heavy chain ferritin conjugates with different gold(I) anticancer drugs, i.e. Auranofin (AF), Aurothiomalate (AuTm) and a monocarbene (Au(NHC)Cl), for the production of ferritin-based nanocarriers for their selective delivery toward cancer cells. I expressed five different human-H chain ferritins in *E. coli* cells: the wild type, three different mutants, where I replaced with Alanine one or more Cysteines (C130A, C90AC102A and C90A) and a ¹⁹F labelled- human ferritin (5-F-Trp93). I exploited the use of recombinant wild type HuHf, as a nanocarrier for the targeted delivery of different gold(I) anticancer compounds; the three mutants to determine the binding sites of the compounds to the protein and the ¹⁹F-labelled human ferritin as a probe for ¹⁹F NMR studies. The approach that has been used for all the HuHf-gold(I) adducts is the same. The reactions were conducted at 37°C in PBS with an excess of gold compound that would be removed via dialysis, ESI-MS spectrometry confirmed the adducts formation and the species present in solution, ICP determined the amount of gold per HuHf cage. Also, biological experiments were performed to evaluate the cytotoxicity of the bioconjugates in five different cell lines i.e. A2780 ovarian cancer cells, U87MG glioblastoma cells, MCF-7 breast cancer cells, HCT-116 colorectal cancer cells and MRC-5 fibroblast cells. In particular the studies regarding the HuHf-AF bioconjugate brought very nice and interesting results [3].

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OR25

Glycolipids synthesis and formulation in biocompatible nanovesicles

Andrea Sodini, Filippo Susini, Francesca Maestrelli, and Cristina Nativi.

Department of Chemistry, University of Florence, Via della Lastruccia 3-13, 50019 Sesto Fiorentino, Italy
E-mail: andrea.sodini@unifi.it

Cancer is a major global health issue, with breast, lung, and colon cancer being the most recurrent types. Triple negative breast cancer (TNBC) is the most difficult to treat due to its aggressive nature, rapid spread, and metastasis. TNBC cells lack Estrogen (ER), Progesterone (PR), and human epidermal growth factor 2 (HER2) receptors, which are well-defined targets in BC treatments. Alternative targets are being investigated, such as Mucins (MUC), which are heavily glycosylated proteins secreted by epithelial cells in mucus. Tumor-Associated Carbohydrate Antigens (TACAs) are overexpressed in cancer cells, modifying cell-cell interactions and signaling. TACAs are used to develop therapeutic cancer vaccines, but they face drawbacks such as reduced metabolic stability and poor T cell independent immunogenicity [1].

Saccharidic-based therapeutic vaccines require multivalent presentation of epitopes for effective immune responses without increased toxicity. Biocompatible lipid nanovesicles, such as niosomes, can be used to present immunogenic antigens.

Niosomes are synthetic nanodimensional structures consisting of non-ionic surfactants, assembled autonomously in an aqueous environment in the form of a lipid bilayer which can be used to present immunogenic antigens [2].

A well-established method to improve the efficacy of an anti-cancer vaccine is using immunogenic adjuvants, which can be co-injected or covalently linked to the antigen. α -GalCer is a synthetic glycolipid derivative of natural compounds isolated from marine sponges and it exhibits an intrinsic immunomodulatory and antitumour activity *in vivo* animal models [3].

Herein I have reported an innovative total synthesis of an α -GalCer analogue, whose synthetic route proved to be an effective and versatile strategy for the synthesis of glycolipid derivatives with a ceramide structure. I have synthesized a mimetic of the tumoral STn antigen and functionalized it with an aliphatic chain for the formulation in niosomes. The resulting glycolipid was presented in a multivalent way by formulating it in biocompatible nanovesicles that were properly produced and characterized in terms of morphology, shape, dimension, and surface charge.

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OR26

Protein-Based Biopolymer Material from Rapeseed Meal: Extraction, Modification, and Peptidomic Characterization for Environmental Sustainability

Sara Aquilia^{a,b,c}, Sabrina Bianchi^c, Michele Pinna^c, Anna Maria Papini^{a,b},
Claudia Bello^{a,b}, Francesco Ciardelli^c, and Luca Rosi^b

^a Interdepartmental Research Unit of Peptide & Protein Chemistry & Biology-PeptLab. University of Florence, Via della Lastruccia 13, I-50019 Sesto Fiorentino, Italy

^b Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia 3-13, 50019 Sesto Fiorentino, Italy

^c Spin-Pet s.r.l., Viale Rinaldo Piaggio, 32 - 56025 Pontedera, Italy
E-mail: sara.aquilia@unifi.it

Petroleum-based polymers are extensively utilized in the production of various every day and high-value products, due to their outstanding attributes, versatility, and cost-effectiveness. Nonetheless, their unregulated disposal and extremely slow degradation have given rise to one of the most pressing environmental challenges over the past two centuries. Consequently, in recent years there has been an increasing focus on developing polymeric materials based on natural biopolymers as a renewable substitute for petroleum-based materials.^[1] The availability of proteins derived from agricultural by-products, along with their favorable properties, has fostered a renewed interest in protein-based materials, promoting research into innovative technologies for bioplastics preparation.^[2] The presented study is the first step toward the development of a protein-based material for multiple applications. Proteins from rapeseed meal have been selected as primary component for our bioplastics. These rapeseed meal samples were obtained as a by-product from the crude oil production process following oil pressing and hexane extraction.^[3] The proposed protein extraction method is eco-friendly, easy scalable, and lead to two protein isolates with good recovery yield. Furthermore, the rapeseed meal was processed using compression molding, and chemical reactions were employed to establish cross-links between protein chains, thereby modulating the material's thermo-mechanical properties while maintaining the viscoelastic response typical of plastic polymer materials. Additionally, the enzymatic hydrolysis of rapeseed meal using specific proteases resulted in hydrolysate mixtures, in order to test them as component of the rapeseed protein-based material. Purification and peptidomic study of the hydrolysates will allow us to characterize the number and sequence of the peptides obtained with the final aim to understand their effects on the properties of the protein-based material. The achieved results will contribute to the green transition achieving the goals of the European Green Deal.

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

Laura Conti, Marco Marradi, and Costanza Montis

Department of Chemistry "Ugo Schiff", University of Florence, via della Lastruccia 3, 50019
Sesto Fiorentino, Florence, Italy.
E-mail: laura.conti@unifi.it

In the past years, RNA delivery demonstrated its unique advantages over traditional biopharmaceutical and vaccine technology. However, to promote its application, RNA's inherent limitations must be overcome by designing delivery vectors able to protect the RNA cargo from the environment and to transport/release it in proximity to its biological target. Among such systems, lipid nanoparticles (LNPs) are particularly promising. To boost their clinical translation, it is crucial to carefully design the LNP composition and structure, in order to ensure: (i) an efficient complexation/protection of RNA (ii) a high ability of LNP-RNA complex to cross the plasma membrane, escape from the endosomes and release the RNA. To this aim, attaining a deep physicochemical understanding of these systems is crucial, as well as investigating their behavior towards biological interfaces.

In this contribution, we present a new formulation of LNPs based on non-lamellar lipid vectors. The cationic nature of the LNPs is designed to efficiently bind siRNA; the residual positive zeta potential of LNPs-siRNA complexes is designed to ensure enhanced ability to interact with the plasma membrane; finally, the topological characteristics of the nanoparticles, of cubic or hexagonal geometry, are designed to enhance the endosomal escape of the complexes. To test their potentiality as RNA carriers, their physicochemical, structural, and colloidal properties were characterized, with and without the RNA cargo, using DLS, ζ -Potential, and SAXS.

The results here presented will contribute to improve the physicochemical understanding of LNPs vectors and promote their application as therapeutics.

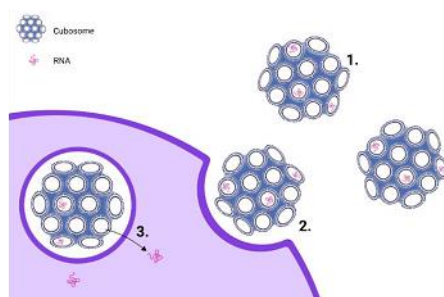


Figure 1: Schematic representation of 1. LNPs 2. LNPs internalization 3. RNA release.

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OR28

An easily customizable glyconanomaterial with biomolecular recognition properties

Chiara Mangini, Jacopo Tricomi, Giacomo Biagiotti, and Barbara Richichi

Department of Chemistry “Ugo Schiff”, University of Study of Florence, Via della Lastruccia
3-13, 50019 Sesto Fiorentino
E-mail: chiara.mangini@unifi.it

The development of reliable custom nanomaterials for precision medicine applications is a sought-after goal. However, harnessing nanoparticles requires thorough control of factors such as nanoparticle composition, morphology, manufacturing process, and fate in biological systems. Furthermore, the attachment of multiple cargos to the nanoparticle surface introduces complexity and significantly affects reproducibility, scalability, and consequently the possibility of effectively utilizing nanotechnology.

During the first year of my Ph.D., I contributed to developing and optimizing a simple and reproducible synthetic strategy for assembling sulfated cellulose nanocrystals (CNCs) and gold nanoparticles (AuNPs), thus providing a novel new modular and functional hybrid glyconanomaterial. Our nanomaterial combines the complementary physiochemical properties of AuNPs and polysaccharide nanomaterials, as well as the preservation of the composition and main structure of the pristine CNC. Due to its unique structure, the surface of our CNC-AuNPs can be easily engineered with one or two different head groups, exploiting a robust click chemistry route, under tightly controlled reaction conditions. These results have prompted the exploration of this programmable nanoplatform as precision delivery system targeting specific receptors on cancer cells [2, 3].

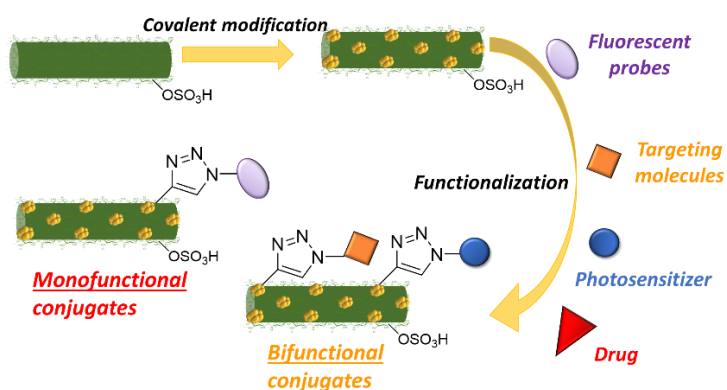


Figure 1: Synthetic strategy

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Development of Porphyrin based two-Qubits Quantum Logic Gates

Davide Ranieri^a, Fabio Santanni^a, Alberto Privitera^{a,b}, Karolina Urbanska^c, Mario Chiesa^d, Giulia Serrano^b, Federico Totti^a, Mathias. O. Senge^{c,e}, Lorenzo Sorace^a, and Roberta Sessoli^a

^a Department of Chemistry “Ugo Schiff” & INSTM RU, University of Florence
Via della Lastruccia 3, 50019 Sesto Fiorentino, Italy

^b Department of Industrial Engineering & INSTM RU, University of Florence
Via Santa Marta, 3 50139 Firenze, Italy

^c School of Chemistry, Chair of Organic Chemistry, Trinity Biomedical Sciences Institute, Trinity College Dublin, The University of Dublin,
152-160 Pearse Street, Dublin D02R590, Ireland

^d Department of Chemistry and NIS, University of Turin,
Via P. Giuria 7, 10125 Torino, Italy

^e Institute for Advanced Study (TUM-IAS), Technical University of Munich, Focus Group –
Molecular and Interfacial Engineering of Organic Nano-systems
Lichtenberg-Str.2a, 85748 Garching, Germany
E-mail: davide.ranieri@unifi.it

Porphyrins are aromatic macrocycles with unique chemical and physical properties. In this PhD Thesis, we exploited the magnetic properties of paramagnetic porphyrin dimers for the realization of two-qubit quantum logic gates. We synthesized novel homo & heterometallic paramagnetic vanadyl-based porphyrin dimers and showed that the vanadyl moiety is crucial for promoting weak-exchange couplings between the two spin-centers [1,2]. We further synthesized linear porphyrin trimers towards the realization of switchable two-qubit quantum logic gates and deposited functionalized porphyrin monomers on the surface to test the capabilities of realizing directly linked porphyrin dimers directly on the surface upon annealing of the monomer porphyrin unit.

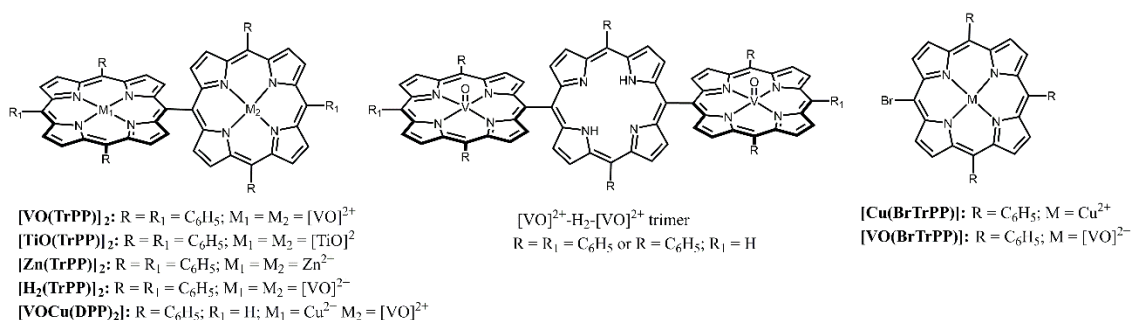


Figure 1: Molecular structure of the three main porphyrinic systems synthesized during the three years of the PhD thesis.

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OR30

Multivalent iminoglyco-NPs for theranostic applications

Francesca Milano^a, Camilla Matassini^a, Alessandra Quarta^b,
Francesca Clemente^a, Francesca Cardona^a, Andrea Ragusa^b, Paolo Paoli^c,
Andrea Goti^a, and Marco Marradi^a

^a Department of Chemistry 'Ugo Schiff', University of Firenze, via della Lastruccia 3-13, 50019 Sesto Fiorentino (FI), Italy

^b CNR-Nanotec, Institute of Nanotechnology, Via Monteroni, 73100 Lecce, Italy

^c Department of Experimental and Clinical Biomedical Sciences, University of Florence, Viale Morgagni 50, 50134 Florence, Italy

E-mail: francesca.milano@unifi.it

Gaucher disease (GD) is a rare autosomal recessive disorder due to mutations in the *GBA* gene which cause a deficiency in the activity of the enzyme glucocerebrosidase (GCCase). This enzyme has indeed multiple roles. Deficiency of GCCase has also been linked to Parkinson's disease, and GCCase is aberrantly activated in cancer, suggesting that therapeutic approaches to modulate GCCase activity could play an important role in treating multiple diseases [1,2]. An innovative therapeutic strategy for the treatment of metabolic disorders which, however, has not yet reached the market for GD, is the use of pharmacological chaperones (PCs), compounds which can be found among competitive inhibitors of GCCase but are able to rescue the enzyme activity when they are used in sub-inhibitory concentrations. In this regard, iminosugars, carbohydrate analogues with a nitrogen replacing the endocyclic oxygen of sugars, are promising candidates as PCs for GCCase [3]. Since the blood-brain barrier (BBB) represents an obstacle for the classic enzymatic replacement treatment of neuronopathic forms of GD, the synthesis of new iminosugars functionalized with specific ligands (e.g. glucose, galactose) capable of enhancing brain uptake through the GLUTose Transporters (GLUT) is being investigated. In addition, since the overexpression of GCCase reduces the toxicity of chemotherapy, the effect of co-administration of iminosugars with chemotherapeutic agents in different cancer cell lines is being studied. Both these applications can be further investigated, by exploiting the enhanced affinity recently demonstrated by GCCase for multivalent iminosugars. Therefore, multimerization of iminosugars on different types of nanoparticles (NPs), e.g. metallic (Au) and fluorescent (quantum dots), is carried out to combine the properties of inhibitors with the multivalence of NPs, thus obtaining intelligent systems having the simultaneous ability to transport and track molecules both *in vitro* and *in vivo*.

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OR31

Challenges and technological approaches for tackling emerging microcontaminants in wastewater

Chiara Sarti^a, Iva Chianella^b, Tao Liu^b, Tania Martellini^a, Fabio Masi^c,
and Alessandra Cincinelli^a

^a Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia 3, 50019 Sesto Fiorentino, Italy

^b Cranfield University, College Road, MK430AL Cranfield, United Kingdom

^c IRIDRA S.R.L., Via Alfonso la Marmora 51, 50121 Florence, Italy
E-mail: chiara.sarti@unifi.it

The presence of emerging microcontaminants (EMs), including organic UV filters (OUVAs), per- and polyfluoroalkyl substances (PFAS), and microplastics (MPs), has been detected worldwide in the aquatic ecosystems. These pollutants, originating from various sources such as personal care products, industrial processes, and plastic waste, can persist and transform within wastewater treatment plants (WWTPs), leading to potential environmental and human health hazard.

In this framework, the present research focuses on two different aims: i) overcome the analytical challenges related to the detection of OUVAs in wastewater samples; ii) evaluate and improve the removal of EMs implementing Nature-based Solution (NBS) systems with electroconductive media.

To achieve the first goal, an innovative electrochemical sensor based on molecular imprinted polymers (MIPs) was developed for a selective detection of Benzophenone-3 (BP-3), one of the most spread OUVA in the aquatic environment [1]. After a first phase of optimization of the MIP layer electropolymerization, the template washing step and the analyte rebinding conditions, the tool was tested both in presence of possible interferents and with real WWTP effluent samples. The study showed interesting results that may lead to a specific and cost-effective approach, allowing widespread monitoring and supporting an early detection of the target compound.

Regarding the second research objective, although, among different NBSs, constructed wetlands (CWs) are an effective and well-known strategy for wastewater treatment, they are associated with high surface area demands. The innovative Microbial Electrochemical Technology Intensified treatment wetland (METland) replaces traditional media (i.e., gravel and sand) with electroconductive material, enabling electroactive bacteria (EABs) to exchange electrons [2]. This enhances electron transfer from donors like carbon within the METland, streamlining the microbial-mediated remediation process, offering a more efficient, sustainable solution while reducing land use [3]. The consequent boost in oxidation reactions within METlands might also lead to an increase in the remediation rates of EMs. In this context, an experiment with different CW pilot systems (with traditional and electroconductive media), provided by Cranfield University, was designed to evaluate the potential differences in terms of target microcontaminants removal efficiency.

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OR32

Development and optimization of nanocarriers for the delivery of Si-RNA

Ilaria Chiarugi, Francesca Maestrelli, Sandra Ristori, and Anna Rita Bilia.

*Department of Chemistry, University of Florence, Via della Lastruccia 13, 50019 Sesto Fiorentino, Florence, Italy
E-mail: ilaria.chiarugi@unifi.it*

Gene knockdown therapies utilizing RNA interference (RNAi) offer a new frontier in the treatment of various diseases, including immune-mediated and inflammatory conditions. Small interfering RNAs (siRNAs), noncoding RNAs consisting of 20-25 nucleotides, play a pivotal role in the RNA interference pathway. This study focuses on the development of lipid nanoparticles (LNPs) as nanocarriers for efficient siRNA delivery [1,2]. The research primarily involves the optimization of parameters and lipid composition to generate LNPs with diverse characteristics. In depth, analysis employing dynamic light scattering (DLS) techniques has been conducted to evaluate the stability, size, and zeta potential of the newly produced LNPs. Moving forward, the study aims to further refine the LNP formulations, assess their cellular transfection capability, and explore functionalization strategies for specific targeting. Additionally, novel nano vectors incorporating modified cyclodextrins will be developed to encapsulate siRNAs [3].



Figure 1: RNA and gene therapy, National Research Center

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OR33

Bridging Smart Materials and Sensing Platforms: Advancements in Liquid Crystalline Elastomers and PDMS Microfluidic Supports

Neri Fuochi^{a,b}, Giovanna Marrazza^a, Daniele Martella^{a,b}, Ilaria Palchetti^a, and
Camilla Parmeggiani^{a,b}

^a *Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia 3-13, 50019 Sesto F.no (Italy)*

^b *European Laboratory for Non-linear Spectroscopy (LENS)t, University of Florence, Via Nello Carrara 1, 50019 Sesto F.no (Italy)
E-mail: neri.fuochi@unifi.it*

Liquid crystals, with their unique state of matter between crystalline and liquid, have proven highly responsive to external stimuli, making them promising for "smart material" applications. Liquid Crystalline Elastomers (LCEs) represent a noteworthy example, combining liquid crystal responsiveness with elastomeric mechanical properties, allowing reversible actuation under various stimuli. Our idea is to expand LCEs application towards the development of intelligent supports for wearable sensors.

By photopolymerization of acrylate-based liquid crystals, it is possible to easily obtain side-chain LCEs while slightly modifying the monomeric mixture and introducing chain extenders lead to main-chain LCEs, therefore modulating material mechanical properties and its responses to external stimulation.

Aiming at pushing the state of art of wearable sensors, preparation and characterization of thermo- and photo-responsive LCEs were presented, together with a more standard approach based on the development of PDMS (Polydimethylsiloxane) microfluidic supports, particularly targeting electrochemical analysis. PDMS microfluidic supports offer a versatile platform for the realization of multifunctional wearable devices, providing a robust foundation for integrating sensors and facilitating the continuous monitoring of various physiological parameters.

This dual approach, involving LCEs and PDMS supports, reflects our commitment to advancing both responsive materials and innovative platforms, with the ultimate goal of contributing to the development of intelligent wearable devices with diverse functionalities.

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OR34

Multivalent iminosugars as enhancers of the lysosomal enzyme GCase activity

Francesca Buco^a, Camilla Matassini^a, Francesca Clemente^a, Francesca Cardona^a, Amelia Morrone^b, and Marco Marradi^a

^a DICUS - UNIFI, via della Lastruccia 13, 50019-Sesto Fiorentino (FI), Italy;

^b AOU Meyer and NEUROFARBA (UNIFI), Viale Pieraccini n. 24, 50139 Firenze, Italy
E-mail: francesca.buco@unifi.it

Iminosugars are sugars mimetics characterized by the presence of a nitrogen atom in place of the endocyclic oxygen atom of carbohydrates and are well known to inhibit carbohydrate-processing enzymes. Recently, their role as pharmacological chaperones (PCs) for the treatment of Lysosomal Storage Disorders (LSDs) has been disclosed. PCs are molecules able to bind and stabilize misfolded enzymes involved in these diseases resulting in enzyme activity's enhancement. No PCs has been yet identified for Gaucher Disease, which is caused by a misfolding of the lysosomal enzyme β -glucocerebrosidase (GCase) [1].

Recent studies showed that *N*-alkylated 3,4,5-trihydroxypiperidines (red moiety **1** in Figure 1) are promising PCs for GCase [1], and even more promising are the results obtained with a trivalent derivative of **1** [2]. The efficacy of multivalency in modulating GCase activity, prompted us to multimerize suitable derivatized moiety **1** bearing a thiol-ending linker onto gold nanoparticles (AuNPs) as a scaffold.

In parallel, since the *C*2-alkylated 3,4,5-trihydroxypiperidine (green moiety **2** in Figure 1) behaves as a better GCase PC compared to the *N*-alkylated analogue [3], a synthetic strategy was started to obtain multivalent systems (both dendrimers and AuNPs) based on **2**. *In vitro* biological assays are ongoing to test the ability of these new nanosystems to act as PCs for GCase.

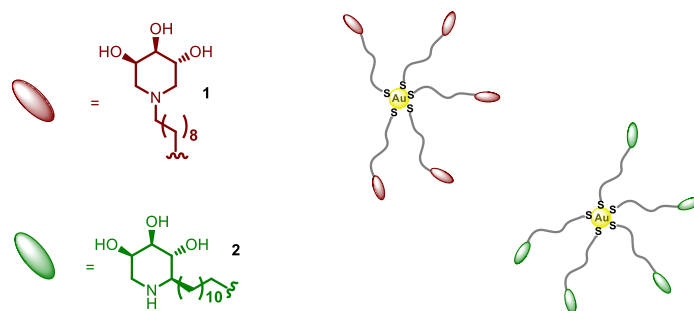


Figure 1: Schematic representation of AuNPs, one of the topics of this project

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OR35

Electrodeposition with modulated currents in optics of a Circular Economy

Elena Mariani^{a,b}, Vincenzo dell'Aquila^b, and Massimo Innocenti^a

^a Dipartimento di Chimica, Università degli Studi di Firenze, Via della Lastruccia 3, 50019, Sesto Fiorentino, Italy

^b Eco-Tech Finish s.r.l., San Zeno, Strada C 27, 52100, Arezzo, Italy

E-mail: elena.mariani@unifi.it

The use of pulsed current is well known as a research tool for studying the electrodeposition mechanism of metals. With increasing emphasis on the properties of the deposits, however, it was realized that this method of deposition could well provide a means of improving their properties [1].

This research aims to find an alternative to the now obsolete use of direct current in galvanic companies, investigating a methodology, that of pulsed currents, whose potential has been known for decades, but never used in this industrial field. The study focuses on a process that allows to obtain products that have similar (or even better) characteristics to those of today but using smaller metal thicknesses, which is essential for a more sustainable industry.

In the pulse electroplating, electrodeposition of the nanostructures depends on two fundamental processes: the nucleation rate and the growth of existing grains. The favorable factors are the ones that cause a high nucleation rate (current density) and a slow grain growth (inhibiting molecules) [2].

The pulsed current plating of this alloy may lead to a more reduced density of pores than that obtained by the conventional direct current plating. Pulse plating can produce a significant change in the morphology of the electrodeposits; by simply adjusting the amplitude and length of the pulses, it is possible to control not only the composition and thickness, in the atomic order, of the deposits, but to improve their characteristics such as grain size, porosity and homogeneity [3].

Research ends in the development of new and innovative electroplating processes that can be used in the electroplating industry, particularly in the industry for fashion and furniture, which increasingly requires process and product innovation aimed at a more conscious, eco-friendly and sustainable vision of the industry.

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OR36

Thia-Bridged Heterohelicenes: synthesis, resolution, and applications

Michela Lupi, Stefano Menichetti, and Caterina Viglianisi

Department of Chemistry "Ugo Schiff" (DICUS) & INSTM Research Unit, University of Florence,
Via della Lastruccia 13, 50019-Sesto Fiorentino, Italy.
E-mail: michela.lupi@unifi.it

Thia-Bridged Hetero Helicenes (TBHH), *Figure 1*, are a peculiar example of helicenes structurally reminiscent of parent triarylamines and phenothiazines. The introduction of thioether bridges in the parent substrates raises the racemization energy barrier making even thia-[4]helicenes configurationally stable at room temperature. The synthesis of these compounds was typically achieved *via* an initial sulfenylation reaction on a triarylamine or a *N*-aryl phenothiazine using phthalimidesulfonyl chloride and a subsequent Lewis Acid-mediated ring closure. Herein, we report a Lewis Base/Hydrogen Bond Donor (LB/HBD) organocatalytic strategy for the synthesis of [4]- and [5]helicenes that were obtained also in enantioenriched form with ee up to 44% using chiral enantiopure chalcogen-containing LBs from the natural chiral pool¹. Additionally, an optical resolution strategy leading to enantiopure [4]- and [5]helicenes using chiral resolving agents² and the application of these compounds as spin filters in spintronic devices will be reported³.

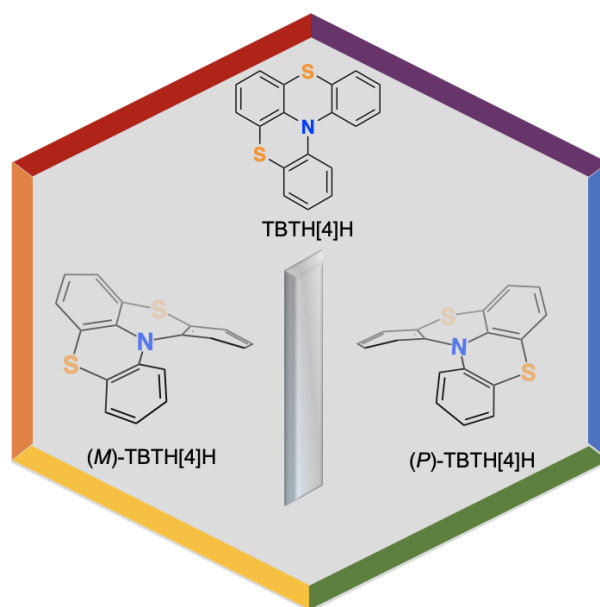


Figure 1: Thia-Bridged Hetero[4]Helicenes.

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OR37

Unusual Behavior of Responsive Peptide Gels

Mert Acar, Duccio Tatini, Lorenzo Pacini, Francesca Nuti, Anna Maria Papini,
and Pierandrea Lo Nostro

*Department of Chemistry 'Ugo Schiff', University of Florence, I - 50019 Sesto Fiorentino (FI)
E-mail: mert.acar@unifi.it*

Peptide-based gels have fine-tuned gelation behavior and mechanical properties. The adaptability of these materials enables the creation of customizable systems, including multi-responsive materials [1]. ACP(65-74) is an active decapeptide fragment of the Acyl Carrier Protein (ACP). We report herein an extensive study on ACP(65-74) gels and in particular on its rheological and fibrillation properties.

We studied 3% w/v gels in water, glycerol carbonate and their mixtures. All samples showed thixotropic behavior and responsiveness to both temperature and pH with fully reversible sol-to-gel transitions. The rheological properties were investigated as a function of temperature and solvent composition. Samples present gel-like, solid material behavior [2]. The zero complex viscosity increases with temperature in all cases, indicating a consistent strengthening of the gel network. Birefringence and Optical Microscopy show the presence of fibrils and ordered regions (See Figure 1). The morphology was investigated by Confocal Laser Scanning Microscopy. Circular Dichroism, Fourier Transformed Infrared, and fluorescence spectroscopy experiments were carried out to further investigate the peptide conformation. The results reveal the presence of a significant amount of β -sheet structure and suggest the formation of fibrils, as with amyloid aggregates. These findings highlight the role of β -sheet fibrils formation in the case of this short peptide fragment.



Figure 1: Bright-field image of ACP(65-74) hydrogel at 10x magnification showing fibrillar structures.

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OR38

Mechanistic studies on antitumor gold compounds

Andrea Geri, Lara Massai, and Luigi Messori

Department of Chemistry DICUS, University of Florence, via della Lastruccia 3-13, 50019 Sesto Fiorentino, Italy

E-mail: andrea.geri@unifi.it

Owing to the great success of Pt-based drugs in anticancer chemotherapy, the study of gold complexes has gained a lot of interest in the view of the discovery of innovative antitumor agents. While Pt drugs exert their actions mostly through binding to genomic DNA and nucleic acids, the main targets of anticancer Au complexes are proteins, typically interacting with the gold center through specific thiol/selenol residues. However, the precise modes of action of gold compounds remain largely unexplored.

During my first PhD year, several ESI-MS binding studies have been conducted according to a well-established experimental protocol developed in our laboratory. Several different experimental conditions were tested to obtain detailed information on the binding mode between selected Au compounds and different model proteins [1-3]. Generally, the analysis of the obtained mass spectra revealed the formation of stable adducts, especially with human thioredoxin reductase (hTrxR), which is considered one of the primary targets of the gold drugs. Careful analysis of ESI MS results allowed us to characterize the nature of the different metal fragments that bind the protein. Notably, the observed patterns of reactivity critically depend on the chemical nature of the gold compound and the structural characteristic of the interacting protein.

Overall, these studies strongly support the view that the selenol-thiol group is the true anchoring site for gold compounds. The present results set the stage to better understand the mechanism of action of these gold compounds and elucidate at the atomic level their mechanism of interaction with model proteins.

In addition, in order to evaluate the gold accumulation and intracellular distribution in A2780 cells, metal uptake studies were performed by ICP-OES. Preliminary results obtained with AF reveal gold distribution in the cytoplasm, nuclei, and mitochondria.

Future studies will involve additional experiments to identify specific protein fragments carrying the metal moiety, and extension of metal uptake studies to the entire panel of gold compounds.

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OR39

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

Laura Vespignani and Antonella Salvini

*Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia 3-13, 50019
Sesto Fiorentino, Italy
E-mail: laura.vespignani@unifi.it*

In recent years it has become increasingly important to identify new materials that can be used in the protection of Cultural Heritage in place of long-chain perfluoroalkyl compounds (PFAS), highly efficient products [1] but with a high environmental impact, and therefore currently under restriction in UE. To develop specific products for the protection of degraded, non-varnishable wooden artifacts, in the last decade new materials have been designed, able to improve the physical-mechanical characteristics of the wood without altering its aesthetic appearance.

Recently, to make wooden surfaces water-repellent, the use of protective agents with characteristics similar to the products used on stone material has been studied. In particular, interesting results have been obtained on wood using two fluorinated products, prepared by reacting an oligo ethylenesuccinamide and a diethylenetriamine with a C6 fluorinated chain epoxide (ESF and DF) [2]. At a later time, another promising product has proved to be an oligo diethylenetriaminosuccinamide functionalized with the same fluorinated chains (DSF). All these compounds have low molecular weights, the presence of polar groups makes them similar to polar materials such as wood while the fluorinated chain gives hydrophobicity and stability to light, but above all they are soluble or easily mixable in eco-sustainable solvents such as 2-propanol. In view of a further probable restriction in the use of C6 fluorinated chemicals, latterly, three other more eco-sustainable products with a shorter fluorinated chain (C4) have been also synthesized (ESF4, DSF4 and DF4).

Systematic tests of wood samples have been done to evaluate and compare these products using a diagnostic protocol developed for this specific application field. The optimal application method has been evaluated for each product. Before and after the treatment, contact angle and colorimetric measurements have been carried out to verify the actual variation in surface wettability with no or minimal alterations to the wood color. Furthermore, the second part of the diagnostic protocol has been developed to test the resistance of these protective materials to natural and artificial photoinduced aging, as well as the resistance to mild abrasion, both on fresh and aged samples, to simulate the effects of manipulating the artefacts.

Best results both in terms of protective efficacy and stability to various types of stress were obtained with ESF and DF, demonstrating the criticality in the use of products with a too low fluorine content.

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OR40

New synthetic pathway to Kesterite nanoparticles with different tin content: an in-depth study of magnetic and optical properties

Alessandro Veneri^a, A. Privitera^{a,b}, B. Muzzi^{a,c}, A. Gabbani^{d,e}, M. Becucci^a, F. Di Benedetto^f, F. Pineider^{d,e}, L. Sorace^a, M. Riede^h, and M. Mannini^a

^a Department of Chemistry "Ugo Schiff", University of Florence and INSTM Research Unit of Firenze, Via della Lastruccia 3-13, 50019 Sesto Fiorentino, Italy;

^b Department of Department of Industrial Engineering, University of Florence, and INSTM Research Unit of Firenze, Via Santa Marta 3, 50139 Florence, Italy;

^c Institute of Chemistry of Organometallic Compounds, C.N.R., and INSTM Research Unit of Firenze, 50019 Sesto Fiorentino, Italy;

^d Department of Chemistry and Industrial Chemistry, University of Pisa, and INSTM Research Unit of Pisa, via G. Moruzzi 13, 56124 Pisa

^e Department of Physics and Astronomy, University of Florence, and INSTM Research Unit of Firenze, 50019 Sesto Fiorentino, Italy;

^f Dipartimento di Physics and Earth Sciences, University of Ferrara, and INSTM Research Unit of Ferrara, Via Saragat 1, 44122 Ferrara, Italy

^h Dipartimento di Physics, University of Oxford, Clarendon Laboratory, Parks Road, OX13PU Oxford, United Kingdom

E-mail: alessandro.veneri@unifi.it

Over the last few decades, significant advancements have been made in the performances of thin film solar cells based on CIGS (Copper Indium Gallium Selenide), CIS (Copper Indium Sulfide) and CdTe technology.[1] However, their reliance on expensive, toxic, and scanty elements like cadmium, tellurium, and indium poses environmental and economic challenges. In this context, $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) emerges as a highly promising inorganic semiconducting compound to produce low-cost thin-film photovoltaic devices because it is composed of easily available, cheap, non-poisonous, and earth-abundant elements. [2] However, the performances of CZTS-based solar cells are below the threshold for effective implementation in the PV-market, thus the integration of greener synthetic approaches with comprehensive material characterization can unlock the full potential of the material, paving the way for the development of efficient and affordable thin-film photovoltaic devices. Here, we propose an innovative low-temperature synthetic pathway to produce $\text{Cu}_2\text{ZnSnS}_4$ nanoparticles. Shape, chemical composition, and phase of the nanoparticles are probed through HR-TEM, XPS, EDX, ICP, and Micro-Raman spectroscopy, moreover, we report on the optoelectrical properties and lattice defects through a multi-technique approach, using Electron Paramagnetic Resonance spectroscopy (EPR), SQUID magnetometry and Magnetic Circular Dichroism (MCD). The performances of hybrid organic-CZTS devices evaluated during my stay at the Oxford University Physics Department highlight that the extensive presence of pinholes is detrimental to the device fabrication, thereby limiting the effectiveness of the bulk heterojunction approach and suggesting the focus of the future research activities I will have to pursue.

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OR41

Evidence of microplastics (MPs) in ground- and well- waters: from sampling to analysis

Laura Sforzi^a, Agostina Tabilio^{b,c}, Tiziana Di Lorenzo^c, Tania Martellini^a, and
Alessandra Cincinelli^a

^a Department of Chemistry "Ugo Schiff", University of Florence, via della Lastruccia 3, 50019
Sesto Fiorentino, Italy

^b Department of Life, Health and Environmental Sciences, University of L'Aquila, Via Vetoio,
67100 L'Aquila, Italy;

^c Research Institute on Terrestrial Ecosystems of the National Research Council of Italy (IRET
CNR), Florence, Italy;

E-mail: laura.sforzi@unifi.it

Microplastics (MPs) are an increasing source of concern. While they are extensively studied in aquatic environments, groundwaters are still little known [1]. For this research, water samples from four Italian groundwater bodies- two karst caves and two saturated alluvial aquifers- have been taken into consideration in order to determine the presence of MPs. Samples were subjected to an oxidative digestion stage using 30% H₂O₂ in order to eliminate any organic matter that would impede further examination. Each sample was vacuum filtrated and a preliminary overview using a stereomicroscope was assessed. The chemical characterization was done by 2D Imaging Fourier Transform Infrared Spectroscopy (FTIR). MPs were found in each sampling site and classified by color, shape, size and composition. In addition, in order to make a preliminary assessment of the potential ecological impacts caused by MPs, the occurrence of these contaminants in the digestive tract of invertebrate fauna found in the same groundwater bodies has been investigated. MPs may enter groundwater bodies through atmospheric depositions, soil infiltrations, and human activity. This poses a risk to the quality of the groundwater and the preservation of biodiversity in these delicate ecosystems, particularly in areas where anthropic pressure is considerable [2]. Further perspectives will focus on the development of an optimal sampling system for MPs in groundwater and also the detection of organic contaminants (i.e., PFAS) in this environment.

This study was supported by National Recovery and Resilience Plan (PNRR), Mission 4, Component 2 "From Research to Enterprise", funded by the European Union NextGenerationEU, CUP B83C22004820002.

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OR42

Bronze disease: synthesis and electrochemical characterization of a new recycled polystyrene-based coating

Daniela Porcu^{a,b}, Emiliano Carretti^{a,b}, and Raffaella Fontana^b

^a Department of Chemistry “Ugo Schiff” and CSGI Consortium, University of Florence, Via della
Lastruccia 3-13, 50019 – Sesto Fiorentino, Fi, Italy

^b National Research Council—National Institute of Optics (CNR-INO), Largo E. Fermi 6,
50125 Florence, FI, Italy

E-mail: daniela.porcu@unifi.it

Polystyrene (PS) is one of the most widely diffused and valuable plastic materials (about 6% of the world's plastic production) with applications from packaging to automotive. Despite its high production volume, high recycling costs are often necessary to transform end-life PS into new valuable materials. For this reason, the development of new protocols aimed at increasing waste PS return in the market is paramount to minimize environmental and health impact. Following a model of circular economics, PS waste can respond to the need to develop new materials suitable for the protection of outdoor bronze surfaces.

Herein, a new protocol for PS upcycling is proposed based on a study by Kurbanova ^[1]. End-life PS was functionalized with an increasing feed of maleic anhydride (MA, 5 to 25% mol) *via* Friedel-Craft acylation reaction, resulting in the formation of carboxylate pendant moieties. In principle, these PS modification could improve coating performances due to the interactions of the newly formed carboxylic moieties with the bronze surface, also producing protecting groups for the copper layer.

PS-MA samples were analyzed by proton nuclear magnetic resonance (¹H NMR), attenuated total reflection Fourier transform infrared (ATR-FTIR), size exclusion chromatography (SEC), and thermogravimetry (DTG).

Aiming to validate our hypothesis, PS-MA films on bronze substrate were prepared and artificially aged ^[2]. Coating thickness was measured by Optical Coherence Tomography (SD-OCT) before and after the artificial aging. To evaluate the corrosion resistance of the coating, potentiostatic electrochemical impedance (EIS) spectroscopy measurements were performed with an agarose gel-polymer electrolyte cell ^[3].

The performance of the tested samples in terms of corrosion resistance, color, thickness, and adhesion is highly promising for the development of a new and effective coating. At last, the PS-MA samples could be further functionalized with target compounds in order to enhance both adhesion and introduce protecting agents for the copper layer.

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OR43

Hard/soft magnetic nanocomposites for high energy product permanent magnet

Alessandro Gerace^a, Federico Totti^a, and Claudio Sangregorio^{a,b}^a *Dipartimento di Chimica, Università degli studi di Firenze, Via della Lastruccia 13, 50019 - Sesto Fiorentino (FI), Italy*^b *ICCOM, Consiglio Nazionale delle Ricerche, Via Madonna del Piano 10, 50019 Sesto Fiorentino (FI), Italy**E-mail: alessandro.gerace@unifi.it*

Permanent magnets (PMs) are classified according to their capacity of storing energy, expressed by the maximum energy product (BH_{max}). The BH_{max} value is obtained from the magnetic hysteresis loop, that is a characteristic magnetization behavior of ferromagnetic materials in the presence of an external magnetic field. By merging the large coercivity of a “hard” phase and the high saturation magnetization of a “soft” one, the BH_{max} can be increased: a valuable strategy is the coupling (exchange or dipolar) of nano-sized grains of the two components [1]. This work moves in this framework aiming at identifying the best building blocks and process parameters to obtain sintered and bonded magnets with no rare earth elements and high energy product. Starting from micrometric or nanometric strontium hexaferrite as hard phase, and metallic iron nanowires as the soft one, various ratios and combining techniques were used. The goal was to discover the best size and shape of the two components, the relative amounts and the key parameters of the process to obtain coupled hard/soft nanocomposites, denoted by a single-phase behavior in the hysteresis loop, without the presence of unusual drops or kinks, that can lead to an improvement in BH_{max} value with respect to single phase hexaferrite [2]. Furthermore, innovative densification technique as SPS and industry manufacturing of magnets have been tested.

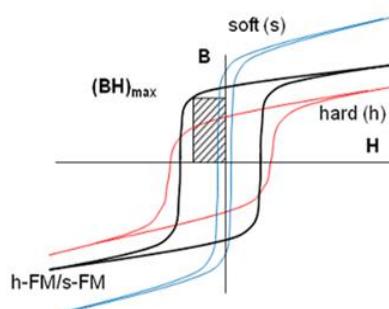


Figure 1: Exemplification of enhanced BH_{max} through hard/soft coupling.

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OR44

Advancing analytical methods for a comprehensive evaluation of emerging and legacy contaminants and their implications on human health following exposure

Saul Santini, Tania Martellini, and Alessandra Cincinelli

*Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia 3, 50019
Sesto Fiorentino, Italy
E-mail: saul.santini@unifi.it*

The abstract describes the result of three years of work in the field of analytical chemistry during the PhD time. In particular, this work focuses on the daily exposure that humans may have through contact or through food. During the discussion, an improvement of the classical analytical approach will be proposed, toxicological phenomena will be observed for certain contaminants in humans, and these analytical methods will then be applied to other matrices. In the first part, a method for the analysis of metals in personal care products was optimized, followed by the analysis of cosmetics commonly sold on the Italian market and evaluation of their toxicological effects on humans by skin contact.

The next topic concerns food and ingestion. Indeed, two common foods were investigated: edible fish and tomatoes. An alternative method to the classical methods for the analysis of polychlorinated biphenyl (PCBs), polybrominated diphenyl ethers (PBDEs), novel brominated flame retardants (NBFRs) and phthalate acid esters (PAEs) was proposed and validated, evaluating their analytical efficiency and sustainability, according to the Green Chemistry criteria. The developed method was then applied to another biotic matrix, *Talitrus Saltator*. For tomatoes, a method was optimised for the simultaneous analysis of 349 multi-residual pesticides and comparing the results and toxicological effects in 504 samples analysed from 2019 to 2022. Finally, a method was developed on another important contaminant, microplastics (MPs). Indeed, through food, MPs can be ingested and can be found within the digestive system such as the intestines and subsequently excreted with faeces. To study MPs contamination in these two matrices, a new method of analysis was developed and validated. Noting the importance of this contaminant for humans, a method was also developed for analysing one of the sentinels of Tunisia's marine areas, the Grey Gull, by collecting regurgitation samples near the saltworks in the coastal city of Sfax.

To summarise, the work described sought to bring about an advancement in analysis processes that would not only observe the purely analytical aspect, but also that of the sustainability of the process and the evaluation, when possible, of the toxicological effects that the presence of certain contaminants causes on humans.



OR45

Study of enzymatic recycling of end-of-life polymers

Benedetta Ciuffi^a, Emiliano Fratini^{a,b}, and Luca Rosi^a

^a Department of Chemistry “Ugo Schiff”, University of Florence, Via della Lastruccia 3-13, I-50019 Sesto Fiorentino, Italy

^b Center for Colloid and Surface Science (CSGI), University of Florence, Via della Lastruccia 3, Florence, 50019, Italy.

E-mail: benedetta.ciuffi@unifi.it

Polyethylene terephthalate (PET) and polyurethanes (PU) are some of the most requested polymers on the market. PET is used to produce beverage and food packaging but also synthetic fiber with exceptional wear resistance, low moisture absorption and durability. Phenomena such as fast fashion have caused an increase in the use of this fiber, with serious problems in the management of end-of-life fabrics that are sent to landfill. According to the new European Directives, closed-loop fiber recycling will become increasingly important. PU rigid foams are used as insulation products. Due to their behavior as thermosets polymers, their mechanical recycling is limited, and more than 50% of PU wastes are landfilled [1]. According to the 12th goal of the 2030 Agenda for Sustainable Development, it is necessary to identify efficient methods for the recycling of plastic waste. Depolymerization mediated by enzymes, has emerged as an efficient and sustainable alternative for plastic recycling [2], thanks to the mild reaction conditions and the prevention in the use of toxic solvents. The monomers obtained in the biodegradation process can constitute molecules with high added value, which can be purified and reused at an industrial level. In the present study, the possibility of valorizing two real polymeric wastes through enzymatic digestion, was evaluated. A synthetic fabric consisting of 72% PET and 18% Elastane (stated on the label), and a rigid DIY PU foam were chosen as substrates. For the enzymatic digestion tests, in accordance with literature, a Lipase from *Candida cylindracea* was used. Enzymatic digestion is an extremely complex process influenced by numerous factors including the chemical-physical characteristics of the polymer. For this reason, during the study some pre-treatments methods have been evaluated to make the substrates more susceptible to biodegradation [3]. The preliminary results have shown that the enzymatic digestion of PET fiber allows the recovery of its high added value building blocks. Conversely, due to the complexity of the substrate and its high degree of cross linking, rigid PU foam is more recalcitrant to the biodegradation process. In the near future, efforts will be made to develop efficient methods of polymers pretreatment in order to improve subsequent biodegradation.

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OR46

Mechanical Rupture of Polyethylene Glycol, Gelatin, Alginate Micro-capsules

Fernando Soto-Bustamante^{a,b}, Martina Raudino^b, Veronica Rossi^b,
Emiliano Fratini^a, and Marco Laurati^a

^a Dipartimento di Chimica and CSGI, Università di Firenze, 50019 Sesto Fiorentino, Italy.

^b BioMérieux Italia, 50012 Grassano FI, Italy

E-mail: fernando.sotobustamante@unifi.it

Micro-capsules can find applications in a variety of fields including drug delivery and microencapsulation. Typically, water-oil emulsions, microfluidics or sacrificial templates are used in their preparation. However, recent studies have shown that employing two immiscible aqueous polymer solutions, such as Polyethylene Glycol (PEG) and Gelatin micro-capsules are produced from water-in-water emulsions [1]. In this project we present the preparation of micro-capsules with different PEG/gelatin/alginate compositions as a mechanical model system of bacterial membranes. The micro-capsules were loaded with a fluorescent dye to measure, and posterior quantify the mechanical rupture of the micro-capsules, to simulate mechanical lysis of bacteria. We found that the composition of PEG/Gel/Alginate resulted in a different size of the capsule, membrane thickness, and therefore in a different response to mechanical rupture.

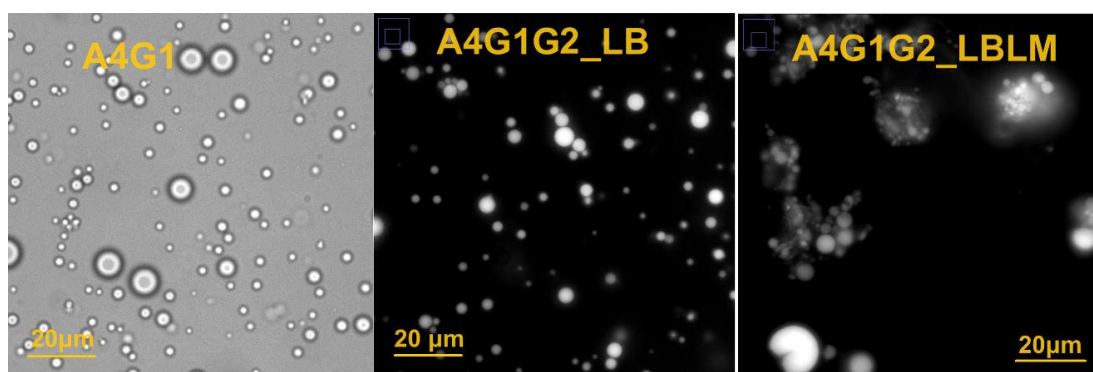


Figure 1: Capsules prepared using PEG/Gelatin/Alginate. From left to right the first image corresponds to the capsules once formed, the middle image corresponds to the capsules with the fluorescent dye and finally the capsules after mechanical rupture.

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OR47

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

Angela S. Tino^{a,b,c}, Anna Maria Papini^{a,c}, Roberta Pierattelli^{a,b},
and Isabella C. Felli^{a,b}

^a *Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia 3, 50019 Sesto Fiorentino, Italy*

^b *Magnetic Resonance Center, Via L. Sacconi 6, 50019 Sesto Fiorentino, Italy*

^c *Interdepartmental Research Unit of Peptide and Protein Chemistry and Biology, Via Madonna del Piano 6, 50019 Sesto Fiorentino, Italy*

E-mail: angelasofia.tino@unifi.it

Many RNA-binding proteins (RBPs) are characterized by modular structures composed by structured domains and intrinsically disordered regions (IDRs). Understanding how these different domains interact to modulate protein function represents an emerging field of research and may stimulate the development of innovative strategies to interfere with these modular proteins. Solution NMR offers the possibility to study both disordered domains and globular domains. In particular, ¹³C detection is a very effective strategy to study modular proteins with intrinsically disordered regions. The Nucleocapsid protein of SARS-CoV-2 represents an example of RBPs [1] which attracted the scientific interest as important alternative drug target because of its low rate of mutations. However, its investigation has been challenging due to its complex modular structure composed of two globular domains and three intrinsically disordered regions that represent 40% of the entire sequence. Nevertheless, by combining ¹H and ¹³C detection, is possible to perform HN/CON multiple receiver NMR experiments, which allow us to get simultaneously complementary information about NMR signals of residues in folded domains and in disordered ones with good resolution in both cases.[2]

My research work deals with two particular constructs of this protein: the well folded NTD construct that is the known RNA-binding domain, and the NTR construct which also includes the two IDRs flanking the NTD. The project is focused on the solution NMR investigation of the interactions between these two protein constructs and some tailored synthetic peptides taking advantages of the solid phase peptide synthesis.[3] We performed NMR titrations to study the interaction between a synthetic peptide and the two different constructs to highlight the different roles of the globular domain and of the IDRs to the interaction. The results confirm an important role played by the IDRs, in addition of course to that played by NTD. In addition, we are planning the synthesis of peptide nucleic acids in order to find a tailored ligand that could better mimic the genomic RNA structure and, ideally, hinder its interaction with the viral protein.

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OR48

Characterization of structurally heterogeneous proteins with NMR

Lorenzo Bracaglia, Isabella C. Felli, and Roberta Pierattelli

Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia 3, Sesto Fiorentino - 50019, Italy

CERM, University of Florence, Via Luigi Sacconi 6, Sesto Fiorentino - 50019, Italy

E-mail: lorenzo.bracaglia@unifi.it

Nuclear magnetic resonance spectroscopy has proven to be an excellent technique for the characterization at atomic resolution of intrinsically disordered regions and multi-domain proteins [1]. The first case of study presented is the TAZ4 construct of the human CREB binding protein (CBP), that comprises the globular zinc-binding TAZ2 domain (89 residues) and the disordered ID4 region (207 residues) [2]. The expression and purification protocol of this construct was designed and optimized to obtain protein samples suitable for NMR applications. The sequence specific resonance assignment has been carried out reaching 80% of the primary sequence. The ^1H - ^{15}N HSQC spectrum and ^{15}N R_1 and R_2 values confirm the folding of the globular region and the presence of a partially folded helix in the disordered region. To fill the gap of the assignment we designed 2D and 3D NMR experiments to discriminate the cross peaks originating from the two regions. This was possible by implementing an inversion recovery block into the pulse sequences, to take advantage of the very different relaxation properties of the two domains of the construct.

Another case of study was the characterization of the interaction of two core proteins of plasma membrane-associated platforms (PMAPs), that are cellular structures that form at the front of migrating tumor cells. The expression and purification of ERC1(270–370) and LL5 β (381–510) constructs was carried out in collaboration with the Vita-Salute San Raffaele University (Milan, Italy). We performed the first NMR characterization of these two constructs. Moreover, we tested their interaction *in vitro* using ^1H - ^{15}N HSQC experiments [3].

The authors thank MUR-Italy ("Progetto Dipartimenti di Eccellenza 2018-2022" allocated to the Department of Chemistry "Ugo Schiff").

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OR49

Plasmonic properties of gold nanoparticles interacting with synthetic lipid bilayers

Ilaria De Santis^{a,b}, Costanza Montis^{a,b}, Marco Marradi^a, and Debora Berti^{a,b}

^a Department of Chemistry "Ugo Schiff", University of Florence, via della Lastruccia 3-13, 50019 Sesto Fiorentino, Italy

^b CSGI - Center for Colloids and Surface Science, University of Florence, via della Lastruccia 3, 50019 Sesto Fiorentino, Italy
E-mail: ilaria.desantis@unifi.it

Despite their revolutionary potential in biomedical applications, the limited number of nanoparticles (NPs) approved for clinical use is attributed to a gap in understanding their biological fate. Biomimetic lipid interfaces represent a promising approach to investigate relevant events occurring at the nano-bio interface, i.e., where NPs meet biological barriers, under simplified and controlled conditions [1]. From a different perspective, the combination of inorganic NPs with lipid membranes is instrumental to build up novel smart hybrid materials, thereby advancing Nanomedicine.

In this context, some recent research reports have focused on the interaction of gold nanoparticles (AuNPs) with synthetic lipid vesicles to enhance our knowledge on nano-bio interfaces. Moreover, the spectral shift of AuNPs localized surface plasmon resonance (LSPR) was shown to depend on some ensemble-averaged properties of lipid assemblies, which can then be determined exploiting the spontaneous clustering of citrate-capped AuNPs on the lipid membrane [2,3].

This contribution explores the plasmon-based relation between AuNPs aggregation and the mechanical response of lipid membranes, aiming at establishing novel plasmonic descriptors for AuNPs-lipid bilayers interactions. By performing UV-Vis measurements, we monitored the evolution of AuNPs LSPR in the presence of a series of synthetic unilamellar liposomes with different rigidities at varying vesicles/AuNPs molar ratios. The analysis of UV-Vis spectra identified a specific concentration range where an isosbestic point emerges, whose wavelength is unique to each lipid composition and dependent on liposomes' stiffness.

Combining UV-Vis data with structural and morphological information, we formulate a unifying hypothesis on the interaction pathway of citrate-coated AuNPs and lipid vesicles and introduce the isosbestic wavelength as a new analytical tool to precisely evaluate the stiffness of membrane-enveloped synthetic and biological nanosized particles.

Overall, the recent results contribute to a comprehensive understanding of the association between AuNPs and synthetic and natural lipid vesicles, disentangling the effect of membrane rigidity from concentration effects on AuNPs plasmonics. This description will enable the design of smart hybrids and provide nanosized analytical probes to sample ensemble-averaged properties of membrane-enveloped particles.

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OR50

Different auxiliary-promoted C(sp³)-H bond activations on a challenging substrate, the *trans*-2-aminocyclopentanecarboxylic acid (ACPC)

Lorenzo Baldini and Andrea Trabocchi

Department of chemistry "Ugo Schiff", University of Florence, via della Lastruccia 3-13, 50019, Italy

E-mail: lorenzo.baldini@unifi.it

The β -amino acid 2-aminocyclopentanecarboxylic acid (ACPC) possesses peculiar capability as monomer for the synthesis of unnatural ordered-oligomers, called foldamers [1]. We applied Pd-catalyzed auxiliary-directed C(sp³)-H activation reactions on such an interesting compound, since they demonstrated to be viable synthetic routes for the stereoselective introduction of FGs. Indeed, many examples are reported concerning the functionalization of saturated carbocycles [2] and α - and β -amino acids [3].

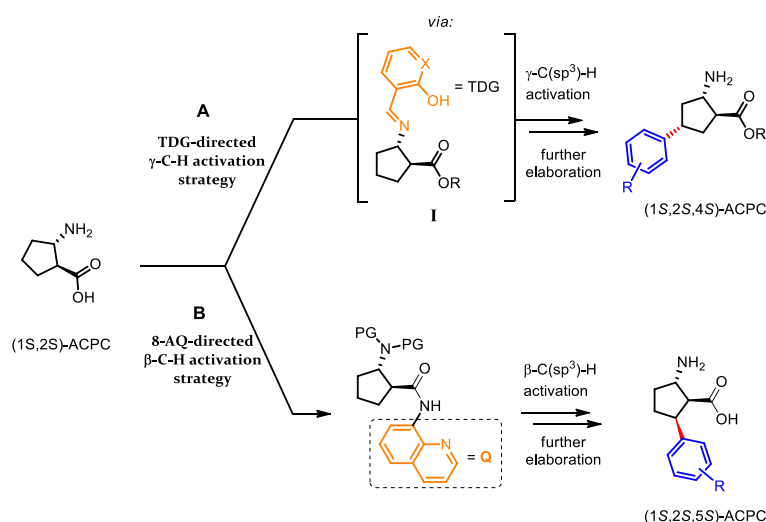


Figure 1: Approach for the two C(sp³)-H activation strategies.

Once the method to access the enantiopure (1*S*,2*S*)-2-aminocyclopentanecarboxylic acid was optimized, we exploited both the FGs beared by ACPC to carry out two distinct CH activations, the carboxylic acid FG for the conduction of C-H activation employing 8-AQ DG, and the amino FG for the exploitation of the TDG strategy. Through these two procedures, we succeeded in stereoselectively inserting aryl moieties in the 4 and 5 positions, respectively, accessing unprecedented functionalized ACPC derivatives.

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OR51

Adsorption of molecular magnets on metal surfaces

Mariano Riccardi, Lorenzo Briccolani-Bandini, Federico Totti, Marco Pagliai,
and Gianni Cardini

*Department of Chemistry "Ugo Schiff", University of Florence, 50019 Sesto Fiorentino,
Italy*

E-mail: mariano.riccardi@unifi.it

The progress of information technology requires the development of ever smaller and faster devices for data storage and information basic units. Active research in this area focuses on molecular magnets (MM), which are considered among the best candidates for the quantum declinations of these fields of research. These applications require the ability to access and control the single molecule, so adsorption on solid surfaces is mandatory.

Computational investigations into the adsorption and organization of these molecules on surfaces require simulating nanoscale systems. However, such simulations can be computationally expensive or even unfeasible depending on the level of theory employed.

To address this challenge we are developing a protocol for the study of these systems by using an external potential that mimics the effect of the metal surface. This approach allows us to avoid explicitly simulating the surface and significantly reduces the computational costs of these calculations.

In this communication, we will discuss a series of preliminary results on the interaction of copper phthalocyanine (CuPc) adsorbed on gold surfaces. We will present a comparison between calculations performed using the external potential approach to mimic the metal surface and fully atomistic DFT calculations, providing insights into the pros and cons of the two strategies.

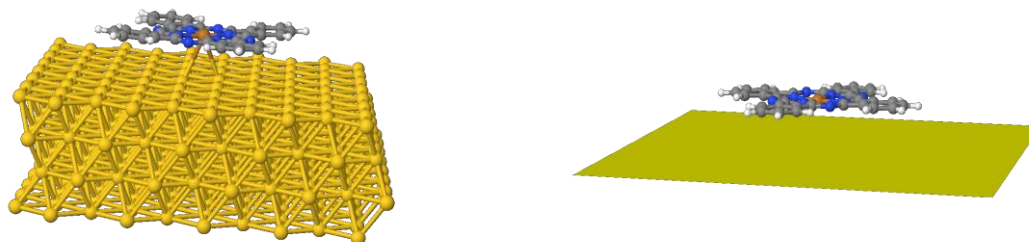


Figure 1: Phthalocyanine simulated with the explicit surface (left) and the external potential (right).



OR52

Microbial Synergy: Exploring Bioremediation and Microplastic Dynamics in Environmental Resilience

Serena Benedetta Cabigliera^a, Tania Martellini^a, David Chelazzi^a,
Alessandra Cincinelli^a, Daniele Cantagalli^b, and Andrew Jenkins^c

^a Department of Chemistry 'Ugo Schiff', University of Florence, Via della Lastruccia 3 – Sesto Fiorentino, 50019, Firenze, Italy

^b ÈCOSÌ, partner company, Via Giovanni Giorgi 12 - Forlì, 47122, Forlì, Italy

^c Faculty of Technology, Natural Sciences and Maritime Sciences, University of South-Eastern Norway, Bø, Norway

E-mail: serenabenedetta.cabigliera@unifi.it

The study employs a multidisciplinary approach to unravel the capacity of microorganisms in utilizing diverse organic materials as sources of carbon and energy, with many of these compounds susceptible to partial or complete breakdown by naturally occurring microorganisms [1]. This entire degradation process is influenced by multiple factors, resulting in variations in the extent and speed of degradation. Bioremediation, a method employing biological processes to remove pollutants and detoxify contaminated environments, presents a promising approach [2]. Recent investigations into plastic degradation offer compelling evidence of microorganisms' proficiency in breaking down plastics and microplastics (MPs) in polluted settings. From a bioremediation standpoint, leveraging the potential of microorganisms to tackle emerging pollutants like MPs shows significant promise. Certain bacterial species have demonstrated impressive capabilities in breaking down carbon chains through specific enzyme activation, as evidenced in previous research [3]. The findings from this study provide valuable insights for selecting bacterial species with high degradation capacity, but further research is necessary to delve deeper into their mechanisms and fully grasp their potential in environmental remediation.

In the realm of bioremediation, a concurrent investigation has been initiated to scrutinize the abundant occurrence of MPs following forest wildfires. This research endeavor aims to discern and proficiently extract MPs from the organic matrix within post-combustion residues in forest soils. This facet of the study underscores the enduring significance of MPs, both in primary and secondary forms, as substantial environmental contaminants. Various methodological approaches, including polymer extraction and digestion, are employed to ascertain optimal techniques for the manipulation of pertinent polymers. Through this multidisciplinary investigation, the research contributes pivotal insights into the persistence of MPs in post-fire ecosystems, illuminating potential ecological implications that warrant thoughtful consideration and proactive measures.

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OR53

Development of materials for the selective coordination of critical elements present in produced waters

Pietro Gentilesca^a, Antonio Bianchi^a, and Samuele Santarelli^b

^a Department of Chemistry, University of Florence, via della Lastruccia 3, 50019, Italy

^b Eni S.P.A., via Felice Maritano, 26, 20097, S. Donato Milanese (MI), Italy

E-mail: pietro.gentilesca@unifi.it

Thanks to the continuous growth in the request of critical elements and the importance of having a sustainable management of water resources, the recovery of saline byproducts generated during oil and gas production is an important economic and ecological goal set by scientists and environmentalists all over the world. To date the main approaches used to recover the critical elements present numerous flaws, that lead to the desire to find new and more functional methods. The main strategy that we used to achieve the recovery of the saline product is based on creating a complex, using the metallic counter ion present in the saline product. One of the most important metal ions in the production water is Li^+ , which is found together with other, more abundant, salts. To create ligands capable of creating a complex with Li^+ we decided to exploit a specific characteristic of it: It is the smallest metal ion. Basing our design on this characteristic we managed to synthesize a ligand, which is now being tested to understand its physical-chemical properties. The next step is to create new ligand and to functionalize them on a solid support, following previously reported procedures [1, 2].

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OR54

A Comprehensive Statistical Analysis of the Structural Properties Exhibited by Glycoproteins

Michele Casoria^{a,b}, Marina Macchiagodena^a, Carla Bazzicalupi^a, Claudia Andreini^{a,c}, Gianni Cardini^a, Anna Maria Papini^{a,b}, and Marco Pagliai^a

^a*Dipartimento di Chimica "Ugo Schiff", Università degli Studi di Firenze, Via della Lastruccia 3-13, I-50019 Sesto Fiorentino, Italy.*

^b*Interdepartmental Research Unit of Peptide and Protein Chemistry and Biology, Università degli Studi di Firenze, Via della Lastruccia 13, I-50019 Sesto Fiorentino, Italy*

^c*Magnetic Resonance Center (CERM), Università degli Studi di Firenze, Via Luigi Sacconi 6, 50019 Sesto Fiorentino, Italy*

E-mail: michele.casoria@unifi.it

Glycoproteins feature a carbohydrate covalently bonded to a protein, with glycan variations like monosaccharides or polysaccharides. Glycosidic linkage can be categorized in O-glycosidic, N-glycosidic, S-glycosidic, and C-Glycosidic, depending on the specific atom of the amino acid involved in the bond with the sugar. The Protein Data Bank (PDB) offers a valuable resource for exploring the three-dimensional configurations of glycoproteins and protein-carbohydrate complexes, aiding our comprehension of glycosylation's impact on proteins. Unfortunately, the glycan components in these structures frequently exhibit several inaccuracies, spanning from minor irregularities to significant errors. Some of these problems have been fixed in PDB-REDO [1], a database reporting protein structures subject to experimental verification to enhance precision and correctness in deposited structures. However, prior examinations of carbohydrates in the PDB lacks in systematic categorizing the sugar components based on glycosidic linkages and have reported only a limited set of structural parameters [2]. Furthermore, the number of computational studies on these systems is quite limited due to the few available Amber-compatible force fields (FFs).[3]

Therefore, we are performing a systematic analysis of the entire PDB database. Following a resolution-based filter, this analysis involves precise categorization of sugars based on their glycosidic linkages, employing the DSSP algorithm to further subdivide sugars based on the secondary structure of the amino acid involved in the glycosidic bond. In the case of each sugar, we provide a comprehensive report on the properties of this moiety, including measures of distance, angle, and dihedral. Using Cremer-Pople Parameters, we analyze conformation, providing deep insights into experimental structures of carbohydrates in the PDB. This data aids comprehensive understanding and potentially advancing force field parameters.

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OR55

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

Chiara Cianci and Rodorico Giorgi

*Department of Chemistry "Ugo Schiff" and CSGI, University of Florence, Via della Lastruccia 3,
50019 Sesto Fiorentino, Florence, Italy
E-mail: chiara.cianci@unifi.it*

This research focuses on the formulation of nanostructured composites with both a macromolecular component and an inorganic component to obtain a reversible and inorganic-substrate compatible product to overcome the limits of traditional synthetic polymers used in conservation. In the current century, Street Art is increasingly impacting worldwide art production. Unfortunately, the constant exposure to environmental conditions of such artworks, for instance, murals, makes their conservation much more problematic. Furthermore, biological agents are non-negligible in urban art degradation [1]. The materials involved in street art are commonly both organic (polymeric paints) and inorganic (concrete, mortar, etc.). For this reason, their physicochemical properties must be considered to develop effective products for their conservation.

This work reports on the study of specifically tailored hybrid coatings for the protection and consolidation of Street art by exploiting the properties of chitosan as a protective agent against salts and microbial agents. Chitosan is a renewable, abundant, non-toxic, and inexpensive biopolymer that exhibits antimicrobial properties [2]. It also shows promising physical properties as it forms semi-permeable and mechanically resistant films [3].

Organic-inorganic hybrid materials (OIHM) based on chitosan and nano-silica are designed and investigated. Chemical stability, color and gloss variations, water vapor permeability, and hydrophobicity are evaluated on spray-painted concrete mockups before and after the application of the nanocomposites, and its long-term stability is assessed through photochemical, hydro-thermal, and thermal aging tests.

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OR56

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

Giulio Pappaianni^{a,b}, Walter Giurlani^a, Dario Morini^b, and Massimo Innocenti^a

^a Department of Chemistry "Ugo Schiff", Università degli studi di Firenze, via della Lastruccia 3, 50019, Florence, Italy

^b Lotti srl, Via Maestri del Lavoro 14/16, 50058, Florence, Italy

E-mail: giulio.pappaianni@unifi.it

The project aims to synergistically exploit the advantages of semiconductors and alloys using electrodeposition as a synthesis method for spin-filtered photoelectrochemical water splitting and optimized hydrogen production directly from solar energy, with a focus on 4.0 industry applications, environmental sustainability, metals recovery and streamlining industrial processes. To accomplish this goal, it is crucial to produce an electrodeposited film tailored for spintronic applications¹. The alloy to be deposited was selected and electrochemical studies were carried out on all the chemical species used by means of cyclic voltammetry techniques, the optimal operating conditions were identified. The sample obtained was characterized using Electron Microscopy (SEM), X-Ray Fluorescence spectroscopy (XRF), X-Ray Diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), magnetometry using Superconducting Quantum Interference Device (SQUID) and magnetoresistance analysis. The deposit is predominantly made of MnAs and MnO₂². Another important step in advancing the project was carrying out experiments on the electrodeposition of thin films and nanostructures of metals on silicon substrates to exploit the advantageous characteristics of both materials³. The selection of metals to be electroplated was carried out through the evaluation of Density Functional Theory (DFT) calculations. Voltammetric studies and Charge-controlled depositions were performed, tests on electroless deposition were made. Ideal deposition conditions were sought. The deposits thus obtained were characterized using SEM and XPS. A study was then conducted with the aim of optimizing industrial electrolysis processes. Using commercial electroplating baths, the results obtained by working in direct current and pulsed current were evaluated. Also, the use of two different commercial systems for optimizing current distributions in galvanic frames was analyzed, comparing the results with those obtained using a standard electrode system. Mapping by X-Ray Fluorescence (XRF) was carried out on the samples thus obtained, which made it possible to evaluate the distribution of precious metal thicknesses on the entire frame. The corrosion resistance of the samples was also studied as the deposition conditions varied, and to do this the salt spray test was employed. A thin film of material containing MnAs was electrochemically deposited, a variety of nano and microstructures of metals were obtained by electrodeposition on silicon. Important information was obtained for the optimization of industrial processes within the industrial electroplating plant.

[1] N. Watanabe et al., *APL Mater.* **2015**, 3(4), 1-6.

[2] M. Solzi et al., *J Magn Magn Mater.* **2010**, 322(9-12), 1565-1568.

[3] X. Zeng et al., *Small Struct.* **2021**, 2, 2000138.



OR57

Archaeometric study of Montelupo Maiolica

Simi Maria Emilia Mangani

*Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia, 3, 50019-Sesto Fiorentino (FI), Italy
E-mail: simimariaemilia.manganil@unifi.it*

Ceramic materials are among humanity's most significant technological achievements, and the Montelupine maiolica production represents a remarkable example of this art during the Late Medieval-Renaissance period.

Although a vast diagnostic campaign was conducted on these artefacts' ceramic bodies [1], their glazes have never been exhaustively explored. In order to fill this gap, this project aims to define a multi-analytical approach suitable for studying the complex stratigraphy of Montelupo glazes: i.e., white opaque glaze, intermediate chromophore-rich decorative layer and possible transparent superficial glaze.

Thanks to the collaboration of the Museum of Ceramics of Montelupo and the Colorobbia Research Centre, forty-two samples were selected to cover the entire Montelupo's chromatic range and the different production periods.

The objects were analyzed, preferring a non-invasive and non-destructive approach, more adequate for future application on well-preserved museum pieces. The MA-XRF scanner detected the colors' characteristic elements working by maps. The micro Raman spectrometer provided information on molecular bonding, while the PIXE-PIGE analyses allowed reliable semi-quantitative data.

Regarding the white areas (white glaze and transparent coating), an interesting trend in the main components' concentration through the centuries is revealed. SnO₂ (opacifier) [2] and PbO (primary fluxing agent) contents, at their peak in the earliest and latest artefacts, seem to reflect the lower technological level of the archaic period and the artistic (and technological) crisis that affected Montelupo since the late 16th century. At the same time, the main chromophores in the decorations are also identified.

The information thus gained and the SEM-EDS results (acquired on seven samples probing each glaze's layer) were then compared to assess the reliability of the non-invasive approach.

A satisfactory agreement is found, even if two critical issues are encountered: the difficulty in identifying the tin-modified Naples Yellows [3] and the inability to determine the presence/absence of transparent glaze directly.

[1] G. Baldi, *Storia della ceramica di Montelupo*. **2003**, 5, 87-115.

[2] M. Martin et al., *Archaeol Anthropol Sci*. **2018**, 11, 1155-1167.

[3] G. Bultrini et al., *Appl. Phys. A*. **2006**, 83(4), 557-565.



OR58

Miniaturized Electrochemical Sensor For Dopamine Detection in Biological Fluids

Ilaria Antonia Vitale, Giovanna Marrazza, Ilaria Palchetti,
and Camilla Parmeggiani

Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia 3, Sesto Fiorentino, 50019

E-mail: ilariaantonia.vitale@unifi.it

Dopamine, a neurotransmitter that plays multiple roles in cells, is linked to various neurological disorders, such as Alzheimer, Parkinson etc. When its levels in biological fluids are altered, several neurological and motor impairment occurs. Nowadays, some of the major therapeutics drugs used for treatment, work by modifying the effects of dopamine. Therefore, it is crucial to develop sensitive, miniaturized, and user-friendly diagnostic platforms to manage personalized and targeted drug treatment.

This study introduces a new analytical wearable platform for screening of dopamine levels on body. Specifically, carbon screen-printed electrodes were enhanced with specific amino acids serving as precursors for the creation of conductive and biocompatible polymers. The modified platforms were characterized using cyclic voltammetry and electrochemical impedance spectroscopy. The sensor analytical performances were evaluated in both standard solution and in samples simulating biological fluids, such as artificial sweat. The proposed platforms were tested in the dynamic range of 1-100 μM . A limit of detection (LOD) of 2 nM was obtained.

Acknowledgements

This work was supported by the European Union by the NextGenerationEu project ECS00000017 'Ecosistema dell'Innovazione' Tuscany Health Ecosystem (THE, PNRR, Spoke 3: Nanotechnologies for diagnosis and therapy).



OR59

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

Yshtar Tecla Simonini Steiner^a, Giammarco Maria Romano^a, Andrea Bencini^a,
Enrique Garcia Espana^b, and Estefania Delgado^b

^a *Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia 3, 50019 Sesto Fiorentino, Florence, Italy*

^b *Instituto de Ciencia molecular, University of Valencia, Catedrático José Beltrán Martínez 2 46980 Paterna, Spain*

E-mail: Yschartecla.simoninisteiner@unifi.it

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, related to their potential toxicological effects towards humans and environment.[1] EPs include mainly chemicals found in pharmaceuticals, such as antibiotics and NSAIDs, waterproofing agents, in particular perfluoroalkyl derivatives, plasticizers etc. In this panorama, the PhD project is devoted to the design and synthesis of new fluorescent chemical sensors targeting different model analytes chosen to be representative of different classes of emerging pollutants, to their physical-chemical characterization, and finally to the analysis of their sensing ability. Our optical probes have been conceived adopting the principles of Supramolecular chemistry for which the interaction between the guest and the receptor unit as a result of appropriate combination of specific intermolecular interactions may induce changes in the luminescence emission of fluorescent chemosensors. [2] For simplicity, the various receptors developed have been classified by their fluorophore unit, including: Monopyrene based chemosensors, proposed as fluorescent probes for the detection of PFOA (perfluorooctanoic acid) in aqueous media; [3] Cyanine based chemosensors and FRET based chemosensors designed for targeting antibiotics. Final results regarding synthesis and analysis of the developed chemical sensors will be presented at the annual PhD symposium in Chemical Sciences.

[1] B. Petrie et al., *Water Research*. **2015**, *72*, 3-27.

[2] B. Valeur, I. Leray, *Coord. Chem. Rev.*, **2000**, *205*, 3-40.

[3] Y. T. Simonini Steiner et al., *Molecules*. **2023**, *28*, 45-52.

OR60**Modified crystalline nanocellulose for the production of hybrid materials for biomedical applications**Francesca Mancusi^a, Luca Torrini^a, Costanza Montis^a, Francesco Pinaider^b,
Alessio Gabbani^b, Beatrice Muzzi^a, and Stefano Cicchi^a^a Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia 3-13,
50019, Sesto Fiorentino, Italy^b Department of Chemistry and Industrial Chemistry, University of Pisa, Via Moruzzi 3, 56124,
Pisa, Italy

E-mail: francesca.mancusi@unifi.it

The use of nanomaterials extracted from renewable biomass, in a world facing a serious ecological problem resulting from the abuse of petroleum-derived substances, is becoming increasingly popular. In this context, nanocellulose has shown promise in various applications because it is biocompatible, has good mechanical properties, and is easy to functionalize. [1] One possible use of this biomaterial is as a *drug delivery system*. For this purpose, nanocellulose was functionalized by introducing carboxyl spacers of different lengths with the aim to obtain nanohybrids with metal oxide nanoparticles. Surface modification of cellulose nanocrystals was performed with different approaches: by TEMPO-catalyzed sodium hypochlorite oxidation, by reaction of primary glucose hydroxyl with monochloroacetic acid and succinic anhydride. Indium Tin Oxide (ITO) nanoparticles have a plasmonic absorption peak in the near-infrared and, following absorption, have non-radiative relaxations that lead to the conversion of the energy absorbed by the electrons into heat that will be exchanged with the surrounding environment. [2] This could be of interest in phototherapy of surface tumors. ITO NPs, having affinity for carboxylic functions, were made to interact in an aqueous environment with the various derivatized nanocellulose samples described above. A fluorescent probe of the BODIPY family and a sugar unit were subsequently introduced that will allow the delivery to be observed and directed toward neoplastic cells. In-cell biological tests will demonstrate the efficacy of the obtained system.

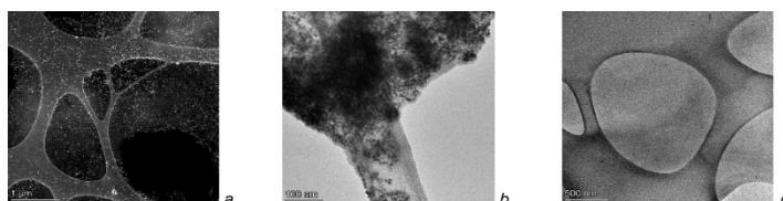


Figure 1: TEM images of the CNC decorated with ITO. From left to right a) CNC-oxidized, b) CNC-succinic c) CNC-carboxymethylated.

[1] N. Lin et al., *Eur. Polym. J.* **2014**, 59, 303-325.

[2] A. Mazzotta et al. *ACS Appl. Mater. Interfaces.* **2022**, 14, 35276–35286.



OR61

Sewage sludge-derived biochar for the adsorptive removal of antibiotics in wastewater

Michelangelo Fichera^a, Massimo Del Bubba^a, and Donatella Fibbi^b

^a Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia, 3, 50019 Sesto Fiorentino (Italy)

^b Gestione Impianti di Depurazione Acque (G.I.D.A.) S.p.A., Via di Baciacavallo 36, Prato, 59100 (Italy)

E-mail: michelangelo.fichera@unifi.it

Antibiotics, despite their health-saving benefits, pose a serious threat to the ecosystem as well as human health and the economy due to their potential adverse effects when released into the environment. Indeed, most of them are poorly absorbed and metabolised by humans and animals and consequently are mostly excreted as such. Even though wastewater treatment plants (WWTPs) play an important role in controlling environmental pollution, often they are not specifically designed for antibiotic removal, thus representing a point-source of pollution for surface water, lakes and sea. Among the technologies developed to remove emerging contaminants from wastewater, biochar could represent a cost-effective and efficient solution as a potential adsorbent for antibiotic removal. Furthermore, the biochar production from sewage sludge pyrolysis is a promising approach to manage hazardous residues from WWTPs. Based on the above-mentioned considerations, the objective of this study was the production of biochar from mixture of biological sludge and waste woody biomass. The materials were investigated for their product characteristics and environmental compatibility taking as a guideline the European Standards for materials suitable for water intended for water consumption [1] to improve their sorption capacity towards different antibiotics, in comparison with a commercially available activated carbon (AC), commonly employed in WWTPs. A model group of 5 antibiotics was selected, including erythromycin (a macrolide) and ciprofloxacin (a fluoroquinolone). Italian consumption data of pharmaceutical compounds in the latest years were considered as election criteria [2]. Moreover, some antibiotic compounds that appeared in European "Watch Lists" for surface water monitoring [3] were included in this study, regardless of their consumption data. Langmuir models were more suitable to describe the adsorption process. Biochar exhibited maximum adsorption amount of the investigated antibiotics 1.6-2.2 lower, in some cases even higher, than AC, thus highlighting its promising sorption performances.

[1] European Committee for Standardization, EN 12915-1/2009.

[2] Rapporto AIFA: The Medicines Utilisation Monitoring Centre. National Report on antibiotics use in Italy. Year 2021. **2023**, Italian Medicines Agency.

[3] European Commission, Commission implementing decision (EU) 2020/1161 of 4 August 2020 establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council. **2020**, *Official Journal of the European Union*.

OR62

Metal-based Antimicrobials to fight Antibiotic Resistance

Stefano Zineddu^{a,b} and Luigi Messori^a^a Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia 3, 50019 Sesto Fiorentino, Italy^b Magnetic Resonance Center (CERM), University of Florence, Via Luigi Sacconi 6, 50019 Sesto Fiorentino, Italy

E-mail: stefano.zineddu@unifi.it

The antibiotic resistance crisis poses a global threat to human health, due to the emergence and spread of multidrug-resistant (MDR) bacteria or "superbugs". Treatment options are becoming more limited. With a currently scarce drug discovery pipeline mostly including derivatives of the known antibiotics, new classes of antibiotics are urgently required and innovative strategies must be implemented.

Owing to their peculiar structural and electronic properties, metal-based compounds represent a rich and still largely unexplored source of new antimicrobial agents endowed with innovative modes of action (MOA) [1]. Remarkably, metal complexes grant access to ligand exchange/release, ROS generation, redox activation, catalytic generation of toxic species and depletion of essential substrates. The chance of overcoming antibiotic resistance is further reinforced by the typical occurrence of multiple modes of action for a single metal compound. Herein I present the case study of the interactions between Trypanothione Reductase from *T. brucei*, a parasitic protozoan, and a selected set of metal-based compounds through an ESI-MS approach. Generally, the analysis of the obtained spectra revealed the formation of stable adducts (Fig. 1). Overall, the present results set the stage to better understand the mechanism of action of these compounds and to elucidate their antimicrobial activity.

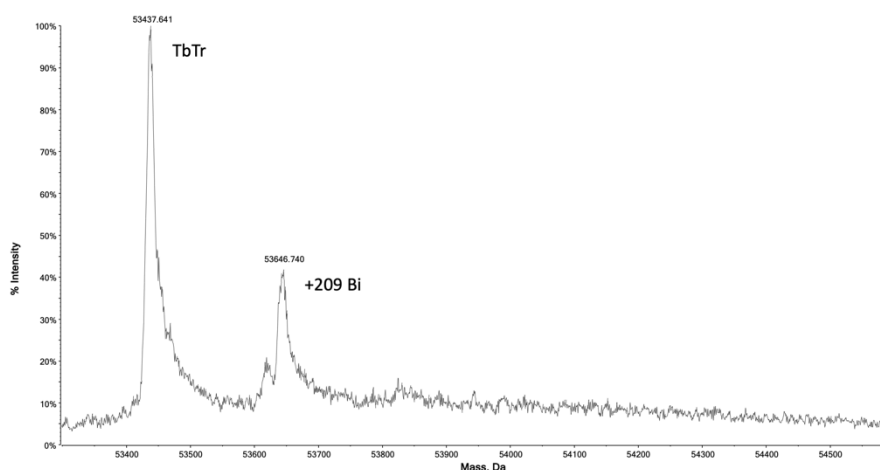


Figure 2: Deconvoluted ESI-MS spectrum of TbTr ($5 \cdot 10^{-6}$ M in ammonium acetate 20 mM) incubated at 37 °C for 24h with a bismuth(III) acetate solution and DTT in a 1:3:14 protein-to-metal-to-reducing agent ratio.

[1] A. Frei et al., *Chem. Sci.* **2020**, *11*, 2627-2639.

Optimization of the sample selection procedure of historical mortars for radiocarbon dating

Sara Calandra^{a,b}, Emma Cantisani^c, Mariaelena Fedi^d,
and Carlo Alberto Garzonio^a

^a Department of Earth Sciences, University of Florence, Via la Pira 4, 50121-Florence, Italy

^b Department of Chemistry 'Ugo Schiff', University of Florence, Via della Lastruccia 3, 50019-Sesto Fiorentino, Italy

^c Institute of Heritage Science, National Research Council of Italy, Via Madonna del Piano 10, 50019-Sesto Fiorentino, Italy

^d National Institute of Nuclear Physics, Unit of Florence, Via Bruno Rossi 1, 50019-Sesto Fiorentino, Italy

E-mail: sara.calandra@unifi.it

The use of radiocarbon (^{14}C) dating of ancient mortars proposed in the 1960s focused on the inorganic binder and organic fragments, but there is no universally accepted protocol that has been validated within the radiocarbon community. For accurate dating of mortar, a multidisciplinary approach is crucial, including a thorough characterization of the mortar and an effective sample selection procedure (Fig. 1), which was developed in the laboratories of DST-UNIFI, ISPC-CNR and INFN-LABEC in Florence and ranges from sampling to Accelerator Mass Spectrometer (AMS) measurements [1-2]. ^{14}C -AMS measurements are conducted on bulk or individual lump samples, with CO_2 extraction adjusted to sample type. Our selection procedure was applied to choose binder samples from Florentine mortars (Trebbio Castle, S. Felicita Church, Medici Riccardi Palace and Baptistery of S. Giovanni) and Pompeian mortars (Eumachia Building, Temple of Genius Augusti, Tabularium and Temple of Apollo), as well as certain organic fragments from the mortars of the Church of St. Philip in Hierapolis (Turkey) [3].

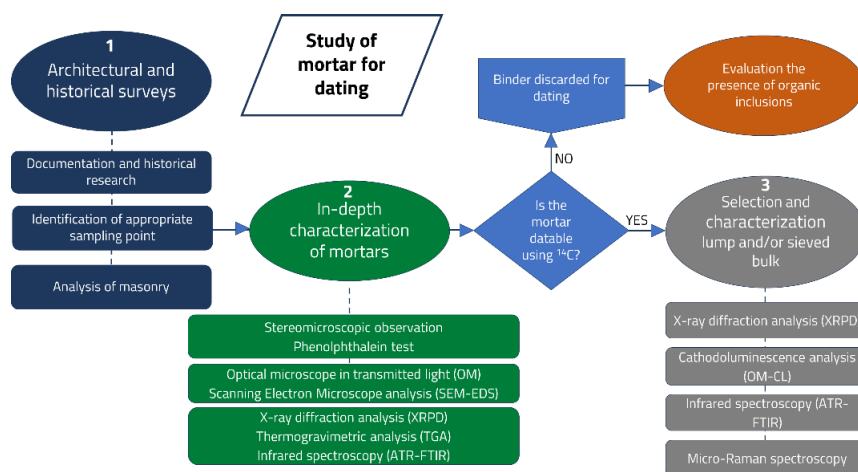


Figure 1: Our procedure for selecting samples for ^{14}C dating of historical mortars.

[1] S. Calandra et al., *IOP Publishing*. **2022**, 2204(1), 012048.

[2] S. Calandra et al., *Analyst*. **2023**, 148, 2861.

[3] S. Calandra et al., *Radiocarbon*. **2023**, 65(2), 323-334.



OR64

Development of immersion and/or runoff measurement techniques for determining the concentration of Urea in water and organic liquids

Lorenzo Quadrini^a, Serena Laschi^a, Claudio Ciccone^b, and Ilaria Palchetti^a

^a *Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia 3, 50019, Sesto Fiorentino (FI), Italy*

^b *Chemitec Srl, Via Isaac Newton 28, 50018, Scandicci (FI), Italy*
E-mail: lorenzo.quadrini@unifi.it

Urea, being a metabolic waste product of mammals, turns out to be abundantly present in the waste from the sewage of intensive livestock farms. The above reason means that there is a growing interest in monitoring urea in sludges and wastewater treatment plants. This reason why, a potentiometric flow analysis (FA) method coupled with an enzymatic bioreactor was assembled. Thus, in this first approach, different types of bioreactors were assembled in which urease was covalently immobilized on a suitable solid phase (glass beads, inner wall of a plastic tube) [1]. The assembled reactors were then coupled to solid-state ammonium sensors as electrochemical readout devices. The analytical performance of each bioreactor was studied as a function of parameters such as cross-linker concentration, amount of immobilized enzyme, and flow rate. The final assembled FA system was then optimized to obtain maximum signal in the shortest possible time. Analytical parameters such as sensitivity, repeatability and durability were evaluated. Then, through collaborative work with the company co-funding the project, the potentiometric measurements were optimized using a flow cell of their own manufacture. Again, we evaluate the potentiometric response by loading solutions of different urea concentrations into the fluidics and derived the calibration curve obtaining parameters such as LOD and %RSD [2].

Urease was successfully immobilized on glass beads in an efficient manner that allows the enzyme to be exploited to achieve hydrolysis of urea and then subsequent quantification by potentiometric measurement. Both batch and flow measurements demonstrated comparable performance.

Future perspectives include further optimization of measurement parameters, study of more complex matrices and real samples.

An additional method of urea quantification, using an amperometric technique, is under development.

[1] K.S. Mangaldas et al., *J. Plant Biochem. Biotechnol.* **2010**, 19, 73-77.

[2] D. Midgley et al., *Trans. Inst. Meas. Control.* **1987**, 1, 25-36.



Abstracts of the Poster Presentations

| | | | |
|--------------|----------------------|--------------|--------------------|
| POS01 | Giulia Agnoloni | POS10 | Thomas Lulli |
| POS02 | Marta Albanesi | POS11 | Amina Mumtaz |
| POS03 | Samuele Baldini | POS12 | Matteo Orlandi |
| POS04 | Alice Beni | POS13 | Valentina Pacciani |
| POS05 | Deborah Bonavolontà | POS14 | Lapo Querci |
| POS06 | Silvia Bracci | POS15 | Matilde Rossi |
| POS07 | Luca Campagiorni | POS16 | Martina Tozzetti |
| POS08 | Valentina Ceccherini | POS17 | Filippo Turchi |
| POS09 | Lapo Gabellini | POS18 | Simone Ventisette |

POS01

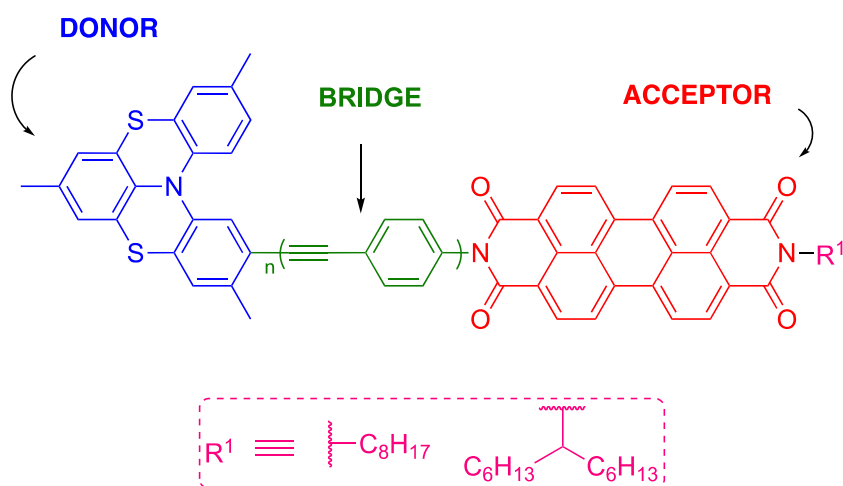
Design, synthesis, and study of chiral systems with spin selectivity in electron transfer processes for the control of molecular spin qubits

Giulia Agnoloni, Caterina Viglianisi, and Roberta Sessoli

Department of Chemistry "Ugo Schiff", University of Florence, via della Lastruccia 3-13, 50019-Sesto F.no (FI), Italy

E-mail: giulia.agnoloni@unifi.it

The topic of this research project is the design, synthesis, and study of donor-acceptor (D-A) dyads, with an enantiopure donor unit. We plan to evaluate the Chiral Induced Spin Selectivity (CISS) effect in the electron transfer processes in these systems by studying the photoinduced electron transfer after photoexcitation of the donor with optical and time-resolved magnetic resonance spectroscopies.¹ As donors we are going to use helical shaped compounds connected, through bridges of various kinds, to perylene diimide acceptor units. Organic donor-acceptor dyads have emerged as attractive systems for several optoelectronic applications. Demonstrating that electrons can be spin-polarized (CISS effect) by moving from chiral molecules will allow the design of new chiral organic devices that, combining optical and magnetic properties, can find application in the new field of opto/spintronic technologies. During this project, we expect to demonstrate the CISS effect in intramolecular electron transfer process in donor-acceptor (D-A) dyads with thia-aza[4]helicene as chiral donor unit.² The study will be focused on the understanding of CISS to exploit its full potential for technological applications in the field of quantum information science (QIS).³

**Figure 1: Donor-Bridge-Acceptor dyads**[1] R. Sessoli et al., *Chem. Sci.*, **2022**, 13, 12208-12218[2] C. Viglianisi et al., *Chem. Commun.*, **2015**, 51, 11452-11454[3] R. Sessoli et al., *Adv. Mater.*, **2023**, 35, 2300472



POS02

Ultra-low temperature magnetic characterization of magnetic molecules assembled on graphene

Marta Albanesi^{a,b}, Lorenzo Poggini^c, Giulia Serrano^d, Andrea Caneschi^d, Philippe Ohresser^b, Roberta Sessoli^a, Edwige Otero^b, and Matteo Mannini^a

^a Department of Chemistry "Ugo Schiff" (DICUS), University of Florence & INSTM RU of Florence, Via della Lastruccia 3-13, 50019-Sesto Fiorentino, Italy

^b Synchrotron SOLEIL, Saint-Aubin, BP 48, 91192 Gif-sur-Yvette, France

^c Institute of Chemistry of Organometallic Compounds (ICCOM-CNR), Via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy

^d Department of Industrial Engineering (DIEF), University of Florence & INSTM RU of Florence, Via Santa Marta 3, 50139 Firenze, Italy
E-mail: marta.albanesi@unifi.it

Magnetic molecules are among the most promising players for the realizations of future qubits, having the unique advantage that their properties can be chemically tuned. A part of the research is devoted to studying the organization of these objects in regular arrays on surfaces while preserving their magnetic properties, which strongly depend on the environment. The final aim is to incorporate them into solid-state devices following strategies developed for other classes of magnetic molecules, including Single Molecule Magnets (SMMs). Promising results have been obtained by depositing molecular qubits on graphene, an innocent substrate which promotes the adsorption of magnetic molecules while preserving their properties [1]. However we still lack detailed information on (i) how to enable magnetic interactions between the magnetic centres both directly and through the substrate and (ii) how to evaluate if these interactions might be observed and controlled in a real device. This PhD project aims to explore these effects by exploiting in-house instruments and large scale facilities. Ad hoc strategies will be adopted to achieve a controlled deposition of intact and ordered molecular qubits on the surface. The morphological and chemical characterization will be performed using the in-house instrumentation, including scanning probe microscopies and X-ray photoelectron spectroscopies. The magnetic characterization will be carried out by magneto-optical techniques using the state-of-the-art equipment available at the DEIMOS beamline at the French Synchrotron SOLEIL. DEIMOS is the beamline dedicated to the measurement of X-ray absorption spectroscopy (XAS), X-ray natural linear dichroism (XNLD) and X-ray circular magnetic dichroism (XMCD) at ultra-low temperatures using polarized light, which allows chemical selectivity and high surface-sensitivity. The ability to perform XAS experiments in operando, available at DEIMOS, will be also exploited to explore the effect of the application of an electric field in a molecular layer embedded in a multilayer device [2], both to probe the interplay between magnetic and electric effects using XAS and to carry out magneto-electric experiments at the synchrotron, thus extending to the nanoscale the capabilities of similar experiments that, up to now, are only possible in bulk [3].

[1] I. Cimatti et al., *Nanoscale Horiz.* **2019**, *4*, 1202.

[2] L. Joly et al., *J. Synchrotron Rad.* **2016**, *23*, 652-657.

[3] B. Kintzel et al., *Angew. Chem. Int. Ed.* **2021**, *60*, 8832.



POS03

Development of chemical organogels and sponges for modern and contemporary artworks cleaning

Samuele Baldini and Emiliano Carretti

*Department of Chemistry "Ugo Schiff" & CSGI, University of Florence, Via della Lastruccia, 3-13, 50019 Sesto, Fiorentino (FI), Italy
E-mail: samuele.baldini@unifi.it*

This project aims to develop a new family chemical organogels and sponges at controlled mechanical properties and porosity that should be effective in the removal of foreign patinas from the surface of modern and contemporary artworks. Traditional conservation procedures use mechanical actions or solubilization processes with organic solvents, which can cause damage, have poor environmental safety, and have low selectivity. A key strategy has been to confine solvents in the micro- and nano-porosity of highly viscous gels to improve selectiveness and control while avoiding damaging the original components of the objects, but a new class of chemical organogels, that ensure good cleaning efficacy and the absence of residue, is needed. As an example, polydimethylsiloxane (PDMS) organogels and sponges guarantee high hydrophobicity, making them suitable for the formulation of systems containing low-polar organic solvents. This project will set up a protocol for the synthesis different classes of organogels and sponges (containing meaningful amounts of organic solvents) at controlled porosity. First, the focus will be on setting up, evaluating, and modulating mechanical properties of the polymer formulations, chemically modifying the reactive species, to improve structural and mechanical properties for cleaning efficiency. In this phase, particular attention will be dedicated to the implementation of a method to rigorously control the porosity (i.e., the pore size and their distribution). A possible approach is the "emulsion template" technique, where droplets of a solvent dispersed into a continuous phase act as templates for the final system [1]. To optimize the formulations, structural analyses using SAXS and SANS techniques or porosity investigation using Scanning Electron Microscopy and X-Ray tomography will be carried out to deeply understand the role of synthetic and structural parameters in cleaning action. The final part of this project will be dedicated to test the solvent compatibility with different chemical gels formulations (with a focus on green and low toxic solvents). Cleaning tests will be conducted using mock-ups and non-invasive techniques on a preliminary phase, and then applying the sponges to real artworks to evaluate their cleaning efficiency.

[1] K. Zimny et al., *Langmuir*. **2015**, *31*, 3215–3221.



POS04

Development of medical devices for wound healing

Alice Beni^a, Natascia Mennini^a, Francesca Maestrelli^a, and Giuliana Gavioli^b

^a *Department of Chemistry, University of Florence, Via della Lastruccia 13, 50019 Sesto Fiorentino, Florence, Italy*

^b *B. Braun Avitum Italy S.p.A. Mirandola, Italy*

E-mail: alice.beni@unifi.it

Skin is the largest organ of the body and it acts as protective barrier against bacteria and other external factors. In presence of wounds the normal alignment of body cells is interrupted, this can be caused by internal (medical illness) or external (injuries, trauma) factors [1]. The research project will concern the development and characterization of advanced dressing for the treatment of skin ulcers. These products will have properties such as to fall into the category of medical devices and characteristics suitable for use on chronic wounds, even infected ones. For this reason, some parameters will be evaluated, such as: fluid management capacity, breathability, odor control, conformability to the wound bed, mechanical resistance, atraumatic resistance to removal, impermeability, biocompatibility, antimicrobial activity against bacteria in planktonic form or organized into biofilms. Standard test, if present, will be used to analyze these parameters [2]. In absence of standard protocols, home-made tests will be developed, operating in experimental conditions as close as possible to those of clinical use, in this way the data obtained in vitro will be predictive of the dressing in vivo performance. If necessary, the prototypes of devices useful for the characterization of new or existing products available on the market, will be designed and created using a 3D printer.

[1] L. Qi et al., *Macromo.l Biosci.* **2022**, 22, 7.

[2] European Standard 13726.

Lipid-based delivery systems for applications in nutraceuticals and cosmetics

Deborah Bonavolontà, Debora Berti, and Costanza Montis

Department of Chemistry "Ugo Schiff", University of Florence, via della Lastruccia 3-13, 50019, Florence, Italy.

E-mail: deborah.bonavolonta@unifi.it

Thanks to their unique properties, such as biocompatibility, structural and physicochemical tunability and easy functionalization, lipid-based nanosystems are among the most attractive building blocks for the development of nanovectors delivering active principles in different application fields as diverse as cosmetics, nutraceuticals, food additives and drug delivery. Among the various lipid assemblies, the inverse lyotropic liquid crystalline (LLC) mesophases, for instance bicontinuous cubic and hexagonal phases, are less explored with respect to the more common lipid vesicles/liposomes, however, they are characterized by particularly interesting properties, such as significant fusogenicity, high interfacial area and capacity to load high amounts of both hydrophobic and hydrophilic molecules.[1] In this framework, the project aims to explore new complex lipid formulations, based on synthetic or natural lipids, forming non-lamellar structures, for the development of suitable biocompatible and efficient nanovectors for possible application in both nutraceuticals and cosmetics. Different lipid formulations will be tested, to probe the ability to encapsulate and release active principles of different sizes and chemical identities. To this aim, common soft-matter related techniques (such as microscopy and scattering techniques) will be employed to characterize the synthesized materials. Microfluidic tools [2] will be developed, to propose new synthetic methodologies to improve the characteristics of the lipid systems and to investigate the interaction of lipid assemblies with bio-relevant interfaces, up to human skin, **Figure 1**.

Overall, the expected outcomes are: (i) to develop new formulations of potential interests for cosmetics and nutraceuticals; (ii) to develop new microfluidic tools to improve the synthesis and evaluate the potential efficiency of the designed systems (iii) to establish clear correlations between the structure and the functional properties of the designed vectors.

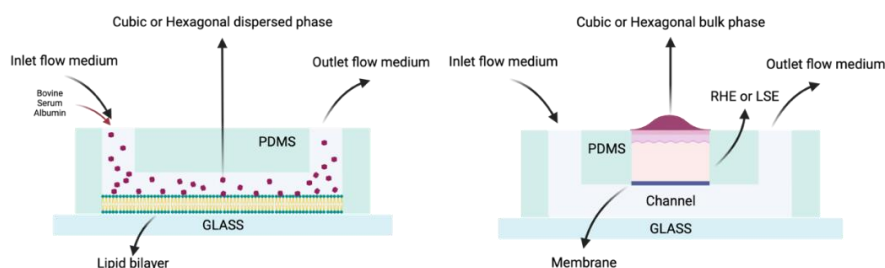


Figure 1: Illustration of microfluidic chips to study the interaction of the developed lipid vectors with biological interfaces.

[1] C. Tan et al, *J. Agric. Food Chem.* **2022**, 70, 1423–1437.

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POS06

Development of diagnostic technologies based on modified synthetic peptides to reveal and characterize autoantibodies as immune response biomarkers

Silvia Bracci^{a,b}, Feliciano Real-Fernandez,^c Paolo Rovero,^{a,d}
and Anna Maria Papini^{a,b}

^a *Interdepartmental Research Unit of Peptide and Protein Chemistry and Biology - PeptLab, University of Florence, 50019 Sesto Fiorentino, Italy*

^b *Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia 3-13, 50019 Sesto Fiorentino, Italy*

^c *Institute of Chemistry of Organometallic Compounds (ICCOM), National Research Council of Italy (CNR), 50019 Sesto Fiorentino, Italy*

^d *Department of NeuroFarBa, University of Florence, Via Ugo Schiff 6, 50019 Sesto Fiorentino, Italy*

E-mail: silvia.bracci@unifi.it

The immune system recognizes and eliminates foreign antigens, while it is tolerant against self-antigens. If self-tolerance is broken down, a pathogenic autoimmune mechanism is triggered and autoreactive antibodies (autoantibodies) and T-cells attack the body, causing chronic inflammation and tissue damage [1]. Possible early misunderstood infections may cause autoimmune diseases that lack definitive cures. Thus, the availability of accurate diagnostic and prognostic assays for early disease detection and monitoring is fundamental to limit chronic damage. Autoantibodies may serve as biomarkers, detectable years before clinical symptoms appear. However, autoantibody identification in complex matrices like human sera requires univocal antigens binding with high affinity. Physiological protein antigens are not always suitable diagnostic probes, mainly due to aberrant post-translational modifications (PTMs) that can trigger non-self immune recognition and can be linked to early bacterial and/or viral infections [2]. The aim of this project is to develop synthetic peptides or proteins, designed to mimic linear and/or conformational epitopes, using solid-phase strategy combined with Native Chemical Ligation. These techniques allow the introduction of single or multiple modifications, that can be installed site-specifically by the building blocks approach. These modified peptides will be used as synthetic antigenic probes (SAPs) to develop *in vitro* assays tailored for different analytical platforms to measure disease-specific autoantibodies. SAPs will be selected using the "chemical reverse approach" that consists in screening antibodies in patient sera vs. healthy control sera provided by clinicians involved in Tuscany Health Ecosystem (THE). SAPs will be used for the development of *in vitro* immunodiagnostic assays [3]. Two techniques will be compared: the more common Enzyme-Linked Immunosorbent Assay and the more innovative Surface Plasmon Resonance biosensor technology, which has been gaining importance in biological and clinical investigations.

[1] A. K Abbas *et al.* *Cellular and Molecular Immunology* 10th edition, Elsevier, 2021.

[2] M. T. C. Walvoort *et al.*, *Sci Rep*, 2016, 6, 39430.

[3] A. M. Papini, *J. Pept. Sci.* 2009, 15, 621-628.



POS07

Study of the physico-chemical properties and hydration reactions of cement formulations based on ground granulated blast furnace slag

Luca Campagiorni and Francesca Ridi

*Department of Chemistry "Ugo Schiff" & CSGI, University of Florence, via della Lastruccia 3,
50019, Florence, Italy*

E-mail: luca.campagiorni@unifi.it

The study is focused on the study of physico-chemical properties and hydration reactions of low-carbon cement formulations containing varying amounts of Portland cement (OPC), ground granulated blast furnace slag (GGBS), and limestone. These formulations make it possible to reduce carbon dioxide (CO₂) emissions, as well as to limit the high carbon footprint in global cement production. These studies are also carried out on formulations containing organic additives (superplasticizers¹) to obtain suitable rheological properties with a low amount of water.

In particular, the water consumption used in the hydration process of the cement mixture is studied through differential scanning calorimetry (DSC), and isothermal calorimetry (IC). Although water confinement is studied with low-temperature differential scanning calorimetry (LT-DSC)².

Finally, the cement matrix porosities can be studied by combining gas porosimetry and mercury intrusion porosimetry (MIP) techniques. The objective is to relate the results to macroscopic properties, such as mechanical properties and durability.

[1] F.Ridi et al., *J.Phys. Chem. C*, **2012**, *20*, 10887-10895.

[2] F.Ridi et al., *J. Phys. Chem. B*, **2009**, *10*, 3080-3087.

POS08

Synthesis of new heterobimetallic ruthenium(II) polypyridyl-based complexes as potential antimicrobial agents

Valentina Ceccherini, Luigi Messori, and Claudia Giorgi

Department of Chemistry "Ugo Schiff", University of Florence, Via Della Lastruccia 3, 50059 Florence, Italy

E-mail: valentina.ceccherini@unifi.it

Antimicrobial resistance represents a serious risk to public health systems and there is an urgent need to find alternatives to the current antimicrobial agents [1]. Ru(II)-polypyridyl complexes have been extensively investigated and have shown considerable antibacterial properties which arise from their interactions with important biological molecules, such as DNA, RNA and proteins. Moreover, these compounds proved to be suitable photosensitizers for Photodynamic Therapy and to be promising candidates to control the photoinduced release of biologically active species in Photoactivated Chemotherapy [2]. Another class of metal complexes which has been extensively investigated as metallopharmaceuticals is that of metal-N-heterocyclic carbene complexes, thanks to their advantageous features of stability, which allow an adequate transport and bio-distribution, and versatility, which offers the possibility to fine-tune their electronic and steric properties. In particular, several gold(I), iridium(I) and silver(I)-NHC complexes have shown to possess antimicrobial activity to varying degrees [3]. In this context, the aim of this project is to synthesize and evaluate on a biological level novel heterobimetallic complexes combining Ru(II)-polypyridyl systems with different NHC units based on the above-mentioned metals, in an attempt to obtain a final compound that can be activated by a controlled photosubstitution that leads to the release of two active metallic species, therefore enhancing the overall antimicrobial properties of the complex.

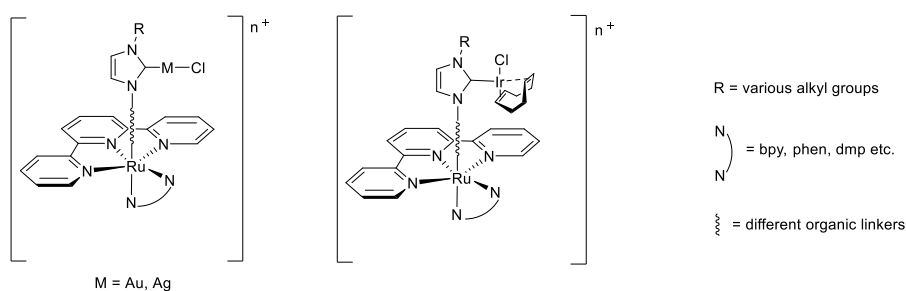


Figure 1: Examples of the generic heterobimetallic compounds proposed for this research project.

- [1] P. Dadgostar, *Infec. Drug Resist.* **2019**, *12*, 3903-3910.
 [2] F. Li et al., *Chem. Soc. Rev.* **2015**, *44*, 2529-2542.
 [3] I. Ott, *Adv. Inorg. Chem.* **2020**, *75*, 121-148.



POS09

Physico-chemical characterization of nanostructured catalysts for green energy conversion

Lapo Gabellini^a, Matteo Mannini^{a,c}, Stefano Caporali^{b,c},
and Andrea Caneschi^{a,b,c}

^a Chemistry Department "Ugo Schiff," DICUS, University of Florence, via della Lastruccia 3-13, 50019 Sesto F.no (FI), Italy

^b Department of Industrial Engineering, DIEF, University of Florence, via di s. Marta 3, 50134 Florence (FI), Italy

^c Consorzio Interuniversitario Nazionale di Scienza e Tecnologia dei Materiali, INSTM, via G. Giusti 9, 50121, Florence, Italy
E-mail: lapo.gabellini@unifi.it

The need to overcome energy production using fossil fuels prompted the research on strategies necessary to smooth and regularize the discontinuity in energy production with renewable sources [1]. By operating in this context, the present project focuses on the realization and the physico-chemical characterization of catalysts suitable for two promising energy conversion schemes: 1) green-hydrogen evolution by water electrolysis using electrical power and 2) fuels synthesis from carbon dioxide using heat from thermal solar plants. Both need the employ of catalysts, to show reaction rates capable of withstanding the present request and the constantly growing energy demand [2, 3]. The activity of these three years involves the realization of the catalytically active materials and their subsequent characterization in terms of chemical composition, stoichiometry, crystallographic phases, and catalytic activity. Particular attention will be paid to novel realization pathways capable of producing porous and nanostructured materials made of transition's metal oxides and nitrides presenting electrochemical and photochemical catalytic activity, employable in the two aforementioned schemes. The physico-chemical characterization will be performed using X-ray photoelectron spectroscopy (XPS), for catalysts' surface elemental composition and oxidation state determination, X-ray diffraction (XRD-powder) for structural information on the crystallographic phases involved and imaging using scanning electron microscope (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM) to identify the overall morphology. The catalytic activity will be evaluated using electrochemical techniques, spectroscopies, and thermal desorption analysis. The entire work will be devoted to studies on catalysis for green energy conversion and storage, an intense and stimulating topic eligible for future large-scale applications.

[1] Q. Chen, et al., *Applied Energy*. **2022**, 312.

[2] X. Li, et al., *Journal of Materials Chemistry A*. **2016**, 31,11973–12000.

[3] E. T. Kho, et al., *Green Energy and Environment*. **2017**, 2, 204–217.

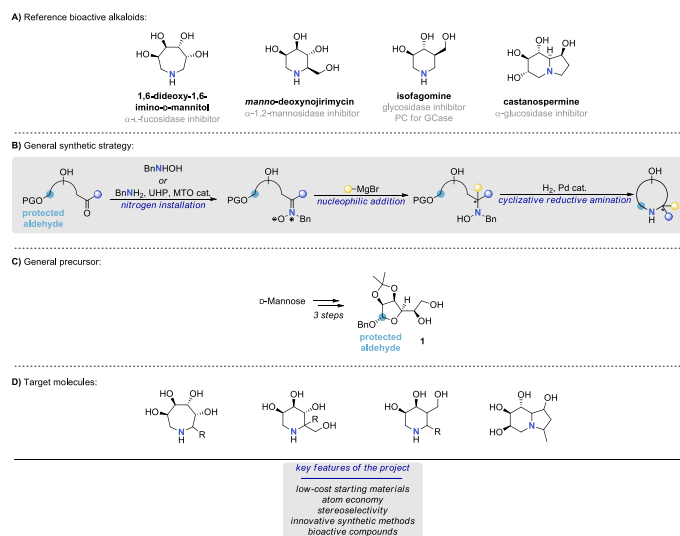
POS10

Innovative approaches to access mono- and bicyclic iminosugars: synthesis biological evaluation

Thomas Lulli and Andrea Goti

Department of Chemistry 'Ugo Schiff', University of Florence, Via della Lastruccia 3-13, 50019 Sesto Fiorentino (FI), Italy.
E-mail: thomas.lulli@unifi.it

Iminosugars are among the most notable classes of glycomimetics known nowadays. Because of their numerous therapeutical applications, these alkaloids continue to receive considerable attention among synthetic chemists. Innovative, stereoselective, and green synthetic routes to mono- and bicyclic iminosugars and their biological evaluation towards selected enzymatic targets are described in this project. Because of their ability to resemble the structures of sugars and mimic their conformations, water solubility, high selectivity towards targets, and stability against processing, iminosugars play a pivotal role among the various inhibitors of carbohydrate-processing enzymes. Due to their potential application as drugs for many diseases, developing more efficient ways to synthesize naturally occurring iminosugars with known bioactivity and original routes to novel congeners is the main challenge in this field. As a natural and easily accessible source belonging to the chiral pool, most synthetic procedures utilize carbohydrates as starting materials, which are lately manipulated in various ways to introduce the nitrogen atom. One of the most straightforward strategies to achieve this task is converting a carbonyl compound into a nitron through condensation with hydroxylamines. The nitron can be further functionalized and cyclized to final structures employing reductive amination reaction (RA) (Scheme 1B). In this context, the diol **1**, easily accessible on a multi-gram scale from inexpensive D-mannose in three steps (Scheme 1C) and already widely used at DICUS to access a variety of polyhydroxypiperidines, can be envisioned as a general precursor of 6- and 7-membered nitrogen heterocycles as well as of bicyclic iminosugars (Scheme 1D).



Scheme 1



POS11

Micropollutants removal from wastewater using new bio-nano/micro-sorbents activated by adsorption/biosorption in a green water management perspective

Amina Mumtaz^a, Claudio Sangregorio^b, and Tania Martellini^a

^a Department of Chemistry Ugo Schiff, Università degli Studi di Firenze, Via della Lastruccia 3, I-50019 Sesto Fiorentino (Florence), Italy

^b CNR-ICCOM, Via Madonna del Piano 10, Sesto Fiorentino I-50019, Italy
E-mail: amna21malik@gmail.com

The presence of micropollutants (especially emerging ones), such as microplastics, dyes, flame retardants, surfactants, and various industrial additives, in surface water and drinking water and their long-term exposure may pose a potential risk to the environment and human health, due to the toxic properties and bioaccumulation capacity of these substances [1]. Many studies have shown that conventional wastewater treatment technologies do not completely remove some substances. Therefore, new approaches are continuously being explored to complement conventional water treatment methods, minimize the costs of treatment processes, and be more effective in the removal of dyes and organic contaminants, with the aim of improving water quality so that it can be reused for civil purposes (e.g. drinking water, cooling or heating systems, street washing), for industrial purposes (e.g. process water) and for irrigation of food and feed crops. Adsorption and biosorption approaches thus represent an ecologically sustainable and cost-effective solution to the aforementioned challenges, offering effective removal of pollutants from wastewater. This research hence proposes the development of inexpensive nanoparticles/microsystems using, for example, biopolymers for pollutant removal. It is also proposed to develop an advanced adsorption/biosorption method, different from those currently in use, to efficiently remove contaminants from wastewater, with a focus on emerging contaminants. The developed materials and methods will be tested on a pilot scale by assessing not only their efficiency but also their regenerability and stability, and their potential full-scale scalability will be investigated. Once the efficiency of the removal systems has been verified, their patentability will be assessed. Magnetic cellulose nanocomposite, mCNFAP/PMAA, *Arenga pinnata* are efficient in dye removal with regeneration and present a cost-effective solution [2]. Phosphate-functionalized supramagnetic Iron oxide nanoparticles demonstrate exceptional selectivity and high loading capacities for the removal of pollutants [3].

[1] L. Bilela et al., *Mar. Pollut. Bull.* **2022**, 193, 115309.

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[3] P. Arosio et al., *Dalton Trans.* **2023**, 11, 29.



POS12

Computational study of metalloproteins and development of new inhibitors for drug resistant bacteria

Matteo Orlandi^a, Piero Procacci^a, Fabrizio Carta^b,
Claudiu T. Supuran^b, and Marco Pagliai^a

^a Department of Chemistry "Ugo Schiff", University of Florence, via della Lastruccia 3, 50019-Sesto F.no (FI), Italy

^b Department of NeuroFarBa, University of Florence, Via Ugo Schiff 6, 50019- Sesto F.no (FI), Italy

E-mail: matteo.orlandi1@unifi.it

Nowadays, drug-resistant bacteria are becoming a real threat to our society. The chance of dangerous pathogens developing resistance to classical antibiotics real and the risk of being unable to fight this impending menace without innovative drugs is drawing ever closer [1]. This project effort will be focused on the development of an accurate and innovative computational protocol to speed up the drug discovery pipeline for a new class of antibiotics, capable of inhibiting the specific bacterial metalloproteins crucial for their survival. Being able to computationally design new ligands that can inhibit their activity, could open new frontiers in the treatment of many pathologies; for example, the selective inhibition of bacterial Carbonic Anhydrase is a promising way to overcome resistant bacteria infections [2]. Since computational studies of metalloproteins are quite challenging, during this project it would be necessary to develop new methods or improve existing ones to accurately reproduce the physical behavior of these macromolecules, such as specific force fields to better match the results of simulations with those of experiments. With HPC, it will also be feasible to perform highly accurate, but computationally expensive, molecular dynamics simulations with enhanced sampling techniques and alchemical transformations, like Hamiltonian replica exchange and virtual double system single box [3], which can reproduce the entire process of molecular recognition of a drug candidate, from the bulk solvent to the protein target site. Under these conditions, it will be possible not only to virtually design new compounds but also to synthesize and evaluate their experimental activity and in vivo safety.

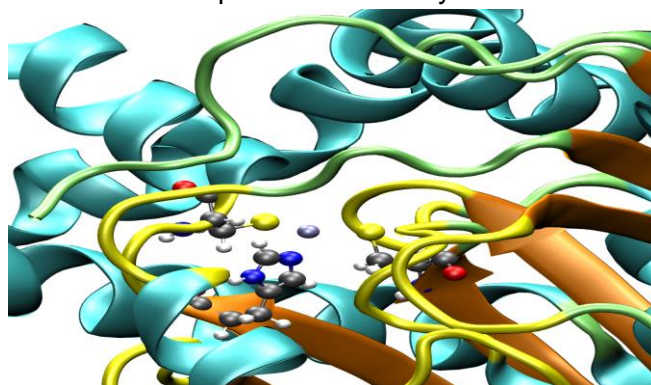


Figure 1: structure of *Mycobacterium tuberculosis* $\beta 2$ Carbonic Anhydrase active site.

[1] World Health Organization (OMS), *Global tuberculosis report 2023*.

[2] A. Aspatwar et al., *J. Enzyme Inhib. Med. Chem.* **2020**, 35:1, 65-71.

[3] M. Macchiagodena et al., *J. Chem. Inf. Model.* **2021**, 61(11), 5320-5326.



POS13

Engineering Liquid Crystalline Mesophases for Biomedical Applications: Tailored Design and Characterization Strategies

Valentina Pacciani^{a,b}, Costanza Montis^{a,b}, and Debora Berti^{a,b}

^a Department of Chemistry “Ugo Schiff”, University of Florence, via della Lastruccia 3-13, 50019, Sesto Fiorentino (FI), Italy

^b CSGI - Center for Colloids and Surface Science, University of Florence, Via della Lastruccia 3, 50019, Sesto Fiorentino (FI), Italy
E-mail: valentina.pacciani@unifi.it

In recent years, there has been a growing interest in leveraging lipid-based nanosystems for drug delivery. Non-lamellar lyotropic liquid crystalline (LLC) nanoparticles, such as hexosomes and cubosomes, have emerged as particularly promising candidates, due to their inherent biocompatibility, high stability, and cargo-loading capacity. The internal structure of these nanoparticles can be modulated by external stimuli, such as pH, ionic strength, or temperature, depending on lipid composition [1]. The transition between different internal LC phases leads to a change in the overall water content within nanoparticles, enabling the design of intelligent nanomaterials capable of targeted release of therapeutic cargoes in specific pathological areas as a response to different biological environments. For instance, the incorporation of charged or ionizable lipids endows LLC nanoparticles with pH-sensitive behavior, thereby allowing selective drug release in response to pH alterations [2].

In this context, an interesting avenue is the integration of synthetic cubosomes/hexosomes with biological functionalities or particles, aiming to combine the unique properties of non-lamellar particles with specific properties, such as targeting, molecular recognition, therapeutic, or immunomodulatory functions, typical of biogenic systems. The primary objective of this project is to explore different strategies for building up synthetic/biogenic hybrid systems. To this purpose, non-lamellar LLC particles will be combined with 1) extracellular vesicles (EVs) and 2) biomolecules, such as peptides, membrane proteins or EVs-derived species.

This study will enhance our understanding of the interplay between composition, structure, and properties of the designed lipid-based nanosystems, providing insight into the development and optimization of hybrid nanomaterials for biomedical applications.

[1] H. M. G. Barriga et al., *Angew. Chem. Int. Ed.* **2019**, *58*, 2958.

[2] O. Mertins et al., *Nanomaterials* **2020**, *10*, 963.



POS15

Development of peptide nucleic acids targeting non-canonical nucleic acids structures

Matilde Rossi^{a,b,c}, Paola Gratter^c, Anna Maria Papini^{a,b}, and Carla Bazzicalupi^b

^a *Interdepartmental Research Unit of Peptide and Protein Chemistry and Biology, University of Florence, 50019 Sesto Fiorentino, Italy*

^b *Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia 3, 50019 Sesto Fiorentino, Italy*

^c *Department of NeuroFarBa, Via Ugo Schiff 6, 50019 Sesto Fiorentino, Italy*
E-mail: matilde.rossi@unifi.it

G-quadruplexes (G4) are non-canonical DNA structures abundant in guanine-rich sequences, characterized by the presence of stacked guanine-based tetrads. G4 are prevalent in promoter regions of oncogenic genes and telomeres, affecting crucial cellular processes. Therefore, G4 have been considered relevant targets in oncology. Several ligands have been designed to stabilize these structures and interfere with biological pathways. However the majority of them display a limited selectivity [1]. Recently, peptide nucleic acids (PNAs) have been considered significant for their potential in DNA targeting [2]. The lack of repulsion from PNAs' neutral peptide backbone, compared with the repulsion caused by DNA's negatively charged phosphate backbone, gave the PNA an edge in binding. Moreover, PNAs are not degraded by nuclease and protease enzymes therefore they are characterized by a great long-term stability. PNAs can be made easily using the same solid-phase synthesis (SPS) strategies used to make other peptides [3]. The first objective of my PhD research project is to operate a rational design followed by SPS of PNAs targeting specific nucleic acids sequences, aiming to stabilize G-quadruplexes, particularly telomeric G4 structures. The design of the PNA molecule, by molecular dynamics studies, will involve also polyamide backbone modifications to increase solubility, as well as binding affinity and selectivity towards the DNA secondary structures. Then, final aim of this project is to characterize the interaction between PNAs and the DNA targets by several techniques, such as circular dichroism, NMR spectroscopy, and X-ray crystallography.

[1] T. Santos et al., *Pharmaceuticals* **2021**, *14*, 769.

[2] P. E. Nielsen et al., *Science* **1991**, *254*, 1497.

[3] C. Suparpprom; T. Vilaivan, *RSC Chem. Biol.* **2022**, *3*, 648–697.

Nanofunctional architectures for diagnosis and therapy

Martina Tozzetti, Gabriella Caminati and Stefano Menichetti

Department of Chemistry "Ugo Schiff", University of Florence, via della Lastruccia 3-13, 50019
Sesto Fiorentino, Italy

E-mail: martina.tozzetti@unifi.it

The aim of the research activity is the design, synthesis and assembly of nanofunctional architectures with a two-fold goal: the development of diagnostic devices for the monitoring of the onset of neurodegenerative pathologies and organ-rejection phenomena and an innovative treatment of coronavirus-related diseases. The study explores different and complementary fields, such as synthetic organic chemistry and physical chemistry of nanomaterials and nanosensors. In the case of nanodiagnostic, the receptor will have the inhibitory portion capable of binding to the analyte and, at the same time, an anchor site that can bind to the sensor-chip for analysis with QCM, SPR and/or SERS. The selected biomarker is the FKBP12 protein, a globular cytosolic protein with a well-established role in the anti-rejection response after organ transplants and in neurodegenerative processes. [1,2]

For nanodelivery the receptor will be studied to bind the FKBP12 protein with the molecule ELTE N378 or to obtain an innovative treatment of coronavirus diseases.

In the second hand, the affinity of some different molecules for the NSP13, a helicase bound to the entire SARS-CoV-2 proteome, or to all coronaviruses in general, does play a key role in virus activity [3], will be tested in vitro. The molecules with the highest affinity will be included in nanocarriers for transport to the lungs with liposomal aerosols, chitosan nanoparticle aerosols, and polymeric core-shell nanoparticles being examined as potential carriers.

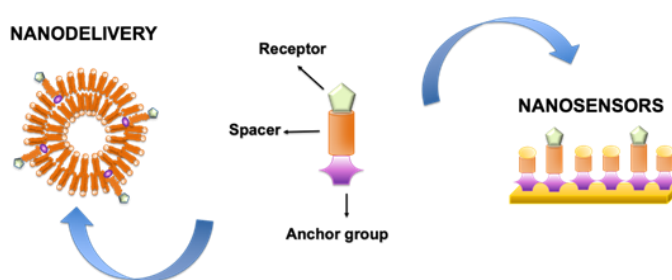


Figure 1: Design proposed for nanofunctional architectures for diagnosis and therapy.

[1] M.W. Harding et al., *Nature*. **1989**, 341, 758–760.

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POS17

Exploring the druggability of intrinsically disordered proteins involved in neurodegenerative disorders through NMR spectroscopy

Filippo Turchi^{a,b}, Francesca Clemente^a, Francesca Cardona^a,
Roberta Pierattelli^{a,b}, and Isabella Felli^{a,b}

^a Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia 3, 50019 Sesto Fiorentino, Italy

^b Magnetic Resonance Center, Via L. Sacconi 6, 50019 Sesto Fiorentino, Italy
E-mail: filippo.turchi@unifi.it

Intrinsically disordered proteins (IDPs) are a large pool of proteins lacking a fixed three-dimensional structure, characterized by structural disorder and flexibility. These proteins challenge the structure-function paradigm, because even if they don't have a 3D structure, they play a fundamental role in various biological processes, such as cellular regulation and protein-protein interactions. IDPs are implicated in several human diseases and represent new potential drug targets. However, IDPs are not generally considered in conventional drug design. In fact, the lack of a 3D structure prevents the design of potential drugs that could optimize interactions with the protein pocket. New approaches are thus needed to identify molecules suitable for interacting with these proteins. Nuclear magnetic resonance (NMR) spectroscopy represents the method of choice in characterizing the dynamic and structural properties of IDPs at atomic level. [1] The objective of my PhD research project is to investigate the drug discovery of α -synuclein (α -syn), a soluble IDP involved in the onset of synucleinopathies, a series of neurodegenerative disorders which also include Parkinson's disease (PD). Aggregates of α -syn (oligomers and fibrils) are found within dopaminergic neurons of people affected by these diseases. It is mainly found in terminal synapses, and it is composed by 140 amino acids divided into three distinct domains: 1) N-terminal domain, which has an amphipathic character; 2) the central domain, known as NAC, which has a hydrophobic character; 3) the C-terminal domain which contains a high number of negatively charged amino acids and has been shown to discourage aggregation. The N-terminal domain and NAC domain, in presence of membranes and phospholipids, form an α -helical structure to interact with them. A very interesting strategy for treating synucleopathies, involves the use of small molecules, called chemical chaperones (CCs), that interact with the monomeric form of α -syn by modulating its aggregation. In this context, we use several advanced NMR methods, to assess how small molecules, such as nitrogen-containing glycomimetics (e.g. iminosugars), can interact with the monomeric state of α -syn. The identification of CCs vs α -syn among iminosugars already recognized as pharmacological chaperones for β -glucocerebrosidase (GCase), an enzyme involved in the pathogenesis of PD, will provide the great advantage to obtain dual targeting compounds able to enhance GCase activity and stabilize α -syn.[2]

[1] I. Felli & R. Pierattelli, *Chem. Rev.* **2022**, *122*, 9468–9496.

[2] F. Clemente et al., *Bioorganic Chem.* **2020**, *98*, 103740.



POS18

Polycatecholamines as innovative systems to detect and replace natural antibodies

Simone Ventisette^a, Maria Minunni^b, and Simona Scarano^a

^a Department of Chemistry "Ugo Schiff" (DICUS), University of Florence, Via della Lastruccia 13, 50019, Sesto Fiorentino (FI), Italy

^b Department of Pharmacy, University of Pisa, Via Bonanno Pisano 12, 56126 Pisa (PI), Italy
E-mail: simone.ventisette@unifi.it

Polycatecholamines (pCAs), such as polydopamine (PDA) and polynorepinephrine (PNE), are very promising bio-inspired materials produced by alkali-induced autoxidation of endogenous neurotransmitters, dopamine (DA) and norepinephrine (NE), and endowed with remarkable adhesive properties on virtually any kind of surface. Simple immersion of the substrate in a dilute aqueous solution of the monomers, buffered to a mild alkaline pH, results in the slow deposition of thin films or, when stirred, the formation of nanoparticles, which can be used for various applications, including surface modification of inorganic materials, drug delivery, and use as polymers for molecular imprinting (MIPs and nano-MIPs) [1, 2]. The primary objective of my Ph.D. research is the development of polycatecholamine-based nanoparticles and nanofilms tailored for deployment in innovative diagnostic and analytical systems, as well as novel drugs and carriers for drug delivery. Initial investigations will focus on non-imprinted structures (NIPs) as a reference before proceeding to investigate their imprinting. In particular, it will be crucial to optimize MIPs and nano-MIPs synthesis in order to make them selective for the recognition of antibodies or other macromolecules, such as proteins, through epitope-directed imprinting technology. Nano-MIPs will be exploited on sensing platforms such as SPR, QCM, and through optical-based spectroscopies to obtain point-of-care (POC) systems by depositing these polymers on optical fibers [3], microfluidic chips, and paper-based supports. Ultimately, this investigation will unlock the extensive potential of polycatecholamines by leveraging nanofilms or nanostructures for detection purposes and exploring their viability as alternatives to antibodies in various bioanalytical analysis techniques, diagnostics, and therapeutics.

[1] H. Lee et al., *Science*, **2007**, 318, 426-430.

[2] F. Battaglia et al., *Talanta*, **2021**, 230, 122347.

[3] S. Zhang et al., *Laser Photon Rev.*, **2022**, 16, 2200009.



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