



TOR VERGATA
UNIVERSITÀ DEGLI STUDI DI ROMA



**Dipartimento di
Scienze e Tecnologie
Chimiche**



1st Workshop X-CHEM
**eXpanding CHEMistry: implementing excellence in
research and teaching**

September 9-10, 2024, Villa Mondragone

*Monte Porzio Catone, September 9-10, 2024
Via Frascati, 51, 00040 Monte Porzio Catone RM*

X-CHEM is the project awarded to the Department of Chemical Science and Technologies recognizing it as a Department of Excellence

With research focused on energy transition, health, and environment, the project aims to foster the creation of new synergies through the interaction and collaboration among different research groups and subject areas and it is pursued through targeted recruitment, funding research projects for young researchers, implementation of equipment, and fostering the activities of the Department two doctoral courses.

As the end of the second project year is approaching, the 1st X-CHEM workshop aims to share and analyze the results obtained and allow a close interaction among Ph D students through the presentation of their activities.

The best poster, selected by the members of the IAB, will receive the *Igor Luisetto Award*. The prize is granted in the memory of our former Ph D Student and Colleague Igor Luisetto who left us prematurely thus interrupting a promising scientific career.

The program foresees an update from the project coordinator and conferences from members of the International Advisory Board. The personnel recruited through X-CHEM will have an opportunity to present their research and former Ph D Students will share their experience describe how it has influenced their career.

We are glad to welcome you all in Villa Mondragone!

The Organizing Committee

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Program

Day 1 –September 9 th , 2024 – Villa Mondragone - Sala degli Svizzeri		
12:00-14:00	Welcome and light lunch	
14:00-14:15	Welcome Address	Rector UTV
14:15-14:30	Update from the Project Coordinator	Valeria Conte, Director DSTC
Lectures IAB Members		
14:30-15:00	Lecture Professor Graca Vicente, IAB	Per-fluorinated BODIPY derivatives: synthesis and regioselective functionalization
15:00-15:30	Lecture Professor Kevin Plaxo, IAB	Molecular vital signs: recent advances in in vivo biosensors
15:30-16:00	Lecture Professor Maurizio Prato, IAB	Carbon Nanodots: the missing link between the molecular and the nanoscale worlds
16:00-16:30	Coffee Break	
Lectures personnel recruited through X-CHEM		
16:30-17:00	Professor Claudia Bizzarri	Sustainable Horizon: Photoactive Earth-abundant Metal Complexes for Carbon Dioxide Reduction and Beyond
17:00-17:30	Dr Paolo Calligari	Exploring the role of protein-protein interactions in the allosteric mechanism of a multi-domain protein: the case of oncogenic tyrosine phosphatase SHP2
17:30-18:00	Dr Gabriele Magna	More than Oranges and Lemons: Recent Advances in Enantioselective Electronic Noses
Day 2 –September 10 th , 2024 – Villa Mondragone - Sala degli Svizzeri		
Lectures Alumni		
09:30-09:45	Professor Giuseppe Pomarico Ph D in Chemical Science	A journey into the multifaceted chemistry of porphyrinoids. And then beyond, where chemistry meets biology
09:45-10:00	Dr Anna Chiara Tizzoni Ph D in Materials for Sustainable Development	A career path in Concentrating Solar Thermal Research: materials challenges and development of sustainable technologies.
10:00-10:15	Dr Alessia Amodio, European Food Safety Authority (EFSA)	From bench research to desk science
10:10-10:45	Coffee Break	
10:45-12:45	Poster session	
12:45-13:00	Closing remarks project coordinator	Valeria Conte, Director DSTC
13:00-14:00	Lunch	

1st Workshop X-CHEM



Book of Abstract

Poster Section

September 9-10, 2024 Via Frascati, 51, 00040

Monte Porzio Catone, Rome, Italy

*Cell-free synthetic biology for transcription factor detection**João Aguiar¹, Simona Ranallo¹, Francesco Ricci¹*

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Transcription factors (TFs) are crucial gene expression regulatory proteins. They achieve this regulation by binding enhancer elements and recruiting cofactors and RNA polymerases to target gene expression. It's estimated that of the approximately 25 000 human genes up to 10% encode DNA-binding proteins the majority of which are thought to function as TFs. As proteins responsible for gene expression regulation, they control a variety of crucial biological mechanisms such as cell proliferation [1].

Considering their crucial biological importance, the development of probes that support the rapid monitoring of TFs is very important. Activity-based probes that respond to the function of the targeted protein can serve as relevant indicators of disease progression. For transcription factor detection this means developing probes that are responsive to DNA binding events.

Herein we envision to design DNA-based biosensors that can bind and respond to specific TF targets. These probes essentially act as DNA switches, synthetic oligonucleotides that undergo binding-induced structural change to signal the presence and functioning of a TF. The biosensors resort to cell-free synthetic biology for signal amplification. These techniques allow us to leverage the core transcriptional and translational components outside of the cellular environment and combine them with the programmability of synthetic DNA responsive elements to create new combinatorial molecular biosensors.

References

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Thermal activation of mobility of lyophilized and weakly hydrated amorphous proteins: molecular dynamics simulations vs. neutron scattering experiments

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Lyophilization is widely used for preserving biopharmaceutical products. However, limited data on the stability and biological activity of biomacromolecules in lyophilized samples makes usage of in-silico studies necessary to understand the impact of freeze drying on such properties [1,2]. Despite the challenges of simulating lyophilized proteins, atomistic molecular dynamics (MD) offers valuable understanding. Here we propose a new in-silico protocol for modelling lyophilized and weakly hydrated proteins that is both experimentally realistic and routinely applicable [3]. Since the outputs from MD simulations align directly with those accessed by neutron scattering [4], the simulation protocol is validated against experimental Quasi-Elastic Neutron Scattering (QENS) data [3].

Our study focuses on amorphous apoferritin and insulin under dry ($h = 0.05$, where $h = g \text{ D}_2\text{O}/g \text{ protein}$) and weakly hydrated ($0.05 < h < 0.38$) conditions ($T = 10 - 290 \text{ K}$) and reveals the influence of biological assembly complexity on local dynamics in the absence and presence of water molecules.

The temperature-dependent mean squared displacement (MSD) of protein hydrogen atoms was used to validate the model descriptions. Subsequent trajectory analysis discloses those mechanisms driving thermal activation of protein atoms and residues. This work also highlights that without cooperative experimental and simulation data, development of simulative procedures with MD alone would prove most challenging.

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Synthesis and characterization of perovskites for hydrogen production: optimizing of synthesis route

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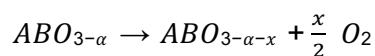
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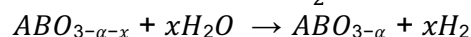
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The European strategy for the energy transition envisages a strategic role for green hydrogen as a fuel in the coming years. The hydrogen production process limits CO₂ emissions and uses renewable energies. Concentrating solar plants (CSP) convert heat from concentrated solar power into chemical energy which can then be used for several applications, such as thermal green hydrogen production. In this regard, two-steps thermochemical water-splitting cycles (TWSC) using perovskite powders are pioneering technologies for contributing to decarbonize the energy sector, as these processes can reduce operating temperatures, facilitating a more efficient coupling with CSP. The present work, carried out within the National framework of “Piano Operativo della Ricerca sull’Idrogeno (POR H2)”, addresses the evaluation of the redox capabilities of different types of perovskites with the final goal of optimizing a two-step thermochemical cycle such as:

Thermal reduction



Water shift



where both reactions are ideally to be performed below 1100 °C and δ should be maximized. Several metals have been considered for A and B sites, together with several preparation methods. The materials have been analyzed by thermogravimetry and characterized by XRD. The results show that a “fast firing” preparation method can produce perovskites more reactive with respect to steam oxidation. The δ value can be evaluated by TGA patterns and the whole cycle suitability can be estimated.

Acknowledgments

This work was carried out within the Operational Research Plan (POR) on green hydrogen developed by ENEA and financed by the Ministry of the Environment and Energy Security - project code: I83C22001170006 -National Recovery and Resilience Plan (Mission 2. Investment 3.5) financed by the European Union as part of the Next Generation EU program.

*Activity-based (bio)sensor for the monitoring of MutyH DNA glycosylase**Erica Belforte¹, Andrea Celeste Di Pede¹, Alessandro Porchetta¹*

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DNA is subject to interactions with mutagens, the most frequent oxidation-induced lesions are 8-oxo-7,8-dihydroguanine, often resulting in G:C to T:A transversion mutations. When oxidation occurs, the base pair will be 8-oxoG:C and cytosine is recognized by the OGG1 and removed. If the damage occurs during replication, it leads to a mismatch of 8-oxoG:A, recognized by a specific glycosylase, MUTYH, which removes A. The literature presents various molecular methods for assessing DNA repair activity, primarily centred on the use of indirect biochemical assays [1]. These methods have a variety of issues as long time of analysis and limited applicability in clinical settings. To enable direct monitoring of MUTYH activity, only few examples using chemically modified DNA probes with fluorescence readout have been reported [2]. They offer advantages as simplicity, rapidity, good specificity and sensitivity. Here we propose developing a synthetic biology toolkit for real-time analysis of MUTYH activity. We design programmable nucleic acid capable of transducing glycosylase activity into downstream CRISPR-powered ultrasensitive detection. This is achieved by using a rationally designed DNA-based hybridization network based on the switching activity of a DNA probe called "DNA activator module" whose structural switch is controlled by glycosylase activity. Only when the DNA activator module populates an ON state the CRISPR/Cas12a is activated, thus generating a fluorescence signal output.

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*Dynamic covalent DNA networks to translate multiple inputs into programmable outputs**Simone Brannetti,¹ Serena Gentile,² Erica Del Grosso¹, Sijbem Otto³, Francesco Ricci¹*

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Intracellular networks that dynamically respond to different biological and chemical cues play a fundamental role in regulating signaling transduction pathways. Researchers have recently explored the possibility of developing artificial systems that, mimicking such dynamic networks, allow to build synthetic systems that respond to different targets with high sensitivity and specificity.

Dynamic combinatorial libraries can be promising tools to engineer artificial networks. In these systems, a set of building blocks forms reversible bond and are allowed to reach thermodynamic equilibrium in the presence of external inputs, resulting in a variety of output libraries [1].

Synthetic DNA has emerged as a versatile biomaterial to engineer nanodevices with potential applications in different fields, like sensing, imaging, and drug-delivery. Taking advantage of the high programmability and predictability of DNA-DNA interactions, several strategies used to design synthetic receptors for a wide range of different targets have been reported [2].

Motivated by the above considerations, here we propose to develop a DNA-based dynamic combinatorial library (DNA-DCL) as a sensing tool able to respond to the presence of multiple targets. To achieve this, we have designed a DCL composed of short reactive DNA strands (Pool) that can interact with each other leading to the generation of a library of products (Output). The presence of specific external inputs (Target) can sequester reactive DNA strands from the pool, inducing the upregulated formation of only a specific product.

To prove the versatility of our approach, we have also designed a DNA-DCN to orthogonally control the assembly and disassembly process of DNA-based nanostructures.

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VS1: a formulation tale of the first STARD3 inhibitor. From stability studies to nanoformulations.

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The rate of incidence of the Colorectal Cancer (CRC) has shown to increase worldwide along with the demand of new, less toxic, and more effective cures [1]. VS1 is an organic compound, which has been identified as the first inhibitor of STARD3, a cellular protein involved in the development of CRC among others. VS1 has already showed promising results when tested in vitro in breast and CRC cancer cells [2]. In order to further explore the potential of VS1 as anticancer compound, a study has been conducted to develop nanoliposomes [3] loaded with VS1 and to investigate their efficacy in vitro. To assess the stability of VS1 in the encapsulation conditions a stability study has been performed. The investigation has been carried out by spectroscopic [4] (UV-Vis, FT-IR, NMR) and microscopic techniques (TEM). The FT-IR and NMR spectra suggested that VS1's pyrido-pyrimidinone moiety may degrade in buffers used to synthesise nanoliposomes, although further investigations on the mechanism of degradation are requested. To this end, to assess the loss of in vitro biological activity of degraded VS1, an antiproliferative activity was performed, and nanocrystals [5] of degraded VS1 and not degraded VS1 have been synthesised, characterized and tested.

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Title Grape shoots: from sustainable polymers extraction to synthesis of biobased bioplastic.

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The actual production of plastic in 2022 was 400.3 million tons, while that of bioplastics (BPs) was 2.3 million tons, equal to 0.5% of the total [1]. The about 48% of the total BPs produced in 2022 were biodegradable [2]. Currently BPs are mainly produced from first generation feedstocks (food crops) even if it's also increasing the production of that materials from 2nd and 3rd generation feedstocks as well as non-edible food waste [3]. Wine production accounts large amounts of waste before (shoots 1.4-2 tons/hectare globally) and after harvesting (grape pomace 20-25% of processed grapes) of which grape shoots are the most abundant [4]. The aim of this work is to valorize these wastes by extracting the polymers they contain (holocellulose and lignin) to produce bioplastic materials based on cellulose acetate (CA). In a first phase, holocellulose and lignin were obtained through a more sustainable organosolv process and different bleaching treatments were tested on shoots, stalks, and seeds. The best starting biomass in term of extraction percentage yield was selected to test different pretreatments (autoclave, sonication, microwave) to try to improve extraction process. The autoclave pre- treatments result to be the best also in term of hemicellulose-cellulose separation. From the best results obtained in this last part, the cellulose diacetate synthesized was used to produce bioplastic film to be characterized in their properties.

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Spectroscopic studies on the mechanism of interaction of antimicrobial peptides with the membrane of live cells and model systems

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Antimicrobial peptides (AMPs) are promising molecules to fight drug-resistant microbes. They usually kill bacteria by perturbing their cellular membranes. This purely physico-chemical process is crucial for AMP clinical potential, due to their very limited propensity to induce bacterial resistance. Spectroscopic and microscopic studies of the interaction of antimicrobial peptides (AMPs) with artificial membranes are pivotal in developing models of the mechanisms of pore formation. However, quantitative data on the mechanism of action of AMPs with the membrane of real cells are scarce. We developed assays allowing for thermodynamic and kinetic characterization of peptide interactions with live bacterial cells [1, 2, 3]. Our data showed that millions of peptides must bind to each cell to cause its death. This number even exceeds the complete coverage of cell membranes. Peptide affinity for bacteria whose membrane has already been perturbed is an order of magnitude higher than for live cells. After membrane perturbation, AMPs accumulate inside the cell, binding to intracellular components. We are currently performing combined thermodynamic and kinetic characterizations that provide a unique perspective of the determinants for the mechanism of action of AMPs in order to design novel antimicrobials with improved properties.

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Green and rapid detection of pesticides through ZnO fluorescent core-based molecularly imprinted polymers

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The extensive use of triazole pesticides is integral to protecting crops, herbs, and spices due to their efficacy against fungal diseases. However, these pesticides pose human health risks, particularly penconazole, which is toxic. Consequently, regulatory bodies have established maximum residue levels in food [1]. Conventional detection methods, such as high-performance liquid chromatography, are effective but costly, time-consuming, and not environmentally friendly. This study introduces a novel, greener detection approach by combining fluorescent methods with molecularly imprinted polymers (MIPs). Specifically, it develops a penconazole- selective MIP with a zinc oxide (ZnO) nanoparticles (NP) core. The ZnO NP surface is modified with (3-aminopropyl) triethoxysilane (APTES), enabling detection through fluorescence intensity changes when penconazole's chlorine interacts with APTES's amino group [2]. MIPs offer an alternative to traditional food analysis methods due to their high selectivity and reduced time requirements. In this MIP synthesis, tetraorthosilicate (TEOS) is the crosslinker and APTES the monomer, and the polymerization occurs around the NPs, modifying the surface to interact with penconazole. The latter serves as both the analyte and the template and is removed post-synthesis leaving a porous MIP with a fluorescent core. ZnO is chosen for its safety, biocompatibility, and ease of preparation, as well as its tunable morphology and properties [3].

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Downregulation or inhibition of insulin degrading enzyme induces accumulation of pre-20s complexes in sh-sy5y cells

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The proteasome is a multi-subunit proteolytic complex that degrades most intracellular proteins. The canonical holocomplex is made up by the 19S regulatory particle and the 20S core particle (composed of four rings; $\alpha\beta\beta\alpha$). During the 20S biogenesis, PAC 1-4 chaperones assist the α -ring assembly. Thereafter, the α -ring serves as scaffold for subsequent insertion of β -subunits through the contribution of the POMP chaperone to constitute the half-20S. Two half- 20S then assemble into a mature 20S.

The activity of proteasome particles can be regulated through decoration with Proteasome Interacting Proteins which modulate their composition and proteolytic specificities. In this regard, Insulin Degrading Enzyme (IDE) has been documented to bind to the 20S, affecting its interaction with the 19S in vitro.

It has been previously reported that downregulation of IDE expression in SHSY5Y cells increases the bulk proteasome activity, envisaging that IDE modulation has global effect on targeted proteolysis [1].

In the present study, we have deepened the molecular features of IDE-proteasome interaction using both siRNA delivery strategies and catalytic inhibition of the enzyme to SH- SY5Y cells. By applying different approaches, we have documented that modulation of IDE expression or activity brings about relevant effect on the abundance of pre20S complexes, likely through a not fully characterized yet interaction with POMP chaperone.

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Self-Powered Flexible and Sustainable Electrochemical Sensor for Oxygen Detection

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The monitoring of oxygen gas in food packaging is crucial for quality surveillance, warning users on spoiled food, happening through aerobic microorganism proliferation [1, 2]. In this scenario, we reported the development of a miniaturized and flexible, Bluetooth-assisted potentiometric sensor for oxygen gas detection in food packaging. In detail, the sensor comprises three layers: a zinc sheet (anode), a conductive silver ink screen-printed on oriented polypropylene (cathode), and a non-toxic deep eutectic solvent (electrolyte) deposited on sustainable office paper. The electrochemical sensor was then integrated with a portable potentiostat for potentiometric oxygen detection, leveraging Bluetooth technology for efficient data transmission.

First, the electrolyte composition and deposition on paper was optimized, and the sensor was characterized by electrochemical impedance spectroscopy, and scanning electron microscopy. Subsequently, the device was tested in standard oxygen atmosphere, obtaining a linear range between 0- 20.9% v/v O₂, with a calibration curve equal to $y = -(0.92 \pm 0.06)x + (1143 \pm 1)$ ($R^2=0.984$).

Finally, the developed device was tested by inserting in packages containing vegetables, obtaining a good correlation between the proposed method and a commercial oxygen gas analyzer.

This work opens up novel opportunities to deliver smart food packaging exploiting sustainable and cost-effective materials for miniaturized, reliable and user-friendly sensor fabrication.

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Green eco-friendly nanocomposite materials for conservation of ancient polychromy: a new proof of concept!

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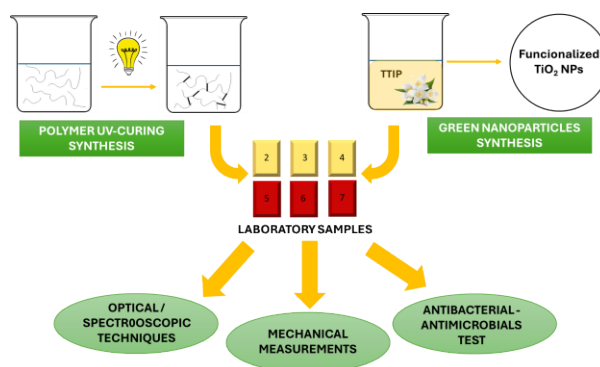
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Ancient sculptures were often characterised by polychromy, that can provide important historical and artistic information. These artifacts are damaged by chemical, physical and biological effects, which contribute to a partial or total loss of the pictorial layers [1]. The aim of the study is to develop green products (by large scale mass production combined with low- cost procedure), to protect the pictorial surfaces. The experimentation is focused on the production of nanocomposite materials, where the polymer entraps nanoparticles, which are produced by green chemistry strategies (simultaneously with the extraction of essential oils from natural plants). The effectiveness of new nanocomposite materials will be investigated by applying laboratory samples, before and after the artificial aging [2]. Several characterisation studies will be carried out, as: the optical test, mechanical measurements and antibacterial/antimicrobial assay, and all results will be compared with the traditional procedures widely used in conservation of ancient polychromy. In this work, highly compatible TiO₂ nanoparticles will be synthesized and applied into different polymers and the expected results will be promising, considering that functionalized TiO₂ shows excellent photocatalytic features and also antibacterial properties (being covered with a layer of essential oils, these latter extracted during the chemical synthesis of nanoparticles).



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Collaborazione di terza missione e trasferimento tecnologico con YOCOCU APS, impresa del territorio laziale operante nel settore della conservazione dei Beni Culturali.

Antibacterial and photocatalytic features of satureja montana essential oil-TiO₂ nanocomposites

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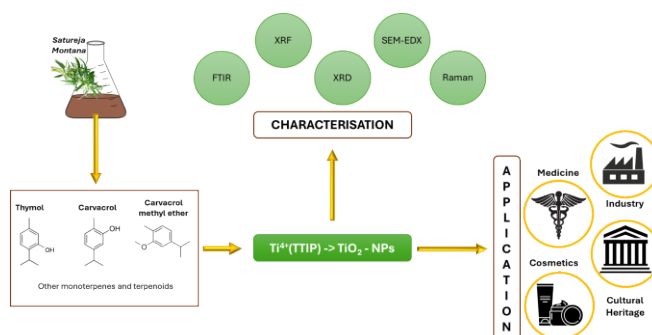
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Satureja Montana is a medicinal plant with known effects against Gram-positive and Gram-negative bacteria and significant antimicrobial properties. The chemical composition of terpenoids, isoprene and other natural substances makes Satureja Montana a green source of concentrated reducing agents capable of precipitating TiO₂ nanoparticles, starting from Titanium isopropoxide having Ti⁴⁺, as precursor [1]. The strategy to synthesize TiO₂ nanoparticles from Satureja Montana' essential oil extracts is due to the further possibility of exploiting the additional antioxidant, and anticorrosive properties within the new manufactured nanocomposites. This last statement is explained based on the chemical composition of the volatile fraction of the Satureja extract, which provides: carvacrol (306 gL⁻¹), thymol (141 gL⁻¹), carvacrol methyl ether (63 gL⁻¹), and the highest phenolic content (i.e. the reducing chemical agents). In this study, the new nanocomposite was then characterized both structurally (with FTIR, Raman and XRD/XRF) and morphologically (mainly with SEM/EDX). The possible industrial applications could range from the medical/pharmacological field to that of nutraceuticals/cosmetics and finally also that of the conservation of historical-artistic surfaces.



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Collaborazione di terza missione e trasferimento tecnologico con YOCOCU APS, impresa del territorio laziale operante nel settore della conservazione dei Beni Culturali.

Synthesis and characterization of a non-stoichiometric perovskite oxide $\text{La}_{0.4}\text{Ca}_{0.4}\text{Ti}_{0.95}\text{Ni}_{0.05}\text{O}_3$ as fuel electrode for Solid Oxide Cells (SOC)

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High Temperature SOCs are among the most interesting devices for energy storage and conversion. SOCs offer high energy efficiency due to the high working temperature (>650°C), which favors thermodynamics and kinetics. The electrode state-of-art materials are perovskite oxides, those containing Fe at the B-site display mixed ionic- electronic conductivity and catalytic activity but poor stability in reducing environment. Among the various perovskite systems, titanates (Ti at B-site) have attracted particular interest due to high structural stability in reducing atmosphere but show low ionic conductivity and electrocatalytic activity [1].

This study presents the synthesis and characterization of an A-site deficient, B-site Ni- doped titanate perovskite $\text{La}_{0.4}\text{Ca}_{0.4}\text{Ti}_{0.95}\text{Ni}_{0.05}\text{O}_3$ (LCTN). The A-site deficiency leads to an increase in oxygen vacancies as compared to the stoichiometric compound, which increase the ionic conductivity. Meanwhile, the Ni doping can improve the electrocatalytic activity also due to exsolution phenomenon [2].

Different synthesis routes are presented. LCTN is characterised by X-ray diffractometry to identify crystalline structure, study the textural properties and assess its structural stability after reduction. Scanning electron microscopy is used to evaluate the exsolution. The electrical conductivity in hydrogen is reported. Finally, the electrochemical properties are evaluated by assessing the electrode area specific resistance on symmetrical cells.

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From NANOpastics to bioplastic toward environmental sustainability: a green algae-based approach

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The increasing plastic pollution in every biome of our planet, especially in our oceans, is becoming of great concern for both the environment and human health. In particular, the threat for human health is caused by the slow release of microplastics, which find an easy way to the human organism through the food chain. The research is currently busy in finding better alternatives to fossil plastics, the most promising one being the development of thermoplastics materials from renewable polymers, called bioplastics. Bioplastics can be obtained out of food and agricultural wastes, from which polysaccharides and proteins can be easily extracted.

NANOGrab project aims at solving plastic pollution problem, by developing high efficiency microalgal strains that produce enzymes able to digest plastic nanoparticles and by converting the microalgal biomass into added value products such as bioplastics.

In this work, we have used the microalgal biomass as additive for bioplastic manufacturing. In particular, the microalgae can be natural pigments; furthermore, they can be natural filler to improve the mechanical properties of bioplastic materials. The bioplastic that we have improved is a protein-based bioplastic from milk waste, produced by the Splastica spinoff, called SP Milk [1,2].

We characterized our proteins-based bioplastic through tensile tests and thermal analysis, showing high resistance and thermoplasticity, two keys' characteristics to obtain an industrially workable material. Moreover, we investigated the positive effects of microalgae as a natural filler and dye. The results suggested that also a small percentage of algae can give rise to a nice colour on the material, and that the mechanical properties can be improved. In particular, the presence of unsaturated fats in microalgae can improve the elongation at break without negatively affecting the mechanical resistance. In some cases, the presence of microalgae improved both the elongation at break and the elastic modulus. These results show the high flexibility of SP Milk to be blended with other natural wastes and filler, to improve his properties and yield.

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Modeling of YBCO film and Thermodynamics aspects of the Barium Oxyfluoride

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The typical layered structure of superconducting cuprates, such as $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ (YBCO), requires proper alignment of conduction planes to ensure optimal transport properties. For this reason, YBCO thin films must be grown with a specific orientation. The best superconducting properties are observed in the YBCO grown along the c-axis, perpendicular to the substrate. Against the background of extensive scientific literature on the growth of YBCO on crystalline substrate by chemical deposition technique [1-5], only a few works concern the study of the nucleation process, although it is crucial for the growth of the film [2-5]. A thermodynamic and kinetic model for the growth of YBCO has been proposed in references [5,6]. This model is based on the calculation of the free energy of oxide formation using thermodynamic data, experimental and theoretical, for the formation reaction of YBCO, to obtain information on the preferential growth of the film along the a or c-axis. Among the parameters that enter the model of [6] and that rule crystal orientation during the growth, the partial pressure of water ($P_{\text{H}_2\text{O}}$) and the temperature of crystallization (T_{cryst}) can be monitored during the film preparation. The study reported in ref. [6] highlights the role of the adhesion work between film and substrate, since it determines the nucleation barrier for oriented growth. This study is significant to identify the optimal conditions for the growth along the c- axis of YBCO crystals. In this work, the epitaxial growth of YBCO films obtained with the fluorine-based Metal Organic Decomposition technique was investigated, with the objective of studying the effect of the process parameters, namely $P_{\text{H}_2\text{O}}$ and T_{cryst} , on the degree of orientation of the film and to verify the model proposed in ref. [6]. The samples have been fully characterized through the analysis of morphology, microstructure, and superconducting properties. This study allowed to deepen the qualitative understanding of the role of these parameters on the epitaxial growth mechanisms. Although the thermodynamic model is in accord with the experimental data, the kinetic model of ref. [6] has been improved to achieve a better description of the experimental output. This is particularly important to produce YBCO on an industrial scale [7]. In addition, we present a study on the thermodynamics of the Oxyfluoride (OF) by processing experimental data on the YBCO growth [8]. The analysis allows one to determine the standard enthalpy and the standard entropy changes for Oxyfluoride formation from Barium oxide and Barium fluoride [9]. To identify the thermodynamically more favorable route to the OF formation in the MOD process, the free energy change for the formation of the precursor, through several reactions involving gas water, has been determined [9]. The free energy of formation via fluoride and water indicates higher stability of oxygen rich Oxyfluoride for $P_{\text{HF}}^2/P_{\text{H}_2\text{O}} < 10^{-6}$ [9]. In the framework of the nucleation theory the present results are needed to study the effect of precursor composition on film orientation [9].

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Asymmetric β -functionalized porphyrins for potential applications in biomimetic process, photovoltaics, PDT and NLO

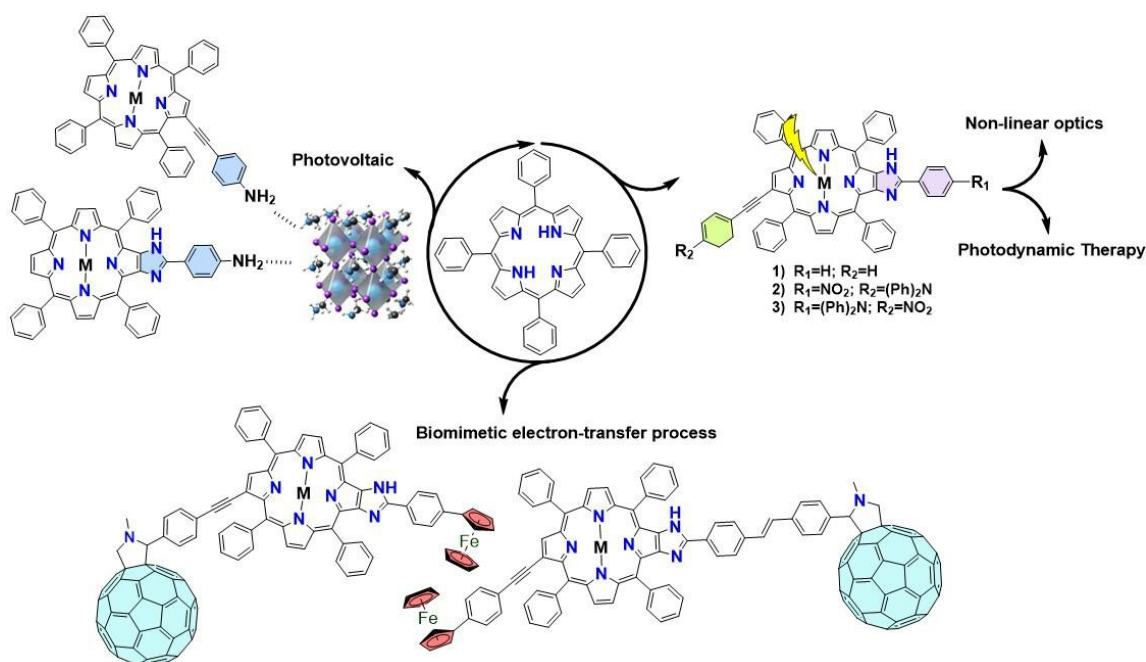
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Porphyrins have always attracted the attention of the scientists for their excellent thermal stability, for their photochemical and electrochemical properties and intense absorption in the visible region. Coordination of metals, functionalization with different substituents, also inducing a molecular symmetry reduction, are the main strategies to achieve a further fine-tuning of their incredible properties, to which their biological versatility is strictly related. The possibility to modulate the porphyrin dipole by altering the molecular structure is a key aspect for subsequent application in many technological fields. In addition to the introduction of different functional groups and substituents in the meso-position, that represents a widely explored synthetic strategy, also the post-synthetic functionalization of the beta-pyrrole positions can be a valid, and most often a more convenient synthetic approach [1] [2].

In our work, we present the synthesis and characterization of innovative asymmetric mono- and bis- β -substituted porphyrins for potential application in biomimetic electron-transfer process, solar cells (dye-sensitized and perovskite solar cells), photodynamic therapy (PDT) and Non-Linear Optical (NLO) materials.



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Improving the sensitivity of CRISPR-based detection of Nucleic Acids via Triplex DNA Switch

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The widespread adoption of CRISPR technology for diagnostics has been fueled by the discovery of the collateral cleavage activities of CRISPR type V (Cas12) and type VI (Cas13) systems, triggered by DNA/RNA binding. Cas12 is an RNA-guided enzyme that combines single- and double-stranded DNA target recognition with collateral cleavage activity, enabling detection and signal amplification in one step [1]. To amplify the signal upon target binding, single-stranded DNA probes functionalized with a fluorophore-quencher pair at the 3' and 5' ends are used, which are cleaved only by Cas12a's collateral activity [2].

We describe a DNA-based hybridization network, utilizing Clamp Triplex DNA to control Cas12a's collateral activity. These Clamp Triplex DNA probes exhibit superior specificity and affinity for recognizing homopurine DNA/RNA targets compared to standard linear or hairpin DNA probes [3]. In the presence of a homopurine DNA/RNA target the Clamp Triplex probe alters its conformation switch into a folded state that is associated to a reaction network leading to Cas12a activation and fluorescence output in a rapid, single-step, one-pot detection. With the same limit of detection (LOD) as standard CRISPR-Cas12-based systems, we overcome two significant limitations of CRISPR-Cas systems in diagnostics: detecting short DNA targets (10 to 20 nucleotides) and achieving high specificity in distinguishing single nucleotide mutations in the target sequence.

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Copper-Substituted Lanthanum Strontium Ferrite (LSF) as a Symmetrical SOEC Electrode for Enhanced CO₂ Reduction

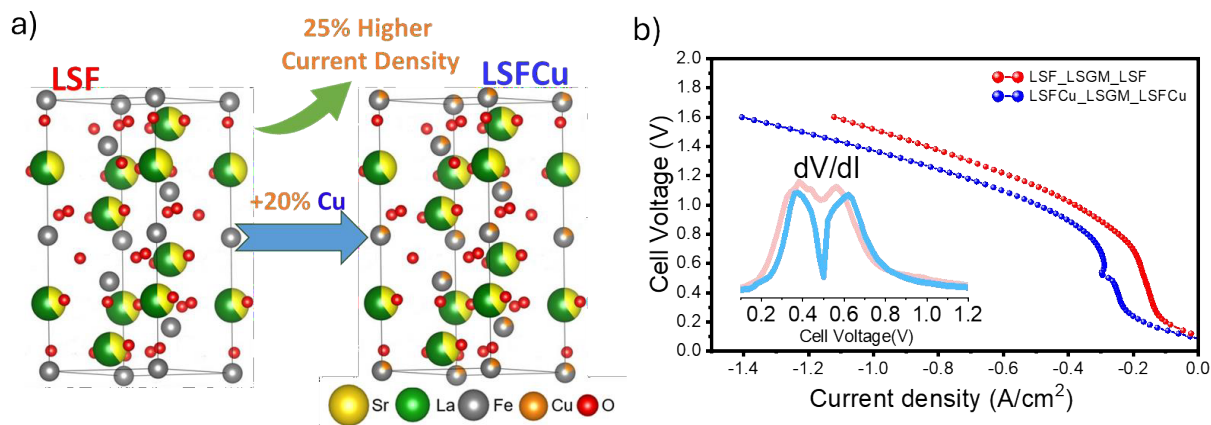
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Mitigating CO₂ emissions is essential for addressing global warming, thereby prompting research into CO₂ electrolyzers [1]. In particular, high temperature CO₂ reduction through solid oxide electrolysis cells (SOECs) has unrivaled efficiency compared to lower temperature technologies [2]. In conventional SOECs, Ni-YSZ composites promote the reduction of CO₂ at the cathode, while Co-containing perovskite oxides catalyze the oxygen evolution reaction at the anode. However, these materials suffer from coking, nickel oxidation, and cobalt diffusion during electrolysis operation [3,4]. Developing Co-free and Ni-free electrocatalysts could advance CO₂-SOEC commercialization.

Here, 20 mol% copper was successfully substituted at the B-site of La_{0.6}Sr_{0.4}FeO_{3-δ} as a multipurpose electrode for symmetric CO₂-SOECs. La_{0.6}Sr_{0.4}Fe_{0.8}Cu_{0.2}O_{3-δ} (LSFCu) is synthesized via the solution combustion method and iron partial substitution with copper is evaluated by XRD, XPS, TGA analyses, and electrical conductivity assessment. LSFCu is tested as the SOEC anode by measuring area-specific resistance versus T and pO₂. LSFCu structural, electrical, and electrocatalytic properties are also assessed in pure CO₂ for cathodic applications. In CO₂ SOEC mode, the LSFCu/LSGM/LSFCu cell exhibits a 25% higher current density at 1.6 V compared to reference LSF cells. Additionally, LSFCu demonstrates a rapid, stable voltage response and excellent durability in galvanostatic mode for 150 hours at 850°C.



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*N-methyl-corroles and their catalytic activity**Alessia Fata¹, Francesco Pizzoli¹, Roberto Paolesse¹, Sara Nardis¹*

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Corroles are one of the most intriguing classes of compounds in the porphyrinoid family, thanks to their peculiar chemistry. They highlight a notable coordinative versatility with the possibility to introduce different metals allowing the expansion of the so-called Periodic Table of Metallo-corroles [1]. Their reactivity and photophysical behavior allow their use as sensing materials in chemical sensors for optical, electrochemical, and conductometric transducers [2]. Their catalytic activity has also been investigated in several literature studies; iron corroles, for example, were found to be more selective catalysts than analogous porphyrins for the aziridination of olefins [3] and the functionalizations on their meso positions can be studied to apply them in electrocatalysis [4]. Furthermore, the use of metallo-corroles together with TBAB resulted in a very powerful cooperative catalytic system for CO₂ fixation with epoxides [5]. In this work, we studied the catalytic activity of meso-arylcorrole complexes and their N-methyl analogs: in particular, we used the N-substituted macrocycles to introduce an interesting dimension, considering their relatively unexplored chirality in catalysis. Investigation of their performances in CO₂ insertion reactions with epoxides and aziridines for cyclic carbonate and oxazolidinones synthesis could provide valuable insights into their potential as enantioselective catalysts and also contribute to the development of greener synthetic methodologies.

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Study of mercury chemical compounds' possible effects, present in the sediment, on benthic communities

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Mercury is an earth crust natural component, containing an abundance of 0.05 mg/kg and significant local variations. Aside from natural phenomena anthropogenic sources have increased Hg levels in the environment [1,2]. Sediments represent both a reservoir and potential contamination source for the pollutants transfer to the water column and finally to the aquatic trophic chain [3,4]. This study specifically focuses on marine benthic macroinvertebrates (macrozoobenthos), which are species inhabit the bottom surface or within the sand for at least one phase of their life cycle. Due to their sensitivity to anthropogenic pressures, macrozoobenthos are considered excellent bioindicators. The PhD program, carried out at Institute for Environmental Protection and Research (ISPRA), investigates the presence of mercury in marine sediment and benthic species. The primary objective is to examine the potential correlation between the mercury content in sediments and that in these organisms. Sediment and organisms' samples were collected during environmental monitoring campaigns carried out in accordance with the MSFD/2008 Framework Directive (Directive 2008/56/EC) in the Italian Seas. The benthos was categorized into major taxa, including mollusks, crustaceans, echinoderms, and polychaetas.

Quantitative mercury determination is conducted for both sediment and benthos samples using a direct mercury analyzer (DMA-80) employing atomic absorption spectrometry [5].

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Advanced Cancer Therapy: SERS Nanostructures Functionalized with ad-hoc oligopeptides Targeting PD-L1

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Immune checkpoint inhibitors have profoundly advanced cancer treatment research, with programmed death ligand-1 PD-L1, playing a pivotal role. PD-L1 is expressed on regulatory cells, and binds the PD-1 receptors on killer T-cells, forming a complex that suppresses immune responses¹. To avoid this interaction, peptide therapeutics is a new frontier, with advantages like low toxicity, minimal immunogenicity and cost-effectiveness. To enhance their targeting and stability in biological environments, peptides can be conjugated to gold nanoparticles (AuNP-NS)^{2,3} which serve as plasmonic nanostructures with surface-enhanced Raman scattering (SERS) signals, enabling novel approaches for imaging and diagnosis³. In this work, the looking for new oligopeptides designed on the basis of the key features necessary for an high affinity to PD-L1 regions interacting with PD-1⁴, and whose efficacy was tested preliminarily through Molecular Dynamics (MD) simulations, is reported. After synthesis, related functionalized AuNP-NS were incubated with PD-L1 over-expressing tumor cells and SERS measurements confirmed their strong affinity for PD-L1. MD simulations of such systems, interacting with PD-L1 provide molecular-level insights into their activities.

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Investigation of ionic liquids as electrolytes for Aqueous Organic Redox Flow Battery (AORFB) application.

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In light of the energy challenges we have faced over recent decades, the imperative to develop new renewable energy sources and energy storage systems has become increasingly pronounced. Redox Flow Batteries (RFBs) stand out among renewable energy technologies due to their extended lifespan and scalable energy and power densities [1]. By harnessing organic compounds, we can fine-tune the properties of the electroactive couple, enabling operation in aqueous electrolytic solutions while minimizing environmental and user risks. This study focuses on a novel water-soluble electroactive couple characterized by high solubility, electrochemical stability, and low aggregation tendencies. Porphyrins, with their well-conjugated systems, were considered for well-defined redox processes, as they exhibit favorable characteristics [2]. Specifically, tetra-(4-sulfonatophenyl) porphyrins (H₂TPPS) and metal tetra-(4-sulfonatophenyl) porphyrins (M-TPPS, where M = Zn²⁺, Cu²⁺, Ni²⁺, VO²⁺) were synthesized and tested. A preliminary Density Functional Theory study revealed that H₂TPPS possesses a planar structure that could promote aggregation. Conversely, NiTPPS exhibited a distorted structure, mitigating π - π stacking, which made it the preferred choice. Additionally, an aggregation study using UV-Visible absorption was conducted. To optimize the electrolyte solution and explore redox processes, cyclic voltammetry of Ni-TPPS was performed in both non-aqueous and aqueous media. Ni-TPPS was characterized in organic and aqueous electrolytic solutions. Particularly, the ionic liquid 1-butylpyridinium tetrafluoroborate ([Bupy⁺][BF₄⁻]) was investigated as electrolyte to enhance the electrochemical properties of NiTPPS.

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3D-printed and reagent-free paper-based phytic acid detection in spinach leaves

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Phytic acid is a phosphorylated derivative of myo-inositol, widely present in plants as their primary phosphorus storage form. Although beneficial for plants, it is considered an antinutrient in human diets. By binding essential minerals like calcium, iron, and zinc, phytic acid reduces their bioavailability, highlighting the importance of its monitoring in food products [1]. In this scene, we have developed a reagent free paper-based biosensor for quantifying phytic acid in spinach leaves integrated in a 3D printed extraction device. Phytase, immobilized on screen-printed electrodes modified with carbon black dispersion, hydrolyzes phytic acid generating phosphate ions that form an electroactive complex with the molybdate pre-loaded on a filter paper pad [2]. The oxidation of phosphomolybdate complex was monitored by using cyclic voltammetry. A linear response was observed across a phytic acid concentration range of 1 to 50 μM with a limit of detection of 0.8 μM in standard solutions. To simplify phytic acid analysis in spinach leaves, a 3D printed funnel was attached to a grinder to directly channel the extracted solution onto a paper electrode. Spinach leaves samples were ground and treated with 0.2 M HCl within the 3D printed device. Developing biosensor for phytic acid detection in foods is crucial for enhancing nutritional quality, ensuring food safety, and mitigating health risks.

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*Design of peptide inhibitors of protein-protein interactions targeted to Src homology 2 domains:
a combined simulative and spectroscopic approach*

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Src homology 2 (SH2) domains mediate protein-protein interactions by recognizing phosphorylated tyrosine residues [1]. Their pivotal role in various signaling pathways has made them important targets for pharmaceutical development. The SHP2 phosphatase, which includes two SH2 domains, is crucial in regulating various cellular processes [2,3]. In the last years, we have developed and patented potent oligopeptides targeting the N-terminal SH2 domain of SHP2 [4]. We are now optimizing these molecules through in silico studies and spectroscopic experiments to bring them closer to clinical applications. Potential of mean force calculations allowed screening of sequence modifications, including non-natural amino acids. The peptides' affinity for the target domain was tested by fluorescence anisotropy binding assays, showing strong correlation between calculated and experimental binding free energies. This led to identify a sequence with a single digit nM dissociation constant. We extended our approach to design inhibitors for the C-terminal SH2 domain of SHP2. Analyzing natural binders, peptide libraries, X-ray structures, and MD simulations, we identified structural determinants for C-SH2 recognition. Binding assays revealed that an eight-residue peptide derived from a natural sequence exhibits a low nM dissociation constant. This SHP2 case illustrates that combining computational and spectroscopic methods can develop highly potent and selective oligopeptide inhibitors for SH2 domains.

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Structural Effects in HAT from the C(sp³)-H Bonds of Lactams to Alkoxy Radicals

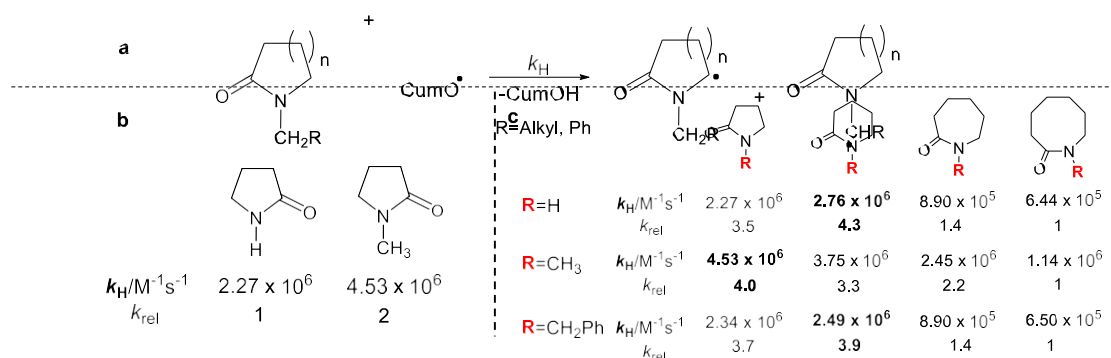
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Nitrogen containing heterocycles are common fragments in active pharmaceuticals and natural products. Among these, lactams represent an important class. A recent kinetic study on hydrogen atom transfer (HAT) from secondary and tertiary lactams to the cumyloxy radical (PhC(CH₃)₂O•, CumO•) has provided information on the role of substrate structure on these reactions [1]. HAT predominantly occurs from the C(sp³)-H bonds that are α- to N, activated by hyperconjugation with the adjacent π-system (Scheme 1a). Interestingly, in the 2-pyrrolidone series a ~2-fold increase in the second order rate constant for HAT to CumO• (k_H) has been measured going from 2-pyrrolidone to 1-methyl-2-pyrrolidone, suggesting that both endocyclic and exocyclic α-C-H bonds contribute to the observed reactivity (Scheme 1b). When considering the effect of ring size, in all the series shown in Scheme 1c, a ~4-fold decrease in k_H has been measured going from the 5- and 6-membered ring derivatives to the 8-membered ones, suggesting that such decrease in reactivity is associated to the greater flexibility of the larger rings compared to the smaller ones.



Scheme 1

In order to obtain a deeper understanding of the structural effects associated to these reactions, it seemed particularly interesting to accompany the kinetic study by product studies on the reactions of a tert-alkoxy radical such as tert-butoxy ((CH₃)₃CO•, t-BuO•) with the N-methyl- and N-benzyl-lactams.² The results of these studies will be discussed.

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Temporal control of in vitro transcription

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In vitro transcription reaction (IVT) is a simple procedure that allows the production of RNA strand from a double-strand DNA template (that contains the promoter region and the coding template). Here we demonstrate a strategy to rationally program the onset of the in vitro transcription reaction. Our approach is based on using blocker strands that through binding to the promoter region of the template and prevent the onset of the transcription reaction. These blockers can, subsequently, be removed via specific enzymatic reactions. The removal of the blocker allows the binding of an input strand that completes the promoter, and thus activate the IVT. The kinetics of the enzymatic blocker degradation control the time at which the transcription starts. Varying the concentration of the blocker and the enzyme we can modulate the onset of the transcription. To show modularity, we designed three different tunable delay systems using RNase H, Uracil-DNA Glycosylase and DNA- formamidopyrimidine glycosylase and their respective blocker strands. We achieved a tunable temporal control of IVT with the half-time of the reaction up to 8.4 hours.

*Halogen atom transfer (XAT) from alkyl iodides to α -aminoalkyl radicals.
A kinetic evaluation of the role of structural effects.*

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Halogen atom transfer (XAT) from a halogenated substrate (R-X) to a radical species (Y^{*}) is an elementary bimolecular reaction that is finding increasing application in modern synthetic chemistry [1]. The versatility of the reaction is related to the possibility of trapping the intermediate carbon centred radical with different reagents to obtain a variety of functionalized products R-FG under mild conditions (Figure 1).

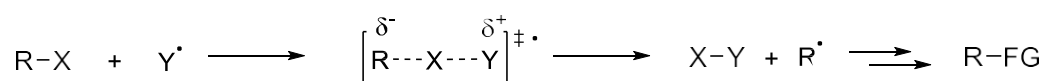


Figure 1

The reaction has been described to occur through a transition state characterized by a certain degree of charge separation, with partial negative and positive charge development on the incipient carbon radical R^{*} and abstracting radical Y^{*}, respectively, in line with the acceleration observed when Y^{*} displays a nucleophilic character.

Along these lines, nucleophilic radicals such as α -aminoalkyls have recently emerged as a new class of XAT reagents [2,3], representing a viable alternative to the commonly employed tin and silicon centered radicals¹. However, despite the increasing applications of the former radical class in synthetically useful procedures, kinetic information on these reactions is still extremely limited [1]. In order to fill this gap and provide a deeper understanding of the role of structural effects on reactivity, we have carried out a detailed time-resolved kinetic study in DMSO on XAT from a series of alkyl iodides to different α -aminoalkyl radicals. The results of this study will be discussed.

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MAIGRET: a CRISPR-based immunoassay that employs antibody-induced cell-free transcription of CRISPR guide RNA strands

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The Clustered Regularly Interspaced Short Palindromic Repeats (CRISPR) and CRISPR-associated proteins (Cas) are the important adaptive immune system in prokaryotes. Besides the gene-editing, many studies showed that the CRISPR/Cas systems can be developed for the field of detection due to their DNase/RNase properties [1]. Here we report a CRISPR-based assay for the sensitive and specific detection of antibodies and antigens directly in complex sample matrices. The assay, called MAIGRET (Molecular Assay based on antibody-Induced Guide-RNA Enzymatic Transcription), is based on the use of a responsive synthetic DNA gene that trigger the cell-free in vitro transcription of a guide RNA strand upon recognition of a specific target antibody [2]. Such transcribed guide RNA is used to activate the Cas12 enzyme, which can lead the cleavage of a fluorophore/quencher-labelled reporter and thus resulting in an increase in the measured fluorescence signal. MAIGRET allows the sensitive (low picomolar detection limit), specific (no signal is observed in the presence of non-specific antibodies) and selective (the system can be employed in complex media, including 50% blood serum) detection of target molecules. Due to the programmable nature of the sensing platform, it can be adapted to different target molecules (using a direct or competitive formats) and for orthogonal detection of two antibodies in the same solution using a different Cas enzyme (i.e., Cas13) associated to another antibody-responsive transcription of Cas13 guide RNA.

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Spinel-type High-Entropy Oxides Electrocatalysts for Anion Exchange Membrane Water Electrolyzers

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Hydrogen is a sustainable energy carrier, and its economy relies on electrochemical water splitting. However, one of the main performance limits of water electrolyzers is the sluggish oxygen evolution reaction (OER) kinetics at the anode, and high-cost and rare platinum-group-metal catalysts are required to enhance efficiency [1,2]. Among the alternative catalysts, multicomponent materials, such as high entropy metal oxides (HEOs), have received much attention due to their tunable compositions and properties, promising performance towards OER, and stability [3,4].

This work explores the use of Mg, Mn, Fe, Co, and Ni-based HEOs as OER catalysts in anion exchange membrane water electrolyzers (AEMWEs). To optimize these materials, different synthesis strategies, calcination conditions, and the stoichiometry of the metal ions in the sites of the spinel structure were investigated. The structure, morphology, and composition of synthesized HEOs were characterized by X-ray powder diffraction, X-ray photoelectron spectroscopy, and scanning electron microscopy. The electrochemical performance was evaluated through rotating disk electrode experiments, in an alkaline medium (pH=14). A lower calcination temperature promoted the formation of single-phase spinel-type HEOs, and the stoichiometry changes, from an equimolar to a near-to-equimolar ratio of the metals, improved the OER activity, with the formation of highly active (oxy)hydroxides species during anodic potential cycling.

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Seawater samples analysis for the detection and classification of microplastics validating the innovative KYTHARA™ device

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Plastics are an important material in our economy, and modern daily life is unthinkable without them. The production of new plastic products since the Second World War revolutionized in a positive way all fields of human activities: medicine, aerospace, transport, health and everyday life. At the same time, however, plastic materials can have serious downsides for the environment and health. The problem is that the conveniences that plastic offers led to a single-use and throw-away culture and revealed the material's dark side: many of these products, which are used only for a few minutes, may persist in the environment for hundreds of years. The breakdown of plastic items, caused by exposure to environmental factors, mainly the sun's radiation and ocean waves, generates microplastics that can be harmful to the environment and animal health.

In this work, we analysed microplastic samples, collected using an innovative device, Kythara™ which is designed to favour microplastic collection at sea, as part of a citizen science project "Plastic Crime Scene Investigation".

Firstly, we performed measurements using the new instrument and compared them to the results obtained using the standard "Manta" instrument, officially used for the sampling activities in the framework of the EU Marine Strategy Framework Directive – MSFD [1]. Twenty-four different samples were collected in the same site with same protocols using the two devices, and the results were compared. The calibration process was conducted following the MSFD protocol, that is by comparing the quantity and type (filaments, granules, fragments, etc.) of particles filtered using the two different devices.

Secondly, we have collected 90 different microplastic samples from six different areas of the Lazio coasts (15 samples for each area) to compare microplastics found in seawater with the plastic world production and the anthropic activities along the coast: Tor Paterno, Foce Di Fiumara Grande, Macchiagrande, Tenuta Presidenziale di Castelporziano, Isola Sacra and Ostia. We characterized the samples by optical microscopy and identified the type of plastic polymer by FTIR. Our results suggest a correlation between plastic World production and the type of plastic found in seawater, which could reflect and depend on anthropic activities on rivers and along the coast.

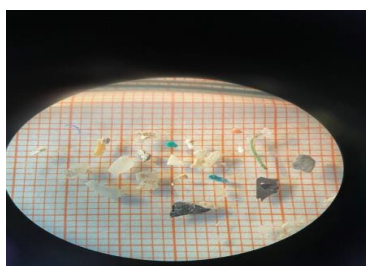


Figure 1: Microplastic particles found in a Tor Paterno sea sample

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N-doped Biochar for Bioelectrochemical Systems

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Biochar, a carbon-rich material derived from biomass, is well recognized as a sustainable source of energy [1,2]. Its porous structure and high specific surface area (SSA) make it promising for Bioelectrochemical Systems, such as Microbial Fuel Cells (MFCs) [3] and Microbial Electrosynthesis Cells (MES) [4]. MES is a rising technology for CO₂ electroreduction into valuable products mediated by electro-autotrophic microbes that accept electrons directly from a cathode or indirectly via H₂, reducing CO₂ to multi-carbon organic compounds.

In this study, biochar samples were obtained from urban green waste (UGW) biomass through controlled pyrolysis and activated via CO₂ at 800°C. Heteroatom doping created N- based active sites for enhancing hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR). Three samples were prepared: CO₂-activated (UGW), CO₂-activated N- impregnated (UGW(N)), and UGW(N) treated with HNO₃ and pyrolyzed at 900°C (UGW(N)_P). BET analysis showed higher SSA for UGW(N)_P (613 m²/g) compared to UGW(N) (450 m²/g) and UGW (546 m²/g). Electrochemical measurements using a rotating disk electrode (RDE) in neutral pH revealed that UGW(N)_P outperformed for ORR, with a more positive half-wave potential (0.55 V vs. RHE) compared to UGW and UGW(N) (0.46 and 0.51 V). Biochar-based electrodes, deposited on carbon cloth by air spraying, were tested in neutral media for HER. UGW(N)_P based electrodes showed higher current densities for HER at -1 V vs. Ag/AgCl (3.87 mA/cm²) compared to UGW and UGW(N) (2.40 vs. 3.36 mA/cm²), ideal for MES applications.

Acknowledgments

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GSSG at the centre of protein oxidative folding scene

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The oxidized glutathione (GSSG) was considered for many years the main actor for the protein oxidative folding but twenty years ago ER oxidoreductin 1 and the protein disulphide isomerase were indicated as the main responsible for this process. However, recent findings are bringing the GSSG back to centre stage. In fact, we discovered that in five proteins a few structural cysteines, only devoted to form disulfides, display astonishing hyper-reactivity toward GSSG when the polypeptide is present in a reduced molten globe (MG) conformation [1]. This is noteworthy because GSSG is present at high concentration in the endoplasmic reticulum. We report here that a similar phenomenon is present in Lactoferrin. The MG state of this protein display four cysteines with a reactivity toward GSSG more than 1000 times higher than that of an "unperturbed" protein cysteine [2]. This hyper-reactivity is specific for GSSG and, such fluorescence study shows, is probably due to a productive transient protein- GSSG complex. Although, this hyper-reactivity is confirmed as a characteristic exclusively present in eukaryotic cells, there are many unclear aspects like its biological and evolutionary meaning. The comparative study within Ovotransferrin, Transferrin and Lactoferrin, all evolved from a common ancestor, outlines only in the latter the presence of hyper-reactivity. The same happens in the casein family where, unlike Lysozyme, lactalbumin and lactoglobulins appear inert towards GSSG.

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Exploring the effect of different synthetic routes on the electrocatalytic activity of LaNiO₃ towards the oxygen evolution reaction

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Hydrogen gas (H₂) is mostly produced through methane reforming (grey hydrogen), a process that also generates CO₂ as a byproduct [1]. Although water electrolysis is a more environmentally friendly way of producing H₂ (green hydrogen), high costs and energy requirements prevent its widespread usage [2]. The overall kinetics of the water splitting reaction is limited by the oxygen evolution reaction (OER), which requires expensive, highly scarce platinum group metal (PGM) electrocatalysts such as IrO₂ and RuO₂ [2,3]. An alternative to PGM-based materials is provided by perovskite oxides (ABO₃), mixed metal oxides with a high degree of structural tunability, remarkable stability and low costs [2,3]. Lanthanum nickelates are especially promising due to their good electrical conductivity and their ability to form a highly OER active NiOOH layer through surface reconstruction [2,3].

In this work, LaNiO₃ perovskite was synthesized with two wet synthesis methods (coprecipitation and solution combustion synthesis) to investigate the relationship between synthesis route and electrocatalytic activity. Phase purity was assessed via X-ray diffraction while specific surface area was obtained from N₂ adsorption isotherms. The electrochemically active surface area (ECSA) was calculated from double layer capacitance (C_{dl}) measurements, activity towards OER was determined via cyclic voltammetry (1.0-1.7 V vs RHE) as well as Tafel plots and electrochemical impedance spectroscopy (EIS).

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Antibody-DNA conjugates triggering CRISPR-Cas12a based detection

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In the rapidly evolving field of biosensing, CRISPR-based systems have established themselves as powerful and versatile tools for nucleic acid detection [1]. However, it has become increasingly urgent to extend the application of CRISPR-Cas based detection beyond its traditional targets [2]. Herein we report the use of CRISPR-Cas12a as transducing mechanism together with nucleotide (ssDNA) modified antibody (Ab-DNA) as recognition element to detect non nucleic acid targets. The proposed approach exploits the enhancing capabilities such as improved sensitivity, due to the catalytic signal amplification of CRISPR- Cas12a, and improved applicability due to the simplicity of assay and reagents required. First, we demonstrated that the antibody modified with the oligonucleotide can activate CRISPR-Cas12a signaling activity on a FRET-based DNA hairpin reporter. The proposed mechanism was first validated for the detection of SARS-CoV-2 spike S protein in a multi well plate ELISA like named CRISPR-based Immunosensing Assay (CIA), where it demonstrated its sensing capabilities and enhanced limit of detection compared to standard colorimetric ELISAs. Next, we deployed the approach into a magnetic bead assay, referred to as CRISPR-based ImmunoMagnetic Assay (CIMA), that proved capable of detecting SARS-CoV-2 spike S protein in both buffer and complex matrix (undiluted saliva).

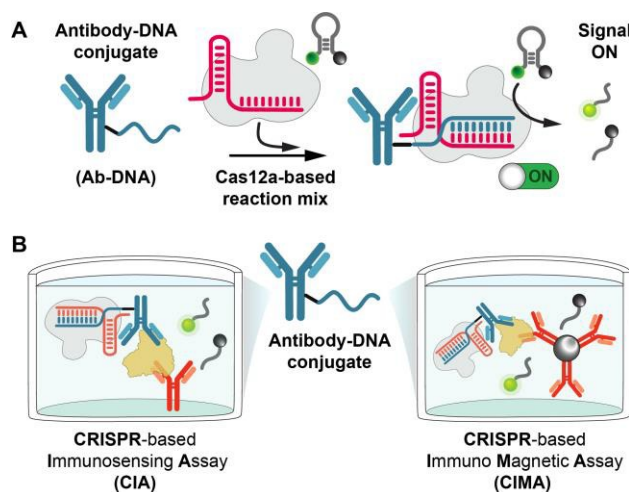


Figure 1: Schematic description of the CRISPR-Cas12a based detection using antibody-DNA conjugate (Ab- DNA). (A) The DNA sequence covalently attached to the antibody is designed to hybridize with the complementary crRNA sequence of the CRISPR-Cas12a complex. (B) On the left, schematic description of a CRISPR-based Immunosorbent Assay (CIA) and, on the right, a magnetic bead-based sandwich assay (CRISPR- based ImmunoMagnetic assay, CIMA).

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Drug-like natural and tailored monoterpenoids: new computational unveiling

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Natural terpenoids and their derivatives are raising new interest as antifungal agents, preventing drug-resistance. Thymol and carvacrol are widely investigated for their activity as antibacterial/antimycotic agents [1]. Further, tailored modifications led to new compounds, such as thymyl acetate and 4-bromothymol, synthesized and purified through eco-friendly approaches [2]. 4-bromothymol antimycotic activity resulted up to 6 times higher than that of thymol even on acclaimed resistant species [3]. To elucidate its mechanism of action, a thorough computational study has been performed, exploiting a hybrid approach that combines Quantum Mechanics (QM) and classical Molecular Dynamics (MD). QM afforded the partition coefficients of the 4-bromothymol, still undisclosed in the literature, while MD, through the Minimum Bias Approach (MBA), reaped the “real” position of active compounds into the simulated double layer of eukaryotic-like membrane, mainly 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (POPC). Overall, the computational findings were in excellent agreement with the experimental results [3]. Simple visual inspection showed that only two poses were allowed, i.e. POSE_1 and POSE_2, but only POSE_1 affected, in a meaningful manner, the $\text{PO}_4^- - \text{N}^+$ dipole. These results clarified, for the first time, the mechanism of action of thymol, carvacrol, and 4-bromothymol, likely explaining their different antimicrobial efficiency (Figure 1).

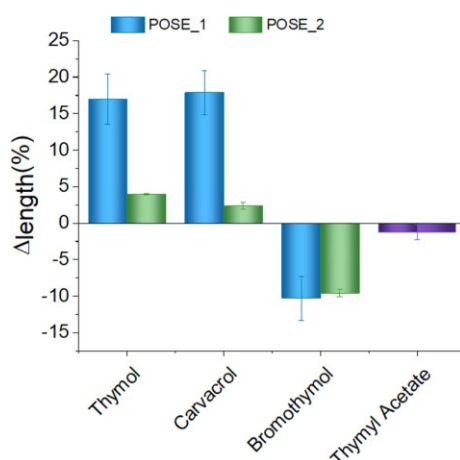


Figure 1: Average tune changing in lipid/s morphology. Percentage of variation of the distance $\text{PO}_4^- - \text{N}^+$ dipole in presence of each compound, setting the POPC one as reference, 0.

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Modeling and Characterization of HuR Protein for the Development of a Promising Cancer Therapeutic Strategy

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RNA-binding protein (RBP) mediated post-transcriptional gene regulation is crucial in eukaryotic gene expression [1]. Among the RBPs, Human Antigen R (HuR) stands out due to its ubiquitous expression in human tissues and its well-characterized role in gene regulation. Chronic activation of HuR is linked to the promotion of tumorigenesis in colon, breast and lung cancers [1].

This work aims to model the full HuR protein structure using classical Molecular Dynamics (MD) simulations, allowing to define and characterize protein-RNA interactions profiles in order to use them to design specific RNA-based inhibitors for the HuR protein.

Two systems (HuR-RNA and unbound HuR) were builded with RosettaFold2NA [2]. Five independent replicas for each complex were simulated using classical MD simulations, each lasting 500 nanoseconds, with the AMBER22 software [3]. The resulting trajectories were analyzed using Gromacs 2023 [4].

MD simulations highlighted an higher stability of HuR-RNA complexes compared to unbound HuR. The stabilizing effect due to RNA was also shown by the identification of a pair of residues (Y26-U22) that perform π - π stacking, which contributes to the overall stabilization of the model. The validation of the HuR-RNA model allowed the identification of important features for the protein-RNA interaction that will be fundamental to rationally design RNA-based inhibitors.

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Towards selective detection of “forever chemicals”: development of optical and opto-electrochemical sensor array for perfluorooctanoic acid (PFOA)

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PFAS (PerFluoro Alkyllic Substances) have recently been reclassified as group 1 carcinogenic substances by the WHO [1]. This makes the development of new sensors capable of effectively and quickly detecting such substances urgent and necessary [2,3].

In this regard, various metal corroles were synthesized, studying their different interactions with PFOA in the organic liquid phase (DCM). The most promising ones were then deposited on different solid supports (color catcher, agarose gel and PVC) and tested on different aqueous solutions of PFOA, performing both static and fluid dynamic measurements.

The second approach we propose consists in a cathodic pre-concentration of PFOA on the surface of biochar-modified screen-printed electrodes (BC-SPE) followed by its defragmentation into partially hydrogenated PFOA chains and release of proportional amount of F⁻ ions [4,5]. The F⁻ concentration was estimated with on-paper-based optical sensor array based on silicon and aluminum corrolates, Si-TTC and Al-PFC respectively. The data of BC-SPE electroreduction currents, fluorescence and luminescence intensity of SiTTC and Al-PFC based optodes fused together were used to construct PLS1 calibration model that has permitted the PFOA quantification in concentration range from 40 ng/L to 4 mg/L.

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PVA Hydrogels applied to Cultural Heritage Conservation.

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An increasing interest has been developed concerning the use of hydrogels and colloidal systems in the field of cultural heritage conservation [1,2]. Recently it has been pointed out that poly-vinyl alcohol (PVA) based systems can be considered suitable and sustainable materials for the preservation of historical artifacts [3].

In such framework, the objective of this work is to highlight the tuneable properties of PVA based chemical hydrogels at different polymer and crosslinker concentrations, synthesized by means of an innovative method; and present some case studies in which PVA hydrogels-based cleaning treatments have been performed on paper artifacts.

In detail, by means of different techniques, the hydrogels' viscoelastic and swelling properties have been studied and correlated, confirming their proper water retaining capacity along with their suitable elasticity [4]. Their pore size homogeneity and average mesh size distribution has been assessed by confocal laser scanning microscopy (CLSM) [5] and FRAP analysis [6]. According to their specific physico-chemical properties, the most suitable materials have been selected and tested to prove their compatibility for paper conservation. The treatments' efficacy has been assessed through pH, colorimetric and FTIR-ATR analysis, performed before and after treatments.

This study has confirmed the useful value of PVA chemical hydrogels for their application in conservation treatments while revealing some new functional aspects.

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Optimizing Silicon/Nanocrystalline-Diamond Cathodes for Photon Enhanced Thermionic Emission

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Photon-enhanced thermionic emission (PETE) [1] is a promising method for efficient solar energy conversion. In PETE devices, absorbed photons generate photoexcited electrons in the conduction band, which then thermalize and are thermionically emitted from the hot cathode surface.

Cathodic materials in PETE devices typically consist of heterostructures designed for light absorption and electron emission. Hydrogen-terminated diamond emitters are noteworthy for their negative electron affinity up to 700 °C, making silicon/diamond PETE cathodes [2] ideal for highly concentrated solar systems.

A study on the evolution and etching of detonation nanodiamond (DND) seeds has been performed to assess the optimal plasma assisted CVD parameters. Studying the temporal evolution of DND seeds [3] during initial CVD diamond growth is crucial to determine the minimum diamond film thickness achievable based on initial seed density [4].

Analysis of PETE performance as a function of NCD film thickness (40 nm to 1 µm) shows that grain boundaries in the diamond layer significantly enhance electron transport and emission. Raman spectroscopy and Kelvin-Probe Force Microscopy (KPFM) [5] reveal that an 80 nm-thick diamond emitter offers the highest emission current density due to optimized grain boundary distribution. To boost photon absorption, the silicon substrate was nanostructured using femtosecond pulsed laser treatments, increasing emission current density tenfold.

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Highly Selective C(sp³)-H Bond Oxygenation at Remote Methylenic Sites Enabled by Polarity Enhancement

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Procedures for selective functionalization of non-activated C(sp³)-H bonds represent one of the most investigated approaches to develop new synthetic methodology[1]. In particular, the development of procedures for site-selective oxidation of both alkyl and cycloalkyl structural motifs is of great importance as it can provide straightforward access to functionalized analogues without resorting to lengthy de novo syntheses [2]. Herein, we report a detailed study on the C(sp³)-H bond oxygenation reactions with H₂O₂ catalyzed by the [Mn(TIP^Smcp)] complex at methylenic sites of cycloalkyl and 1-alkyl substrates bearing 19 different electron- withdrawing functional groups (EW FGs) [3]. Oxidations in MeCN were compared to the corresponding ones in the strong hydrogen bond donating (HBD) solvents 1,1,1,3,3,3- hexafluoro-2-propanol (HFIP) and nonafluoro tert-butyl alcohol (NFTBA). Formation of the products deriving from oxygenation at the most remote methylenic sites was observed, with yields and the site-selectivities for oxygenation at the most remote over the next methylenic sites that significantly increased going from MeCN to HFIP and NFTBA (Figure 1). The results are rationalized on the basis of a polarity enhancement effect via synergistic electronic deactivation of proximal methylenic sites imparted by the EWG coupled to solvent HB. This study uncovers a simple procedure for predictable, high-yielding, and highly site- selective oxidation at remote methylenes of cycloalkyl and 1-alkyl substrates that occurs under mild conditions, with a large substrate scope, providing an extremely powerful tool to be implemented in synthetically useful procedures.

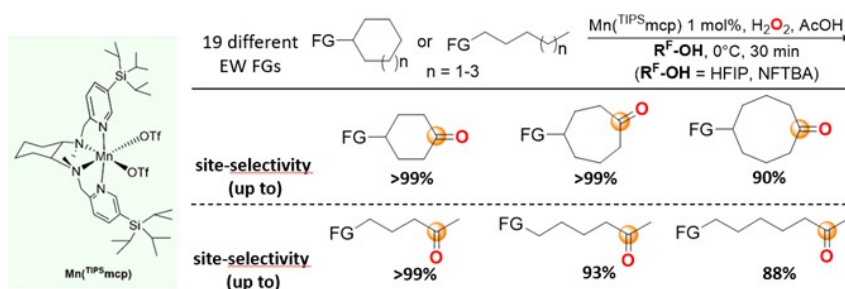


Figure 1: Site-selectivities for oxygenation of remote methylenes of 1-cycloalkyl and 1-alkyl substrates.

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Advanced nanocarriers for the release of anti-vegetative compounds for the protection of artworks

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Nanomaterials are widely employed in the field of protection of Cultural Heritage. Our efforts are directed towards the development of nanocarriers loaded with active antimicrobial agents, intended for dispersion in coatings, consolidants, and adhesives.

Thyme and Oregano essential oils (EOs) have been selected as active species. EOs are active volatile compounds that work through the sublimation as well as the water leaching of several active species, including thymol. The selected EOs showed strong antifouling activity, as shown in Figure 1.

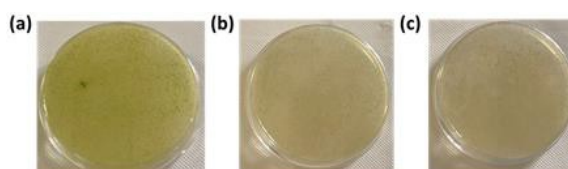


Figure 1: a) Control; b) Antifouling activity of Thyme Oil and c) Oregano Oil after 7 days.

The direct application of EOs in their free forms is limited due to several reasons such as high volatility. Therefore, nanoencapsulation could be a powerful approach.

Mesoporous Silica Nanoparticles (MSN) [1] and Halloysite Nanotubes (HNTs) have been selected as inorganic carriers, while Zein nanoparticles as protein-based organic one [2]. All the loaded nanoparticles exhibit a low sublimation kinetic of active species, whereas the release in water is not affected by the embedding in the nanocarriers.

To tailor the release of active species even in water, the nanocarriers need to be coated to realize a barrier for the permeation of active species from inner particles to the environment. One strategy is to form around the nanocarriers a network made by Tannic Acid (TA) crosslinked with Sodium tetraborate decahydrate (Borax) to form catechol-borate di-esters [3]. The plan is to evaluate parameters such as TA:Borax molar ratio or pH, in order to have the best cover hydrophobic behavior. The engineered nanocarriers will be studied in terms of release kinetic, and compatibility with sustainable polymeric matrix.

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Programmable binding-induced transcriptional switches

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We demonstrate here a novel approach to rationally control cell-free transcription. To achieve this, we re-engineered a double-stranded DNA template into a structure-switching one, by linking the two ends of the promoter with a loop and introducing a nick in the promoter region. Such switch is in a thermodynamic equilibrium between an open (OFF) and a closed (ON) conformation (Figure 1), characterized by the switching equilibrium constant (K_s). The transcriptional activity can be finely modulated by simply changing the K_s . Furthermore, we created stimuli-responsive switches that, upon binding to different molecular cues, can induce cell-free transcription and provide a measurable signal. We did this by redesigning the structure-switching template's loop domain to recognize a specific target, so that this binding event can induce a conformational change from the open to the closed state. Targets include nucleic acids, small molecules, enzymes, and antibodies. This engineering strategy could enable simultaneous, controlled production of different RNAs triggered by different inputs, and provide a novel way to control metabolic processes in artificial systems.

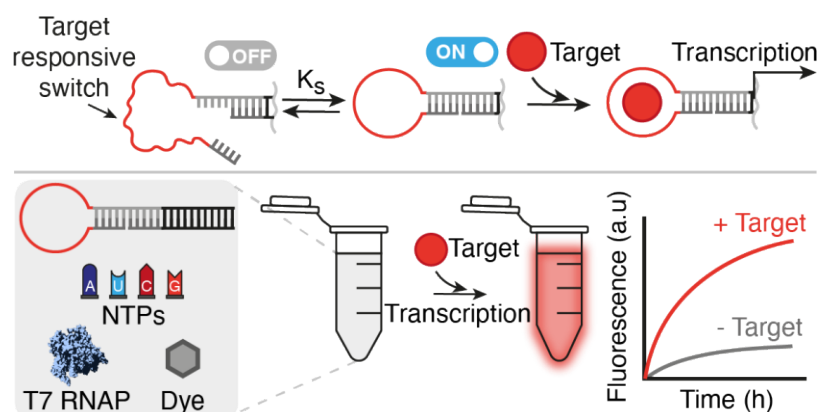


Figure 1: Programmable binding-induced transcriptional switches. The double-stranded DNA template was re-engineered by introducing a loop connecting the two ends of the promoter and a nick in a promoter region, giving the template structure-switching properties. The transcriptional switch can respond to different molecular cues.