Société Chimique de France
Le réseau des chimistes

Società Chimica Italiana

JFIC2022

10th edition of the Franco-Italian Days of Chemistry

Palais Neptune, Toulon, France

April 26 and 27th, 2022

BOOK of ABSTRACTS

UNIVERSITÉ DE TOULON

MERCK
SIGMA-ALDRICH

cloup
SHIMADZU

WELCOMING WORD

Dear colleagues,

We would like to thank you for your participation to the 10^{the} edition of the Franco-Italian Days of Chemistry, JFIC2022.

The “**Liguria**” and “**Piemonte/Valle d’Aosta**” sections of the **Società Chimica Italiana** and **the Provence-Alpes-Côte d’Azur** section of the **French Chemical Society** organize the JFIC this year in Toulon on April 26th and 27th , 2022. It will be held in the Neptune palace during the scientific days of **University of Toulon**. We would like to thank the University of Toulon for their logistic, communication and financial support.

These Franco-Italian Chemistry Days are inter-disciplinary and have established a lasting contact between researchers of Provence-Alpes-Côte d’Azur region and those in the regions of Liguria and Piedmont-Aosta Valley, in order to get closer interaction at European level both scientifically and culturally.

This event, which takes place every two years and is organized alternately in the two countries, took place in **2002** in **Juan-les-Pins**, **2004** in **Genoa**, **2006** in **Turin**, **2008** in **Nice**, **2010** in **Genoa**, **2012** in **Marseille**, **2014** in **Turin**, **2016** in **Avignon**, **2018** in **Genoa**. The 2020 edition was supposed to be held in Toulon but, because of Covid epidemia, has been canceled 1 month before. And here we are : this edition is back in **2022**, in **Toulon**, as it was supposed to be in 2020.

The program covers all the chemical areas, including organic chemistry and bio-organic chemistry, physical and inorganic chemistry, chemical engineering, analytical and pharmaceutical chemistry, environmental chemistry, industrial chemistry and materials chemistry.

During these days we have scheduled four prestigious plenary lectures, four invited speakers by the conference organizing committee, additional 38 oral presentations, highlighting young researchers, and about a hundred posters.

This congress is a real opportunity for all, included for the PhD students to share large research topic related to chemistry, to inform ourselves on last technologies, merging research fields, but it’s also a great pleasure to exchange with our colleagues, in particular our italian ones.

The SCF organizing Commitee

Scientific committee

Società chimica italiana and French Chemical Society members :

- Prof. Pinuccia CERRATO Turin, SCI Piémont/Val d'Aoste (Italie)
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Organizing committee

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- Alain BURGER, Université Côte d'Azur
- Lionel SANTINACCI, Aix-Marseille University

JFIC2022 PROGRAM

Tuesday April 26th		**Amphi COLBERT**
8h00		Welcoming of the participants
8h45		Opening of the day - welcome speech
9h00-9h40	**PLENARY CONFERENCES** (30' oral+ 10' Q)	**Uwe MEIERHENRICH, Côte d'Azur University** (Grand Prize 2022 SCF-Sud PACA) "3D Presentation: ESA's Mission Rosetta-Philae - the search for organic molecules on a comet"
9h40-10h20		**Piero UGLIENGO, Turin University** (Grand prize 2022 SCI-Piemonte) " From Astrochemistry to Prebiotic Chemistry through the Eyes of Computer Molecular Modeling"
10h20-10h30		**Presentation of the Youth Club of the SCF and SCI**
10h30-11h15		**Coffee break and** POSTERS SESSION

	10' oral + 5' Questions	**Amphi Colbert** **SESSION 1: ORGANIC AND BIO-ORGANIC CHEMISTRY**	**Room Raimu 1** **SESSION 2: CHEMISTRY OF MATERIALS AND ENVIRONMENTAL CHEMISTRY**
11h15-11h30	Oral Communication	**Federica MINUTO**, Univ. Genova A novel photoinduced multicomponent reaction to β-Lactams: Ketene 3-Component Staudinger Reaction (K-3CSR)	**Lorenzo FENOCCHIO**, Univ. Genova High Entropy Alloys (HEAs): Thermodynamic Simulations for High-Temperature Applications
11h30-11h45	Oral Communication	**Manuel BARDAY**, AMU, ISM2 NHC-catalysed atroposelective desymmetrisation of maleimides: complete control towards highly functionnalised heterocycles.	**Marta MENEGHELLO**, AMU, BIP Electrochemical studies of CO2-reducing metalloenzymes
11h45-12h00	Oral Communication	**Mariacristina FAILLA**, Turin Metallo β-Lactamases inhibitors: new tools against Bacterial Multidrug Resistance	**David Javier CASTRO RODRIGUEZ**, Politecnico di Torino Experimental Array to Evaluate Different Operative Parameters in Bioremediation of Hydrocarbon-Polluted Soil
12h00-12h15	Oral Communication	**Iryna SHCHEHOLEVA**, UCA, ICN Diversity-oriented synthesis of small molecules applied to the discovery of new inhibitors of oncogenic miRNAs production	**Christian CRAVOTTO**, Univ. Avignon Higher yield and polyphenol content in olive pomace oil extracted using 2-methyloxolane
12h15-12h30	Oral Communication	**Francesconi VALERIA**, Univ. Genova Multitarget agents in Alzheimer's disease: development of xanthenone-based derivatives	**Giovanni PAMPARARO**, Univ. Genova Cu-SiO2 catalysts made by Aerosol Assisted Sol-gel method as promising materials for ethanol non oxidative dehydrogenation
12h30-13h45		**BUFFET and POSTER Session**	

		Amphi Colbert	**Room Raimu 1**
	10' oral + 5' Questions	**SESSION 1: ORGANIC AND BIO-ORGANIC CHEMISTRY**	**SESSION 2: CHEMISTRY OF MATERIALS AND ENVIRONMENTAL CHEMISTRY**
13h45-14h00	Oral Communication	**Enzo VAIEDELICH**, AMU, ICR Shifting nitroxides as the new Overhauser-enhanced MRI probes for in-vivo evaluation using enzymatic activities.	**Ashwini Reddy NALLAYAGARI**, AMU, Madirel Role of carbon quantum dots and anion exchange ionomer as a multiphase electrode for the oxygen reduction reaction
14h00-14h15	Oral Communication	**Tullio CROVETTO**, Univ. Genova Synthesis of new solid state fluorescent furo[2,3-c]isoquinolines via Ugi reaction and subsequent Pd-catalyzed transformations	**Nicolò GHIBAUDO**, Univ. Genova Application of a D-Optimal Design of experiments to a photocatalytic pilot plant for environmental issues.
14h15-14h30	Oral Communication	**Guillaume LESEIGNEUR**, UCA, ICN La Stéréochimie des Hydrocarbures Isoprénoïdes comme Fossiles Moléculaires: Conséquences pour la Recherche de Vie Ancienne sur Mars / The Stereochemistry of Isoprenoid Hydrocarbons as Molecular Fossils: Implications for the Search of Extinct Life on Mars	**Brahim AKHSASSI**, UTLN, IM2NP Photodegradation of organic pollutant rhodamine B by a zinc phosphate-based composite
14h30-14h45	Oral Communication	**Dinesh DHUMAL** , AMU, Cinam Dynamic self-assembling supramolecular dendrimer nanosystems as potent antibacterial candidates against drug-resistant bacteria and biofilm	**Davide PALMA**, Univ. Turin Re-thinking the role of natural organic matter in water treatment processes
14h45-15h00	Oral Communication	**Arthur GAUCHERAND**, AMU, ISM2 Simultaneous Control of Central and Helical Stereogenic Elements on Small Molecules	**Alessandro COSSARD**, Univ. Turin Topology of the Electron Density and of its Laplacian from Periodic LCAO Calculations on f-Electron Material
15h00-15h15	Oral Communication	**Marta GALLO**, Univ. Turin Vitamin D3: three possible strategies for its topical delivery	**Léo CHAUSSY**, AMU, ISM2 Benchmark on cobalt systems relevant for reactivity
15h15-15h30	Oral Communication	**Tereza HORACKOVA**, AMU, Cinam Towards a new generation of (di-)zwitterionic quinones and macrocycles	**Emanuele PRIOLA**, Univ. Turin Solid state peculiarities and polymorphism in imidazo[1,5-α]pyridine dyes
15h30-15h45	Oral Communication	**Nicolas GIACOLETTO**, AMU, ICR Coumarin-Based Oxime Esters : New photoinitiators for visible light photopolymerization	**Marta CAMPOLUCCI**, Univ. Genova Mn – based Hybrid Metal Halides for Optoelectronic Applications
15h45-16h30	**Coffee Break and POSTER SESSION**		
16h30-16h35	**Presentation IUPAC (Sylvain Marque, AMU, ICR)**		
	20' oral + 10' Questions	**Donation of the PhD thesis award**	
16h35-17h05	Award-winning speaker	**Enrico SARTORETTI** , **Politecnico di Torino, Italy** "Doped ceria nanostructures for the oxidation of pollutants: investigations into the role of defect sites"	
17h05-17h35	Award-winning speaker	**Guillaume BARNOIN**, **UCA, France** "Intermolecular dark resonance energy transfer (DRET): Applications to the fluorogenic detection of nucleic acids"	
	20' oral + 10' Questions	**Invited Speakers**	
17h35-18h05	Invited speaker	**Silvia BODOARDO**, **Turin University, Italy** "Post Li-ion and disruptive technologies for advanced and innovative batteries: what is Europe doing?"	
18h05-18h35	Invited speaker	**Jalila SIMAAN**, **Aix-Marseille University, France** « structure-function relationships in copper-containing enzymes: from fundamental studies to the development of bioinspired catalysts »	

Wednesday April 27th		**Amphi COLBERT**
8h30		Welcoming of the participants
9h00-9h40	**INVITED CONFERENCES** *30' oral + 10' Questions*	**Carla VILLA, Genova University, Italy** « Ecofriendly microwave extraction of agrofood waste for cosmetic and pharmaceutical applications"
9h40-10h20		**Christine BRESSY, Toulon University, France** "When chemistry deals with marine biofouling"
10h20-11h00		**Coffee break and POSTER SESSION**

		Amphi Colbert	**Room Raimu 1**
	10' oral + 5' Questions	**SESSION 1: ORGANIC AND BIO-ORGANIC CHEMISTRY**	**SESSION 2: CHEMISTRY OF MATERIALS AND ENVIRONMENTAL CHEMISTRY**
11h00-11h15	Oral communication	**Louise MITON**, AMU, Ecole Centrale Anion-pi interactions in confined space	**Maria Alessia VECCHIO**, Univ. Genova Strontium isotopic analysis of Antarctic snow samples by multi-collector inductively coupled plasma mass spectrometry
11h15-11h30	Oral communication	**Milane SAIDAH**, AMU, ISM2 Enantioselective construction of tetrasubstituted carboncenter.	**Erika Michela DEMATTEIS**, Univ. Turin Mn-substituted TiFe alloys for large scale hydrogen storage: a neutron diffraction study
11h30-11h45	Oral communication	**Alessio GIOVE**, UTLN, Mapiem Synthesis of new selective monomers for the design of original Ni(II) and Co(II) ion imprinted polymers	**Sawssen SLIMANI**, Univ. Genova Interplay between magnetic anisotropy and interparticle interactions in crystalline-amorphous nanocomposite
11h45-12h00	Oral communication	**Emilie GENTILINI**, UCA, ICN Asymmetric Gold-Catalyzed Addition of Carbonyl Compounds on 1,6-Enynes	**Alessia GIORDANA**, Univ. Turin Biostimulant and biofertilizer from waste valorisation: the different behaviour of humic and fulvic acid on hydroxyapatite
12h00-12h15	Oral communication	**Guillaume BRULAY** , AMU, ICR Synthesis and studies of SBA-15 materials functionalized with transcient radical precursors.	**Barbara BENEDETTI**, Univ. Genova Evaluation of polycyclic aromatic hydrocarbons contamination in botanical extracts for human consumption: development of a specific sample pre-treatment method followed by GC-MS analysis
12h15-12h30	Oral communication	**Xueyang LIU**, AMU, ISM2 Indirect Enantiocontrol of Tertiary Alcohols and Quaternary Centers by Acylative Organocatalytic Kinetic Resolution	**Monica RIGOLETTO**, Univ. Turin Valorization of an agro-industrial waste: synthesis of soybean hulls derivatives-based hybrid materials for water purification
12h30-13h30		**BUFFET + POSTER SESSION**	

Amphi COLBERT

13h30-13h40		**winner of the grand prizes**
13h40-14h20 (30' oral + 10' Q)	**PLENARY CONFERENCES** *(30' oral + 10' Q)*	**Philippe KNAUTH, Aix-Marseille University, France** (Grand Prize 2021 SCF-Sud PACA) « Ion-conducting nanomaterials: a lot of movement in small domains"
14h20-15h00		**Paola RIVARO, Genova University, Italy** (Grand Prize 2022 SCI) "Variability in chemical properties of the Ross Sea (Antarctica) waters and links to climate change: the results of our observations from 90's to today"
15h00 – 15h10		**Poster awards**
15h10 – 15h20		**Closing Ceremony**

Plenary Talks

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KNAUTH Philippe	**Aix-Marseille University, France**	« Ion-conducting nanomaterials: a lot of movement in small domains"	8
MEIERHENRICH Uwe	**Côte d'Azur University (France)**	"3D Presentation: ESA's Mission Rosetta-Philae - the search for organic molecules on a comet"	9
RIVARO Paola	**Genova University, Italy**	"Variability in chemical properties of the Ross Sea (Antarctica) waters and links to climate change: the results of our observations from 90's to today"	10
UGLIENGO Piero	**Turin University**	" From Astrochemistry to Prebiotic Chemistry through the Eyes of Computer Molecular Modeling"	11

Ion-Conducting Nanomaterials: a Lot of Movement in Small Domains

Knauth Philippe

Aix Marseille University, CNRS, MADIREL (UMR 7246), campus Etoile St Jérôme, 13013 Marseille, France

In this plenary talk, I will present our work related to ionic conduction and diffusion in nanostructured materials, starting with a short retrospective on our pioneering studies on nanocrystalline metals especially diffusion-controlled grain growth [1,2]. I will then move on to the studies of ion-conducting nanoceramics and nanocomposites ("Nano-ionics"), where I will focus on the influence of size and shape (nanospheres, nanocubes, nanorods, nanotubes…) on the ion conduction properties [3-6].

The last part will be devoted to ion-conducting nanostructured polymers in the framework of the International Laboratory "Ionomer Materials for Energy" jointly created by Aix-Marseille University, CNRS and the University of Rome Tor Vergata in 2015. Ionomers are nanophase-separated polymers with anchored ionic groups. I will focus on materials for lithium batteries [7-10], including the conformal electrochemical deposition of ionomer films directly on nanotubular electrodes [10]. Concerning ionomers for fuel cells and redox flow batteries [11-14], I will present especially stability improvements by cross-linking ionomers [11] and studies on the tortuosity and percolation of ionic transport paths [14].

[1] P. Knauth, A. Charaï, P. Gas, Grain growth of pure nickel and of a Ni-Si solid solution studied by differential scanning calorimetry on nanometer-sized crystals, Scr. Metall., 28, 325 (1993).

[2] S. Villain, P. Knauth, G. Schwitzgebel, Electrodeposition of Nanocrystalline Silver: Study of Grain Growth by Measurement of Reversible E.m.f., J. Phys. Chem. B, 101, 7452 (1997).

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[5] B. L. Ellis, P. Knauth, T. Djenizian, Three-dimensional self-supported metal oxides for advanced energy storage, Adv. Mater., 26, 3368 (2014).

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[14] P. Knauth et al., Effective ion mobility in anion exchange ionomers: relations with hydration, porosity, tortuosity, and percolation, J. Membrane Sci., 617, 118622 (2021).

3D Presentation:

ESA's Mission Rosetta-Philae - the search for organic molecules on a comet

Uwe J. Meierhenrich (1)

(1) Université Côte d'Azur, UMR 7272 CNRS, Institut de Chimie de Nice, 06108 Nice, France

ESA's Rosetta mission had made spectators from all over the world dream: On 12 November 2014, the Rosetta mission posed the little robot Philae on the nucleus of comet 67P/Churyumov-Gerasimenko. The Rosetta Space Probe collected information about the composition of the comet nucleus and the origin of the Solar System [1]. Rosetta is the first probe to place itself in orbit around the comet and to place a lander on the surface of a cometary nucleus. After 10 years of travel, the separation of the Philae lander from the Rosetta orbiter was carried out on November 12, 2014. The cometary sampling and composition (COSAC) instrument, a device onboard Philae, which we developed in an international partnership lead by the Max Planck Institute for Solar System Research, is a gas chromatograph using eight stationary phases coupled with a mass spectrometer time of flight type. 25 minutes after Philae's landing and bouncing on the cometary nucleus, COSAC successfully performed the first chemical analysis of cometary surface material that cannot be analyzed from the Earth. 16 organic molecules were identified in the cometary sample by using COSAC's MS-only mode [2]. The first results of the analysis of the cometary nucleus surface by the COSAC instrument will be presented. These *in situ* cometary results will be interpreted in relation to laboratory experiments that allow for the simulation of cometary ices by condensing volatile molecules such as H_2O, NH_3, CO, CO_2, and CH_3OH in an ultra-high vacuum from the gas phase onto a cooled surface of $T = 12$ K. The room temperature residues of the cometary ice analogues were shown to contain amino acids [3], aldehydes [4] and ribose [5] as produced in form of simulated cometary ices in the laboratory [6]. The laboratory simulation experiments thereby confirm data on the chemical inventory of comets and the early Solar System obtained by the Rosetta-Philae cometary probe.

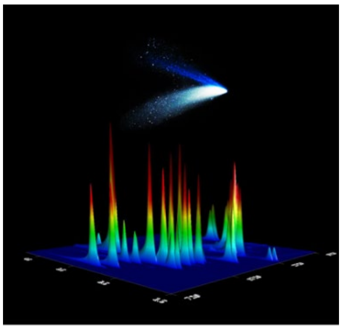

Figure 1 : The Rosetta space probe landed on a comet nucleus and analysed its organic inventory.

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[3] G. Munoz Caro, U. Meierhenrich et al., *Nature* **412**, 403 (2004).
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Chemistry Area :

- ☐ **Material Chemistry or**
- **X Environmental and Analytical Chemistry or**
- ☐**Organic and Bioorganic Chemistry or**
- ☐**Physical Chemistry**

Variability in chemical properties of the Ross Sea (Antarctica) waters and links to climate change: the results of our observations from 90's to today

Rivaro P.

Department of Chemistry and Industrial Chemistry, University of Genova, via Dodecaneso 31, 16146 Genova, Italy

The Ross Sea (Antarctica) plays a significant role in the Southern Ocean carbon cycle by functioning as a major regional oceanic CO_2 sink and in the regional cycling of other essential bio elements, such as nitrogen, phosphorus and iron.

Sea ice dynamic controls the surface waters (AASW) physical and chemical features and influence phytoplankton composition, which has been shown to affect the relative concentrations of dissolved inorganic carbon and bioelements. Climate change feedbacks (AASW warming, reduction in sea ice extent and convective mixing) could decrease the supply of iron to surface waters during the growing season, although these impacts might be balanced out by increased inputs of iron-rich glacial ice melt water (Smith et al., 2012). Substantial shifts in the chemistry of the oceans driven by anthropogenic CO_2 have occurred in recent times causing the phenomenon known as Ocean Acidification (OA), which is measurable by a decrease in pH and a shift in the carbonate equilibria. The Ross Sea is vulnerable to OA due to its relatively low total alkalinity (A_T) and because of increased CO_2 solubility in cold water.

Finally, the Ross Sea contributes to the larger global ocean's overturning circulation, through the formation of dense High Salinity Shelf Water (HSSW) and the flow of Antarctic Bottom Water (AABW) off the shelf with profound effects on the heat budget of the Earth and impacts the regional and global climate.

AABW plays a significant role in the cooling and in the ventilation of the deep layers north of the western Ross Sea as it contains high oxygen concentration, consistent with the deepening of the surface water involved in the HSSW formation and in the export of inorganic carbon, particularly in the capture of the anthropogenic CO_2. Dropping formation rates, which lead to a reduced ventilation of Antarctic deep and bottom water masses, could have far reaching consequence like a declining uptake of CO_2 by the oceans, which would certainly amplify an ongoing global warming.

The chemical properties in the Ross Sea shelf area have been extensively studied by Italian Antarctic Research Program (PNRA) CLIMA, T-Rex, RoME, CELEBeR and ESTRO Oceanographic Projects between 1998 and 2020, which has lead to an improvement in our understanding of their variability to ongoing climate perturbations.

The most relevant findings will be presented in this communication.

Chemistry Area :
X Physical Chemistry

From Astrochemistry to Prebiotic Chemistry through the Eyes of Computer Molecular Modeling

Piero Ugliengo

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Life, as we know today, is mainly characterized by proteins, nucleic acids and membranes. The basic building blocks, *i.e.* amino acids, nucleic bases and lipids are handled by the complex metabolism of the actual cells to make all the needed polymers essential to life. The first question is to understand how and where these building blocks where synthesized before the existence of living organisms. Deep interstellar space, where one is not expecting to find molecules more complex than H_2 shows, instead, more than 200 complex molecules detected by radio astronomy. Comets and meteorites are rich of organic molecules, from amino acids to simple lipids which can be brought to the primordial Earth by early bombardment. Also, intense geochemical and volcanic activities coupled with the primordial atmosphere of the early Earth or through submarine hydrothermal processes, may have provided many of the needed chemical building blocks. A question remains, however: how these building blocks can merge together to end up with the primordial nucleic acids and proteins or polysaccharides? All these reactions are condensation reactions, in which a water molecule is eliminated during the polymerization and are thermodynamically disfavored in liquid water. There is evidence that mineral surfaces help for the condensation reaction to occur (Fig. 1). Many of the above topics are addressed experimentally [1]. However, atomistic details are usually missing, and accurate quantum mechanical calculations are of help to elucidate the reaction mechanisms and energetics [2]. This talk shows selected examples from astro- to prebiotic chemistry of the role of computer modeling [3].

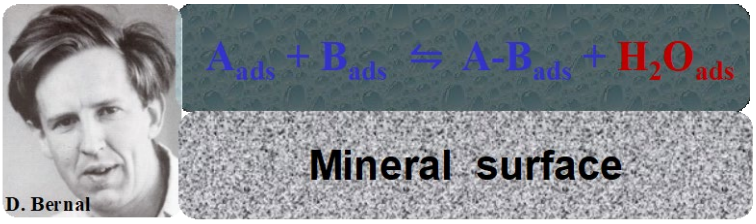

Figure 1: D. Bernal's hypothesis: condensation reactions occur at the mineral surfaces

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Invited Speakers

Author	Affiliation	Title	Page
Silvia BODOARDO	**Turin University, Italy**	"Post Li-ion and disruptive technologies for advanced and innovative batteries: what is Europe doing?"	13
Christine BRESSY	**Toulon University, France**	"When chemistry deals with marine biofouling"	14
Jalila SIMAAN	**Aix-Marseille University, France**	« structure-function relationships in copper-containing enzymes: from fundamental studies to the development of bioinspired catalysts »	15
Carla VILLA	**Genova University, Italy**	« Ecofriendly microwave extraction of agrofood waste for cosmetic and pharmaceutical applications"	16

Chemistry Area :
X Material Chemistry or
☐Environmental and Analytical Chemistry or
☐Organic and Bioorganic Chemistry or
X Physical Chemistry

Post

Li-ion and disruptive technologies for advanced and innovative batteries: what is Europe doing?

Silvia Bodoardo, Julia Amici, Carlotta Francia, Federico Bella, Lucia Fagiolari, Daniele Versaci, Anna Mangini, Davide Dessantis, Piera Di Prima, Andrea Marchisio, Roberto Colombo, Maria Laura Para, Sabrina Trano, Simone Siccardi, Matteo Gandolfo

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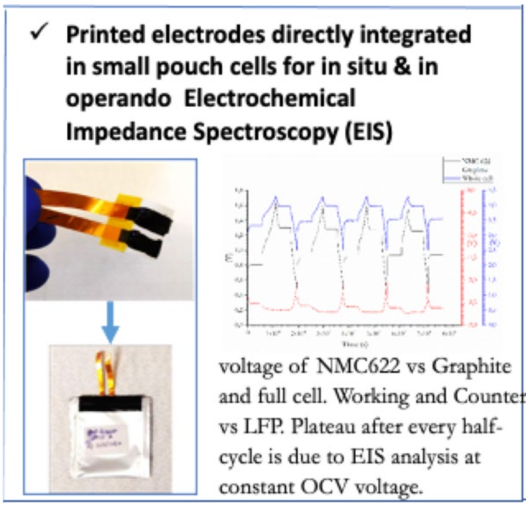
New digital technologies they are taking up more and more space in our lives. To this, also electric vehicles are replacing old combustion vehicles. More and more energy is so required and should be obtained by renewable sources which are not continuous and need to be stored. Today's battery technology is lagging behind adjacent technological advances, with most devices using lithium-ion batteries that bring with them some concerns. Some of the materials used in Li-ion batteries are scarce and their mining has negative impacts on the environment. Other challenges are safety, low energy density, recyclability. In addition, it is becoming more and more important to assure batteries availability in Europe.

To create a European energy platform for the future, bringing together renewable energy sources, electric transportation and a connected Internet of Things, a new solution for battery technology will need to be found. During the lecture I will explore how current challenges can be overcome through the application of advances in new materials, how to implement the so called post-lithium ion technologies as well new disruptive concepts, as the use of self-healing materials and sensors placed inside the battery cells (Fig.1). Starting from Battery2030 roadmap[1] it will be presented how sustainability can drive the choices for the European batteries of the future. It is discussed what is Europe doing in the field of batteries, the need of skilled people and how the future of battery technology can contribute to build a better, greener and connected world



✓ Printed electrodes directly integrated in small pouch cells for in situ & in operando Electrochemical Impedance Spectroscopy (EIS)

voltage of NMC622 vs Graphite and full cell. Working and Counter vs LFP. Plateau after every half-cycle is due to EIS analysis at constant OCV voltage.

Figure 1 : Example of printed sensors placed inside the cell developed in SENSIBAT project[2]

(1) https://battery2030.eu/research/roadmap/
(2) https://sensibat-project.eu

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When chemistry deals with marine biofouling

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Any surface immersed in seawater is prone to colonization by marine organisms, known as biofouling (Figure 1). Marine biofouling is a worldwide problem, costing billions of dollars per year in many civil or military marine applications. In marine shipping industry, Self-Polishing Coatings (SPCs) and Fouling Release Coatings (FRCs) are common strategies used to prevent and control the natural colonization process of ship hulls [1]. In recent past, research into novel antifouling and fouling release strategies with lower environmental impact and higher performances has gained considerable interest.

SPCs are mainly composed of polymers bearing seawater hydrolyzable side groups or hydrolyzable main chains allowing the renewal of the coating surface by an erosion process and the control of the release rate of active molecules. Both the chemistry and microstructure of the hydrolyzable polymers influence the performance of the resulting coatings. In our research group, silyl ester and siloxysilyl ester groups have been investigated as labile side groups of (meth)acrylic polymer backbones [2, 3]. Copolymers with poly(dimethylsiloxane) (PDMS) precursors with low surface energy were synthesized. The distribution and length of the PDMS side or main chains were found to be key parameters influencing the antifouling and erosion properties of coatings. The microstructures of the prepared polymers were tailor-made by reversible deactivation radical polymerization (RDRP) to achieve well-defined random, diblock, and graft copolymers with simultaneous control of molar masses, dispersities, and molar compositions.

FRCs are mainly composed of a poly(dimethylsiloxane) (PDMS) elastomer matrix. Their specific fouling release property is related to the hydrophobicity and the low surface energy of PDMS, also influenced by parameters including surface roughness, elastic modulus and coating thickness. Amphiphilic copolymers were synthesized and dispersed in PDMS elastomer matrices with the aim of developing new surface-active materials [4, 5].

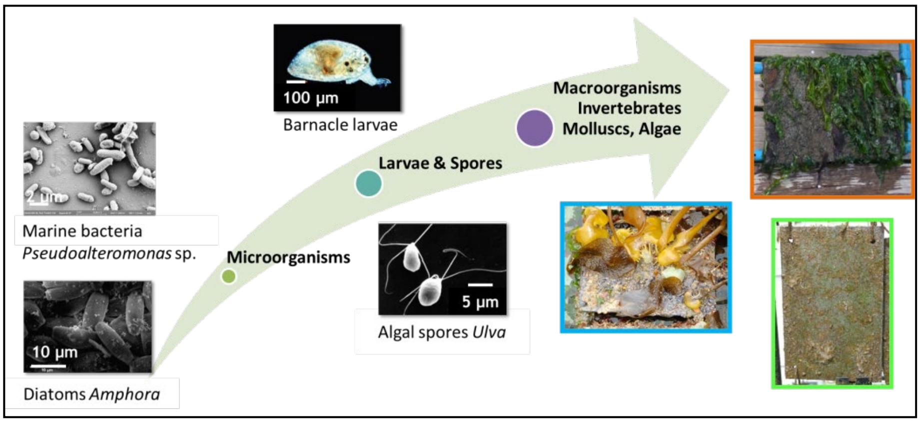

Figure 1: Colonization of surfaces by marine biofouling

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Chemistry Area :

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Structure-function relationships in copper-containing enzymes: from fundamental studies to the development of bioinspired catalysts

Gomez Pineiro R., Munzone A., Pujol M., Concia A.L., Gamboa Ramirez S., Leblay R., Wang Y., Orio M., Iranzo O., Decroos C., Réglier M., **Simaan A.J.***

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Copper-containing enzymes have gained attention in the past decades following the discovery of oxygenases with high potential for fuel production. In particular, LPMOs copper-containing enzymes produced by some bacteria and fungi, among a consortium of enzymes that act collectively to degrade recalcitrant polysaccharides such as cellulose or chitin [1,2]. LPMO enzymes were shown to oxidatively cleave polysaccharide chains of the polymeric recalcitrant substrates, in contrast to the well-known hydrolysis reactions carried out by hydrolase enzymes. LPMO active center is constituted of a mononuclear copper ion ligated by two histidines including the *N*-terminal histidine ligated in an unusual bidentate binding mode (**Fig 1A & B**). LPMO catalyzes the hydroxylation of a strong C-H bond at the glycosidic linkage of polysaccharides leading to glycosidic bond cleavage (Fig 1C). It is not clear whether the natural oxidant employed by LPMO consists of O_2 or H_2O_2. Furthermore, the nature of the reactive copper-oxygen species responsible for the initial activation of the strong C-H bond (>90 kcal/mol) remains to be established. The preparation of relevant bioinspired models provides important mechanistic tools and can lead to the development of catalysts for strong C-H bond activation. Our group combines studies on enzymatic systems (including LPMO) to the development of bioinspired complexes [3,4]. Our recent results directed towards the understanding of structure-function relationships and strong C-H bonds activation at copper centers will be presented.

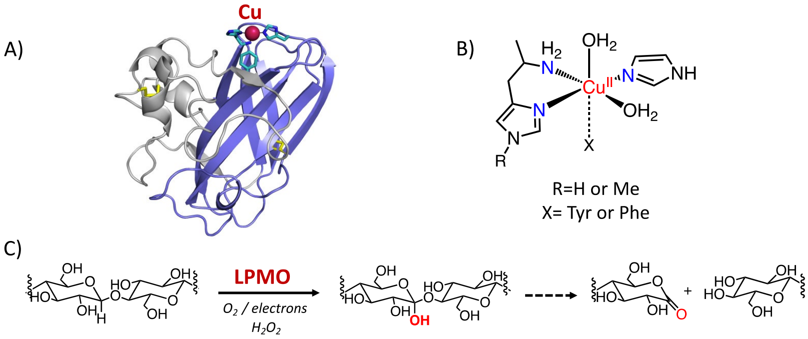

Figure 1 : A) structure of a bacterial LPMO [3a] B) schematic representation of LPMO active site. C) C1-oxidation of cellulose catalyzed by LPMO

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ECOFRIENDLY MICROWAVE EXTRACTION OF AGROFOOD WASTE FOR COSMETIC AND PHARMACEUTICAL APPLICATIONS

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Nowadays, in a context of sustainability, a great industrial interest in the development of green processes and green bioactive compounds has significantly increased due to their wide spread in food, cosmetic and pharmaceutical products. “Green" can not only mean “botanical”, ingredients can’t be considered "greener" "or safer" simply when they come from plants, but when all details of sourcing, manufacturing, disposal (including information concerning energy and water use, as well as eco- and human toxicity) have beeb taken into account[1] by a systematic approach to analyze, quantify, and then minimize the environmental/resource-depleting impact of any process and technology.
From an extractive point of view, the exploitation of renewable sources, especially plant wastes, are attracting greater and greater attention. The agro-alimentary sector produces a large amount of organic residues that often are both highly polluting and quite expensive to treat. Their conversion from worn out plant matrices with high environmental impact into recycled natural sources with significant added values represents a great challenge, due to the industrial need of a “Responsible Care” of the environment together with a high quality of products and processes and a general attention to circular economy[2].
Taking into account all of these statements and our interest in green cosmetic and pharmaceutical ingredients[3-7], the aim of this research was the study and application of eco-sustainable extractive procedures to obtain new “green” bioactive ingredients from organic waste, following the Green Chemistry and Green Extraction targets[8-10]
Thus the project included the recycle of agro-food by-products as substrates from renewable sources such as grape marc (from wine-making process), pomegranate peel (from fruit juice industry) and safflowers without stigmas (from saffron production), the choice of microwave heating (MW) as an alternative energetic source and the use of green solvents (such as NADES or water) or no solvents. The green extracts were characterized and evaluated by means of *in vitro* studies.

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[10] Chemat, F; Abert-Vian, M.; Zill-e-Huma, Y.J. In Green Chemistry Research Trends; Pearlman, J.T., Ed.; Nova Science Publishers, 2009.

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Oral Communications

Chemistry Area:
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Photodegradation of organic pollutant rhodamine B by a zinc phosphate-based composite

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Rapid population growth is leading to an abnormal increase in the level of harmful organic pollutants worldwide. The reduction of these contaminants is becoming a major challenge in the whole world. However, conventional treatments for these substances are not effective in mineralizing the recalcitrant organic compounds. In this work, heterogeneous photocatalysis was used as a consistent process to remove an organic dye: Rhodamine B, in an aquatic environment. In a typical procedure, the photocatalytic activity of zinc phosphate was enhanced by establishing a composite between this later with another oxide (zinc oxide). This composite catalyst was synthesized by a simple approach, the solid-state reaction, which is easy to implement and does not require high energy and cost. Various characterization techniques were used to investigate the formation of the composite, such as X-ray Powder Diffraction, Scanning Electron Microscopy coupled to Energy-dispersive X-ray spectroscopy and Fourier-transform infrared spectroscopy techniques. All analytical findings reveal the formation of zinc phosphate, zinc oxide and their mixed phases $Zn_3(PO_4)_2/ZnO$ photocatalysts. Furthermore, this new $Zn_3(PO_4)_2/ZnO$ composite owns significant photocatalytic properties rather than the pristine zinc phosphate. The degradation kinetics was pursued by the UV-visible spectrophotometry unit. As an outcome, we found that composite catalyst with 20% of zinc oxide exhibits high activities on Rhodamine B decontamination [1]. In addition, the efficient catalyst resisted facing the degradation of the pollutant after a variety of photocatalytic application cycles, which makes it a prospective photocatalyst for the degradation of organic contaminants.

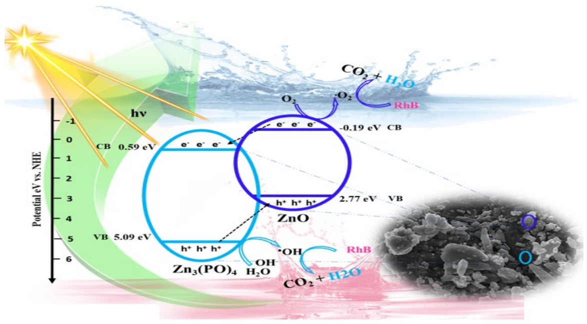

Figure 1: Scheme of enhanced photocatalytic degradation

[1] B. Akhsassi et al., Enhanced photocatalytic activity of $Zn_3(PO_4)_2/ZnO$ composite semiconductor prepared by different methods, Chem. Phys. Lett. 783 (2021) 139046. https://doi.org/10.1016/J.CPLETT.2021.139046.

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NHC-catalysed atroposelective desymmetrisation of maleimides:

complete control towards highly functionnalised heterocycles.

Manuel Barday*(1), Pierre Bouillac(1), Jessica Rodrigues(1), Jean Antoine Rodriguez(1), Muriel Amatore(1), Thierry Constantieux(1)

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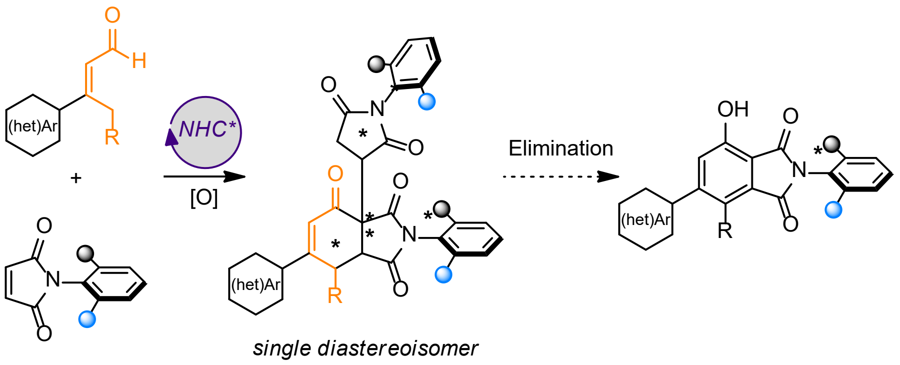
The atroposelective research field, dedicated to the stereoselective synthesis of molecules bearing a stereogenic axis, has received a huge interest lately, due to the large number of applications exhibited by those compounds (*i.e.* natural products, molecular machines, chiral ligands / catalysts).[1] Although the access to biaryls atropisomers has been well documented, examples of configurationally less stable molecules are scarce. In this category can be found, among others, pentacyclic atropisomers and stereogenic axis around a C–N bond.[2] Moreover, this field has been dominated by organometallic catalysis, and it's only recently that organocatalysis has proven as efficient as the latter.

In this context, we have applied the chemistry of azolium dienolates, generated in oxidative conditions from an *α,β*-unsaturated aldehyde and a *N*-Heterocycle Carbene (NHC), to the desymmetrisation of pro-chiral maleimides.[3] This reaction afforded the access to functionnalised heterocycles bearing up to 6 chirality elements in a highly controlled manner. Moreover, this methodology allowed for the remote control of 2 stereogenic axis. The corresponding succinimide derivatives were obtained as a single diastereoisomer with yields ranging from moderate to quantitative and excellent enantioselectivities. The products could be further transformed in one step to chiral phthalimides with no loss of the chiral information.[4]



- C–N/pentacyclic atropisomers
- 6 chirality elements
- remote control
- 17 examples
- up to quantitative yield
- up to 99% ee

Figure 1 : NHC-catalysed desymmetrisation of maleimides / Elimination

[†] **J. K. Cheng, S.-H. Xiang, S. Li, L. Ye, B. Tan, *Chem. Rev.* 2021, *121*, 4805.**
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Intermolecular dark resonance energy transfer (DRET): Applications to the fluorogenic detection of nucleic acids

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Recent discoveries of the involvement of nucleic acids in a wide range of biological processes have highlighted the importance of being able to detect and localize them precisely within cells. To achieve this, many strategies have been developed. The process of resonance energy transfer between two fluorescent molecules (FRET) has largely contributed to meet this challenge. However, problems related to spectral overlaps between the donor and acceptor limit its sensitivity.

Researchers have recently discovered the possibility of performing resonance energy transfer from a quenched donor (Dark-RET: DRET). By revisiting this concept through an intermolecular approach, we developed a novel method for fluorogenic detection of nucleic acids. This has the advantage of reducing considerably the background noise in a very simple way.

The push–pull fluorophore DFK, which fulfillls all the requirements of a quenched donor for intermolecular DRET, was synthesized as an amidite and then incorporated into numerous nucleic acid sequences. The resulting donor probes were annealed with their complementary sequence labeled with Cy5, a bright acceptor.[1] One of these hybridizations generated a record amplification factor of 256. This result confirmed the ability of DRET to confer on a quenched donor, the fluorescence potential of the acceptor with which it is associated.

The proof of concept was then performed *in cellulo* for the detection of the oskar mRNA sequence. The fluorescence signal corresponding to its localization then emerged very clearly from the residual background. The development of such fluorogenic tools would shed new light on many biological processes, offering another angle of examination.

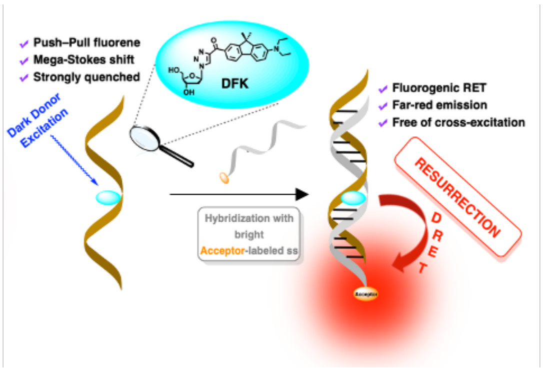

Figure 1: Fluorogenic detection of specific nucleic acid sequences by intermolecular DRET.

[1] Barnoin, G. *et al.* Intermolecular dark resonance energy transfer (DRET): upgrading fluorogenic DNA sensing. *Nucleic Acids Res.* **49,** e72 (2021).

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Evaluation of polycyclic aromatic hydrocarbons contamination in botanical extracts for human consumption: development of a specific sample pre-treatment method followed by GC-MS analysis

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Plant-derived nutraceutical products are extracts or macerates rich in bioactive compounds, which are increasingly spreading in the market. Among them, an innovative category is represented by bud-derivatives, which contain high concentration of polyphenols [1]. The amount of buds and young sprouts naturally available is relatively scarce, since their presence on the tree lasts a rather short time and a significant depletion must be avoided. An alternative and convenient source of these products could be represented by cities pruning, which is generally considered as waste, but could be exploited within a circular economy approach. A concern connected with the use of buds coming from urban trees, is the possible contamination by micropollutants. The particulate generated by vehicular traffic and other anthropic activities adsorbs organic compounds and, transported by the wind, can deposit them onto leaves and sprouts. Polycyclic aromatic hydrocarbons (PAHs) are ubiquitously present in urban areas, since deriving from incomplete combustion, and some of them are classified as possible carcinogens. For this reason, it is fundamental to verify their presence in bud extracts intended for human consumption. In this work, an accurate analytical procedure was developed to investigate the presence of 16 priority PAHs in *Tilia tomentosa* bud-extracts, obtained by maceration or ultrasonic extraction of the buds in a mix of glicerin:ethanol. The developed methodology was based on GC-MS analysis and the use of magnetic microparticles covered with a molecular imprinted polymer (MagMIP) to selectively extract PAHs from the considered complex matrix [2]. First of all, the recovery of the analytes from a blank sample spiked with known amount of PAHs was optimized, by studying the several variables involved. In particular, a D-optimal experimental design allowed to perform a limited number of experiments to obtain response surfaces, describing the single PAHs recoveries as a function of the studied factors. The volume of sample/microparticles ratio, the number of extractions and the extraction mode significantly affected the recoveries. Their optimal values were therefore chosen based on the obtained mathematical models. A pooled sample made up of real *Tilia tomentosa* bud extracts was spiked with a known amount of PAHs and those were extracted with the MagMIP particles by choosing the best conditions indicated by the D-optimal results. Recoveries in the range 96-133% were reached, as well as acceptable repeatability of the whole sample treatment (RSD in the range 2-18%). The optimized methodology was applied to 9 *Tilia tomentosa* bud extracts deriving from sites characterized by different anthropic impact, to detect any possible contamination. Preliminary evaluation of the results indicated very low concentration of few PAHs in all the analyzed samples.

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SYNTHESIS, AND STUDIES OF SBA-15 MATERIALS FUNCTIONNALIZED WITH TRANSCIENT RADICAL PRECURSORS.

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Organic radicals and materials have already a long common history. Organic radical precursors have been adsorbed in zeolites, grafted onto silicas and onto nanostructured silicas.[1] In these studies the organic radical precursor was positioned in the material by simple adsorption or by post-grafting, in other words with no means to control the distribution of the radical precursor in the inorganic material.

Recently, our group focused his attention on the effect of nanostructuration on the behavior of sulfur-[2,3] or oxygen-centered[4] radicals covalently linked to SBA-15 silicas. These systems enabled an amazing increase of the radical lifetime; the main weakness of these materials was a too low radical concentration for developing an application. In this communication, we will present how the nature of the radical precursor embedded in the framework and the irradiation process had a dramatic impact on the amount of phenoxyl radicals generated, opening the way to new developments.

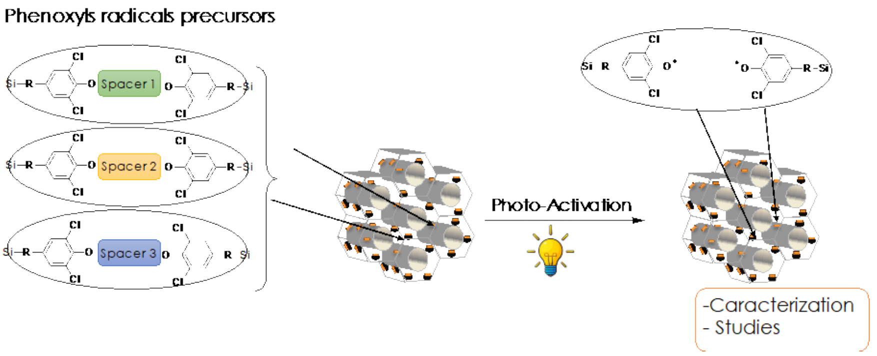

Figure 1: Functionalized SBA-15 with phenoxyl transient radical precursors and photoactivation towards radical species generation.

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Mn – based Hybrid Metal Halides for Optoelectronic Applications

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Starting from the well-studied ABX_3 (A = $CH_3NH_3^+$, Cs^+; B = bivalent metal cation, X = Cl^-, Br^-, I^-) perovskite, new derivates can be obtained with the partial or full substitution of the A and B cations with different metal ions [1]. The introduction of larger or smaller cations in the A site favors the formation of polymorphs of a lower dimensionality (2D or 0D). To date, one of the most promising strategies to tune and confer excellent optoelectronics is the insertion of an organic cation instead of an inorganic one. The resulting structures are named "hybrid metal halides" [2]. Promising compounds can be obtained starting from the emissive Mn-based stoichiometries $AMnX_3$, of which $CsMnBr_3$ constitutes an interesting red-emissive material having a PLQY of 54% [3].

Here, we present our recent results achieved in the preparation of emissive 2D Mn-based hybrid metal halide as single crystals. Starting from the reported synthesis of $CsMnBr_3$, the Cs^+ cation was progressively substituted with the butylammonium ($BA^+ = C_4H_{12}N^+$) cation leading to a phase presenting an orange emission. The obtained sample crystallizes in the orthorhombic system and present the BA_2MnBr_4 stoichiometry; the crystal structure consists of monolayers of connected $[MnBr_6]$ octahedra stacked by two BA^+. The synthesis used is based on the dissolution of the precursors ($MnCO_3$ and BABr) in an acid media (HBr), followed by the slow solvent evaporation. The characterization of these materials was carried out using XRD, FTIR, DTA-TG coupled with GC-MS, ABS, PLE, PL.

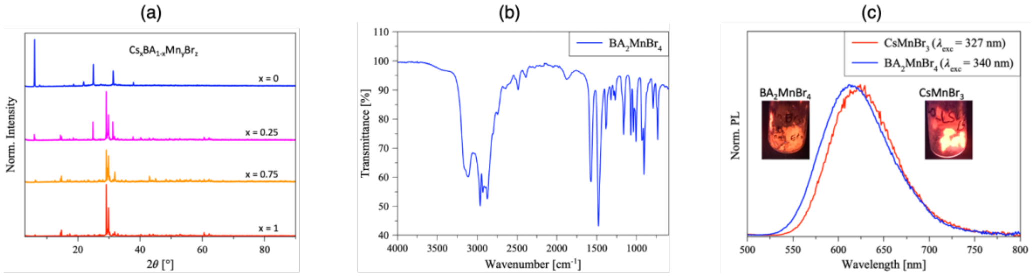

Figure 1: (a) Experimental powder patterns of the samples with $Cs_xBA_{1-x}Mn_yBr_z$ composition, with increasing amount of BA. (b) FTIR spectra of BA_2MnBr_4. (c) PL spectra with images under UV lamp (λ = 365 nm) of crystals' $CsMnBr_3$ and BA_2MnBr_4.

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Chemistry Area:

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Experimental Array to Evaluate Different Operative Parameters in Bioremediation of Hydrocarbon-Polluted Soil

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Pollution by hydrocarbons is associated with different industrial activities which may harm the environment and human health Shahryar (1). It is generally accepted that this kind of pollution has an anthropogenic origin, often due to accidental spills from production units and transport pipelines, leakages from storage facilities and underground tanks, mining, human activities in the production, transportation, and improper or illegal behaviors in waste treatment and disposal. These contaminants can be accumulated in soil due to their low degradation rates, affecting the physical, physiological, and biochemical properties of this valuable resource Raffa et. al (2). The bioremediation of soils polluted with hydrocarbons demonstrated to be a simple and cheap technique, even if it needs a long time Gutiérrez et. al (3). The current paper shows the application of statistical analysis, based on two factors involved in the biological process at several levels. We focus on the Design of Experiments to determine the number and kind of experimental runs, whereas the use of the categorical factors has not been widely exploited up to now. This method is especially useful to analyze factors with levels constituted by categories and define the interaction effects. Particularly, we focused on the statistical analysis of 1) experimental runs carried out at laboratory scale (test M, in microcosm), on soil polluted with diesel oil, and 2) bench scale runs (test B, in biopile), on refinery oil sludge mixed with industrial or agricultural biodegradable wastes. Finally, the main purpose was to identify the factor's significance in both the tests and their potential interactions against the different response variables, by applying ANOVA.

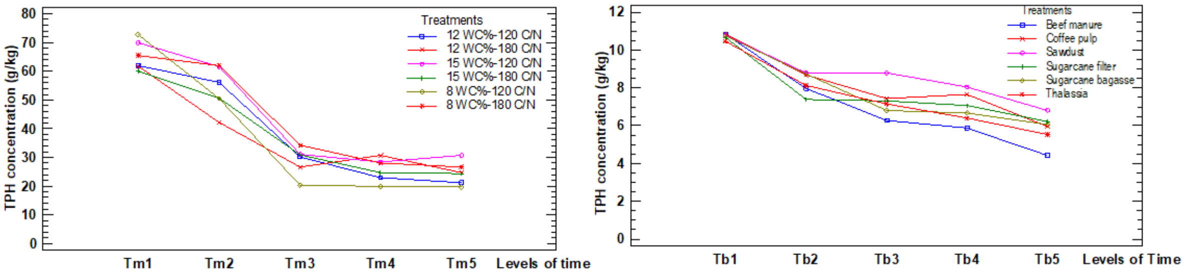

Figure 1: Interaction plot for the factors. a) test M b) Test B

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Benchmark on cobalt systems relevant for reactivity

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The high cost and low availability of second- and third-row transition metals push more and more researchers to explore the chemistry of the first-row transition metals. Among known reactivities, cobalt complexes have been used for more than ten years to perform cycloaddition reactions. Their use in catalysis needs a fine understanding of their electronic properties, which could be achieved by theoretical approaches. Nevertheless, the computational study of first-row transition complexes and their reactivity rises numerous questions, as several electronic states could be accessible.

Recently, in our group, a [CpCo] mediated chemodivergent cycloaddition has been studied.[1] General mechanisms proposed for this kind of reactivity usually rely on density functional theory calculations (employing hybrid functionals) and involve a two-state reactivity. However, for some key intermediates, and as expected from the so called "exchange" integrals treatment, a pure density functional would predict a more stable singlet state, while a hybrid functional, such as B3LYP, would predict a more stable triplet state. We used wavefunction based methods on a series of model cobalt and rhodium systems to compute singlet-triplet splittings in order to benchmark the performances of common density functionals in our mechanistic studies. This also represents an opportunity to gain methodological insights on the computational treatment of organometallic catalysts. Using correlated wavefunction methods such as MRCI and CASPT2/RASPT2 on systems of increasing size, we assess the influence of the relevant parameters.[2, 3] Coupled Cluster calculations were also performed to check the extent of their reliability in treating these strongly correlated transition metal complexes.[4, 5] In the process, we aim at finding a suitable cost/accuracy balance to treat systems of chemical interest, select the appropriate density functional and assess the validity of proposed mechanisms.

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Topology of the Electron Density and of Its Laplacian from Periodic LCAO Calculations on f -Electron Material

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The nature of the chemical bonding (CB) of f-electrons is as fascinating as still puzzling. Many aspects of this intricate phenomenon are widely studied since its full rationalization would have both fundamental and technological relevance. The main objective of our research work is the development of new methodologies for a better description of CB features for materials containing Lanthanides and Actinides. The most general, formally rigorous technique allowing for a consistent and quantitative description of multiple aspects of CB is represented by Bader's quantum theory of atoms in molecules and crystals (QTAIMAC). At the core of this methodology is the topology of the electron density and of its Laplacian, and therefore, it can in principle be adopted both experimentally and theoretically, thus allowing for a mutual validation of the two approaches. The QTAIMAC is a very general theory so it can be used to extract atomic charges, to find information about the spatial distribution of the electrons and to characterize the critical points of the electron density ρ(r) which allows to identify the interaction type. In this context our work, focuses on the theoretical description of ρ(r) for Lanthanides and Actinides complexes and materials. We have extended the TOPOND library of the CRYSTAL code[1], which worked only up to d-orbitals, to f- and g- type basis function. Then, we applied our new methodologies to systems that have already been experimentally studied in order to validate our approach with already existing data. However, despite a broad consensus on its ability to describe subtle features of the chemical bonding, only very recently could the QTAIMAC be successfully applied to actinide compounds. In particular, Gianopoulos et al. computed the charge density of the UF_6 molecular fragment extracted from the $[PPh_4][UF_6]$crystal (figure 1, center), performed a QTAIMAC study, and compared their theoretical results with those from the experiment on the crystals[2]. Also Zhurov et al., some years before, studied from ax experimental point of view an uranium containing compound, the $Cs_2UO_2Cl_4$ [3] (figure 1, left). By our side, we studied these systems from the theoretical point of view, and we got a really coherent description of many aspects of the chemical bond with experimental data[4,5]. Since a remarkable qualitative and quantitative agreement represents a strong mutual validation of both approaches experimental and computational, we decided to study a common system, the UCl_4 (Fig. 1, right), with Prof. Pinkerton of the Toledo university and to try understanding if a union of the experimental and theoretical methodology could give us a further improvement.

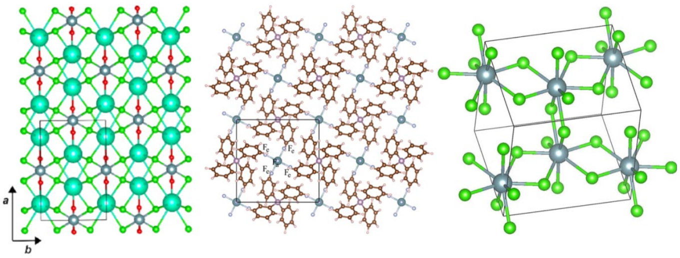

Figure 1 : the three systems under investigation (from left to right: $Cs_2UO_2Cl_4$, $[PPh_4][UF_6]$, UCl_4 *)*

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Higher yield and polyphenol content in olive pomace oil extracted using 2-methyloxolane

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(2) Avignon Université, INRA, UMR 408, GREEN Extraction Team, Avignon, F-84000, France

Despite its severe toxicity and negative environmental impact, hexane is still the most commonly used solvent for the extraction of edible oils. This is in contrast with the constantly growing demand for sustainable and green extraction processes.

A variety of alternatives to hexane have been investigated in recent years, and these include 2-methyloxolane (2-MeOx), which has emerged as a promising bio-based alternative. This study evaluates the possibility of replacing hexane, in the extraction of olive pomace (OP) oil, with 2-MeOx, both dry and saturated with water (4.5%), the latter of which is called 2-MeOx 95.5%. The three solvents have been compared in terms of extraction yield and quality, as well as the lipid and polyphenol profiles of the oils. Furthermore, a comparison with an extra-virgin olive oil (EVOO) of the same OP cultivar is presented. The work concluded that both dry 2-MeOx and 2-MeOx 95.5% can replace hexane in OP oil extraction, resulting in higher extraction yields of oils that are richer in phenolic compounds. This alternative solvent can satisfy 11 of the 17 SDG (Sustainable Development Goals) adopted by all United Nations Member States in 2015 to provide a shared blueprint for peace and prosperity for people and the planet.

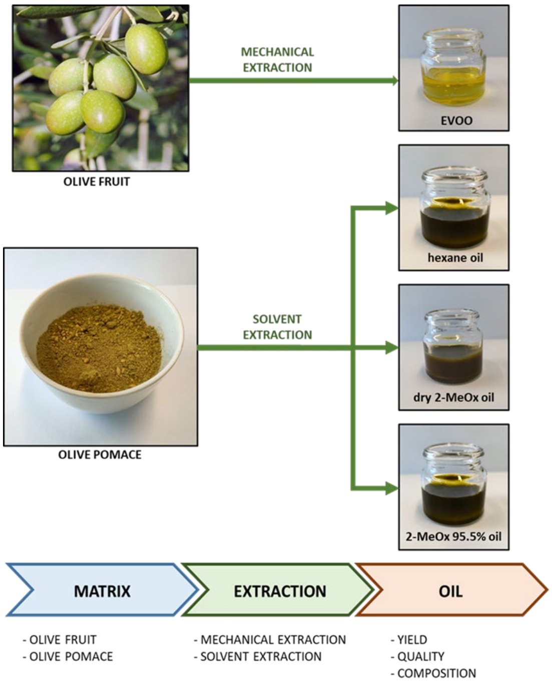

Figure 1. *2-MeOx (dry and 95.5%) as a promising bio-based alternative to hexane in the extraction of olive pomace oil.*

Keywords: 2-methyloxolane, hexane, olive pomace oil, polyphenols.

Synthesis of new solid state-fluorescent furo[2,3-c]isoquinolines via Ugi reaction and subsequent Pd-catalyzed transformations

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(2) Institut für Organische Chemie und Makromolekulare Chemie Heinrich-Heine-Universität Düsseldorf (Deutschland).

The synthesis of a novel class of organic fluorophores featuring the unusual furo[2,3-*c*]isoquinoline core has been explored. The synthetic approach is characterized by an Ugi multicomponent reaction coupled with a subsequent one-pot palladium-catalyzed insertion–alkynylation–cycloisomerization cascade[1,2]. The use of suitable aromatic methyl propargyl ethers in the process leads to furoisoquinolines that can extend the π-conjugation throughout a final elimination (Figure 1). The resulting molecules not only exhibit a red-shift both in the absorption and emission bands with respect to the previously synthesized ones with no increased π-conjugation, but also "switch on" the fluorescence at the solid state. This peculiar phenomenon, known as *Aggregation-Induced Emission* (AIE)[3], holds an enormous application potential in the field of functional materials (e.g. OLEDs, sensors, bio-imaging) and, consequently, it has been recently listed as one of the "Top Ten Emerging Technologies in Chemistry"[4]. Our current work has been focused on the introduction of (hetero)aryl rotors in the alkenylidene moiety of the furoisoquinolines to further extend the π system and to improve the restriction of intramolecular motions (RIM), which are known to be a key feature for the AIE luminophores. Besides, we also studied the linkage of auxochromic functionalities to modulate even more the fluorescence and to portray a wider picture of the substitution-photophysics correlation.

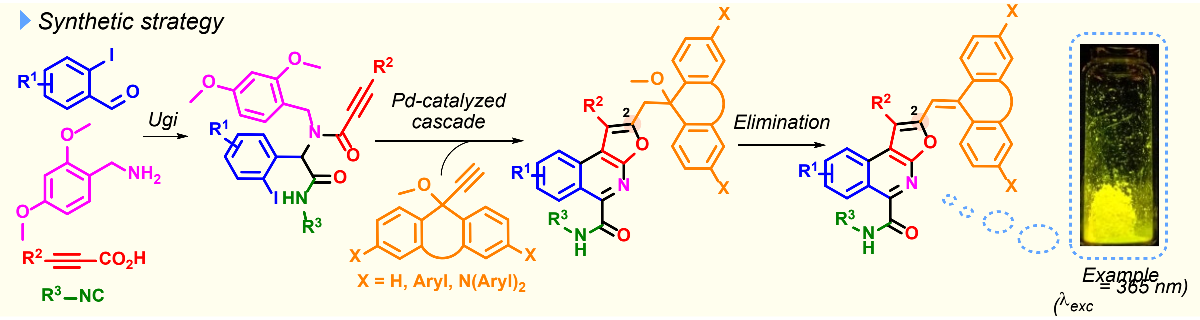

Figure 1: synthetic pathway that leads to the furo[2,3-c]isoquinolines with extended conjugation at C$_2$.

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Mn-substituted TiFe alloys for large scale hydrogen storage: a neutron diffraction study

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Looking forward a greener energy scenario, hydrogen, as an efficient energy carrier, can drive the widespread use of renewable energy sources. Its safe storage in the solid state can be achieved in TiFe intermetallic compound, storing up to 1.86 wt.% H_2 in mild condition of pressure and temperature.[1] Elemental substitution at the Fe site allows mild activation of the compound during the first hydrogenation. Among several possible substitutions, Mn has been selected to tailor the hydrogenation properties of TiFe intermetallic. In fact, $Ti(Fe,Mn)_{0.90}$ alloys can lead fine tuning of equilibrium pressure of hydrogenation to adapt them to the final application.[2]

The crystal structure of $TiFe_{(0.90-x)}Mn_x$ alloys (x = 0, 0.05 and 0.10) and their deuterides has been determined in this study by in-situ neutron diffraction, while recording Pressure-Composition Isotherm curves at room temperature. The structural study aims at understanding hydrogen storage and basic structural properties of materials with optimised compositions, to support the industrial application of TiFe-type alloys for integrated hydrogen tank in energy storage systems. Hence, the materials have been tested towards their implementation in an integrated, renewable, large-scale stationary hydrogen storage tank within the framework of the HyCARE European project (www.hycare-project.eu). The influence of Mn and Ti substitutions at the Fe site for TiFe-type alloys have been determined and structural properties are studied during reversible deuterium loading at ILL and ISIS neutron facilities [3,4]. The in-situ evolution of deuteride phases is followed as a function of deuterium pressure to determine domains of existence for the alpha (α: D-solution in pristine alloy), beta (β: mono-deuteride) and gamma phases (γ: di-deuteride).

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Dynamic self-assembling supramolecular dendrimer nanosystems as potent antibacterial candidates against drug-resistant bacteria and biofilm

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The alarming increase and prevailing nature of antibiotic resistance urge for new antibacterial agents, preferably those differing substantially from conventional antibiotics [1]. Amphiphilic antibacterial agents are particularly appealing to tackle this crisis because they can mimic the antibacterial features of natural antimicrobial peptides and antibacterial detergents [2]. Additionally, self-assembled supramolecular nanostructures of these amphiphilic agents can contribute towards the antibacterial activity via cooperative and multivalent interaction. [3] In this perspective, we have developed amphiphilic dendrimers [4] and explored their potential as antibacterial candidates. We report here novel antibacterial candidates based on self-assembling amphiphilic dendrimers composed of a hydrophobic alkyl chain and a hydrophilic poly(amidoamine) dendron bearing different terminal functionalities. Remarkably, the dendrimer with amine terminals exhibited strong antibacterial activity against both Gram-positive and Gram-negative as well as drug-resistant bacteria and prevented biofilm formation. In addition, the amphiphilic dendrimer is able to form nanomicelles and co-deliver antibacterial agents. Our study presents a novel concept for generating potent antibacterial candidates and offers a new perspective for combatting antibacterial resistance.

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Metallo β-Lactamases inhibitors: new tools against Bacterial Multidrug Resistance

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Bacterial multidrug resistance poses a real menace to public health, calling for new discoveries and innovation in antibiotic research.[1] One of the principal ways through which bacteria acquire resistance is the development of β-lactamases capable of breaking the β-lactam ring of β-lactam antibiotics. Conventionally, β-lactamases are divided into four classes: A, B, C and D. Enzymes from classes A, C and D contain in the active site a nucleophilic serine, while class B Metallo-Beta-Lactamases (MBLs), carries two zinc ions promoting the formation of a nucleophilic hydroxide substituting the serine residue. This class is divided into 3 subclasses according to the zinc coordination shell; subclass B1 contains the most clinically relevant members including VIM, NDM and IMP.[2] Efficacious inhibitors for MBLs are still missing, in fact, many MBLs are carbapenemases, BLs able to hydrolyse even the last resort antibiotics. The co-production of carbapenemases belonging to different classes, highlights the importance of developing new ligands acting as broad-spectrum inhibitors. The aim of this work is to find promising structures able to inactivate MBLs so that antibiotics can preserve their activity. Here we present a library of new 4H-1,2,4-triazole-3-thiol derivatives, with general structure **A**, which were designed starting from compound **1** (R_1 = H, R = Br).[3] New molecules have been synthesised carrying the same moiety but using different substituents with different electronic features to optimize the interactions with the enzymes. All the molecules were subjected to *in vitro* studies to determine their inhibition potency towards isolated enzymes. The results suggested the good inhibitory activity of some of the new compounds which might be promising lead in developing of new broad-spectrum inhibitors able to fight antibiotic resistance.

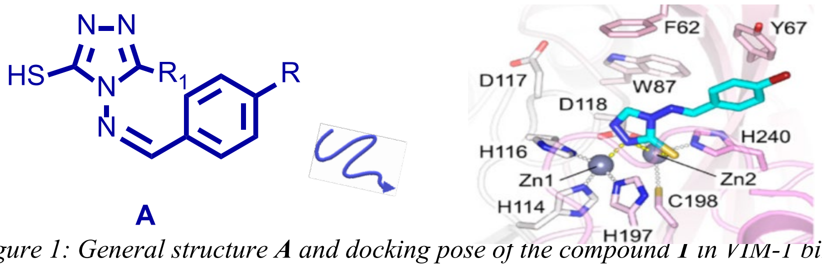

*Figure 1: General structure **A** and docking pose of the compound **1** in VIM-1 binding site.*

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High Entropy Alloys (HEAs): thermodynamic simulations for high-temperature applications

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Università di Genova, Dipartimento di Chimica e Chimica Industriale, Via Dodecaneso 31, 16146 Genova, Italy

The rise of global energy request is pushing science to develop materials increasingly resistant and performing at high temperatures. High Entropy Alloys (HEAs) and their unique features represent a new tool to achieve this goal thanks to their high corrosion resistance, yield strength and hardness[1]. On the other hand, these alloys complexity makes their study via trial-and-error method expensive, time consuming and hardly viable.
The aim of this work consists in developing a thermodynamic database to simulate HEAs behaviour at high temperature, expanding an existing database previously built in our research group (containing Al, B, C, Co, Cr, Fe, Hf, Mo, Ni, Re, Ta, Ti, W, and Y). The main interests regard the systems of Si (since it is also used in commercial superalloys) and of refractory elements belonging to groups 4 and 5, whose presence is connected to high-temperature applications. First results on the Si insertion in the database allowed the correct modelling of several binary and some ternary subsystems, presented here.
The main advantages of this approach regard the exploration of the whole compositional and temperature range and the extremely wide applicability of the database. With its completion, in fact, any multicomponent system constituted by elements included in the database could be simulated and investigated for potential applications.

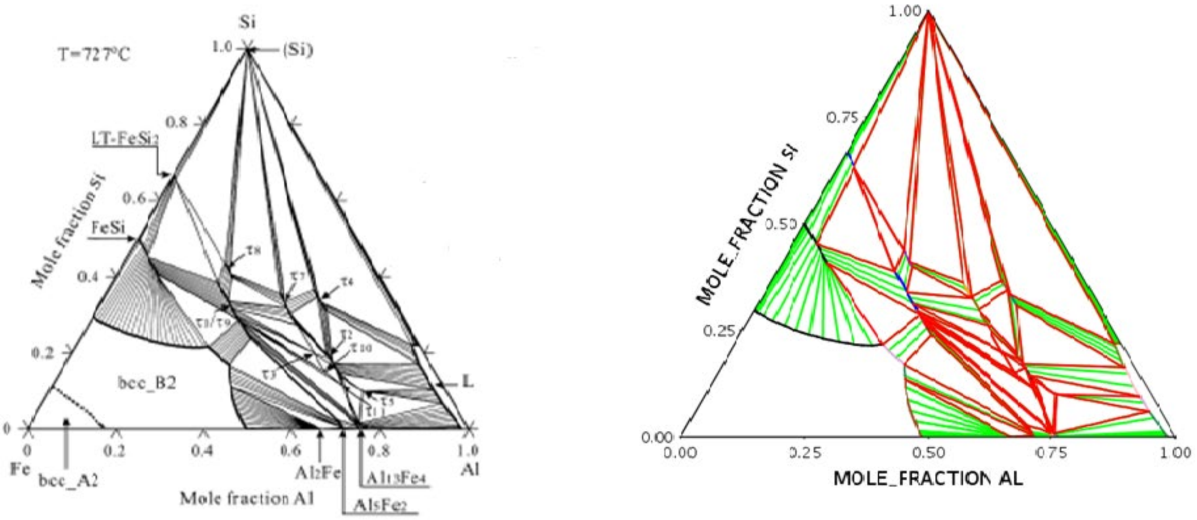

Figure 1 : Al-Fe-Si ternary isothermal section at 800°C reported in literature[2] (on the left) and calculated with our database via Thermo-Calc software (on the right).

[1] D.B. Miracle, Acta Materialia, 122 (2017), 448-511
[2] Y. Du et al., Intermetallics, 16 (2008), 554-570

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Chemistry Area :

- ● **Material Chemistry or**
- ☐**Environmental and Analytical Chemistry or**
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- ☐**Physical Chemistry**

Vitamin D_3: three possible strategies for its topical delivery

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Apart from its fundamental role in bone formation, cholecalciferol, known as Vitamin D_3 ($VitD_3$), has a beneficial effect against a wide variety of diseases, which includes psoriasis [1]. The use of $VitD_3$, however, is hindered by its low water solubility and its susceptibility to rapid degradation when exposed to UV light, heat, oxygen and/or acidic conditions. To tackle this problem it is possible to resort to a drug carrier. The ideal carrier for $VitD_3$ should be able to shield this active principle from degradation and to deliver it with appropriate kinetics in the desired administration site (i.e., the skin). In this perspective, mesostructured silica, thanks to its stability and the beneficial effect of silicates to skin [2], is an appealing candidate for $VitD_3$ topical delivery. In the present study, a commercial mesoporous silica (SBA-15) was loaded with $VitD_3$ through two different impregnation techniques: the traditional incipient wetness impregnation from a solution (IWI) and the more innovative impregnation with supercritical CO_2 ($scCO_2$). In parallel, a third strategy was also examined: the direct incorporation of $VitD_3$ during the synthesis process, which resulted in a mesostructured hybrid material made of silica, surfactant (CTAB) and $VitD_3$. Samples of the SBA carrier loaded with the two impregnation techniques (SBA_IWI and SBA_$scCO_2$) as well as the hybrid material (Meso_SiO_2_$VitD_3$) were analyzed by means of FTIR spectroscopy (Figure 1, right), nitrogen sorption at 77K, thermogravimetry, X-ray diffraction and Scanning Electron Microscopy. Moreover, the $VitD_3$ content and its stability were estimated by means of ethanol extraction and UV-visible analysis (Figure 1, left). Meso_SiO_2_$VitD_3$ resulted to be a mesostructured material with 2D hexagonal symmetry (typical of MCM-41 precursors), where $VitD_3$ and CTAB intimately interact acting as co-surfactants. Results show that $VitD_3$ was successfully incorporated in significant amount in all samples (25 w/w% in SBA_IWI, 20 w/w% in SBA_ $scCO_2$ and 9% in Meso_SiO_2_$VitD_3$, respectively). However, $VitD_3$ suffered degradation when it was incorporated in the SBA carriers, independently of the adopted technique. On the contrary, the active principle incorporated in the hybrid sample Meso_SiO_2_$VitD_3$ was effectively preserved. Consistently with what reported in the literature for protein-based systems containing $VitD_3$ [3], the compact structure of the hybrid system is crucial for the preservation of the drug against oxidative/thermal/UV degradation, whereas the porous structure of commercial mesoporous silica is not able to avoid $VitD_3$ degradation.

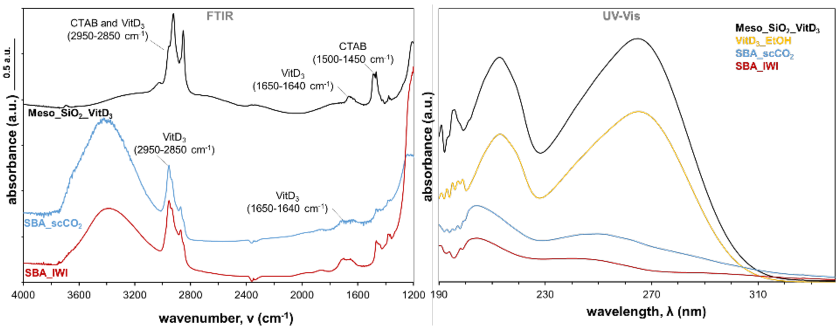

Figure 1: FTIR spectra of $VitD_3$-loaded commercial silica and $VitD_3$-containing mesostructured hybrid material (left); UV-Vis spectra of the same samples in ethanol (right).

[1] Weinberg, J.M., *Treatment of psoriasis*; Birkhauser Basel, 2008.
[2] Seaborn, C.D., Biol.Trace Elem. Res. 2002, 89, 251-261.
[3] Abbasi, A., Food Chem. 2014, 143, 379-383.

Chemistry Area :

☐ Material Chemistry or

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☐Physical Chemistry

Simultaneous Control of Central and Helical Stereogenic Elements on Small Molecules

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Small molecules featuring different types of stereogenic elements are very challenging synthetic targets, especially when displaying configurationally labile helical chirality. Previously, we developed a method to access enantiomerically enriched atropoisomers [1] and dioxa[6]helicenes [2] via centrally chiral dihydrofurans formation. Herein, based on these works, we propose an enantioselective organocatalytic approach for the synthesis of small molecules bearing both central and helical stereogenic elements, starting from achiral substrates. Products were obtained with excellent enantioselectivity in most cases with simultaneous control of the helicity and two stereogenic centers. Such obtained products could handle post-functionalization with good retention of enantiopurity.

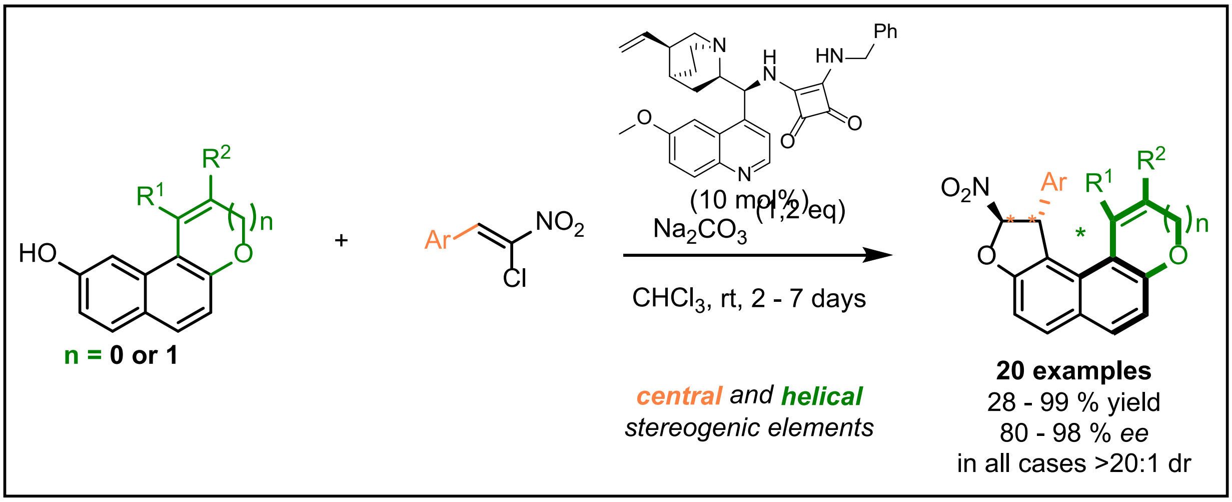

Figure 1: Enantioselective organocatalytic heteroannulation to access centrally and helically chiral molecules

[1] J. Am. Chem. Soc. 2017, 139, 2140-2143
[2] J. Am. Chem. Soc. 2020, 142, 16199-16204

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Asymmetric Gold-Catalyzed Addition of Carbonyl Compounds on 1,6-Enynes

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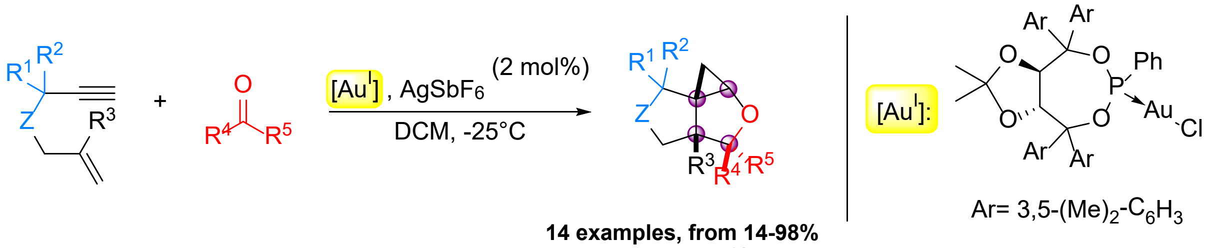
Interest in homogeneous gold catalysis has noticeably increased during the last decades.(1) Gold complexes possess a carbophilic Lewis acid character which provides it a particular reactivity able to activate π-systems towards nucleophilic additions. This reactivity offers new possibilities of chemical synthesis, such as cycloisomerizations and domino reactions of enynes and carbonyl compounds which allows to reach various carbocyclic or heterocyclic scaffolds, starting from simple substrates, enhancing significantly the molecular complexity.(1,2) Nevertheless, asymmetric gold catalysis still represents a great challenge considering the linear geometry of gold (I) complexes and the difficulty to synthesize gold (III) complexes. One of the strategies to perform efficient enantioselective transformations with gold (I) complexes is to diligently design ligands in order to bring the chiral information closer to the substrate.(3) Based on the work of our group,(4) this project was focused on an unprecedented asymmetric domino gold-catalyzed cycloisomerization of 1,6-enynes towards carbonyl addition. This Prins-type reaction was first reported by the group of Helmchen.(5) We developed an efficient gold-catalytic system for this enantioselective transformation. We evaluated the scope of the reaction under racemic conditions, obtaining a range of derivatives with moderate to excellent yields. Our investigations on the asymmetric version have shown that chiral gold (I) catalysts could induce promising enantioselectivities: a complex with a phosphonite ligand containing a TADDOL pattern allowed us to reach for the first time moderate to good enantiomeric excesses over our scope.(6)



14 examples, from 14-98%
ee up to 82%

(1) Toste, F. D.; Michelet, V. *Gold Catalysis: An Homogeneous Approach*, Catalytic Science Series; Imperial College Press, **2014**; Toste, F. D.; Hashmi, A. S. K. *Modern Gold Catalyzed Synthesis* Wiley-VCH, Weinhein, **2012**; Rappoport, Z.; Liebman, J. F.; Marek, I. *The Chemistry of Organogold Compounds.* In Patai's Chemistry of Functional Groups; Eds.; John Wiley & Sons, Inc.: Hoboken, NJ, **2014**; Slaughter, L. M. *Homogeneous Gold Catalysis.* In Topics in Current; Chemistry;, Ed.; Springer: Berlin, **2015**.
(2) Jiménez-Núñez, E.; Echavarren, A. M., *Chem. Rev.* **2008**, *108*, 3326–3350; Belmont, P.; Parker, E., *Eur. J. Org. Chem.* **2009**, 35, 6075–6089; Toullec, P. Y.; Michelet, V., *Top. Curr. Chem.* **2011**, 302, 31–80; Zhang, D.-H.; Zhang, Z.; Shi, M., *Chem. Commun.* **2012**, 48, 10271–10279;
(3) Zi, W.; Dean Toste, F., *Chem. Soc. Rev.* **2016**, *45*, 4567–4589.; López, F.; Mascareñas, J. L., *Beilstein J. Org. Chem.* **2013**, *9*, 2250–2264; Li, Y.; Kwong, F.; Yu, W.; Chan, A., *Coord. Chem. Rev.* **2007**, *251*, 2119–2144; Zuccarello, G.; Escofet, I.; Caniparoli, U.; Echavarren, A. M., *ChemPlusChem* **2021**, *86*, 1283–1296; Collado, A.; Nelson, D. J.; Nolan, S. P. *Chem. Rev.* **2021**, *121*, 8559–8612.
(4) Dupeux, A.; Michelet, V., *J. Org. Chem.* **2021**, *86*, 17738–17747, and references cited therein; Schelwies, M.; Dempwolff, A. L.; Rominger, F.; Helmchen, G., *Angew. Chem. Int. Ed.* **2007**, *46*, 5598–5601; (Schelwies, M.; Moser, R.; Dempwolff, A. L.; Rominger, F.; Helmchen, G., *Chem. Eur. J.* **2009**, *15*, 10888–10900.
(6) Dupeux, A.; Gentilini, E.; Michelet, V. *Unpublished results.*

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☐ **Physical Chemistry**

Coumarin-Based Oxime Esters: New photoinitiators for visible light photopolymerization

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(1) Université de Haute-Alsace, CNRS, IS2M UMR 7361, F-68100 Mulhouse, France
(2) Université de Strasbourg, France
(3) Aix Marseille Univ, CNRS, ICR, UMR 7273, F-13397 Marseille France

Light-induced polymerization process has become a green chemistry technology, due to its numerous advantages such as low energy consumption, low or no volatile organic emission, high efficiency, and spatiotemporally controllable characteristics. Since most of the benchmark photoinitiating systems require high-intensity UV light sources, the search for new visible light photoinitiators is a significant challenge and this topic has received an increasing attention in recent years. In this field, oxime-esters (OXEs) have long been known as efficient Type I photoinitiators due to their high reactivities in photopolymerization reactions. Generally, their high efficiency is attributed to the direct photocleavage of the N–O bond, to produce iminyl and acyloxy ($R'C(=O)O^{\bullet}$) radicals, which in turn can undergo further decarboxylation reactions.

Recently, a series of coumarin chromophore-based oxime-esters were designed and synthesized as visible light photoinitiators (PIs).[1] Interestingly, coumarin-based OXEs could exhibit a dual initiating ability since heat or light could be indifferently used to initiate the decomposition of oxime-esters and efficiently induce free radical polymerizations (FRP). Markedly, coumarins could also act as Type II photoinitiators when combined with an iodonium salt. Chemical mechanism supporting the high polymerization efficiency was fully investigated. In order to evidence the interest of these new structures, direct laser write experiments were carried out (See Figure 1).

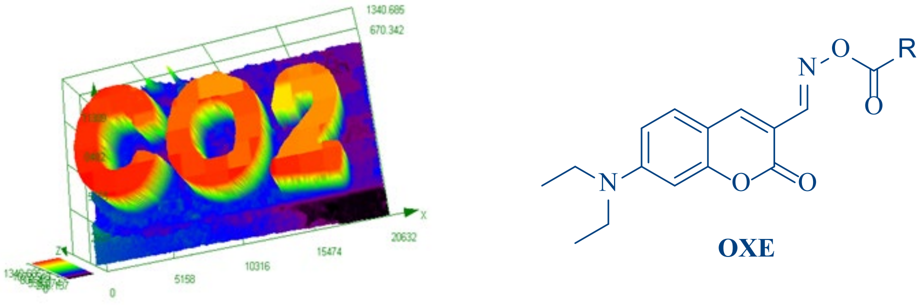

Figure 1: Example of 3D-patterns obtained by direct laser write and chemical structures of investigated OXEs.

[1] F. Hammoud, N. Giacoletto, G. Noirbent, B. Graff, A. Hijazi, M. Nechab, D. Gigmes, F. Dumur and J. Lalevée *Mater. Chem. Front.* **2022**, DOI: 10.1039/d1qm01310f.

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Chemistry Area :

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Application of a D-Optimal Design of experiments to a photocatalytic pilot plant for environmental issues.

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Department of Chemistry and Industrial chemistry, University of Genoa, Genoa, 16146, Italy

Environmental problems related to the presence of emerging pollutants within the environment is finally receiving the proper attention, due to the dangerous side-effects that arise due to the presence in the environment of these biologically active compounds (pharmaceuticals and personal care products, PPCPs). The research on this topic doesn't just involve the detection of all the compounds that are input every day from multiple sources, but also comprehend their environmental fate and the investigation on processes for their degradation. Actual wastewater treatment plants are not able to deal with these micro-contaminants, thus, it's mandatory to find new water treatment technologies to efficiently counteract the spread of these new contaminants [1]. In this work, we set up a design of experiment to take into consideration different kind of variables, both quantitative and qualitative, on a photocatalytic process using TiO_2-based photocatalysts for pollutants abatement [2].

A pilot plant with volume of 1L was set-up according to Figure 1: a reactor placed under magnetic stirring with an adjustable volume was connected to a peristaltic pump, whose flow was directed to a glass coil, placed under solar simulated irradiation lamps. The circuit was then closed by the flow reaching the mixing reactor. We decided to investigate the significance of 7 different variables: photocatalyst concentration, initial pH, treatment time, lamps positions, stirring rate, type of pollutants (dye) and type of photocatalysts. Being these variables of different nature (quantitative and qualitative), a D-Optimal design of experiment was chosen to extract the significance of each investigated variable, possible interactions among them and eventually the optimized conditions to carry out the photocatalytic process. In addition, investigated variables could be modified over different levels and considering their difference, also levels varied considerably. The practical implication is that, on a mono-variate approach, the number of experiments would be equal to 1620, while with this type of approach the number was reduced to 32. As a conclusion, deduced information will lay the foundation for the industrial scale up that will allow the exploitation of photocatalysis as part of water treatment processes in order to degrade the environmental burden caused by the presence of emerging pollutants.

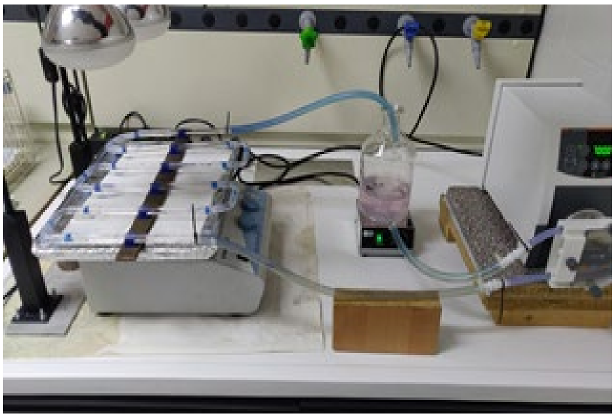

Figure 1: Photocatalytic pilot plant and its components: reactor, peristaltic pump and glass coil

This work was partially supported by the AMGA Foundation through the PROJECT 4.0 2020.

[1] A critical review on application of photocatalysis for toxicity reduction of real wastewaters. J.J. Rueda-Marquez et al. / Journal of Cleaner Production 258 (2020) 120694.

[2] TiO_2 assisted photocatalysts for degradation of emerging organic pollutants in water and wastewater. H.K. Paumo, S. Dalhatou, L.M. Katata-Seru et al. Journal of Molecular Liquids 331 (2021) 115458.

Chemistry Area :

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Biostimulant and biofertilizer from waste valorisation: the different behaviour of humic and fulvic acid on hydroxyapatite

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The ability to enhance productivity reducing the environmental impact represent one of the major challenges of agronomy in the prospective of a sustainable development.

Nanofertilizers represent an interesting alternative to traditional systems, allowing a slow/controlled release of the macro/micronutrient and an optimal nutrient use efficiency. Hydroxyapatite nanoparticles ($Ca_{10}(PO_4)_6(OH)_2$, HAp) have an intrinsic biocompatibility and biodegradability and have been proposed as carrier of P fertilizing element. [1] One of strategies proposed to improve its bioavailability is to modify HAp nanoparticles surfaces with nontoxic and soil-friendly materials capable of increasing solubility and/or avoiding the formation of agglomerates. [2] As surface modifier, humic substances represent an interesting possibility for surface modification by virtue of their ability to stimulate plants. These organic molecules are classified as biostimulant, defined as any substance or microorganism applied to plants with the aim to enhance nutrition efficiency, abiotic stress tolerance and/or crop quality traits, regardless of its nutrients content. [3]

In this study we employed as humic substances a residual product derived from the digestion of Turin municipal organic waste, rich of both fulvic and humic acids. The obtained multifunctional materials show a slow release of macronutrient and humic substances, proving their potential as fertilizers and biostimulants. To explain this behaviour we try to study the interaction by FT-IR: results indicates that, even if humic and fulvic acids have similar structures, the absorption and the release mechanisms on Hap nanoparticles are very different.

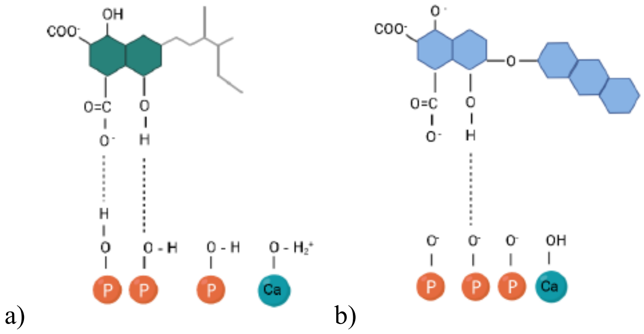

Figure 1 : Supposed interaction mechanism between HAp surface and fulvic (a) and humic (b) acids.

[1] Kottegoda, N. et al. ACS Nano 2017, 11, 1214−1221
[2] Yoon, H.Y. at al. ACS Omega 2020, 5, 6598−6610
[3] du Jardin, P. Scientia Horticulturae 2015, 196, 3–14.

Synthesis of new selective monomers for the design of original Ni(II) and Co(II) ion imprinted polymers

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(2) *Université de Toulon, MAPIEM, Toulon, France*

In the last 2 decades, imprinting technology has been widely applied for the production of ion imprinted polymers (IIPs) to prepare selective adsorbent materials for the solid phase extraction (SPE) of metal ions in solution[1]. The selectivity of IIPs is strongly dependent on the interaction between the functional chelating monomer and the template ion. To increase the efficiency of IIPs, it is therefore essential to produce new functional monomers that can interact in a highly specific way with the target ion. In this work, two chelating ligands, 2-(aminomethylpyridine) (AMP) and bis-2-(pyridylmethyl)amine (bis-AMP) (Fig.1a), were functionalized by a vinyl group to produce two new monomers for the synthesis of original Ni(II) and Co(II) imprinted polymers.

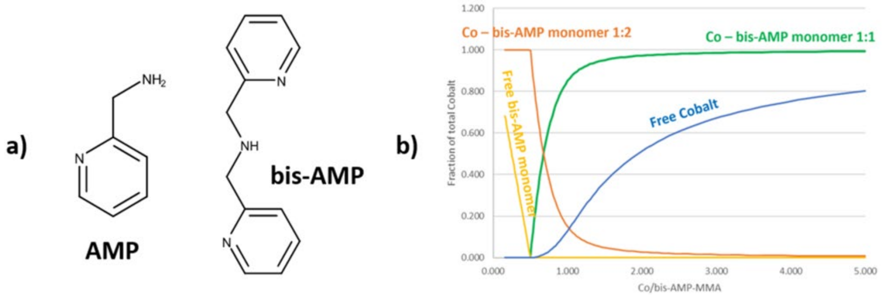

Figure 1: a) Structure of AMP and bis-AMP; b) Distribution of complexes calculated from UV-Vis spectra with HypSpec program between $Co(NO_3)_2$ and bis-AMP monomer in DMSO at 80°C.

The selectivity of IIPs is closely linked to the stoichiometry of the functional monomer-target ion complexes. Therefore, the complex formation between the two monomers and Ni(II) or Co(II) ions was first studied *in-situ* in the conditions of the IIP preparation (solvent and temperature) in order to optimize the prepolymerization mixture. For each monomer/ion couple, UV-Vis spectra were collected and analysed with HypSpec program to extrapolate the distribution of the complexes at equilibrium and estimate their stability constants[2] (Fig.1b). With the AMP monomer, it was possible to isolate the 1:2 complex with Ni(II) ion while with bis-AMP monomer, both 1:2 complexes with Ni(II) and Co(II) ions could be isolated. At this stage, both AMP and bis-AMP monomers were copolymerized with ethylene glycol dimethacrylate (EGDMA) under the optimal ratio conditions determined through the previous study in order to produce IIPs for Ni(II) and Co(II) and their corresponding non-imprinted polymers (NIP). The incorporation of functional monomers within the respective IIPs and NIPs was evaluated by NMR and FTIR spectroscopy. Finally, the morphology of each synthetised polymer was evaluated by SEM. The first results of the study of the binding and selectivity properties of the IIPs towards the target ions will be presented.

[1] Y. El Ouardi, A. Giove, M. Laatikainen, C. Branger, K. Laatikainen, *J. Environ. Chem. Eng.* **2021**, 9(6), 106548.
[2] K. Laatikainen, C. Branger, B. Coulomb, V. Lenoble, T. Sainio, *React. Funct. Polym.* **2018**, 122, 1-8.

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Chemistry Area :

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Towards a new generation of (di-)zwitterionic quinones and macrocycles

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The well-established chemistry of classical calixarenes can be reasonably changed by the introduction of heteroatoms instead of the common CH_2 bridging units, which results in significant changes in the macrocycle behaviour (cavity size, electronic properties). For instance, azacalixarenes (ACA), an evolved class of heteracalixarenes, have attracted much attention as anion receptors,[1] or as precursors of a new type of macrocycles called azacalixquinarenes (ACQ).[2] Indeed, upon insertion of tetraaminobenzene rings within ACA, the oxidation of these electron-rich units leads to the formation of ACQ, which are composed of two aromatic rings and two diaminobenzoquinone diimine units (Figure 1a).

If we now consider the [1+2] adduct (Figure 1b), we showed that the canonical (uncharged) quinoid rings can be converted into a stable zwitterionic form following intramolecular proton transfer.[3] This intramolecular acid-base reaction occurred due to the presence of strong electron-withdrawing groups (EWG) which increases the acidic character of the N-H proton. Thus, because of the possible presence of both canonical and zwitterionic quinones within a single structure, ACQ possess fascinating electrochemical and optical properties, such as absorption in the red range. Therefore, the development of such systems is of growing interest for detection applications (*e.g.* anions or polar gases).

Recently, we discovered that the engineering of EWG can have a strong influence on the electronic form of the quinones. We incorporated nitrile moieties into the molecule that turned out to promote the zwitterionic ground-state structure due to the absence of intramolecular hydrogen bonding.

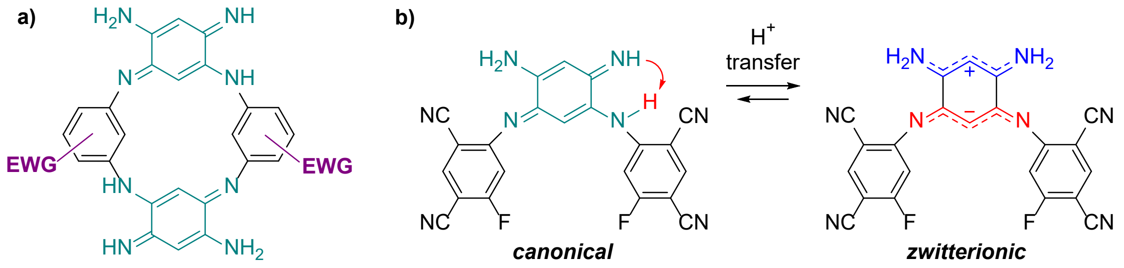

Figure 1: a) Azacalixquinarene structure; b) Illustration of the canonical-zwitterionic equilibrium in quinones.

[1] Canard, G.; Edzang, J. A.; Chen, Z.; Chessé, M.; Elhabiri, M.; Giorgi, M.; Siri, O. *Chem. Eur. J.* **2016**, 22 (16), 5756–5766.
[2] Pascal, S.; Lavaud, L.; Azarias, C.; Varlot, A.; Canard, G.; Giorgi, M.; Jacquemin, D.; Siri, O. *J. Org. Chem.* **2019**, *84* (3), 1387–1397.
[3] Pascal, S.; Lavaud, L.; Azarias, C.; Canard, G.; Giorgi, M.; Jacquemin, D.; Siri, O. *Mater. Chem. Front.* **2018**, 2 (9), 1618–1625.

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Chemistry Area :
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Indirect Enantiocontrol of Tertiary Alcohols and Quaternary Centers by Acylative Organocatalytic Kinetic Resolution

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Institute Address : Aix-Marseille Université, CNRS, Centrale Marseille, iSM2, Marseille, France

The stereocontrol of chiral tertiary alcohols and quaternary stereocenters represent a recurrent challenges in organic synthesis. In our laboratory, we elaborated a simple, efficient, and indirect strategy to enantioselectively prepare both of these challenging targets througt a chiral isothiourea* catalyzed selective acylation of adjacent secondary alcohols. This transformation enables the kinetic resolution (KR) of easily prepared racemic diastereoenriched precursors. In the first challenge, secondary/tertiary diols provided both monoesters and starting diols in highly enantioenriched forms (s-value>200).

In the second challenge, this indirect method was also used to control the quaternary centers, providing desired product with s value up to 185.

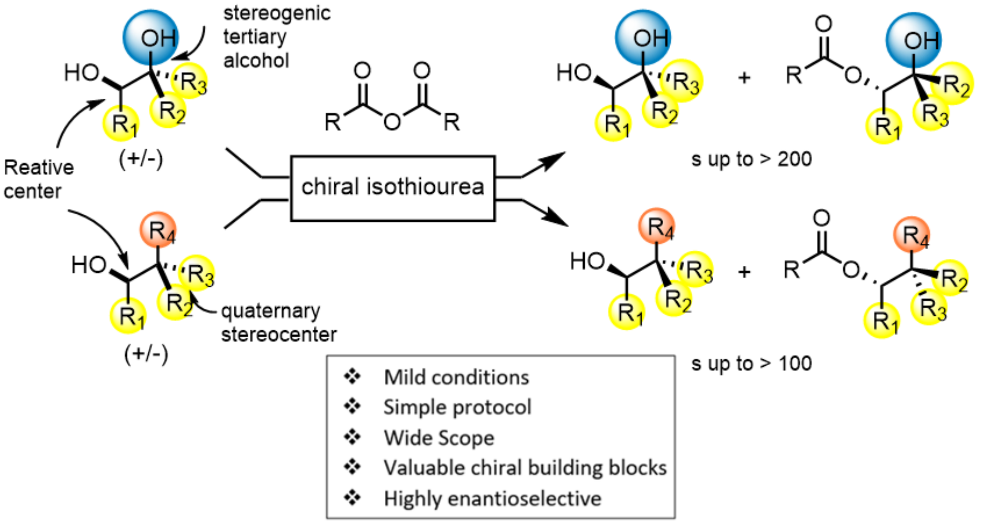

Figure 1 : Indirect enantiocontrol of tertiary alcohols and quaternary centers

[1] Liu X.*, Desrues T.*, Pons J. M., Monnier V., Amalian J. A., Charles L., Quintard A., Bressy C., *Org. Lett.* **2021**, *23*, 4332-4336.
[2] Liu X, Pons J. M., Monnier V., Charles L., Quintard A., Bressy C., *Eur. J. Org. Chem.* **2022**, e202101475

Chemistry Area :

☐ Material Chemistry or

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☐ Physical Chemistry

Electrochemical studies of CO_2-reducing metalloenzymes

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There are only two enzymes in nature capable of directly reducing CO_2: CO dehydrogenase (CODH), which produces CO at a [$NiFe_4S_4$] active site, and formate dehydrogenase (FDH), which produces formate at a mononuclear Mo or W active site. Both metalloenzymes are very fast, energy-efficient and specific in term of product. There is a strong incentive in studying their catalytic mechanisms given the high importance of CO_2 reduction in biology and technology, to convert a highly stable compound into more reactive and useful organic compounds.

In our group, we connect both these enzymes to electrodes in order to study their catalytic properties and mechanisms using electrochemical techniques. This method is called Protein Film Electrochemistry (PFE) and consists in immobilising the enzyme on the electrode surface in a configuration in which it catalyses its reaction, producing an electrical current proportional to the turnover frequency [1].

We recently used PFE to discriminate between CO_2 and HCO_3^- as the substrate for the reductive reaction of CODH and FDH: with a very simple and inexpensive method, we definitively demonstrated that both metalloenzymes reduce CO_2 [2]. Moreover, we have purified and characterised through electrochemistry the two CODHs from *Thermococcus* sp. AM4 [3], determining their catalytic properties such as Michaelis constants, product inhibition and oxygen inhibition. Finally, combining site-directed mutagenesis with PFE, we investigated the gas channels in these CODHs.

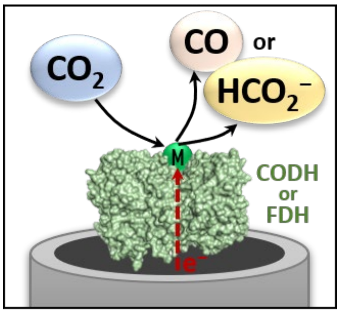

Figure 1: Schematic representation of Protein Film Electrochemistry to study CODH or FDH.

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A novel photoinduced multicomponent reaction to β-Lactams: Ketene 3-Component Staudinger Reaction (K-3CSR)

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A novel photoinduced three component reaction was performed to obtain β-lactams through the Staudinger reaction.[1]

In literature it has been reported the bicomponent photoinduced Staudinger reaction between preformed imines and diazoketones. This process is carried out under highly energetic UV irradiation to favour the Wolff rearrangement of diazoketones to the corresponding ketenes.[2]

The innovative methodology reported in this contribution uses visible-light instead,[3] and both ketenes and imines are generated in situ and directly employed in the Staudinger [2+2] cycloaddition. Synthetic simplicity, high efficiency and complete stereoselectivity are some features of the Ketene 3-Component Staudinger Reaction (K-3CSR). Due to the intrinsic reactivity of ketenes and amines, the key to the success of the process was performing the reaction in the dark and switching the light on only upon imine formation. An optimization of the reaction conditions was performed, and the outcome was compared with that of the classic two component reaction. Moreover, the quantum yield of the visible-light mediated Wolff Rearrangement was calculated and found to be close to 100%. Finally, a library of compounds was realized exploiting this new methodology.

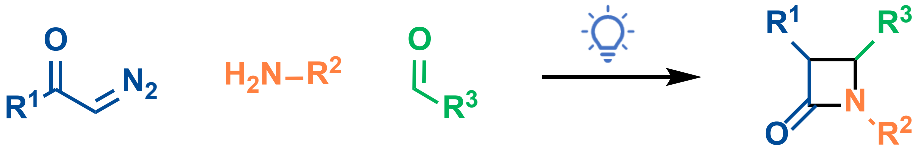

Figure 1 : Ketene 3-Component Staudinger Reaction (K-3CSR).

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Anion-π interactions in confined space

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Noncovalent interactions involving aromatic rings play a key role in many processes of molecular recognition. Among them, π-π and cation-π interactions have been widely studied and are known to be important bonding forces in biological systems. Furthermore, these interactions are also observed in many supramolecular assemblies with artificial hosts.[1] On the contrary, anion-π interactions, which can be broadly defined as the attraction of anions to electron deficient π-systems, have been recognized theoretically only since the beginning of this century.[2] The vital role of anions in many key chemical and biological processes, and the involvement of π-rings in molecular anion recognition and transport, indicate that anion-π contacts could be prominent players in medicinal and environmental applications.[3]

Molecular cages, defined as hollow structures delineating a three-dimensional cavity, are attracting considerable attention in modern supramolecular chemistry due to their possible applications in molecular recognition, catalysis, drug delivery, biosensing, separation and storage. Among the classes of molecular containers, crown ethers, cucurbiturils, cyclodextrins; cryptophanes and hemicryptophanes, have recently received growing interest.[4] Hemicryptophanes are heteroditopic host compounds built from a cyclotriveratrylene (CTV) unit with another C3-symmetrical moiety are able to recognize various charged or neutral guests, such as ion pairs, zwitterions, ammoniums, carbohydrates and fullerenes.

We have developed a series of molecular cages based on electron-deficient units in order to encapsulate anionic species. A drastic modulation of the recognition properties was achieved demonstrating the selectivity of our systems.

The synthesis of hemicryptophanes, their special conformational isomerism and the study of their molecular recognition properties will be highlighted.

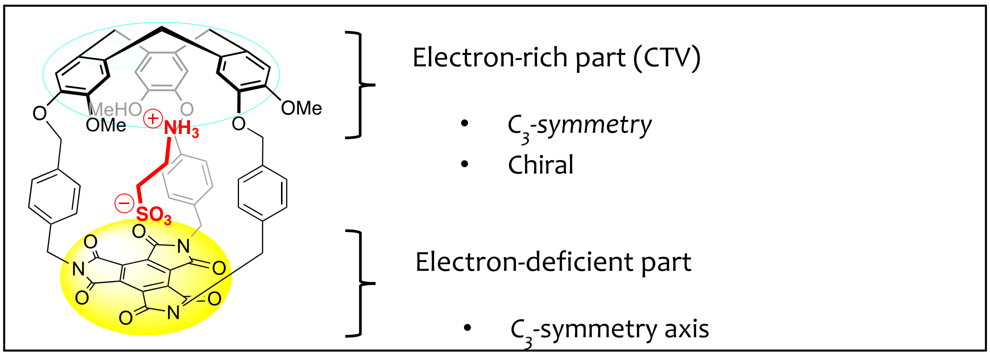

Figure 1 : Schematic representation of the encapsulated taurine guest within the cavity of the heteroditopic hemicryptophane.

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The Stereochemistry of Isoprenoid Hydrocarbons as Molecular Fossils: Implications for the Search of Extinct Life on Mars

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Life on Earth is homochiral: in biology, amino acids are almost universally L-chiral while sugars are D-chiral. Less known, the chiral hydrocarbons in nature are also found in an enantiomerically pure form. In fact, homochirality is observed in all families of molecules used by life [1]. Of interest for us, due to their chemical inertia and thermal stability, hydrocarbons are expected to survive billions of years even in harsh environments, making them much better molecular fossils than the more reactive amino acids and fragile sugars when probing for very ancient life.

We focus on the most abundant chiral hydrocarbons found in primitive organisms: the isoprenoid alkanes pristane ($C_{19}H_{40}$) and phytane ($C_{20}H_{42}$). These are notably a major part of the cellular membrane of archaea [2], as well as the side chain of most chlorophylls (including those used by cyanobacteria) [3].

We now know that Mars most likely had oceans about 4.4 Gy ago [4], where it is believed that a lot of the conditions required for a potential Martian life to emerge were met [5]. The ExoMars space mission from ESA is set to land on the red planet in 2023 with the main scientific goal of looking for extinct or extant life. To do so, it contains the MOMA instrument: a gas chromatograph linked to a mass spectrometer for detailed in situ analysis of the Martian surface and subsurface [6].

Experiments are ongoing to test how well the instrument can separate the stereoisomers of pristane and phytane, but the first results are promising [7]. Then, if similar molecules are found on Mars, being able to distinguish between a racemic or homochiral sample will give enormous weight to a potential biological origin.

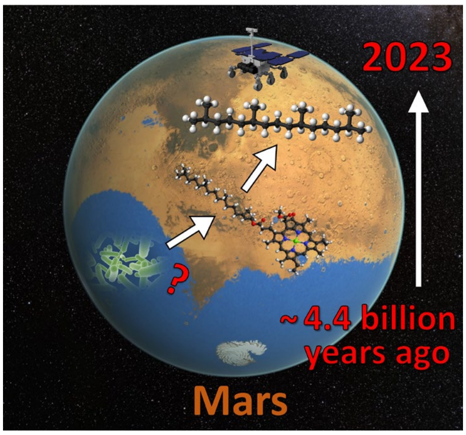

Figure 1 : Remnants of primitive lifeforms

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Role of carbon quantum dots and anion exchange ionomer as a multiphase electrode for the oxygen reduction reaction

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The oxygen reduction reaction (ORR) is the most fascinating electrochemical reaction, especially in fuel cell applications. Proton-exchange membrane fuel cells (PEMFC) were already commercialized but the cost involved to produce the PEMFC is high due to the platinum catalyst. Over the last few years, researchers steadily shifted towards alkaline anion exchange membrane fuel cells (AEMFC) that can perform with non-platinum-based catalysts. Taking this streamline, we used a metal-free catalyst including carbon quantum dots (CQDs) synthesized hydrothermally from green sources [1]. Our work discusses nitrogen-containing CQDs with aminated polysulfone ionomer [2]. Ionomers contribute to less aggregation of CQDs and improve the electrocatalytic performance. We have examined various methods of electrode preparation such as drop-casting and electrospinning and observed the effect on the ORR in alkaline medium. The electrocatalytic activity was analyzed by rotating disc electrode measurements including Koutecky-Levich and Tafel plots [3]. A promising catalyst activity was observed.

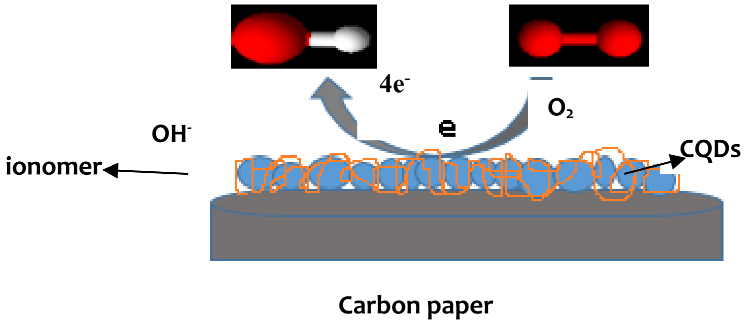

Figure 1: Electrode design with an ionomer and carbon quantum dots.

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Re-thinking the role of natural organic matter in water treatment processes

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In water treatment processes, Natural Organic Matter (NOM) is commonly considered an undesired constituent of natural waters and is typically removed in the early stages of the treatment chain. This is done to avoid the formation, in the presence of chlorine-based disinfectants, of NOM toxic by-products such as haloacetic acids. However, NOM also presents photo-sensitizing properties capable of inducing the transformation of organic compounds in irradiated waters [1]. Furthermore, the metal-complexing ability of NOM, that on the one side can hinder the removal of metal cations, on the other hand could be exploited to maintain in solution Fenton-activating metal cations over a wide range of pH values therefore expanding the potential applications of such treatment processes.

In this study, Suwannee River NOM (SRNOM) was used to promote the abatement of commonly encountered water contaminants using two different approaches: on the one side, the ability of SRNOM to produce $HO^•$ radicals under UVC irradiation was investigated. Glyphosate, a highly recalcitrant compound, was selected as target pollutants and was efficiently abated in the presence of the sole SRNOM under irradiation @254nm; an effort was made to identify SRNOM photo-active moieties and to propose a reaction mechanism for the photochemical production of $HO^•$.

Secondly, the role of SRNOM as iron complexing agent was investigated with the goal of performing a modified photo-Fenton process at circumneutral pH. The role of SRNOM concentration, iron concentration and oxidation state, and pH on the removal of aqueous caffeine were evaluated under irradiation with simulated solar light (λ>340nm). Increasing concentrations of SRNOM demonstrated to accelerate caffeine removal reasonably due to the formation of photo-active iron complexes (Fig. 1). Caffeine degradation rate constant obtained in the optimized photo-Fenton carried out at pH 6 in the presence of SRNOM 40 mg/L was 0.0183 min^{-1}; in comparison, a classical photo-Fenton carried out at pH 3 in the absence of NOM gave a rate constant of 0.0126 min^{-1}.

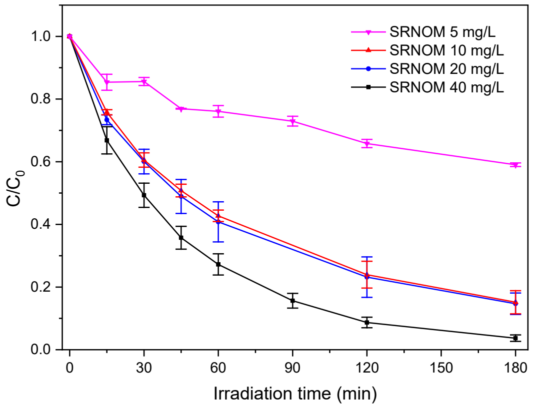

Fig. 1. Degradation profiles of caffeine 5 mg/L in the presence of Fe(II) 1 mg/L, H_2O_2 51 mg/L, and different concentrations of SRNOM (5-40 mg/L).

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Cu-SiO$_2$ catalysts made by Aerosol Assisted Sol-gel method as promising materials for ethanol non oxidative dehydrogenation

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Recently, in a move towards more sustainable chemical processes, the interest in using biomass as carbon source to produce chemicals has been reinforced. Among these, ethanol produced by fermentation of lignocellulosic biomass is expected to become a primary platform chemical [1]. One of the most important intermediates that can be obtained from bioethanol is acetaldehyde, that allows producing several other important industrial chemicals [2]. Acetaldehyde can be produced through non-oxidative dehydrogenation of (bio)ethanol. For this reaction, copper-based formulations such as Cu-ZnO-Al$_2$O$_3$, Cu-MgAl$_2$O$_4$, Cu-SiO$_2$, Cu-Al$_2$O$_3$ have been widely studied in literature [3-5].

These studies showed a strong impact of the preparation procedure on catalyst performances. In particular, it is crucial to precisely control the active site speciation and catalyst texture. This prompted us to study the potential of the aerosol-assisted sol-gel process (AASG) for the preparation of efficient ethanol dehydrogenation catalysts. Aerosol processes are currently emerging as promising synthetic routes to synthesize efficient supported catalysts controlling active site dispersion and porosity [6]. Based on the atomization and fast drying of a precursor's solution or suspension, this bottom-up technique allows the one-step and continuous production of tailored nanomaterials. In fact, the rapid drying of the droplets allows forming solids in metastable states, including highly homogeneous metallo-silicates, which are of wide interest in the field of heterogeneous catalysis. Interestingly, to the best of our knowledge no one still used this process to synthesize active catalysts in ethanol non oxidative dehydrogenation.

Thus, the present work aims at exploiting Aerosol Assisted Sol Gel process (AASG) to prepare Cu-SiO$_2$ catalysts for (bio)ethanol dehydrogenation, comparing their catalytic performances with conventional impregnated Cu/SiO$_2$ catalyst using an AASG SiO$_2$ support. In particular, the effect of the Cu loading and of synthetic procedure on the catalyst performances were investigated and a deep characterization of fresh and used catalysts were carried out. These catalysts show excellent catalytic performances, up to 76% acetaldehyde yield with selectivity higher than 95%, with higher dispersion of the active phase and more resistance to Cu coalescence respect to the impregnated ones.

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Solid-state peculiarities and polymorphism in imidazo[1,5-α]pyridine dyes

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Imidazo[1,5-α]pyridines are a family of heteroaromatic polycyclic compounds that showed in the last decades a multitude of applications: from luminescent compounds for OLED technology to ligands for a multitude of different metals. In medicine, they have been applied as anticancer molecules or enzymatic inhibitors.[1][2] An enormous effort in perfecting the synthesis of all the different kind of derivatives and to maximize the performances has been done.[3][4] However, although some structural results have been collected in literature, no systematic analysis has been performed. We manage to crystallize and analyse with X-ray diffraction a family of 15 differing molecules (4 of them in more than one crystal forms), and some surprising general trends have been observed: from the tendency to polymorphism, to a frequent appearance of non-centrosymmetric space group in absence of chiral centres, or the presence of more than one non-equivalent molecules in the asymmetric unit. These characteristics are much more that exotic games and can either influence the known properties or open new frontiers of research into this stimulating theme of research.

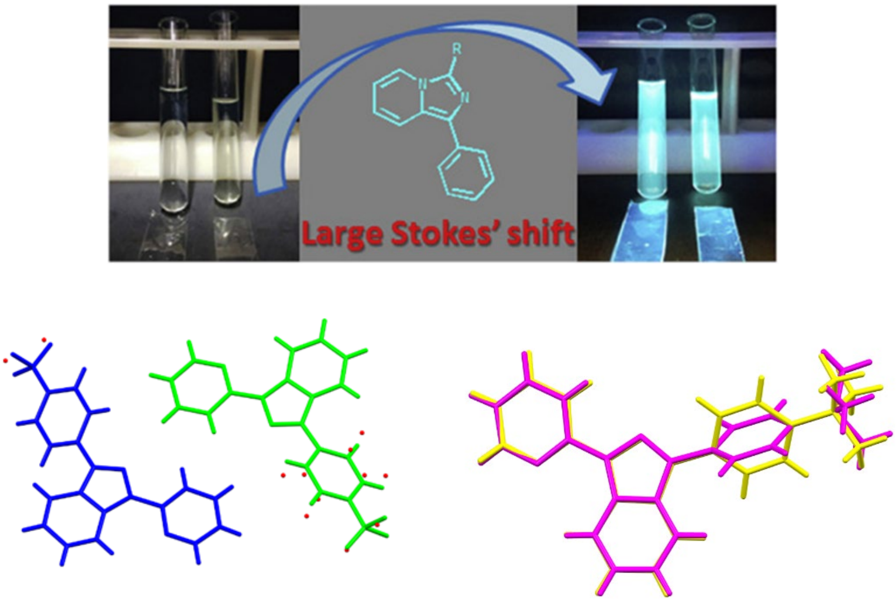

Figure 1 : Luminescence, pseudosymmetry and conformational polymorphism in imidazo[1,5-α]pyridine.

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Valorization of an agro-industrial waste: synthesis of soybean hulls derivatives-based hybrid materials for water purification

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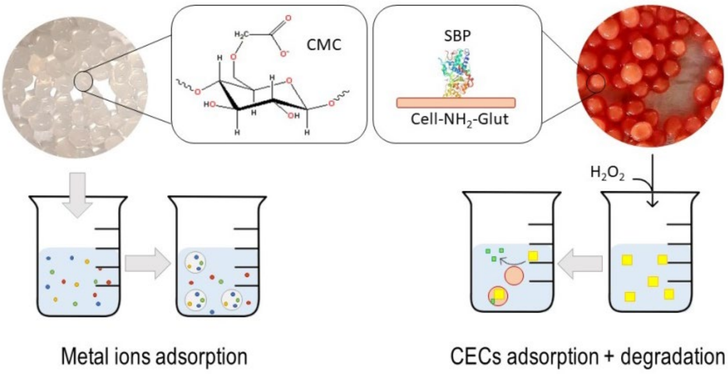

The development of green approaches for environmental treatments, together with the concept of circular economy, is becoming more and more important.

Many wastes are rich in components that can be exploited and valorized, therefore their reuse as source of secondary raw materials is increasing. Our study aimed to the almost complete valorization of a common agro-industrial waste, *i.e.* soybean hulls, in the preparation of hybrid materials useful for the removal of contaminants of emerging concern (CECs) and potentially toxic elements (PTEs) from water.

From the hulls we extracted cellulose [1] and an enzyme, soybean peroxidase (SBP) [2]. These components have been used to prepare two types of alginate-cellulose hybrid hydrogels. For the first type of hydrogel, SBP was coupled to cellulose previously functionalized with (3-aminopropyl)triethoxysilane and glutaraldehyde. These hydrogels will be tested in the removal of Triclosan, Bisphenol A and 2,4,6-Trichlorophenol in presence of H_2O_2. We obtained good preliminary results, also in comparison with similar hydrogels containing SBP immobilized on silica through a previously published procedure [2, 3]. For example, more than 90% of Triclosan (5 mg/L) can be degraded in 5h with 0,033 g/ml of wet hydrogel.

The second type of hydrogel was prepared by using cellulose previously carboxymethylated [4] to enhance the ability to remove PTEs from water by adsorption. This material was tested in the removal of seven metal ions (Pb, Cu, Cd, Zn, Ni, As, Hg) at the concentration of 10^{-5} M in MilliQ water solution at pH 5. It showed good efficiency towards five ions (in the order: Pb > Cu > Cd > Zn > Ni, with abatements in the range 90-50% using 1 g/L of dried hydrogels) and limited effects on As and Hg. To enhance the efficiency of hydrogels towards all the ions, new functionalizations of cellulose are currently in progress.

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Enantioselective Construction of Tetrasubstituted Carboncenter

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Chirality represents an indefinite challenge that has aroused chemists' interest for decades. In view of the emergence of organocatalysts compounds as powerful tools for asymmetric catalysis, the development of processes involving chiral ion pairs has proven successful. Notably, Asymmetric Counterion-Directed Catalysis (ACDC) is well-known to be an efficient strategy for enantioselective reactions involving cationic species and enantiomerically pure counteranions[*]. More specifically, recognized methodologies for the synthesis of chiral non-racemic C5-functionnalized g-lactams involve a prochiral 5-membered cyclic N-acyliminium ions (NAI) as cationic intermediates in the presence of chiral phosphoric acid or thiourea compounds.[†] Although this intermolecular enantioselective functionalization is quite well established for the construction of trisubstituted stereocenter-containing pyrrolidinones with high enantiocontrol, the preparation of fully substituted stereogenic center is more challenging and still topic relevant.

Based on the ACDC concept, an enantioselective construction of tetrasubstituted carbon stereocenters *via* chiral phosphoric acid-catalyzed aza-Friedel-Crafts alkylation of indoles with a,b-unsaturated-hydroxylactam is presented herein. Taking advantage of the different interactions between the chiral counteranion and the NAI intermediate, enantioenriched a,b-unsaturated-2-pyrrolidinones containing a carbon tetrasubstituted center are obtained in good yield and excellent enantioselectivities.

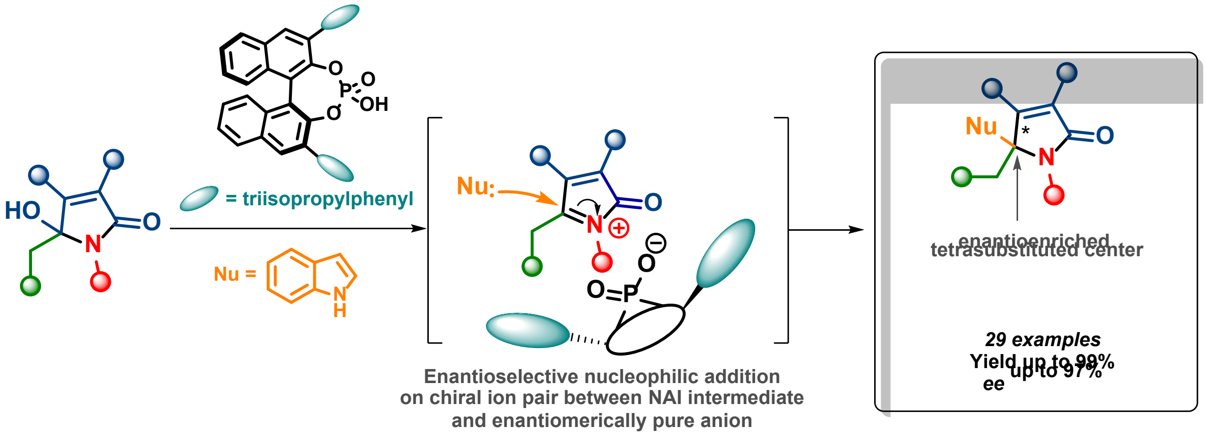

Figure 1: Construction of Enantioselective Tetrasubstituted Center

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1. (a) K. Brak, E. N. Jacobsen, *Angew. Chem. Int. Ed.* **2013**, *52*, 534–561. (b) M. Mahlau, B. List, *Angew. Chem. Int. Ed.* **2013**, *52*, 518–553.
2. Y. S. Lee, M. M. Alam, R. S. Keri, *Chem. Asian. J.* **2013**, *8*, 2906–2919.

Chemistry Area :

- ■ **Material Chemistry or**
- ☐**Environmental and Analytical Chemistry or**
- ☐**Organic and Bioorganic Chemistry or**
- ☐**Physical Chemistry**

Doped ceria nanostructures for the oxidation of pollutants: investigations into the role of defect sites

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Thanks to their promising oxidative performances, ceria-based catalysts are regarded as attractive alternatives to expensive noble metals in the field of pollutant abatement. Ceria activity is linked to its unique redox behavior and oxygen storage capacity, but several other factors, such as morphology, reducibility or defectiveness, influence the final catalytic performances. In this work, different ceria-based nanostructured catalysts doped with Cu and Mn were examined, with the intent of shedding light on the relevant structural and physico-chemical properties defining the catalytic activity and on the reaction pathways involved. In particular, the defect sites formed in ceria structure upon doping were investigated via in situ Raman spectroscopy, monitoring their behavior throughout thermal cycles and during soot oxidation [1] and CO oxidation [2]. Three different types of structural defects were recognized, namely oxygen vacancies, Frenkel interstitial-vacancy pairs and vacancy-free substitutional sites. Spectral evolution suggested that oxygen vacancy clusters can form in reducing atmosphere; these clusters could reorganize not only in the presence of O2 but also upon a temperature decrease, forming isolated vacancies and then evolving into Frenkel and dopant-containing oxidized sites when exposed to oxygen. A correlation was found between defect abundance and catalytic activity towards CO oxidation. Instead, an increase of vacancy-free sites after soot oxidation suggested that the deactivation of reactive oxygen species can occur on catalysts presenting excessive oxygen vacancy concentration [3]. Hence, Cu-doped ceria was characterized by the best CO oxidation activity, thanks to its high specific surface area, reducibility and defect abundance; however, it featured poor soot oxidation activity. Conversely, Mn-doped ceria exhibited the best soot oxidation activity, thanks to an intermediate density of oxygen vacancies and to its well-defined morphology.

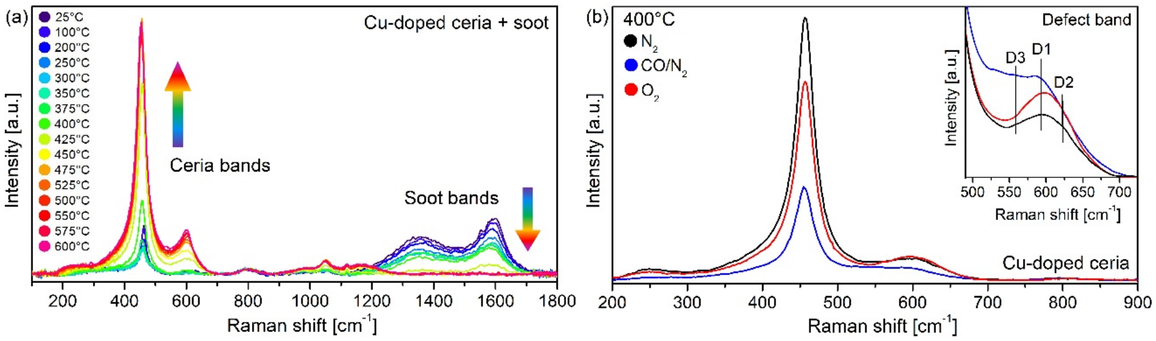

Figure 1: in situ Raman spectra of Cu-doped ceria recorded (a) at different temperatures during soot oxidation and (b) at 400 °C under different atmospheres (in the inset the normalized defect band is magnified).

[1] E. Sartoretti et al., Scientific Reports 9, 3875 (2019).
[2] E. Sartoretti et al., Applied Catalysis A: General 596, 117517 (2020).
[3] S. Liu et al., Catalysis Today 281, 454 (2017).

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Chemistry Area :

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Diversity-oriented synthesis of small molecules applied to the discovery of new inhibitors of oncogenic miRNAs production

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Targeting therapeutically relevant RNAs continues at a great pace, with several strategies being currently employed: antisense oligonucleotides and small molecules being the main ones.[1] Small molecule binders offer advantages over oligonucleotides, having better pharmacological properties.[2] Here we report *de novo* design, the synthesis and the biochemical activity assessment of a microRNA-focused library directed at the maturation inhibition of the microRNA-21. MicroRNAs (or miRNAs) are small non-coding RNAs responsible for the regulation of gene expression. The overexpression of microRNAs has been linked to a number of pathologies such as cancers and the inhibition of their production upon binding to their precursors is a recognized strategy to inhibit cancer progression. MiRNA-21 has been reported to be consistently upregulated in numerous cancers and we chose it as a model target for the development of new RNA binders and inhibitors of its biogenesis.

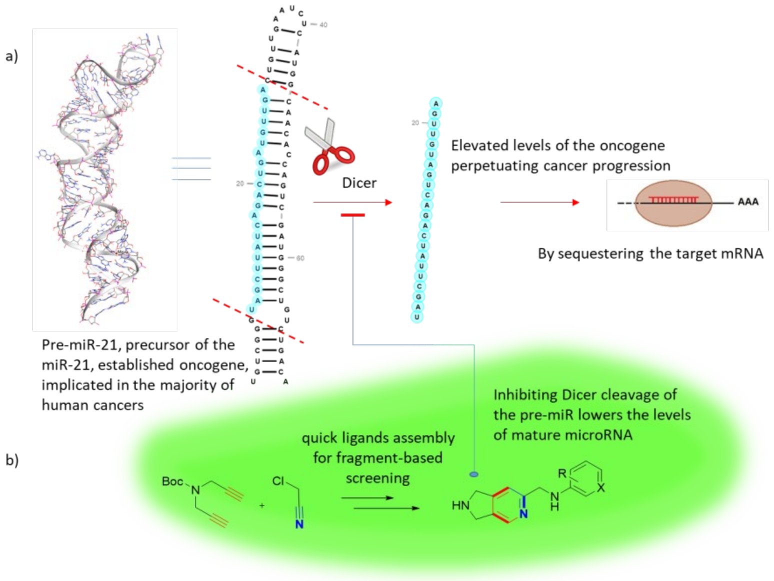

Figure: a) Inhibition of the oncogenic miR maturation by direct binding to its precursor, b) simplified synthesis scheme

Our *de novo* drug design features dihydropyrrolo-[4,3-c]-pyridine scaffold because it combines the pyridine moiety, recurring among reported RNA binders, and condensed aliphatic heterocycle, aiding in aqueous solubility and molecular complexity. The 5-steps synthetic strategy allows for a quick and modular synthesis of the library, involving a metal-catalyzed-[2+2+2] cyclization for the construction of the main core.[3]

Measurement of affinity, selectivity, and biochemical activity of the synthesized compounds allowed for the identification of several hits able to inhibit the biogenesis of pre-miR-21. The mode of interaction was studied by docking, molecular dynamics simulations, enzymatic footprinting, and STD-NMR allowing for a better understanding of the molecular mechanism of action and for the design of optimized ligands.

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10èmes Journées Franco-Italiennes de Chimie
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Interplay between magnetic anisotropy and interparticle interactions in crystalline-amorphous nanocomposite

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Generally, the presence of an amorphous component is often considered a weakness of the synthesis method of the nanostructured magnetic materials. This stems from the fact that the amorphous fraction is often considered as a “dead” magnetic component, showing little to no contribution to the magnetic properties. e.g., saturation magnetization. Here we investigated a hybrid-structured nanoarchitecture combining crystalline $CoFe_2O_4$ and the amorphous parent material. The nanocomposite was prepared by coprecipitation method without further steps employed after the main synthesis process. Transmission electron microscopy (TEM) analysis evidenced small crystalline particles ($<D_{TEM}> \sim 3$nm) embedded in amorphous matrix. By Applying the Debye-Scherrer formula to the most intense reflection of the XRD pattern peak confirm an average size of the crystalline structure of about 3 nm. The investigation of the magnetic properties by SQUID magnetometer and the magnetic structure by means of Mössbauer pointed out that the amorphous phase contributes partially to the total magnetic moment accompanied by a strong variation in the anisotropy (i.e., $H_c = 1.3(1)$ T, at 5K) and the presence of a significant interparticle interacting regime(i.e., T_b=95(9)K).Cross-checking the obtained information from structural and magnetic characterization, we have proposed a micromagnetic model using the software Mumax3, which sheds light on the contribution of each component elucidating the active role of the amorphous phase as a "non-dead magnetic phase", but a magnetically canted structure, with low effective magnetization and very large magnetic anisotropy coupled with the regular core structure[1].

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Chemistry Area :

☐ Material Chemistry or

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☐Physical Chemistry

Shifting-nitroxides as the new Overhauser-enhanced MRI probes for *in-vivo* evaluation using enzymatic activities.

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(1) Université Aix Marseille, Institut de Chimie Radicalaire, Marseille
(2) Université de Bordeaux, Centre de Résonance Magnétique des Systèmes Biologiques, Bordeaux

Fast and efficient detection of enzymatic activity in particular media such as turbid media or even detection of proteases activity in vivo are really challenging. Developing such sensitive method for detection of lipases and proteases activities could be applied in food industry, in biotechnology but also for medical diagnostic for a large range of diseases including pulmonary inflammations and almost all types of cancers. Indeed, those diseases generally involve an overexpression of a particular kind of protease. As a result, the development of a powerful and selective method for early detection of those diseases by monitoring the overexpressed enzymes activities would be an efficient diagnostic tool.

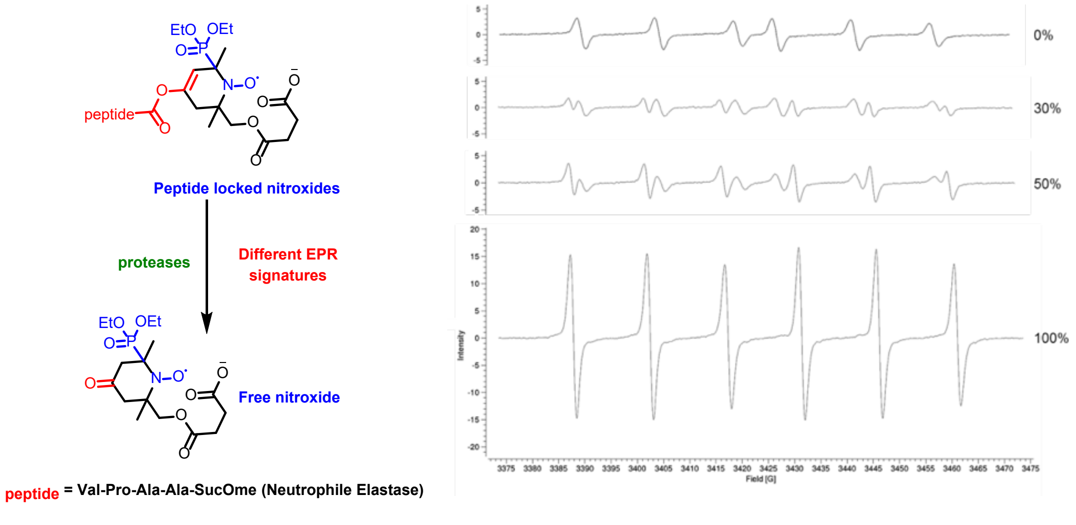

Figure 1. *EPR kinetic hydrolysis of the peptide locked nitroxide by the Elastase Neutrophile to nitroxide.*

Herein, we present the synthesis of new nitroxide probes, peptide locked nitroxides based on the same principle: the probes are hydrolyzed by proteases to give another free nitroxide with a different EPR signature.[1,2] Moreover, the EPR signatures of substrate and product are different enough to allow selective irradiation. Consequently, our methodology will permit to detect the presence of specific enzymes *in vivo* and so, an early detection of diseases.

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Multitarget agents in Alzheimer's disease: development of xanthenone-based derivatives

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Alzheimer's disease (AD) is a neurodegenerative disorder characterized by a gradual decline of cognitive processes. Bulk of evidence supports the AD multifactorial nature as a result of an intricate network of neurochemical factors that need to be simultaneously modulated for a better disease outcome. In fact, the marketed anti-Alzheimer drugs, namely, the acetylcholinesterase (AChE) inhibitors and the NMDA receptor antagonist memantine, are regarded as merely symptomatic, since they work against a single target. This scenario has drawn greater attention on the multitarget-directed ligands (MTDLs) strategy as these molecules may exhibit significant potential on the road to therapeutics for AD [1,2]. Previously, we reported a series of xanthenone-based derivatives, inhibiting animal cholinesterases (ChEs) and Aβ aggregation [3]. Due to the crosstalk between Aβ and tau leading to AD pathological burden, we deemed interesting to deepen the multitarget profile of the library including some novel analogues. Thus, we explored the ability to inhibit human ChEs and tau protein, as a novel biological property with more credentials for a disease-modifying effect. The most promising derivatives were also tested for their ability to restore cell viability against the toxic effects exerted by Aβ42 in primary cultures of cerebellar granule cells from postnatal rats. Therefore, the present work sheds light the multitarget mechanism of action of thioxanthenone derivatives, that may represent valuable therapeutic leads for Alzheimer's disease.

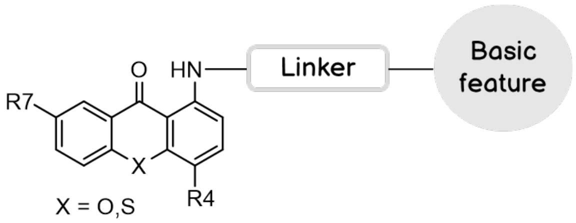

Figure 1: Chemical structures of the investigated xanthenone-based derivatives

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Chemistry Area :

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Strontium isotopic analysis of Antarctic snow samples by multi-collector inductively coupled plasma mass spectrometry

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Determination of Sr isotopic ratios in snow samples from polar regions can provide information about the sources of atmospheric particulate and reconstruct changes in their (relative) contributions over time. This is possible because Sr shows pronounced natural variation in its isotopic composition as one of its isotopes (^{87}Sr) is the decay product of the naturally occurring, long-lived radioisotope ^{87}Rb [1].

This work developed a method to isolate Sr from the matrix, in order to avoid overlapping signals from the isobaric nuclides ^{87}Sr and ^{87}Rb. Due to the low analytical concentration [2, 3], the samples were first pre-concentrated 20 times by freeze-drying, after that Sr was chromatographically isolated from the matrix and analysed by multiple-collector inductively coupled plasma mass spectrometry. Sensitivity was maximized by using an Aridus II membrane desolvating system, high-transmission interface, and an innovative 10^{13} Ω amplifier technology for ^{86}Sr and ^{87}Sr, instead of the standard 10^{11} or 10^{12} Ω amplifiers. The accuracy of the procedure was assessed by replicate analysis of NIST SRM 987 $SrCO_3$ isotope reference material.

Precise and accurate determination of the ^{87}Sr/^{86}Sr isotope ratio was performed in 132 snowpit samples and 12 surface snow samples, collected at Dome C, on the East Antarctic plateau. Strontium concentration was 1-25 ppt, and the measured ^{87}Sr/^{86}Sr isotopic ratios ranged from 0.70819 to 0.71191, in excellent agreement with literature data. Moreover, the achieved precision was fit for the purpose of discriminating between potential source areas with high temporal resolution.

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Posters

Poster Nuùmbers	Name, Surname	University	Title	Theme	Authors
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3	Chemat Aziadé	Avignon	Valorization of spent coffee grounds by 2-methyloxolane as bio-based solvent extraction. Viable pathway towards bioeconomy for lipids and biomaterials.	Environnement	Chemat A.*, Ravi H., Hostequin A., Burney H., Tomao V., Fabiano-Tixier A.S.
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10	Hippolyte Léa	AMU, IMBE	PCA evaluation of parameters influencing the radio-oxidation of XLPEs containing additives in electric cables of power plants	Chimie Physique	Lea Hippolyte, Sandrine Amat, Muriel Ferry and Nathalie Dupuy
63	HOTI GJYLIJE	Turin	Nano spray drying technique as a novel approach to synthesize dextrin-based polymers nanoparticles	Matériaux/chimie organique	Gjylije Hoti*, Fabrizio Caldera, Claudio Cecone, Alberto Rubin Pedrazzo, Adriàn Matencio, Yousef Khazaei Monfared, and Francesco Trotta
53	JOLY Jean-Patrick	AMU, ICR	Activatable Alkoxyamine-based prodrugs that are cytotoxic in the presence of Neutrophil elastase only	Chimie Organique	Joly J-P., Seren S., Bouchaud V., Audran G., Marque S., Voisin P. et Mellet P.

50	Julliard Paul-Gabriel	AMU, Cinam	Meso-poly-halogeno-alkyl-dipyrromethanes as a building block for the synthesis of functional corroles and porphyrins	Chimie Organique/bio-organique	Julliard Paul-Gabriel, Pascal Simon, Siri Olivier, Cortés-Arriagada Diege, Sanhueza Luis, Canard Gabriel
61	Labate Maria	Torino	Non-invasive analysis of late mediaeval goldsmith's materials: piedmontese reliquary busts in comparison	Matériaux	Labate Maria, Aceto Maurizio, Castronovo Simonetta, Operti Lorenza, Agostino Angelo
48	LEFAY Catherine	AMU	A versatile and straightforward process to turn plastics into antibacterial materials	Matériaux	S. Hadiouch, M. Maresca, Y. Guillaneuf et C. Lefay *
54	Leseigneur Guillaume	UCA, ICN	La Stéréochimie des Hydrocarbures Isoprénoïdes comme Fossiles Moléculaires: Conséquences pour la Recherche de Vie Ancienne sur Mars / The Stereochemistry of Isoprenoid Hydrocarbons as Molecular Fossils: Implications for the Search of Extinct Life on Mars	Chimie physique/Chimie Organique	Guillaume Leseigneur, Uwe Meierhenrich
66	Luca Andreo	Turin	Novel organic-inorganic gold iodide perovskites: a new synthetic approach	Matériaux	Luca Andreo, Emanuele Priola, Alessia Giordana, Stefano Pantaleone, Lorenza Operti et Eliano Diana
24	Mabrouk kamel	AMU, ICR	Synthesis and Structure-activity Relationship study of New antimicrobial peptides derived from Polistes gallicus hymenopteran venom.	Chimie Organique	Chloé Mollet, Hamza Oleik, Soioulata Aboudou, Yasmine Boughanmi, Awatef Ouertani, Amor Mosbah, Harold de Pomyers, Didier Gigmes, Marc Marresca & Kamel Mabrouk
15	Marra Francesco	Turin	A lithium amide-promoted preparation of BINOL-derived carboxamides under bench-type aerobic conditions	Chimie Organique	Marra F., Antenucci A., Ghinato S., Prandi C., Blangetti M.
33	MARTINAUX Philippe	UCA	Gold Catalysis: an Entry to Hedonic Materials for Fragrance Industry	Chimie Organique	Martinaux P., Marin C., Michelet V.
49	Massardo Sara	Genova	Non-ambient structural and spectroscopic studies on different doped ceria systems for energy applications	Matériaux	S. Massardo*, C. Artini, M. M. Carnasciali, and M. Pani
64	MASSON Kevin	AMU, ISm2	An Original Donor-Acceptor Cyclopropane for the Thermal Synthesis of Carbocyclic Eight-Membered Rings	Chimie Organique	Kevin MASSON, Jean-Luc PARRAIN, Laurent COMMEIRAS, Paola NAVA and Gaëlle CHOURAQUI

29	Matencio Adrián	Turin	Dextrin-based Nanosponges as an interesting material for drug delivery and bioapplications	Matériaux/Chimie organique	Adrián Matencio, Gjylije Hoti, Fabrizio Caldera, Claudio Cecone, Alberto Rubin Pedrazzo, Silvia Lucia Appleton, Yousef Khazaei Monfared and Francesco Trotta
36	Miranda Murillo Jean-Pierre	Genoa	SYNTHESIS OF COBALT-IRON NANO-STRUCTURED ALLOYS BY HYDROGEN ANNEALING OF SPINEL IRON OXIDE NANOPARTICLES	Matériaux/Chimie Physique	Jean-Pierre Miranda Murillo, Maryam Abdolrahimi, Alexander Omelyanchik, Pierfrancesco Maltoni, Fabio Michele Canepa, Diego Colombara, Davide Peddis
69	Miton Louise	AMU, Ecole Centrale	Anion-pi interactions in confined space	Chimie Organique	Louise Miton; Yoann Cotelle; Alexandre Martinez
8	Moragues Adrien	AMU, Sondes Moléculaires en Biologie et Stress Oxydant	Novel bifunctional probes for oxidized proteins identification/localization	Chimie Organique	Adrien Moragues , Sylvia Pietri, Marcel Culcasi et Sophie Thétiot-Laurent
21	MOUROT Benjamin	AMU, Centre Interdisciplinaire de Nanoscience de Marseille	Coupling principle among polymethines	Chimie Organique	Benjamin Mourot, Simon Pascal and Olivier Siri
58	Munteanu Tatiana	AMU, Cinam	Phenazines chemistry: an unexpected synthetic route towards N- and C-substituted dyes	Chimie Organique	Tatiana Munteanu, Simon Pascal, Olivier Siri
34	Mustière Romain	AMU	Pharmacomodulations of antiplasmodial thienopyrimidinone hit with multi-stage activity	Chimie Organique	Mustière R., Hutter S., Dell'Orco V., Amanzougaghene N., Tajeri S., Amrane D., Paoli-Lombardo R., Deraeve C., Azas N., Verhaeghe P., Mazier D., Primas N. and Vanelle P.
44	Orlandi Valentina	Genoa	Monitoring of the lipid oxidation of dehydrated by-products coming from tuna processing	Environnement	Turrini F., Grasso F., Orlandi V., Dondero L., Grasselli E. et Boggia R
27	Panosetti Marc	UCA, ICN	Design, synthesis and biological evaluation of new RNA ligands targeting miRNA-210: modulation of the circadian clock for cancer therapy	Chimie Organique	Panosetti Marc, Grimaldi Benedetto, Di Giorgio Audrey and Duca Maria
23	Paoli-Lombardo Romain	AMU, ICR	Synthesis and antileishmanial SAR study of new 5- and 7-substituted 3-nitroimidazo[1,2-a]pyridine using SNAr	Chimie Organique	Paoli-Lombardo R. * (1), Primas N. (1), Hutter S. (2), Castera-Ducros C. (1), Bourgeade-Delmas S. (3), Sournia-Saquet A. (3), Valentin A. (3), Azas N. (2),

			and cross-coupling reactions		Verhaeghe P. (3), Rathelot P. (1) and Vanelle P. (1)
68	Papatola Francesco	Genova	Magnetic Nanostructures: A smart platform for biomedical applications	Chimie Organique	F. Papatola 1, M.Salvador 3 , M.Rivas 3, F. Canepa 1 D. Peddis 1,2 and S. Slimani 1,2
13	Pascal Simon	Centre Interdisciplinaire de Nanoscience de Marseille	Quinonediimine ligands for the design of oligomeric coordination complexes and molecular wires	Matériaux	Simon Pascal,* Tatiana Munteanu, Lucien Lavaud, Hassib Audi, Gabriel Canard, Vijai M. Santhini, Christian Wäckerlin, Aleš Cahlík, Jack Hellerstedt, Jesús I. Mendieta-Moreno, Pavel Jelínek, Olivier Siri
65	Pasquini Lucas	AMU, Madirel	Investigation of the hydration and the ionic conductivity of cation and anion – conducting ionomers in buffer solutions	Matériaux/chimie organique	Pasquini L., Knauth P., Di Vona M. L.
20	Percivale Matteo	Genoa	A study of modified Co/SiO2 catalysts for CO2 hydrogenation	Matériaux	Percivale Matteo, Riani Paola* et Garbarino Gabriella*
45	POISSON Marie	AMU	Dihydrogen bioinspired photoproduction	Envionnement /Chimie Organique	Poisson M. Papadakis M. Charalambidis G. Ladomenou, K. Coutsolelos A. G. Massin J. Orio M. Hardré R.
77	Poungsripong peeranuch	Aix-Marseille Université	Nanomaterials synthesis and assembling towards solution-processed elaboration of rectenna devices	Matériaux	Poungsripong Peeranuch, Duché David, Margeat Olivier, and Sciacca Beniamino
17	Pujol Manon	AMU	Engineering of Lytic Polysaccharide MonoOxygenases	Chimie Organique	Pujol M. *(1), Munzone A. (1), Réglier M. (1), Royant A. (2,3), Simaan A. J. (1) and Decroos C. (1)
57	Ralahy Brigino	AMU, CiNAM	Fluorinated dendrimers as 19F-MRI imaging probes	Matériaux	Zhenbin Lyu(1), Brigino Ralahy(1), Ling Ding(1), Yifan Jiang(1), Aura Tintaru(1), Teodora-Adriana Perles-Barbacaru(2), Angele Viola(2) and Ling Peng(1)*
18	Recupido Antonio	AMU	Bifunctional Iodoazolium Salts: Searching for Cooperation Between Halogen Bonding and Hydrogen Bonding.	Chimie Organique	Antonio Recupido, David Givaudan, Bohdan Biletskyi, Olivier Chuzel, Thierry Constantieux et Xavier Bugaut

14	Rico Alexandre	AMU, ICR	Bis-chalcone derivatives derived from natural products as promising near-UV/visible light sensitive photoinitiators of polymerization	Matériaux	Rico A., Chen H., Noirbent, G., Gigmes, D., Lalevée J. et Dumur F
11	Rigoulet Florian	AMU, iSm2	Synthesis of azonia polycylic aromatic atropisomers	Chimie Organique	Florian Rigoulet, Brian Castro Agudelo, Jean Rodriguez et Yoann Coquerel*
43	Rigoulet Florian	AMU, Ism2	Synthesis of azonia polycyclic aromatic atropisomers	Chimie Organique	Florian Rigoulet, Brian Castro Agudelo, Jean Rodriguez et Yoann Coquerel*
52	Roussel Tom	Centre Interdisciplinaire de Nanoscience de Marseille	Self-assembling supramolecular dendrimer nanosystems for tumor imaging	Matériaux	Ling Ding, Tom Roussel, Jingjie Tang, Philippe Garrigue, Beatrice Louis, Ahlem Bouhlel, Aura Tintaru, Zhenbin Lyu, Samantha Fernandez, Laure Balasse, Suzanne Giorgio, Benjamin Guillet, and Ling Peng*
40	Roux Hugo	AMU	Synthesis of new broad-spectrum inhibitors for enterovirus	Chimie Organique	Roux H., Khoumeri O., Touret F., Coluccia A., Gattacecca F., Fanciullino R., Silvestri R., Nougairede A., Roche M. et Vanelle P.
67	SHAO NA	AMU, Ism2	Synthetic economies in 1,3-diols preparation	Chimie Organique	Na SHAO, Jean RODRIGUEZ, Adrien QUINTARD
62	Spennati Elena	Genoa	A study of Ni/SiO2 catalysts for CO2 hydrogenation	Matériaux	Elena Spennati, Paola Riani, Guido Busca, Gabriella Garbarino
79	Tarpa Vlad	Aix-Marseille Univ. – CINaM	One-pot synthesis of a bis-zwitterionic macrocycle via transamination reactions	Organic/Bioorganic Chemistry	Vlad Tarpa, Jean-François Longevial, Michel Giorgi, Gabriel Canard, Simon Pascal, Denis Jacquemin, Olivier Siri
32	Truchon Alexis	UCA, ICN	Gold-Catalyzed One-Pot Cycloisomerization/Nucleophilic Addition /Rearrangement of Acenaphtylene Carbaldehyde	Chimie Organique	Truchon A, Dupeux A, Olivero S, Michelet V.
51	Vivado Davide	Genova	Combining voltammetric and mass spectrometric data to evaluate iron organic speciation in subsurface coastal seawater samples of the Ross Sea (Antarctica)	Environnement / Matériaux	Davide Vivado, Francisco Ardini, Annalisa Salis, Gianluca Damonte, Paola Rivaro

60	YEN-PON Expédite	AMU, Stéréo	Heterohelicenes through 1,3-Dipolar Cycloaddition of Sydnones with Arynes	Chimie Organique	YEN-PON Expédite, FREDERIC Lucas, BUTTARD Floris, THUERY Pierre, TARAN Frédéric, PIETERS Grégory, CHAMPAGNE Pier Alexandre, AUDISIO Davide

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- ☐ **Physical Chemistry**

Orange Peel Waste valorization: a pilot scale biorefinery study

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In a circular economy framework, the valorization of side-products, coming from the orange industries, is very attractive. Thousand tonnes of Orange Peel Waste (OPW) are produced every year, (considering *approx.* 55-60% of raw fruit weight) as a side-product of orange juice production chain [1]. Their untapped potential can represent a viable way to achieve high sustainability level, using innovative technologies, in a large-scale production system. The aim of this work was to employ environmental-friendly processes, non-conventional green extraction methods and possibly scalable solutions on OPW valorization. Essential oils (EOs, consisting mainly of D-limonene) and pectins (recovered from maceration water) were extracted from OPW, performing a microwave-assisted hydrodistillation, using only water as dispersing medium and microwaves as energy source. Scalability of the process was investigated by means of a pilot reactor (Ethos XL, Milestone srl), able to work up to 10 kg of biomass [2]. High added-value products, such as polyphenols (naringin, hesperidin, narirutin and others), were extracted using microwave-assisted subcritical water extraction (MASWE), in a Synthwave reactor. Different condition set (time and temperature) were exploited in order to enhance selectivity and achieving enriched extracts (flavonoids-rich or pectins-rich). Those extraction were also transposed in a pilot-scale subcritical water extraction (SWE) plant, (160L water and 20kg of biomass). The polyphenols obtained were analysed by LC-MS and colorimetric methods, whilst pectins were exploited for ionotropic gelation. Particular attention was paid to downstream process design, adopting scalable and wide-spread technologies. In detail, membrane filtration (nano- or ultrafiltration) allowed to fractionate and concentrate different production streams.

Spray dried extract from aqueous solutions showed unaltered active polyphenols. This case-study led to a biorefinery approach, exploiting non-conventional techniques and process intensification to achieve four different product streams, considering industrial scalability. The most valuable products were EOs, pectin-rich and flavonoid-rich fractions. The residual biomass, rich in primary metabolites, could be further valorized.

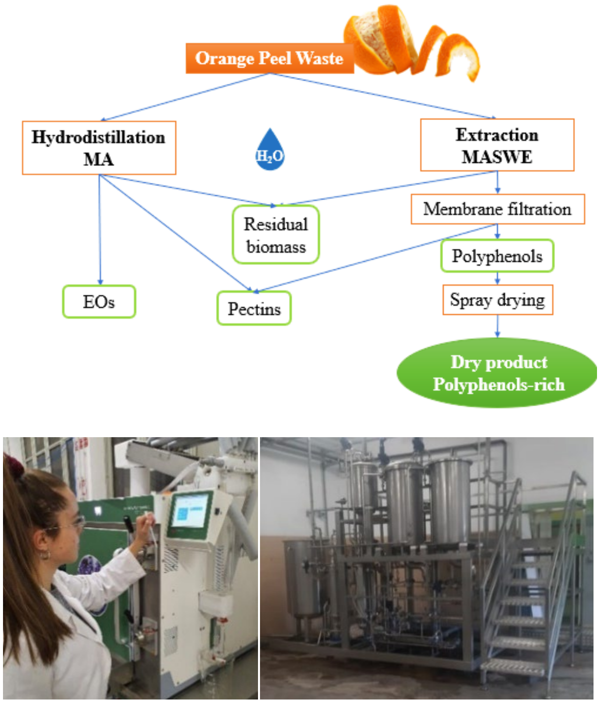

***Figure**: OPW Biorefinery flow chart; Ethos XL; SWE pilot-scale plant.*

[1] Divyani Panwar *et al.*, *Trends Food Sci. Technol.* (2021) 549–562.
[2] Ciriminna R. *et al.*, *ACS Sust. Chem. Eng.* (2017) 5 (*6*) 5578–5587.

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Influence of gamma irradiation on electric cable models: study of additive effects by infrared spectroscopy and dielectric materials

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1. *Aix Marseille Univ, Avignon Université, CNRS, IRD, IMBE, Marseille, France*
2. *Department of Electrical, Electronic, and Information Engineering, 'Guglielmo Marconi', University of Bologna, Viale Risorgimento 2, Bologna 40136, Italy*
3. *Institut de Radioprotection et de Sûreté Nucléaire, PSN-RES, SEREX, 13115 Saint-Paul-lez-Durance CEDEX, France*

Cables, especially their insulation and jacket materials made of polymers, are vulnerable to ageing degradation during normal operation of a nuclear power plant. However, they must remain functional for the entire life of the facility, or even in the event of an accident for cables with a safety requirement. To understand the ageing behavior of cables insulation, this study focuses on crosslinked polyethylene (XLPE)-based model materials. Various additives are added to the polymer formulation to evaluate their impact on ageing. Structure modifications and the behavior of additives are thus investigated in conditions representative of a nuclear power plant atmosphere. The samples are irradiated at room temperature by several gamma doses, up to 374 kGy, with three dose rates (8.5, 77.8 Gy/h and 400 Gy/h) and compared with a non-irradiated sample used as reference. To understand the impact of gamma irradiation on the materials, principal component analysis (PCA) was achieved on infrared spectra and dielectric spectroscopy analyses. The results highlight the effects of ageing depending on the dose rate and on the formulation of the materials, with the identification of different degradation products. A curve resolution study compares the effects of different additives on polymer oxidation and shows that the lower dose rates lead to a higher degradation than the high dose rate.

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Visualizing electron delocalization in contorted polycyclic aromatic hydrocarbons with 3D IMS contour maps

Artigas, A. *(1), Hagebaum-Reignier, D. (1), Carissan, Y. (1)*, Coquerel, Y. (1)*

(1) Aix Marseille Université, CNRS, Centrale Marseille, ISM2, 13397 Marseille, France

Meaningful interactive 3D contour maps of isotropic magnetic shielding (IMS, the negative of isotropic NICS) can be plotted around molecules using pseudo-van der Waals surfaces generated by overlapping spheres made of ghost atoms. 3D IMS maps are reminiscent of the Clar π-sextet model of aromaticity and provide an intuitive, yet detailed and quantitative evaluation of the aromatic, non-aromatic, and antiaromatic character in (highly) contorted polycyclic aromatic hydrocarbons (PAHs). The difference in delocalization patterns between the two faces of the electron circuits in contorted PAHs was clearly visualized. Notably, for large contorted PAHs, some splits of the π system resulted in recognizable patterns typical of smaller PAHs. Importantly, the differences between the delocalization patterns of diastereomeric chiral PAHs could also be visualized. Mapping IMS on pseudo-van der Waals surfaces around contorted PAHs allows the visualization of their superimposed preferred circuits and hence their local and global aromaticity patterns. In this communication, select examples of contemporaneous chemical problems related to aromaticity will be discussed from the 3D IMS contour maps perspective.

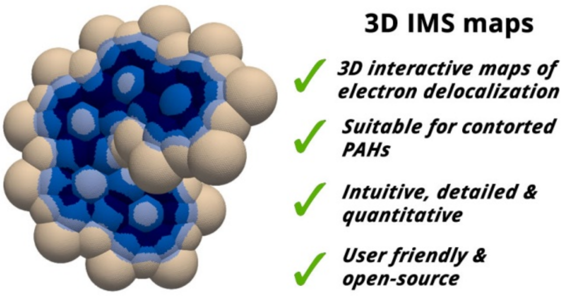

Figure 1 : 3D IMS contour map of [5]helicene.

[1] Artigas, A.; Hagebaum-Reignier, D.; Carissan, Y.; Coquerel, Y. *Chem. Sci.* **2021**, *12*, 13092.

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Ab initio characterization of vanadium species at TiO_2 anatase surfaces

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The selective catalytic reduction (SCR) of NO and NO_2 (NO_x) by NH_3 to N_2 and H_2O is a well-established technology to control the emission of NO_x formed during combustion in diesel engines, power plants and other pollution sources. This type of catalysis is heterogeneous and the most widely used catalyst for the SCR process in power plants is vanadium oxide (vanadia) dispersed on titania oxide (anatase) [1],[2]. Although these systems have been studied extensively in the past, no clear conclusion about a catalytic mechanism, especially on the atomic level, has been made which demonstrates the complexity of the catalytic chemistry of the SCR process [1],[2],[3]. What is known is that *in operando* condition a vanadium +5/+4 redox cycle occurs. Vanadium +4 surface complexes are characterized by the presence of a single unpaired electron in the 3d orbitals and so Electronic Paramagnetic Resonance (EPR) is a useful technique to characterize these systems [4]. Infrared (IR) spectroscopy is also informative as it can monitor the TiO_2 coverage and evaluate the acidity of catalytic sites through the analysis of OH stretching bands [5].

In this work the CRYSTAL code [6] is used to characterize and investigate vanadyl complexes at TiO_2 surfaces. A great advantage in studying catalysts with CRYSTAL is the possibility of easily use hybrid functionals (mixture of the Hartree-Fock and Density Functional Theory approaches): the presence of an exact exchange term deriving from Hartree-Fock calculations allows to deal with electron correlation, something to take in account describing transition metals centres in which the electrons can be highly localized and correlated.

With CRYSTAL different models of vanadium complexes have been modelled considering monomers and dimers on (101) and (001) TiO_2 surfaces, as shown in Figure 1. IR spectra and EPR parameters can be accurately predicted and compared with experimental data to validate the proposed surface complexes and to establish an unambiguous correlation between structure and hyperfine couplings or IR frequencies.

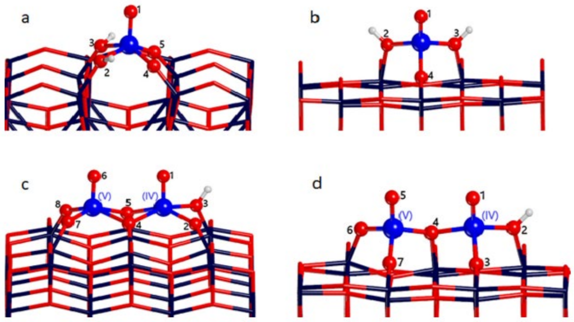

Figure 1 : Computed optimized structures of a) monomeric VO^{2+} at the TiO_2 (001) surface b) monomeric VO^{2+} at the (101) surface c) dimeric V-O-V structure at the (001) surface and d) dimeric V-O-V structure at the (101) surface. Color code: V blue, oxygen red, Ti black, H white. From Ref. [5].

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Generation of powerful organic electron donors by water-assisted decarboxylation of benzimidazolium carboxylates

Guillaume Tintori,(1) Arona Fall,(1) **Nadhrata Assani,**(1) Yuxi Zhao,(1) David Bergé-Lefranc,(2) Sébastien Redon,(1) Patrice Vanelle,(1) and Julie Broggi.(1)

(1) *Aix Marseille Univ, CNRS, Institut de Chimie Radicalaire ICR, Faculté de Pharmacie, 13005 Marseille, France. E-mail: julie.broggi@univ-amu.fr, patrice.vanelle@univ-amu.fr*
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Organic electron donors (OEDs) are powerful reducing agents possessing a neutral organic structure.[1] These OEDs are increasingly used for the reduction of polyfunctional substrates and the initiation of polymerization reactions by spontaneous electron transfer.[2] However, their sensitivity to air and long-term instability necessitate short shelf-life storage under inert atmosphere. To overcome these constraints and improve the practicality of OEDs, new air- and moisture-stable carboxylate precursors, that are easily activated to *in situ* generate the potent electron donor, have been synthesized.[3] The water-assisted decarboxylation of these precursors takes place at room temperature and generates the OED for the reduction of aryl halide derivatives. The resulting aryl radicals are engaged in intermolecular addition reactions.

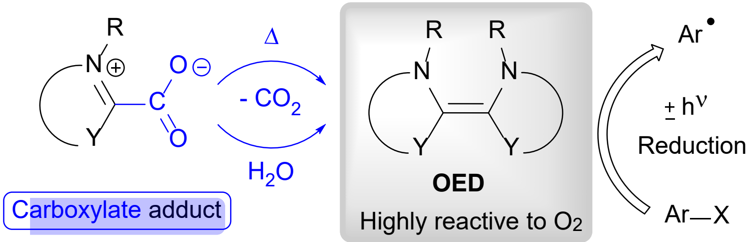

Figure 1: OED formation from air-stable precursors

[1] J. Broggi, T. Terme, P. Vanelle, *Angew. Chem. Int. Ed.* 2014, **53**, 384-413.
[2] J. Broggi, M. Rollet, J-L. Clément, G. Canard, T. Terme, D. Gigmes, P. Vanelle, *Angew. Chem. Int. Ed.* 2016, **55**, 5994-5999.
[3] a) G. Tintori, P. Nabokoff, R. Buhaibeh, D. Bergé-Lefranc, S. Redon, J. Broggi, P.Vanelle *Angew. Chem. Int. Ed.* 2018, **57**, 3148-3153, b) G. Tintori, A. Fall, N. Assani, Y. Zhao, D. Bergé-Lefranc, S. Redon, P.Vanelle, J. Broggi, *Org. Chem. Front.* 2021, **8**, 1197–1205.

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10èmes Journées Franco-Italiennes de Chimie
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Innovative structures for neglected diseases: original amidoximes as antileishmanial agents.

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Leishmaniasis remains one of the most neglected diseases in the world. This disease, caused by a protozoan parasite from over 20 *Leishmania* species, is endemic in 98 countries (mainly developing countries), leading an estimated 700 000 to 1 million new cases and 50.000 deaths annually [1].

Since 2010 and until recently, our project concerns the synthesis of compounds that can be considered as original structures with antiprotozoan properties, it involves amidoximes [2] derivatives presenting a 2,3-dihydrofuran heterocyclic scaffold that could offer a new option for the treatment of leishmania disease. Our work, which focuses on oral treatments, safer and less expensive, is essential due to its status as a neglected disease [3].

The following figure summarizes the principal scaffold modifications developed in a ligand-based approach **(a)** and then the consequent HIT identified **(b and c).** We present herein the process of modulating a diversity of chemical substituents mainly at position 4 **(d)** with the objective to improve the activity, without significantly increasing toxicity and enhancing physicochemical properties such as solubility [4,5].

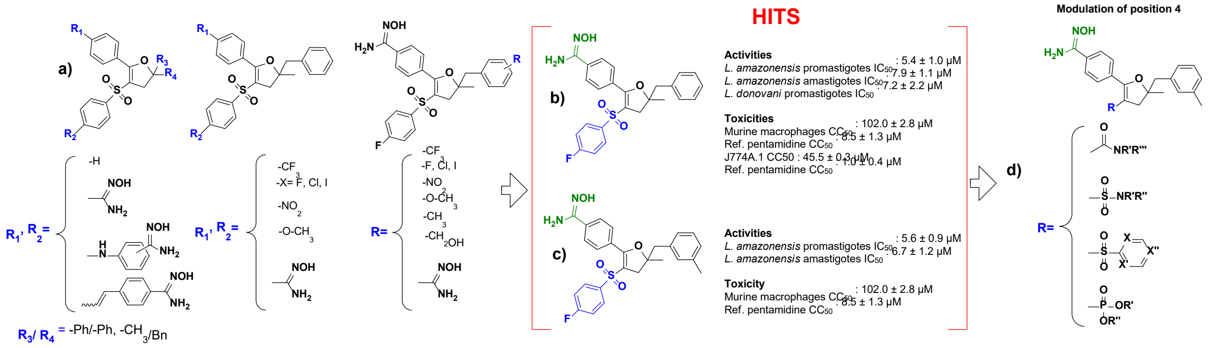

Figure 1: Principal scaffold modifications of compounds presenting a 2,3-dihydrofuran heterocyclic and amidoxime group with interesting biological results on Leishmania strains.

[1] World Health Organization. Leishmaniasis [On line]. Available: https://www.who.int/health-topics/leishmaniasis. [Access February 03, **2022**]

[2] Amidoximes and Oximes: Synthesis, Structure, and Their Key Role as NO Donors. Sahyoun T., Arrault A., Schneider R. *Molecules*, **2019**, *24 (13):2470*, 1-19.

[3] Synthesis and evaluation of original amidoximes as antileishmanial agents. Bouhlel A., Curti C., Dumètre A., Laget M., Crozet M., Azas N., Vanelle P. *Bioorg. Med. Chem.*, **2010**, *18*, 7310-7320.

[4] Synthesis and evaluation of monoamidoxime derivatives: Toward new antileishmanial compounds. Paloque L., Bouhlel A., Curti C., Dumètre A., Verhaeghe P., Azas N., Vanelle P. *Eur. J. Med. Chem.*, **2011**, *46*, 2984-2991.

[5] Original antileishmanial hits: Variations around amidoximes. Tabélé C., Faiões V., Grimaud F., Torres-Santos E., Khoumeri O., Curti C., Vanelle P. *Eur. J. Med. Chem.,* **2018**, *148*, 154-164.

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[*] oscar-leonardo.avendano-leon@etu.univ-amu.fr, christophe.curti@univ-amu.fr

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Mn(OAc)3 free radical chemistry for new antimalarial quinones

Benech A.[*(1)], Khoumeri O.[(1)], Curti C.[(1)], Vanelle P[(1)].

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Our work aimed to synthetize new quinone cycloperoxide derivatives for antimalarial purposes, through radical reactions catalyzed by manganese (III) acetate.[1]
First, a derivative substituted by two aromatic rings was synthesized, serving as a starting material for the development of its methylation.
Then, methylation was applied to other derivatives. In parallel, *in vitro* biological tests evaluated the activity of the first methylated compound on *Plasmodium falciparum* K1 and its cytotoxicity on HepG2 cells.

New molecules have been produced, with yields from 40 to 88%. Methylation, using iodomethane and potassium carbonate, was successful for the starting material (63%).
The IC50 of this first original derivative tested is above 10µM and the CC50 above 25µM. Water solubility of the derivative was limiting for biological evaluation, guiding further synthetic work towards derivatives with aliphatic or alicyclic substituents, and increased solubility.

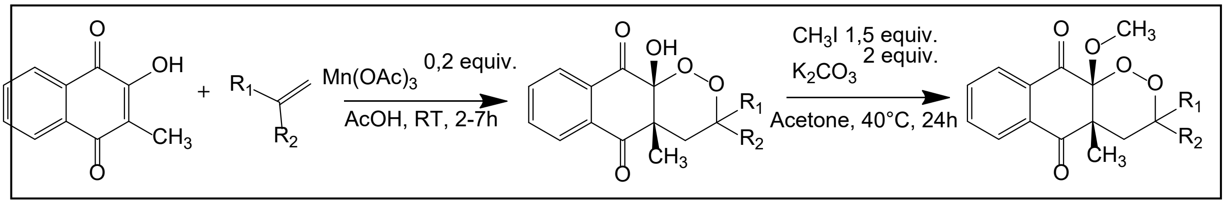

Figure 1 : General scheme for the synthesis of naphtoquinone cycloperoxide derivatives.

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Chemistry Area :

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New ferrocene derivatives as molecular diodes for rectenna applications

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Aix Marseille Univ, CNRS, Institut Nanomatériaux Microélectronique Nanosciences de Provence, UMR 7334, F-13397 Marseille (France)

The proliferation of portable devices, their growing integration into human lives and the surrounding environment, and the necessity to keep them powered have led to an increasing interest in radio frequency (RF) energy harvesting and its use in wireless mobile devices charging. The obvious advantage of harvesting this type of energy is that it is free and green. To scavenge the ambient RF energy emitted by a large number of radio transmitters around us and to convert it as a usable energy, the rectenna i.e. the rectifying antenna should exhibit a specific design. Building on the strong foundations of antenna theory, a rectenna is constructed from a carefully designed antenna that collect/interact with the electromagnetic waves and a diode rectifier which turns this energy into a direct current power (see Figure 1).[1] To allow a maximum transfer of electricity, the response time of the molecular diode is a critical parameter and this latter is intimately related to the size of the gap because it creates an ultra-fast tunnel junction between the rectenna's two electrodes but also to the excited state lifetime of the molecular rectifier. By combining an antenna of adapted size and shape to an ultrafast-converting molecular diode, devices yielding a DC current and operating an efficient electromagnetic wace-to-electron conversion can be obtained. However, such a combination is still a challenge that has been taken up by many and has yet to be accomplished.

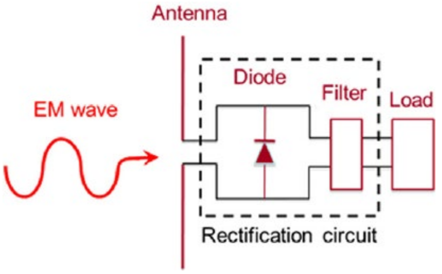

Figure 1 : Working principle of a rectenna

Here, we present unprecedented works on ferrocene derivatives designed as molecular rectifiers. Especially, a special effort is devoted to provide the most favorable orientation of the molecular diode with respect to the antenna and the rectification circuit.

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Chemistry Area :

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Combination of radical and coordination-insertion polymerization controlled by organometallics

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This ongoing work aims to perform the living copolymerization of olefins (ethylene and 1-alkenes) and vinyl polar monomers (VPM, e.g., acrylates or vinyl esters), leading to original copolymer structures.

Coordination-insertion polymerization (CIP) being efficient at polymerizing olefins [1], and radical polymerization (RP) being efficient at polymerizing VPM [2], we are developing a polymerization method simultaneously involving these two modes. Titanium species are active in both CIP and RP: on the one hand, cationic titanium(IV) complexes catalyze the CIP of 1-alkenes [3]. On the other hand, when reduced to neutral titanium(III), titanocene complexes are active in various radical reactions [4], including some that can initiate radical polymerizations, and control them along an organometallic-mediated radical polymerization (OMRP) pathway (Figure 1) [5].

Finding a mechanism to switch between these two forms of titanium could lead to combined CIP-OMRP. As a first step towards this, we evaluate the activity of titanocene(III) chloride (Cp_2TiCl) as a radical inhibitor in the polymerization of various VPM.

In Ti-OMRP, the homolytic dissociation of the Ti-C bond is the step that controls the concentration of radicals. Thus, we also use molecular modelling to evaluate the bond dissociation enthalpy (BDE) of various organometallic titanium complexes.

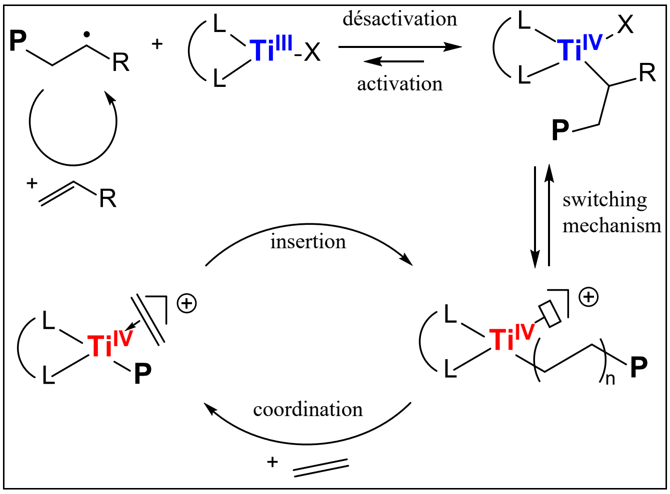

Figure 1: mechanism to switch between cationic/neutral organotitanium complexes for combined CIP-OMRP

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Chemistry Area :

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From animal venoms to new antitumoral molecules: Identifications, physicochemical and pharmacological characterizations

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Cancer is the second leading cause of death in the world (the first in France) after cardiovascular disease. It is predicted that there will be 23.3 million new cases of cancer worldwide by 2030. So far, the success of cancer treatments has been unsatisfactory. This is because the synthetic chemicals used in chemotherapy and radiotherapy, in addition to their low solubility, have extremely high cytotoxicity and cause extensive collateral damage to normal tissues. In addition, many cancer cells can develop chemoresistance or radio resistance after a period of treatment. It is therefore essential to develop new molecules that can block cancer cell division and have less toxic effects on healthy tissues.

Unlike most conventional chemotherapies, many anti-cancer peptides have the ability to specifically and selectively target cancer cells and can also be used in combination with other anti-cancer therapies, with which synergistic effects have been shown to improve outcomes (Lepinoux-Chambaud & Eyer., 2013). Animal venoms contain numerous bioactive peptides, sometimes rich in disulfide bridges, of different lengths, potent, stable, and exerting various multipharmacological actions (Koh et al.2006). In this paper, the results of screening about 100 animal venoms for their ability to inhibit the proliferation of several tumour cell lines will be discussed.

Venoms that do not appear to be described in the literature were selected from all active venoms. All these venoms were fractionated, and their fractions tested for their biological activities. The active sub-fractions were purified and characterised by analytical HPLC and mass spectrometry. The design of lead antitumoral peptides by chemical synthesis and the determination of the mode of action of all these active peptides will be presented and discussed.

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Host-Guest interactions between cyclodextrins and β-phosphorylated nitroxides

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The design of new supramolecular systems could become the next step in the evolution of chemistry in the 21st century. The development of new molecular complexes in which the properties of well-known host molecules are enhanced by the new functions of the attached molecules could be useful in medicine and nanotechnology fields. The synthesis of new supramolecular complexes between cyclodextrins and β-phosphorylated nitroxides is a breakthrough in Host-Guest systems. In fact, these systems can be considered as potential probes to study supramolecular assemblies of cyclodextrins with biomolecules, as reduction agents in aqueous solutions, as polarizing agents for DNP signal enhancement in NMR studies of proteins, and as efficient and selective fluorescence quencher (1).

In this work, a new β-phosphorylated nitroxide was synthesized and the chemical interactions with different types of cyclodextrins were investigated by Electron Paramagnetic Resonance (EPR). In the first time, the results showed a concentration-dependent complexation and a high affinity between the synthesized nitroxide and β-cyclodextrins. In the second time, after recording, this new nitroxide exhibit the expected 6-line EPR signal due to the coupling between the nuclear spins of the nitrogen atom (I_N = 1) and phosphorus atom (I_P = 1/2) and the odd electron on the nitroxyl moiety (2). However, after the nitroxide-cyclodextrin binding, the EPR signal displays several changes compared to the initial spectrum of free nitroxide. These changes allow to identify the type of cyclodextrins involved in the Host-Guest complex.

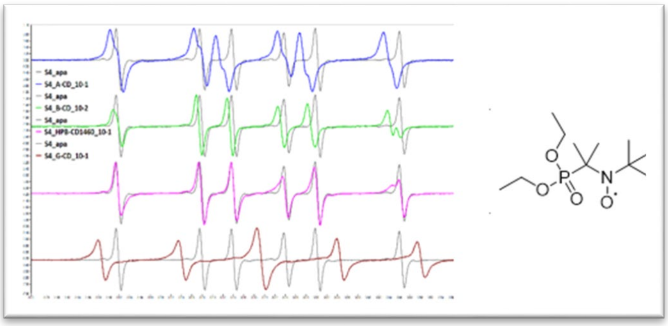

Figure 1: EPR signals between Nitroxide-Cyclodextrins and free nitroxide, in grey, for comparison

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COLLOID-POLYMER MIXTURE IN PROTEIN LIMIT
SANS STUDY

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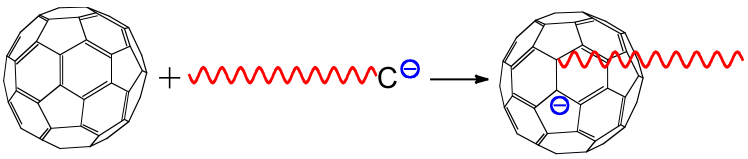
Abstract

Since the work by S. Asakura and F. Oosawa (1), it is known that the addition of non-adsorbing polymers with radius of gyration Rg to a suspension of colloidal particles of much larger radius R (Rg<<R) causes phase separation to occur. This behaviour is of technological importance and results from the so-called depletion interaction. In this work, we consider an inverse asymmetry parameter $\xi=Rg/R>>1$ (Rg>>R) that corresponds to the association of non- adsorbing long polymers with small colloids, referred as "protein limit" (2-5). We study the stability of mixed systems involving long polystyrene chains (PS) and soft nanoparticles made of fullerene coated with short PS chains (6 chains of PS grafted on C60 molecule: C60(PS)6 (6).

Keywords
Protein limit, nanoparticles, inverse asymmetry rapport, adsorption, longs chains of polymer



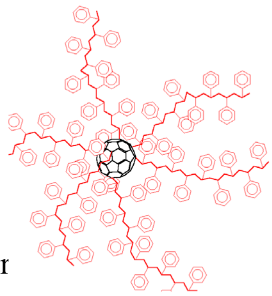


Figure 1: Fullerene C_{60} molecules coated with 6 PS chains (6-ar

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Chemistry Area :

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Who is triaza-macrocycle Cinderella? A study to find the perfect match for Fe(III) complexation

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In recent years, the biomedical research has started to investigate a new generation of contrast agent for MRI based on high spin Fe(III) complexes.[1] The change from the actual Gd(III) based agents concerns not only the properties that determine their efficiency as contrast agents, but also the ligand requirements to ensure the thermodynamic, kinetic and redox stabilities, essential for their approval for clinical use. The stability of a metal complex is determined by the ligand structure and its donor atoms; in particular the donors and the cavity size should be compatible with the chemical properties and the dimension of the Fe^{3+} ion.

The most common chemical structures reported in the literature for Fe(III) complexation are based on the functionalized nine-membered macrocyclic triamine 1,4,7-triazacyclononane. Starting from the 9-membered macrocycle, in this work we systematically evaluated four triazamacrocycles, expanding the size from a 9-membered ring to 10, 11 and 12- membered rings with the aim to determine the most suitable size for Fe(III) complexation. The best basic structure was also evaluated by comparing the functionalization of the three secondary amines with acetic arms or 2-hydroxybenzilic arms. Two of these macrocycles (9 and 12-terms) are commercially available, while the other two (10 and 11-terms) were synthesized using the modified Richman-Atkins procedure, that exploits tosylamides and glycol-tosylates.[2] The protonation constants of the ligands and the stability of the Fe(III) complexes were determined by potentiometry and UV-vis spectrophotometry, evaluating the changes in absorbance as a function of pH at precise wavelength values. In conclusion, the higher is the sum of individual protonation constants, the more basic is the ligand and therefore potentially capable of forming highly stable Fe(III) complexes.

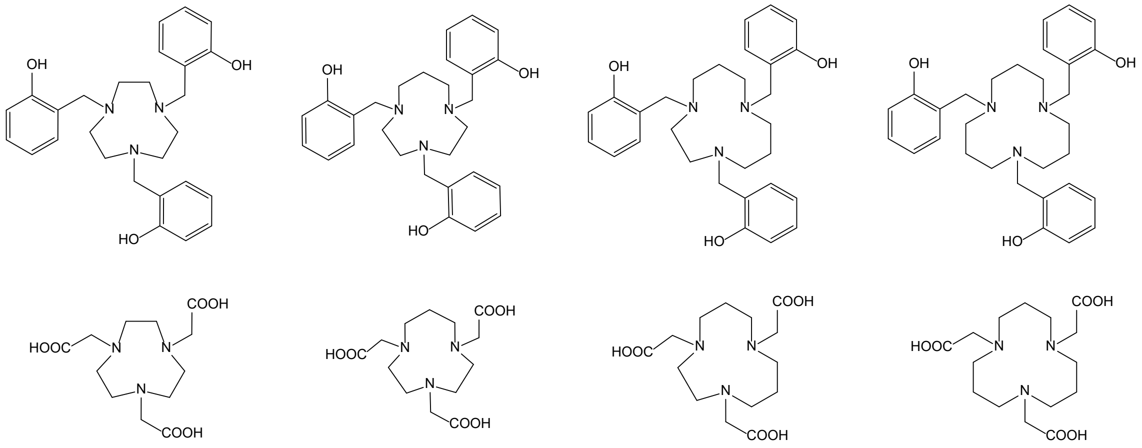

Figure 1: Acetic and 2-hydroxybenzylic macrocycles series studied.

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Designing Benzenoids With Defined Properties

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(2) Aix Marseille Univ, Université de Toulon, CNRS, LIS, Marseille, France

We present the BenzAI program, an open-source software available at the following URL: https://benzai-team.github.io/. This program allows for the generation of benzenoids under structural constraints. Then, it allows for the determination of the local aromaticity of the hexagons and the calculation of IR spectra provided that the generated benzenoids have less than 10 hexagons. In this poster, we show concrete applications of this software in astrochmistry, molecular design and molecular magnetism.

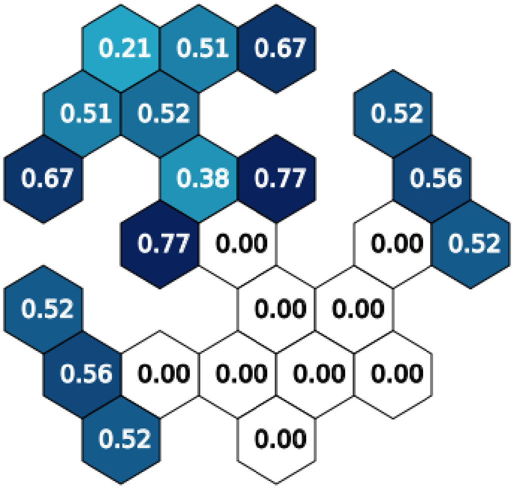

Figure 1 : Benzenoid generated with a given irregularity parameter of 0.8.[1] Values indicate local aromaticityas computed by the BenzAI software within the Lin and Fan approach[2]

[1] Carissan et al. Principles and Practice of Constraint Programming 690–706 (2020)
[2] Carissan et al. Principles and Practice of Constraint Programming 673–689 (2020)

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INFLUENCE OF $Cd_{1-x}Zn_xS$ ON THE AGEING OF LINSEED OIL

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(2) *Swedish National Heritage Board, Dep. of Conservation, Artillerigatan 33A 62138, Visby, Sweden*

$Cd_{1-x}Zn_xS$ solid solution have been employed as pigments since the 1840s, thanks to their bright shades from yellow to orange. They were produced by means of either dry or wet process and present cubic, hexagonal or amorphous phases [1,2]. Paintings in which these pigments were used can show remarkable, but not homogeneous, signs of degradation after limited time periods. The aim of this work is to understand how the pigments differences, to parity of elemental composition, can influence the degradation of a linseed oil binder. Pigments with progressive substitution of Cd were synthetized by adapting the procedures described in early literature, obtaining powders with different crystalline structure and morphology. The starting materials were characterized by means of XRF, XRD, SEM, FTIR-ATR, Reflectance Spectroscopy and PL. The powders have been used to reproduce paint samples with a binder/pigment ratio of 1:1 that were exposed to artificial ageing and analyzed with FTIR-ATR and µ-Fader for characterization and monitorization of binder and overall color changes, respectively. Artificial ageing was carried out for 8 weeks under two different environmental settings: a) outdoor environment, exposure to simulated sunlight and b) indoor environment, exposure in the dark to 65% relative humidity at 30°C in a climate chamber; for each sample, weekly analyses were performed Multivariate chemometric methods such as Principal Component Analysis (PCA) were applied to the spectroscopic and colorimetric data. The results of the accelerated ageing trials for the two ageing methods showed that alterations trends are different based on structure and degree of crystallinity of the pigments. Moreover, these preliminary results show how changes in the IR spectra suggest a degradation detectable before the yellowing of the binder.

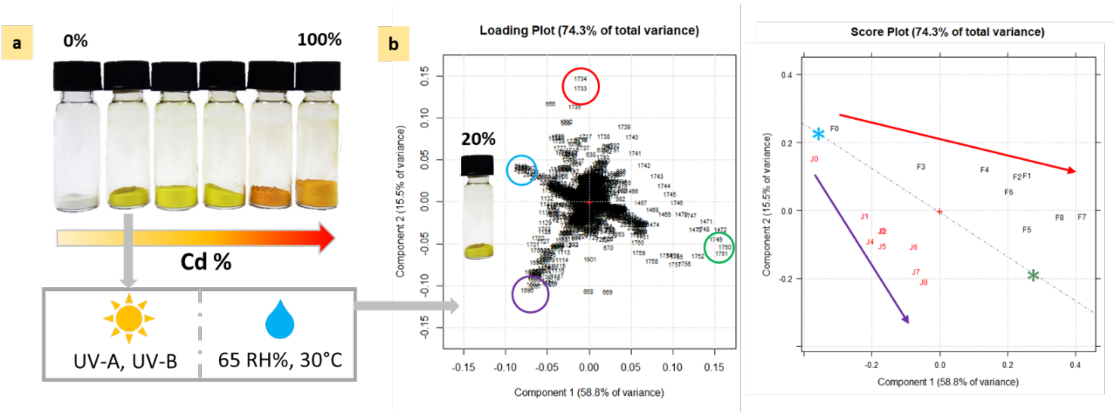

Figure 1: a) Pigment powders of Zn.CdS solid solutions, 20% Cd content increase; b) Loading and Score plots of FTIR-ATR data of sample Cd-20% with 8 weeks ageing

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Chemistry Area :

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Valorization of spent coffee grounds by 2-methyloxolane as bio-based solvent extraction. Viable pathway towards bioeconomy for lipids and biomaterials.

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(2) Atelier LUMA, Parc des Ateliers, F-13200 Arles, France

This study attempts to shed light on the efficacy of the solvent 2-methyloxolane (2-MeOx) as an alternative for hexane in defatting spent coffee grounds (SCG). Higher lipid yields were obtained with the bio-based solvent dry 2-MeOx (13.67%) and water-saturated 2-MeOx (15.84%) compared to hexane oil yield which is of petroleum origin and is a known neurotoxin. Palmitic acid and linoleic acid were the principal fatty acids identified. The fatty acid profile of coffee oils obtained with hexane, dry 2-MeOx and aqueous 2-MeOx were similar. Lipid hydrolysis was observed in oils extracted with 2-MeOx which warrants further investigation. The residual caffeine content in the defatted SCG was highest when hexane was used highlighting better solubility of methylxanthine compounds in the solvent 2-MeOx. Within the purview of the biorefinery framework defatted SCG was pressed (Atelier Luma, Tarbes, France) to obtain a board-type material which when optimized can be used as a packaging alternative. Even stationaries such as enclosures for pens were fabricated where 50% of the SCG was used as ingredient in the formulation.

Figure 1. *Biorefinery of spent coffee grounds focusing on non-food applications of spent coffee grounds.*

[1] Aziadé Chemat, Harish Karthikeyan Ravi, Anne Claire Hostequin, Henna Burney, Valérie Tomao and Anne-Sylvie Fabiano-Tixier. Valorization of spent coffee grounds by 2-methyloxolane as bio-based solvent extraction. Viable pathway towards bioeconomy for lipids and biomaterials. OCL, 29 (2022) 7
DOI: https://doi.org/10.1051/ocl/2021052

Chemistry Area :

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Amphiphilic poly(aminoester) dendrimer for effective delivery of siRNA therapeutics

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(2) *Aix-Marseille University, CNRS, Centre Interdisciplinaire de Nanoscience de Marseille (CINaM), France*

Dendrimers, by virtue of their well-defined dendritic structure and cooperative multivalency, are particularly promising materials for biomedical applications.[1-2] Specifically, we will present here a biodegradable amphiphilic dendrimer bearing poly(aminoester) dendron for the delivery of small interfering RNA (siRNA) and gene silencing.[3] Notably, this dendrimer was able to interact with siRNA, protect siRNA against degradation and promote cellular uptake, while being readily disintegrated upon enzymatic action and releasing siRNA for effective gene silencing. More importantly, this dendrimer combines delivery advantages of both lipid and polymer vectors, demonstrating superior siRNA delivery and gene silencing performance without notable toxicity. Our study provides a new perspective in the application of dendrimer chemistry for safe and effective siRNA delivery, which can be further extended and translated in the clinical implementation.

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A small ring into the bigger picture

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Benzocyclobutenes (BCBs) derivatives are of significant interest due to the cooperative effects between the thermodynamic stability coming from the aromatic ring and the high reactivity of the strained cyclobutene moiety. In this regard, BCBs have been used as an original building block for the synthesis of natural products[1] and also as precursors for the development of polymers.[2]

On the other hand, small rings represent a valuable three-atoms building element in the search to reach molecular complexity in an atom economical manner and often participate in fascinating chemical transformations.[3] This release of ring tension usually allows for a scalable, rapid and controlled synthetic access to the expected target molecules.

In this context, a new class of donor-acceptor cyclopropanes-DACs **1** has recently been developed in our laboratory combining a silyl protected cyclopropanol with an α,β-unsaturated ester. Gratifyingly, the latter delivered the corresponding highly functionalized benzocyclobutenes **2** in good yields.

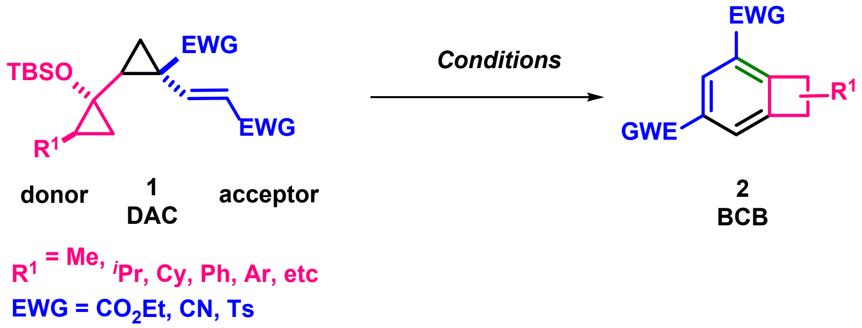

Figure 1: Cascade reaction from donor-acceptor cyclopropane to benzocyclobutene

Strategies, synthesis of precursors, scope and limits of the reaction and mechanistic studies will be described and discussed.

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[2] a) G. Mehta, S. Kotha, *Tetrahedron,* **2001**, *57*, 627-634. b) X. Wei, H. Hu, X. Li, Q. Yin, L. Fan, Y. Huang, J. Yang, *J. Appl. Polym. Sci.,* **2019**, *136*, 47458.
[3] B. Biletskyi, P. Colonna, K. Masson, J.-L. Parrain, L. Commeiras, G. Chouraqui, *Chem. Soc. Rev.*, **2021**, *50*, 7513-7538.

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Chemistry Area :
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Aryne atropisomers: enantioselective generation and synthetic applications

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Arynes are strained short-lived species that must be generated in situ, most commonly through the *ortho*-elimination of suitable aromatic precursors [1]. Arynes are generally planar molecules, but enantioenriched aryne atropisomers having a biaryl stereogenic axis vicinal to the reactive triple bond were recently demonstrated to exist, which unlocked new options for the synthesis of enantioenriched atropisomers [2]. The half-life of an aryne atropisomer in the presence of furan in solution was determined experimentally to be less than 100 ns at –20 ºC [3]. Synthetic equivalents of bis(aryne) atropisomers can also be easily produced in situ and undergo the standard aryne cycloaddition chemistry in an enantiospecific manner [3]. Among others, the (bis)aryne atropisomer synthetic equivalents have allowed the practical syntheses of a small (bis)nanographene atropisomer, a (bis)triptycene atropisomer, and an isotopically chiral (bis)anthracene atropisomer, with full (or nearly so) retention of the stereochemical information from the aromatic precursors (Figure 1).

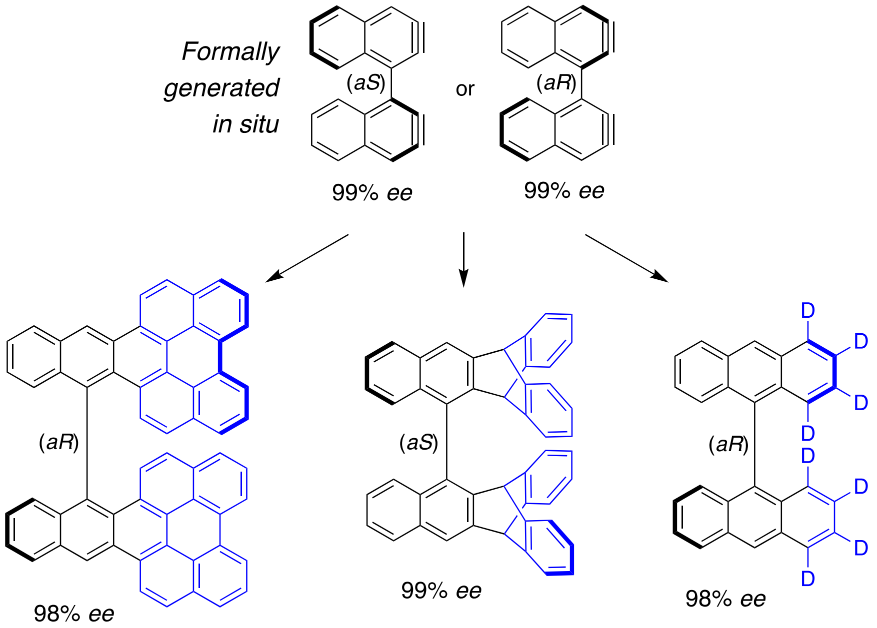

Figure 1 : Bis(aryne) atropisomers for the enantiospecific synthesis of atropisomers

[1] J. Shi, L. Li, Y. Li, o-Silylaryl Triflates: A Journey of Kobayashi Aryne Precursors. *Chem. Rev.* **2021**, *121*, 3892–4044.
[2] Y.-L. Wei; G. Dauvergne, J. Rodriguez, Y. Coquerel, Enantiospecific Generation and Trapping Reactions of Aryne Atropisomers. *J. Am. Chem. Soc.* **2020**, *142*, 16921–169.
[3] Unpublished.

Ultrafast chemo- and regioselective anionic Fries rearrangement promoted by lithium amides under aerobic conditions in sustainable reaction media

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The regiospecific preparation and modification of (poly)substituted aromatic compounds constitute a fundamental synthetic approach towards selected target molecules of biological and agrochemical interest. The anionic *ortho*-Fries rearrangement (A*o*F) represents an interesting protocol for the preparation of salicylamide derivatives.[1] This process arises from the directed *ortho*-metalation (D*o*M) of *O*-aryl carbamates promoted by organolithium reagents and proceeds in the absence of an external electrophile upon slow warming to room temperature.[2] Strictly reaction conditions, such as low temperatures, dry ethereal solvents and inert atmosphere, are typically required for this transformation. However, in recent years the chemistry of polar organometallic compounds has experienced a deep revolution. The use of Deep Eutectic Solvents (DESs) and cyclopentyl methyl ether (CPME) as sustainable reaction media under simple experimental conditions (room temperature, open air) has been recently reported for organometallics-promoted transformations.[3] Building upon these findings, we have investigated the possibility to promote the anionic *ortho*-Fries rearrangement of *O*-aryl carbamates using alkyllithium reagents and lithium amides under aerobic conditions in CPME and DESs as sustainable reaction media. In particular, we focused our attention on the use of hindered lithium amides as metalating agents to promote D*o*M/A*o*F processes under aerobic conditions, which has never been explored so far. Our findings in terms of selectivity, substrate scope and applications will be presented.

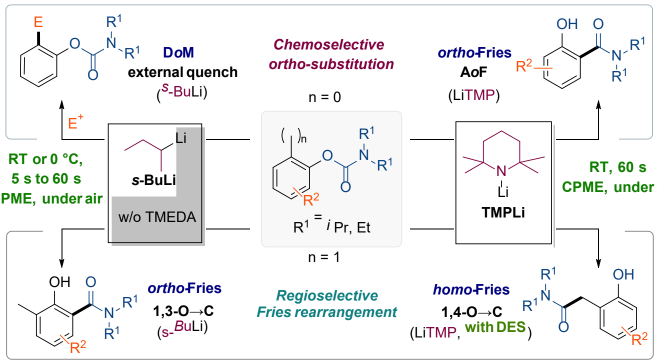

Figure 1: Ultrafast chemo- and regioselective anionic Fries rearrangement under aerobic conditions.

[1] M. A. J. Miah, M. P. Sibi, S. Chattopadhyay, O. B. Familoni, V. Snieckus, *Eur. J. Org. Chem.* **2018**, *2018*, 440-446
[2] M. P. Sibi, V. Snieckus, *J. Org. Chem.* **1983**, *48*, 1935-1937
[3] (a) S. Ghinato, G. Dilauro, F. M. Perna, V. Capriati, M. Blangetti, C. Prandi, *Chem. Commun.* **2019**, *55*, 7741-7744; (b) D. Arnodo, S. Ghinato, S. Nejrotti, M. Blangetti, C. Prandi, *Chem. Commun.* **2020**, *56*, 2391-2394; (c) S. Ghinato, D. Territo, A. Maranzana, V. Capriati, M. Blangetti, C. Prandi, *Chem. Eur. J.* **2021**, *27*, 2868-2874; (d) S. E. Garcia-Garrido, A. Presa Soto, E. Hevia, J. Garcia-Alvarez, *Eur. J. Inorg. Chem.* **2021**, *2021*, 3116-3130.

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Chemistry Area:

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Production of nanoplastics and their ecotoxicological effects on the photosynthetic pigments of marine microalgae

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The ubiquity of nano/microplastics in the environment could pose a largely unknown threat to aquatic ecosystems and public health. The MEDITPLAST project (Véolia, Agence de l'Eau RMC) aimed to determine the sources of this pollution in the Bay of Toulon (discharges from wastewater treatment plants, etc.) and its fate through the development of innovative methods of nano/microplastics sampling and analysis. The ecotoxicological risk represented by these particles on marine coastal plankton, the basis of foodweb, was also studied.

Nanobeads (~100-200 nm) of different plastics (PS, HDPE, LDPE, PP, PVC and PET) were first synthesized from raw plastic particles of 250 µm to 5 mm according to a modified protocol from Balakrishnan et al. (2019). The concentration and the size distribution were determined by nanoparticle tracking analysis (NTA NS-500, Malvern), while their shape was inspected by scanning electron microscopy (SEM).

The green microalga *Chlorella vulgaris* Beijerinck, 1890 and the red microalga *Porphyridium purpureum* (Bory) KM Drew & R Ross, 1965 were then exposed to each of these nanobeads at concentrations from 10^3 to 10^7 particles/mL. Their physiological state was monitored during a five-day experiment by UV-visible spectroscopy and compared to a control. A dose-effect relationship was assessed based on daily changes in the spectral characteristics of photosynthetic pigments: chlorophylls (~640-720 nm) and carotenoids (~390-530 nm) for *C. vulgaris* ; chlorophylls (~645-705 nm), carotenoids (~400-455 nm) and phycoerythrin (~480-585 nm) for *P. purpureum* (Figure 1). The study of peak areas could provide relevant information on the photosynthetic efficiency of marine microalgae in case of environmental disturbance.

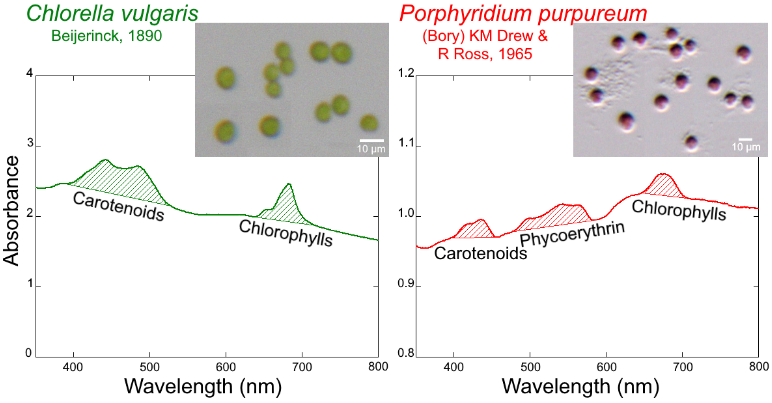

Figure 1: Absorbance spectrum and composition in photosynthetic pigments of the green microalga Chlorella vulgaris *and the red microalga* Porphyridium purpureum.

[1] Balakrishnan G, Déniel M, Nicolai T, Chassenieux C, Lagarde F (2019) Towards more realistic reference microplastics and nanoplastics: preparation of polyethylene micro/nanoparticles with a biosurfactant. Environmental Science: Nano 6 (1): 315-324.

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Some Ionic liquids catalyzed Biginelli reaction under solvent free conditions

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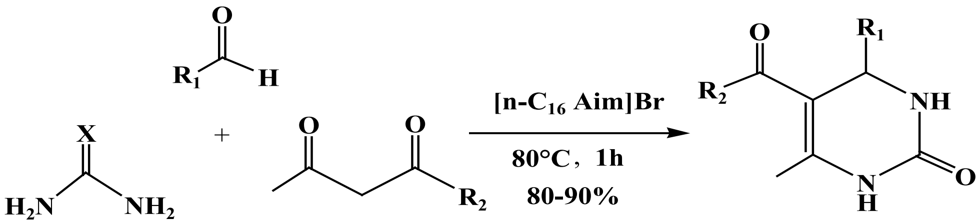
3,4-Dihydropyrimidin-2(1H)-ones were synthesised in high yields by one-pot three component Biginelli condensation[1] in the presence of room temperature ionic liquids such as 1-hexadecyl-3-allylimidazolium bromide [n-C_{16}Aim]Br as catalysts under solvent-free conditions. These DHPMs represent a heterocyclic system of remarkable pharmacological efficiency, including antiviral, antibacterial and anti - inflammatory activities.[2,3] This method, in comparison with the classical Biginelli reaction, has several advantages including high yield, short reaction time and experimental simplicity. The structures of the synthesized compounds have been elucidated by IR and NMR.



R_2=EtO, MeO ; R_1=Ph, 4-OH-C_6H_4, 4-MeO- C_6H_4

Figure 1 : Synthesis of 3,4-dihydropyrimidin-2(1H)-ones catalyzed by ionic liquids.

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[3] *RamandeepKaur[a]SandeepChaudhary[a]KapilKumar[a]Manish K.Gupta[b]Ravindra K.Rawa* European Journal of Medicinal Chemistry **2017** Vol 132, 26 , 108-134.

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Chemistry Area :
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Efficient synthesis of *N*-substituted 1,3-thiazin-2-ones containing sulfonamide

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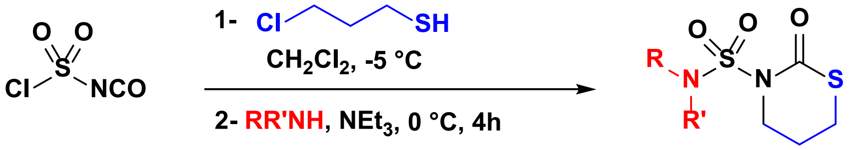
Thiazinones[1] containing sulfonamides are experiencing increased interest due to their importance in the design and development of new molecules of potential pharmaceutical interest. The synthesis of a series of new *N*-substituted 2*H*-1,3-thiazin-2-ones[2] containing sulfonamide is described. The compounds were synthesized in good yields in a one-pot reaction starting from commercially available chlorosulfonyl isocyanate (CSI), 3-chloro-1-propanethiol, and various primary and secondary aliphatic, aromatic or heteroaromatic amines. The structure of one of these compounds was established by X-ray crystallography. The compounds are being evaluated for their biological activity.



20 examples: rapid, efficient, inexpensive

Figure 1: Synthesis of N-substituted 2H-1,3-thiazin-2-ones.

[1] Bentley R. *Chem. Soc. Rev.* **2005**, *34*, 609-624.
[2] Bendif B., Dumur F., Ibrahim-Ouali M. Arkivoc **2021**, *8*, 253-264.

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In situ generation of Ag nanoparticles during photopolymerization : 3D/4D printing applications

Chen H.(1,2), Noirbent G.(3), Liu S.(1,2), Gigmes D.(3), Lalevée J. (1,2) et **F. Dumur**(3)

(1) Université de Haute-Alsace, CNRS, IS2M UMR 7361, F-68100 Mulhouse, France Institute Address
(2) Université de Strasbourg, France.
(3) Aix Marseille Univ, CNRS, ICR, UMR 7273, F-13397 Marseille France

Silver nanoparticles (AgNPs) play a crucial role in biology and medical research as their extensive and efficient antibacterial activity and high electrical and thermal conductivity. However, the generation of them with a certain morphology under mild conditions (under air, solvent-free, room temperature, etc.,) is still a huge challenge. Herein, a simple one-step method is proposed to generate AgNPs in situ at room temperature under air by combining the photopolymerization process with the formation process of AgNPs within a few minutes. In detailed, 12 different dyes based on 2,5-diethylene-cyclopentan-1-one were first synthesized and used as high-performance type II photoinitiator. When using in conjunction of *bis*-(4-*tert*-butylphenyl)iodonium hexafluorophosphate (Iod) and ethyl 4-dimethylaminobenzoate (EDB), they can effectively boost the free radical photopolymerization (FRP) of polyethylene glycol diacrylate (PEG-DA) and the cationic photopolymerization (CP) of 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate (EPOX) upon irradiation with LED@405 nm. Furthermore, all the formulations containing/without AgNPs can be successfully used to perform the direct laser write experiment. However, even if all of the obtained 3D patterns exhibited reversible swelling performance and shape-memory effects caused by swelling and dehydration for the access to 4D printing, the presence of AgNPs will affect these properties (See Figure 1)

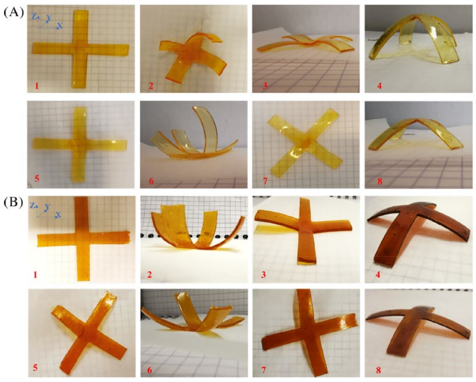

Figure 1 : Examples of 4D-printed polymers

[1] H. Chen, G. Noirbent, S. Liu, Y. Zhang, K. Sun, F. Morlet-Savary, D. Gigmes, P. Xiao, F. Dumur and J. Lalevée *J. Polym. Sci.* **2021**, *59*, 843–859.

Chemistry Area :

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Alkoxyamines Designed as Potential Drugs against Plasmodium Parasite

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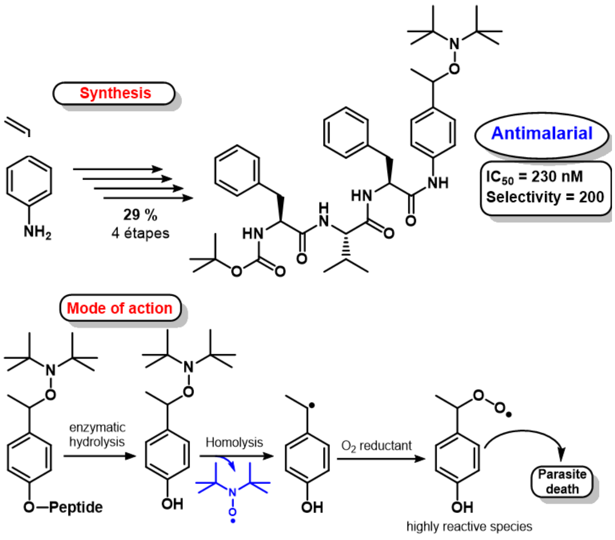
Université Aix Marseille, Institut de Chimie Radicalaire, Marseille

Malaria is a disease caused by *Plasmodium falciparum* : the most harmful parasitic species for humans. According to the World Health Organization (WHO), this disease affects 625,000 people a day and 1,120 die.

Faced with this major public health problem, several treatments have been used for several years, mainly "Artemisinin-based Combination Therapies" (ACTs). These drugs were quite effective in the 90s and 2000s in treating malaria. However, since 2013, the emergence of resistant strains to these treatments has revealed their limits.

Therefore, the research for more active substances is a major challenge for the eradication of this pathogen. During our project RADICAL, we have tested more than 100 different alkoxyamines that exhibited moderate antiparasitic activities.[1]



So, we recently turned our interest to the above-described enzymatic activation Boc-Phe-Val-Phe-alkoxyamine prodrugs. The synthesis of the peptide-linked to alkoxyamine was realized in 4 steps with an overall yield of 29%.

This very simple alkoxyamine based on an anilido moiety linked to a tripeptide targeting a *P. falciparum* protease digestive vacuole (plasmepsin) was tested.

This prodrug exhibited a very promising activity, with **IC_{50} value = 200 nM against *P. falciparum***, and a **selectivity index larger than 200.** This molecule also exhibits antischistosomal activity. **This result is very encouraging for exploring more carefully this approach.**

As reported in the above scheme, the mechanism of action of the peptide-linked to alkoxyamine is : first - hydrolysis of the peptide to lead the formation of phenol derivative. Then, this phenol is unstable and homolyses to afford reactive alkyl radicals and a nitroxide. Finally, the radical alkyl react to oxygen to give a ROS would destroy the pathogen by oxidative stress.

[1] Reyser, T. et al *Molecules* **2020**, *25*, 3838

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Reversible or irreversible catalysis of H^+/H_2 conversion by FeFe hydrogenases

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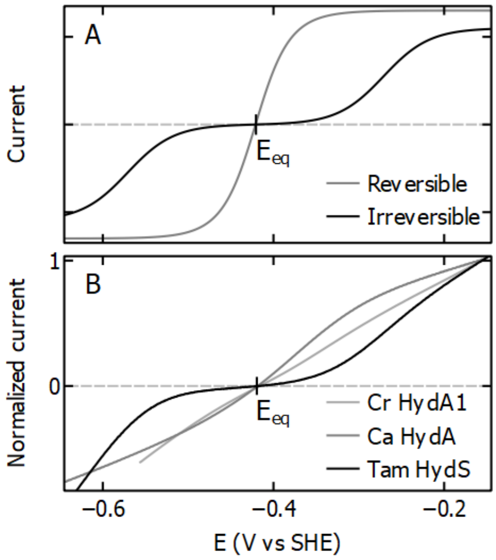
b. Molecular Biomimetics, Department of Chemistry-Ångström, Uppsala University, Uppsala, Box-523, 751 20, Sweden.



FeFe Hydrogenases are metalloenzymes present in bacteria, archaea and eukaryotes. These enzymes catalyse the oxidation and evolution of molecular hydrogen, an important energy vector in the metabolisms of these microorganisms.

Different hydrogenases can have very different catalytic properties. One of these properties is catalytic reversibility, which is defined here in relation to the thermodynamic driving force (overpotential in the case of electrochemical experiments) the enzyme needs to start catalyzing the reaction in either one or the other direction[1]. Prototypical hydrogenases, (i.e. HydA1 from *Chlamydomonas reinhardtii* and *Clostridium acetobutylicum,* grays in panel B) are reversible catalysts: a tiny departure of the electrode potential from the equilibrium potential of the H+/H_2 couple leads to a significant hydrogen oxidation or proton reduction current. Recently, sensory hydrogenases (HydS) have been characterized. A particular putative sensory hydrogenase, from *Thermoanaerobacter mathranii* (*Tam*), has a catalytic response (shown in black in panel B) very different from that of prototypical hydrogenases, as it requires a large overpotential to start catalysing the reaction in either direction[2]. We characterized this irreversible catalytic response using protein film electrochemistry[3], demonstrating that: (1) an ordered reaction mechanism can lead to an irreversible catalytic response; (2) slow electron transfer between the electrode and the enzyme is not the reason behind this irreversible behaviour[4]. We therefore conclude that irreversibility is an intrinsic property of *Tam* HydS; this finding opens new questions about the molecular differences with the prototypical hydrogenases, and the physiological function of such irreversibility.

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DETECTION ET QUANTIFICATION DES CENTRES AZOTE-LACUNE DANS LES DIAMANTS SYNTHETIQUES PAR RPE

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L'amélioration de la sensibilité est un enjeu majeur dans le domaine de la Résonance Magnétique Nucléaire. Afin d'atteindre cet objectif, la Polarisation Dynamique Nucléaire (DNP) est une technique déjà largement utilisée mais possédant de nombreuses contraintes. D'autres méthodes alternatives prometteuses sont en cours de développement. Parmi elles, l'utilisation des centres Azote-Lacune (centres NV) [1,2], défauts présents dans les diamants, en tant qu'agents d'hyperpolarisation grâce à un rayonnement laser (532 nm). Cependant, cette méthode requiert de connaître la quantité de centres NV présents dans les diamants. Pour cela, une quantification est effectuée à l'aide d'un appareil de Résonance Paramagnétique Electronique (RPE) à onde continue. Les diamants sont placés dans des tubes en quartz et à 1 cm du centre du résonateur afin d'éviter toute saturation. Le logiciel EPR Xenon_Nano permet par la suite de donner la quantité d'espèces présentes dans le diamant analysé. Nos résultats montrent que la quantité d'irradiation subie par le diamant dans le but de créer les centres NV influence bien la valeur des concentrations en centres NV. Nos résultats montrent aussi que le positionnement et l'orientation du diamant dans l'appareil RPE modifient la position des raies des centres NV sur le spectre RPE, ce qui permet de connaître l'orientation des centres NV dans l'espace.

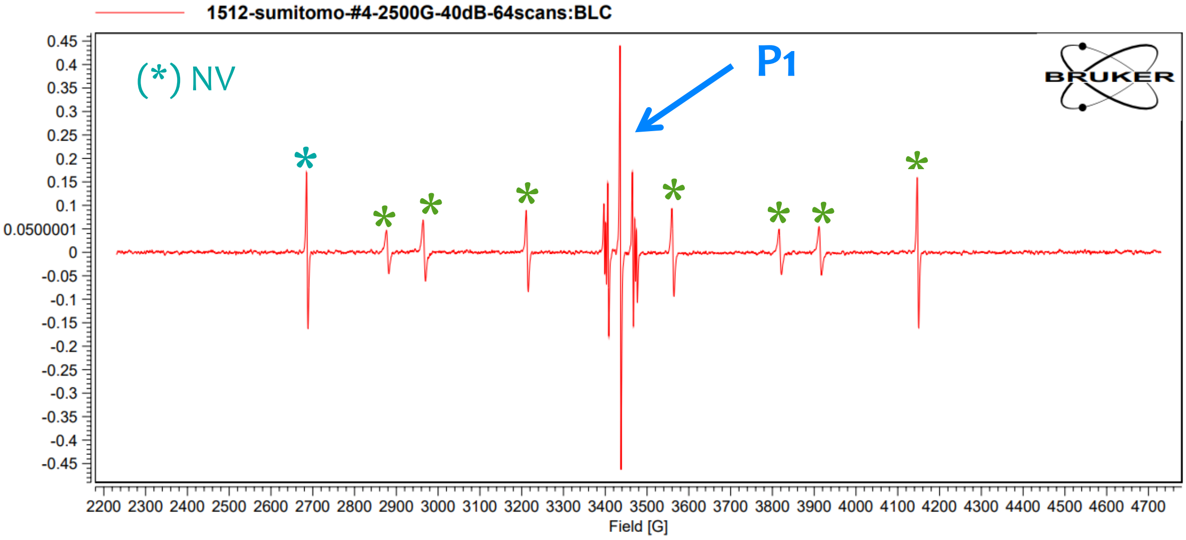

Figure 1 : Spectre RPE d'un diamant HPHT Sumitomo (1.5x1.5x1.2mm) irradié afin d'obtenir des centres NV.

[1] Suter, D.; Jelezko, F. *Progress in Nuclear Magnetic Resonance Spectroscopy* **2017**, *98–99*, 50–62.
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[3] Drake, M.; Scott, E.; Reimer, J. A. *New J. Phys.* **2015**, *18* (1), 013011
[4] Scott, E.; Drake, M.; Reimer, J. A. *Journal of Magnetic Resonance* **2016**, *264*, 154–162.

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Design of new iminium salts involved in the fight against Malaria

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(2) Aix Marseille Univ, IHU Méditerranée Infection, UMR VITROME, Équipe 7, Marseille, 13005, France

Like most parasites, *Plasmodium falciparum,* responsible for the most severe forms of malaria, has developed resistances to known marketed drugs such as chloroquine. [1] With this resistance emergence, the number of deaths from malaria increases each year (WHO: 627 000 in 2020 up which 80% are children under the age of 5) [2]. In order to fight this scourge which particularly affects African populations, our research focus on the development of new drugs against *P. falciparum*.

In that respect, we synthetized and tested different families of iminium salts (pyridinium, quinazolinium, quinolinium and imidazolium) on the *Plasmodium falciparum K1* strain. Our structure activity relationship study showed that the quinolinium and quinazolinium structures were the most promising series. The best activities were observed for *N*-heterocyclic structures bearing electron-donor substituents. As well, the connection of two iminium salts through a carbon chain drastically improved the activity. Our best candidates possess chloroquine-like activities (IC_{50} = 0,5 µM vs 0,23µM for the chloroquine) and low cytotoxicities on HepG2 human hepatocytes ($CC_{50} >$ 75 µM).

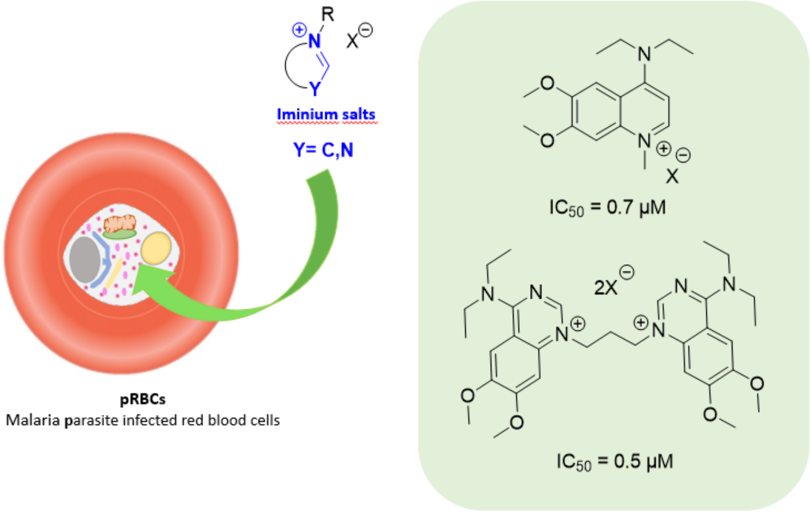

Figure 1: Iminium salts tested on P. falciparum

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[2] World Health Organization (WHO); World Malaria Report 2021

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Difference between NiAl-NO_3 and NiFe-NO_3 LDHs applied as anodes in Sodium Ion Batteries (SIBs) based on sodium alginate binder.

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In recent years, the demand of lithium for batteries grown up dramatically leading to a sharp increase in price and shortage. For this reason, currently, the research moves toward the use of different elements for metal ion batteries, such as sodium.

In this work, basing on previous results of our research group [1], was studied the appliability of two different layered double hydroxides (LDHs) as negative electrodes active materials in Sodium Ion Batteries (SIB) using sodium alginate as binder.

In particular the two compounds NiAl-NO_3 and NiFe-NO_3 LDHs were investigated to underline the ifluence of the trivalent metals (Fe/Al) on both the specific capacity and the stability of the electrode.

All the active materials were characterized by means of PXRD and FE-SEM analysis, the electrodes were prepared spreading a mixture of active material (LDH), conductive carbon (Timcal C65) and binder (Na-alginate) (70:20:10) on a copper foil. Those electrodes were tested in Swagelock T-cells with 1M solution of $NaClO_4$ in EC/DMC with a 5% of fluoroethylene carbonate FEC as electrolyte, metallic Na as counter electrode and glass fiber as separator. The electrodes were tested in the potential range 0,01-3 V vs. Na/Na^+. In both cases (fig.1) the cells were discharged/charged at 50 mA/g and 500 mA/g showing a very high initial specific capacity (more than 1000 mAh/g) and a quite good stability. The NiAl based electrode seems to be more performing at higher current, while the NiFe based electrode shows an opposite behaviour.

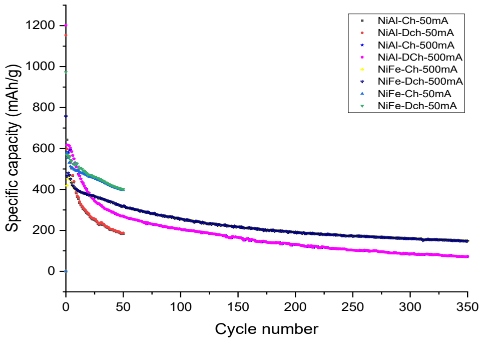

Figure 1 GCPL of NiAl and NiFe at different current (50-500 mA/g)

[1] Li, X., Fortunato, M., Cardinale, A.M. *et al.* Electrochemical study on nickel aluminum layered double hydroxides as high-performance electrode material for lithium-ion batteries based on sodium alginate binder. *J Solid State Electrochem* **26,** 49–61 (2022). https://doi.org/10.1007/s10008-021-05011-y

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Radical synthesis of original persubstituted furans

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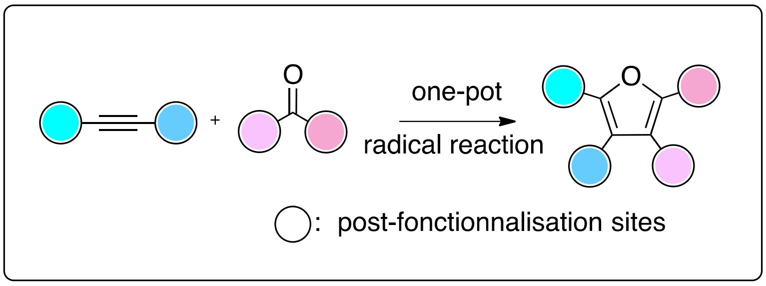
Furans belong to one of the most important class of five-membered ring heterocycles. Present in various natural products derived from plants and marine organisms, persubstituted furans are used as pharmaceutical agents, perfumes, or insecticides [1] and are important synthetic intermediates for the elaboration of more complex structures. [2] Several strategies have been developed for the elaboration of furan ring however few of them are concerned with the synthesis of persubstituted furans bearing functionalities that can be involved in further transformations. [3]



One-pot radical synthesis of persubstituted furans

Our laboratory is interested in the development of new methodologies involving radical species. [4] Here we proposed the one-pot synthesis of persubstituted furans, based on radical reaction between judiciously disubstituted triple bonds and carbonyl compounds. The furans obtained with good to excellent yields are originals and highly functionalized.

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[3] (a) Haut, F.-L.; Habiger, C.; Wein, L. A.; Wurst, K.; Podewitz, M.; Magauer, T. *J. Am. Chem. Soc.* **2021**, *143*, 1216 and refs cited there in. (b) Oonishi, Y.; Sato, Y.; Miyairi, A. *Org. Biomol. Chem.* **2021**, *19*, 9396–9400
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Asymmetric Gold-Catalyzed Addition of Carbonyl Compounds on 1,6-Enynes

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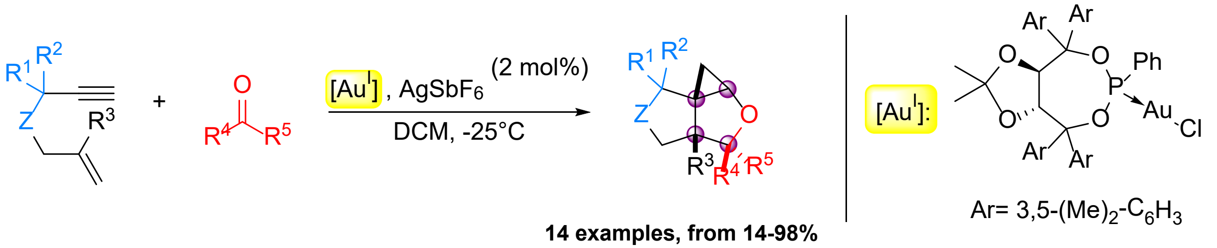
Interest in homogeneous gold catalysis has noticeably increased during the last decades[1]. Gold complexes possess a carbophilic Lewis acid character which provides it a particular reactivity able to activate π-systems towards nucleophilic additions. This reactivity offers new possibilities of chemical synthesis, such as cycloisomerizations and domino reactions of enynes and carbonyl compounds which allows to reach various carbocyclic or heterocyclic scaffolds, starting from simple substrates, enhancing significantly the molecular complexity[1,2]. Nevertheless, asymmetric gold catalysis still represents a great challenge considering the linear geometry of gold (I) complexes and the difficulty to synthesize gold (III) complexes. One of the strategies to perform efficient enantioselective transformations with gold (I) complexes is to diligently design ligands in order to bring the chiral information closer to the substrate.[3] Based on the work of our group,[4] this project was focused on an unprecedented asymmetric domino gold-catalyzed cycloisomerization of 1,6-enynes towards carbonyl addition. This Prins-type reaction was first reported by the group of Helmchen.[5] We developed an efficient gold-catalytic system for this enantioselective transformation. We evaluated the scope of the reaction under racemic conditions, obtaining a range of derivatives with moderate to excellent yields. Our investigations on the asymmetric version have shown that chiral gold (I) catalysts could induce promising enantioselectivities: a complex with a phosphonite ligand containing a TADDOL pattern allowed us to reach for the first time moderate to good enantiomeric excesses over our scope.[6]



14 examples, from 14-98%
ee up to 82%

[1] (a) Toste, F. D.; Michelet, V. *Gold Catalysis: An Homogeneous Approach*, Catalytic Science Series; Imperial College Press, **2014**. (b) Toste, F. D.; Hashmi, A. S. K. *Modern Gold Catalyzed Synthesis* Wiley-VCH, Weinhein, **2012**. (c) Rappoport, Z.; Liebman, J. F.; Marek, I. *The Chemistry of Organogold Compounds.* In Patai's Chemistry of Functional Groups; Eds.; John Wiley & Sons, Inc.: Hoboken, NJ, **2014**. (d) Slaughter, L. M. *Homogeneous Gold Catalysis.* In Topics in Current; Chemistry;, Ed.; Springer: Berlin, **2015**.
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Monitoring of the lipid oxidation of dehydrated by-products coming from tuna processing

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(2) Department of Earth, Environmental and Life Sciences, University of Genoa, 16100, Genoa, Italy

The increase in waste generated by the fish supply chain has a significant impact on environment and moreover it represents a big economic problem; in addition, it is necessary to consider the loss, within fish leftovers and their processing by-products [1], of precious compounds with high nutraceutical interest, with a view of a "zero waste economy". University of Genoa is one of the 34 partners in EcoeFISHent, a European Union's Horizon project (H2020-LC-GD-2020-3, https://cordis.europa.eu/project/id/101036428/it) implementing systemic solutions through multilevel circular value chains for an eco-sustainable valorization of fishing and fish industries side-streams.

By-products coming from canned tuna processing, made up of fillets scraps, fishbones, heads, once separated from viscera, have been dehydrated by a patented process in order to stabilize this highly perishable biomass and obtaining a powdered material with a residual humidity of about 5%. The bromatological analysis of the biomass before and after the dehydration step have been performed (humidity, protein, lipid, ash, and carbohydrates contents). Since lipid oxidation [2] may be considered one of the most dangerous modification in such an unsaturated food matrix, its monitoring seems mandatory in order to evaluate the possibility of further valorize these by-products. As far as fish oils are concerned, the analytical determinations suggested by Codex Alimentarius [3] are the Peroxide value (PV) and the Anisidine value (AV) to evaluate primary and secondary oxidation products respectively and combining them in the Total oxidation value (ToTox).

Looking for greener and more rapid approaches exploitable for the lipid oxidation monitoring of tuna by-products, the following determinations have been proposed:

- the Hara-Radin method to extract the lipid fraction has been proposed to replace the Folch method in order to avoid the use of halogenated solvents ;
- the spectrophotometric analiysis of the conjugated dienes was performed alternatively to PV test for the primary oxidation products evaluation ;
- the TBARS (Thiobarbituric Acid Reactive Substances) test [4] directly applied on the food samples, avoiding the lipid extraction step, has been proposed to evaluate the secondary oxidation products.

[1] Alfio VG et al. *Molecules*. 2021;26(4):1002. DOI: 10.3390/molecules26041002.
[2] Abeyrathne EDNS et al. *Antioxidants*. 2021; 10(10):1587. DOI:10.3390/antiox10101587.
[3] Codex Alimentarium Commission Standard for fish oils Codex Stan (2017).
[4] Hu Z et al. *Food Chemistry*. 2010;123(3):794-799. DOI: 10.1016/j.foodchem.2010.05.012.

Acknowledgements: EcoeFISHent project (Demonstrable and replicable cluster implementing systemic solutions through multilevel circular value chains for eco-efficient valorization of fishing and fish industries side-streams) Grant agreement ID: 101036428 has received funding from the European Union's Horizon 2020 EU.3.5. Green Deal, Call H2020-LC-GD-2020

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Authentication and traceability of the *Mandorla di Avola* almond by means of trace elements distribution

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The *Mandorla di Avola* is recognised all over the world as one of the best almond varieties. It is cultivated in a small area inside the provinces of Siracusa and Ragusa (Sicily, Southern Italy). The famous Sicilian writer Leonardo Sciascia used to describe it as "the almond with a perfect oval". The denomination *Mandorla di Avola* accounts for three different cultivars: *Pizzuta*, *Fascionello* and *Romana* or *Corrente d'Avola*. These are used in the traditional Sicilian cuisine for both salty and sweet foods and of course in artisan pastry, apart from being consumed as a fruit. Thanks to the collaboration with the *Consorzio di tutela della Mandorla di Avola*, a project has been started aiming at favouring the achievement of the IGP (Indicazione Geografica Protetta - Protected Geographical Indication) brand for this product.

Due to its extraordinary organoleptic and beneficial features, the *Mandorla di Avola* is frequently counterfeit with almond varieties of lower quality coming from other countries. While its nutraceutical features have been studied, highlighting its great polyphenol content and antioxidant activity [1], the possibility of authenticating it with respect to other varieties has not been explored. In this work we used microelements as chemical descriptors to distinguish samples of *Mandorla di Avola* almonds from almonds coming from California and Spain, which are usually employed as substitutes in pastry. A set of 46 elements has been determined by means of Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES) and Inductively Coupled Plasma – Mass Spectrometry (ICP-MS). Among the different elements determined, Mn and P resulted to be the best descriptors for authentication.

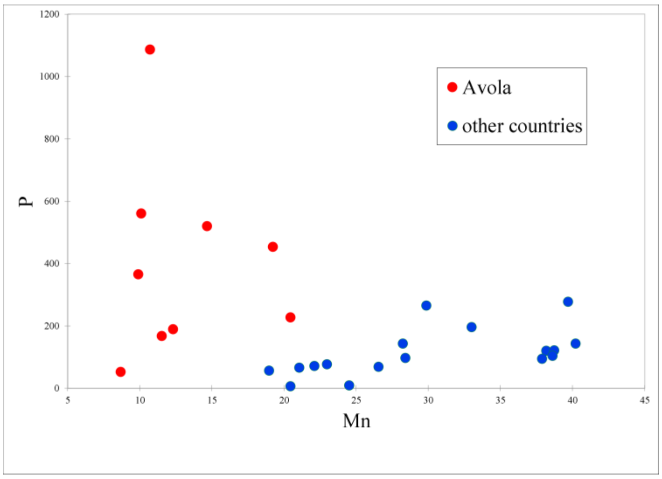

Figure 1: Mn vs P plot in almonds

[1] Kahlaoui M., Borotto Dalla Vecchia S., Giovine F., Kbaier H.B.H., Bouzouita N., Pereira L.B., Zeppa G., 2019, Characterization of polyphenolic compounds extracted from different varieties of almond hulls (*Prunus dulcis* L.), Antioxidants (Basel), 8(12) 647, doi: 10.3390/antiox8120647

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"Development of sulphur-containing carbon derived from hyper-cross-linked polymers for CO_2 capture"

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(2) *Dipartimento di Scienze e Innovazione Tecnologica (DISIT), Viale Teresa Michel, 11 – 15121 – Alessandria, Italy*

In recent years, the increase of carbon dioxide emissions into the atmosphere has caused global warming. The capture and subsequent storage of greenhouse gases, such as CO_2, through solid porous sorbents, is a promising method to reduce pollution.

In this perspective, the main objective of this work was the development and characterization of new hyper-cross-linked polymers and their transformation into activated carbon with high surface area to optimize the adsorption of CO_2 in gas phase. The focus was the use of Diphenylsulfide monomer which contains a sulfur heteroatom placed between two phenyls. The monomer used was chosen after careful bibliographical research, which had as its objective the understanding of the interaction mechanisms that may occur between carbon dioxide molecules and the electronic the heteroatom. Different materials have been prepared changing both the type of catalyst and the ratio catalyst/monomer, in order to optimize the synthesis procedures also in view of a subsequent industrial scale-up. In particular, six hyper-cross-linked polymers (HCPs) were synthesized through two different catalysts: a catalyst widely used in literature for the Friedel-Crafts reaction, Ferric Chloride ($FeCl_3$) and Zirconium Chloride ($ZrCl_4$) with different catalyst/monomer molar ratios, in particular: 8, 4, 2. The polymers obtained using the catalysts $FeCl_3$ and $ZrCl_4$, have been named DZ(x)-y, where "DZ" indicates the monomer, "x" the catalyst and "y" means the catalyst/monomer ratio used. The HCPs were chemically activated at high temperature [1] to obtain porous carbons. The obtained materials have been characterized through various techniques, in order to study their superficial, morphological, thermal and structural properties. In addition, the adsorbent properties of the derived carbon were measured through a gas adsorption volumetric system of up to 20 bar. The structural analysis of polymers, carried out through IR-DRIFT has confirmed that the synthesized materials are crosslinked. Finally, the presence of two peaks respectively assigned to the stretching mode of groups $-SO_3H$ and the stretching mode of C-S bonds, confirms the presence of sulfur in the structure and groups that can interact with CO_2.

The porous carbon obtained, tested through a home-made line, showed excellent adsorption capacities (Figure 1), comparing to Zeolite 13X[2] due, theoretically, to a stabilization of adsorption through hydrogen and electrostatic bonds between carbon dioxide and the sulfonic groups present in the carbon structure.

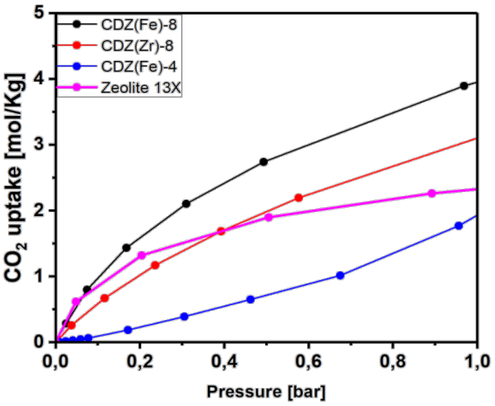

Figure 1 CO_2 adsorption analysis performed on CDZ(Fe)-8, CDZ(Zr)-8 and CDZ(Fe)-4 at 298 K comparing with Zeolite 13X

[1] Giorgio Gatti, Mina Errahali, Lorenzo Tei, Maurizio Cossi and Leonardo Marchese, Polymers **2019**, 11, 588.
[2] P.J.E. Harlick, F.H. Tezel, Micropor. Mesopor. Mater., 76 **2004**, pp. 71-79

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Formation of glyceraldehyde and glycerol in interstellar ice analogs: a water and radical-assisted mechanism?

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Complex organic molecules (COMs) are defined in the astrochemist community as carbon-bearing organic molecules containing six or more atoms. They have been unambiguously identified in a large variety of objects and environments in space. Among them, glycolaldehyde (GA) and ethylene glycol (EG) are the largest detected COMs in the interstellar medium. These molecules were recently shown to be efficiently formed experimentally from a Visible-UltraViolet photolysis of pure formaldehyde [1] or H2O/H2CO [2] ices at very low temperature (13K).

It is thought that EG and GA are perfect precursors for the formation of Glyceraldehyde (GCA), the simplest of all common sugars and Glycerol (GCO), its saturated polyol derivative. Recent laboratory experiments performed at low temperatures in H2O/H2CO ices have evidenced the formation of GCA and GCO, suggesting a general route for aldose and polyol formation in interstellar medium[3].

In this study, we examine water and radical-assisted formation mechanisms of glyceraldehyde and glycerol using DFT calculations. We show a spectacular lowering of the tautomerism reaction barriers in early formed radicals due to water cluster assistance. After hydrogen transfer, the newly formed radicals can undergo further reaction with formaldehyde molecules and lead to the carbon chain extension of the COM. It is shown that, according to these new water-assisted mechanisms, the formation of glycerol seems to be favored compared to the formation of glyceraldehyde as well as the formation of PolyOxoMethylene (POM), the polymerized form of formaldehyde (Figure 1).

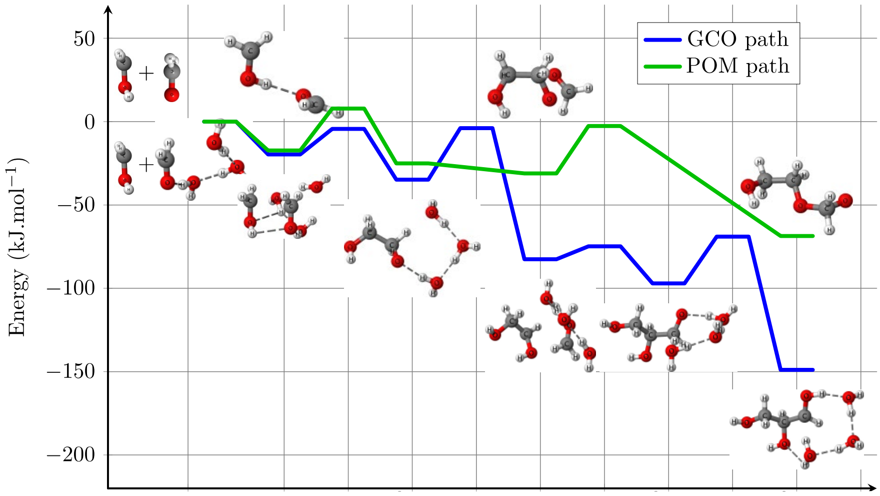

Figure 1: Full reaction path leading to the formation of glycerol in competition with POM formation

[1] T. Butscher, F. Duvernay, P. Theule, G. Danger, Y. Carissan, D. Hagebaum-Reignier, T. Chiavassa, *Mon. Not. R. Astron. Soc.*, **2015**, DOI:10.109

[2] T. Butscher, F. Duvernay, G. Danger, T. Chiavassa, *Astron. Astrophys.*, **2016**, DOI:10.1051/0004-6361/201628258.

[3] Y. Layssac, A. Gutiérrez-Quintanilla, T. Chiavassa, F. Duvernay, *Mon. Not. R. Astron. Soc.*, **2020**, DOI:10.1093/mnras/staa1875.

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PCA evaluation of parameters influencing the radio-oxidation of XLPEs containing additives in electric cables of power plants

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Abstract: Electric cables (insulation and jacket in polymers) must remain functional for the entire life of a nuclear power plant (NPP), in normal conditions but also in accidental conditions in the case of cables with safety requirements. Very different kinds of polymers are used to manufacture electric cable parts: can be cited for instance halogenated polymers such as PVC (polyvinylchloride) or Neoprene® and aliphatic polymers as EPR (ethylene/propylene copolymers) or XLPE (crosslinked polyethylene). This study focuses on XLPE, this polymer being nowadays one of the polymers mainly employed produce the insulation part of cables dedicated to NPPs.

The objective of this article is to understand the aging mechanism of formulated crosslinked polyethylene upon radio-oxidation. To perform this study, formulated model XLPEs with increasing quantities of different added additives and filler were gamma radio-oxidized at room temperature. Three different dose rates (8.5, 78 Gy/h and 400 Gy/h) and three different doses, up to 374 kGy, were employed. To quantity gases emission and oxygen consumption, polymers have to be irradiated in closed containers. Hence, a second irradiation was performed, at doses as low as possible in comparison to the initial dose in order to keep the material's signature. Gas emitted from aged polymers were compared with a non previously irradiated sample which was used as reference.

To understand the impact of gamma irradiation on the materials and the effect of the presence of additive and filler in the polymer, the principal component analysis (PCA) method is applied on gases released and on oxygen consumption during irradiation. We evaluated the impact of the formulation of the material, of the dose rate and of the dose on the gases emitted and consumed. We hence evaluated the main parameters influencing the ageing of the polymers under study, and this methodology gave information on primary processes that modify the polymers at different ages.

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Nano spray drying technique as a novel approach to synthesize dextrin-based polymers nanoparticles

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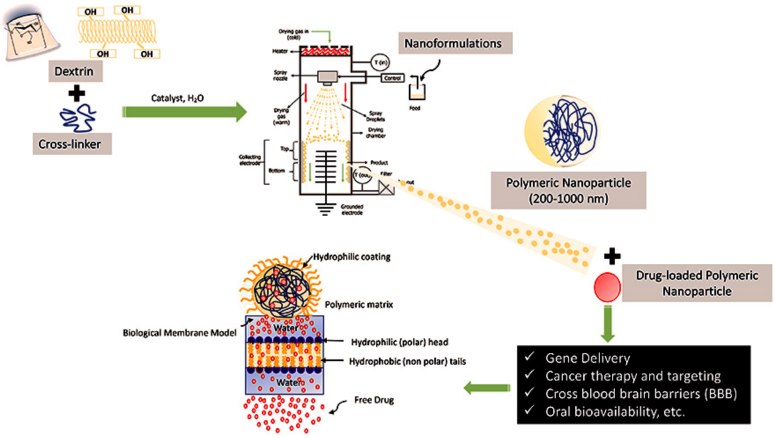

- ✓ Gene Delivery
- ✓ Cancer therapy and targeting
- ✓ Cross blood brain barriers (BBB)
- ✓ Oral bioavailability, etc.

Figure 1: Schematic representation of the synthesis of dextrin-based polymers nanoparticles using the Nano Spray Dryer B-90

The development and optimization of drug-delivery systems are related to the complexity of various diseases and the toxicity related to certain drugs [1]. To improve existing therapies and to develop novel ones, nanotechnology, a multi-disciplinary scientific field, produces nanoparticles (NPs). Nanoparticle drug delivery systems are one of the most significant areas of study [2]. The size of NPs less than 200 nm is essential for nanomedical application [3], [4], as at this length scale, NPs with encapsulated drugs, can enhance the solubility and bioavailability of the drug, can enter the pulmonary system, cross the blood-brain barrier (BBB), can be absorbed along the tight junctions of the skin endothelial cells, etc [3]. Dextrins [5], particularly cyclodextrin (CD)-based nanosponges (NSs) or chemically cross-linked polymers, due to their biocompatibility and versatility, have shown their full potential as drug delivery systems [6], [7], [8]. The extensive literature about the applications of CD-NSs instructed the investigations of linear dextrins-based NSs. As the nanoparticles of dextrin-based NSs are ordinarily achieved by mechanically grinding the synthesized polymer, in this study, we present a new method to prepare dextrin-based crosslinked nanoparticles by spray drying the monomers solution (dextrin and cross-linking agent). After curing, the obtained dry powders were characterized using dynamic light scattering (DLS) measurements, nanoparticle tracking analysis (NTA), and scanning electron microscopy (SEM). An average size in the nanometer range (200-1000 nm) is observed. The vast majority of synthesized nanoparticles were spherical. The spray-dried syntheses were then compared with the conventional ones, and their effect on water absorption capacity (WAC) was investigated. The focus will be given to the in vitro and in vivo performance of the synthesized dextrin-based NSs nanoparticles. It will enable us to understand the effect of nanoparticle size on their delivery efficiency and to further optimize the nanoparticle synthesis process. The future research will be promising for the trends of the global market that have indicated strong growth of the nanotherapy sector.

[1] B. Begines *et al.*, *Nanomaterials*, vol. 10, no. 1403, pp. 1–38, 2020.
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Activatable Alkoxyamine-based prodrugs that are cytotoxic in the presence of Neutrophil elastase only

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Current chemotherapies suffer low specificity and sometimes drug resistance. Neutrophil elastase activity in cancer associates with poor prognosis and metastasis settlement[1]. More generally tumors harbor persistent and various protease activities unseen in healthy tissues. In an attempt to be more specific we designed a prodrug that is activatable by neutrophil elastase. Upon activation these alkoxyamine-based drugs release cytotoxic alkyl radicals that act randomly to prevent drug resistance[2,3]. As a result U87 glioblastoma cell displayed high levels caspase 3/7 activation during the first hour of exposure upon concurrent presence of HNE and the prodrug in vitro. Apoptosis process pursued and cell death occurred between 24 and 48 hours after exposure with a half lethal concentration of 150 µM. These prodrugs are versatile easy to synthetize and can be adapted to many enzymes.

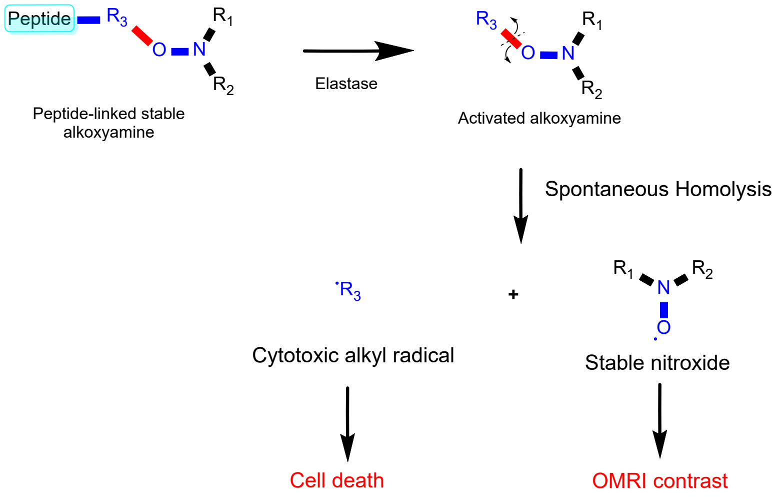

Figure 1 : General scheme for elastase-activated alkoxyamines.

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Meso-poly-halogeno-alkyl-dipyrromethanes as a building block for the synthesis of functional corroles and porphyrins

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If porphyrins and more recently corroles have been studied extensively, only very few examples of *meso*-poly-halogeno-alkyl derivatives have been brought up to light.[1] These substituents are yet unique because i) they increase the lipophilicity and/or the metabolic stability of the macrocycles, ii) they can induce non planar distortion or photo-stability, iii) they may enhance the catalytic activity through an electron withdrawing effect, all leading to numerous possible applications.[2] This presentation will describe how poly-halogeno-alkyl-dipyrromethanes **1** were used in the preparation of original A_2B_2-porphyrins **2** bearing either two perfluoroalkyl chains, formyl groups or rarely observed fluoro acyl moieties,[3] but also innovative A_2B corroles **3** *via* a tetrapyrrole intermediate and ABC corroles **4** after hydrolysis of one of the poly-halogeno-alkyl chains leading to unprecedented *meso*-keto-corroles. A physico-chemical characterization of these new derivatives will be also enlightened by their distinctive electrochemical and photophysical properties that vary significantly with the nature of the functional substituents.

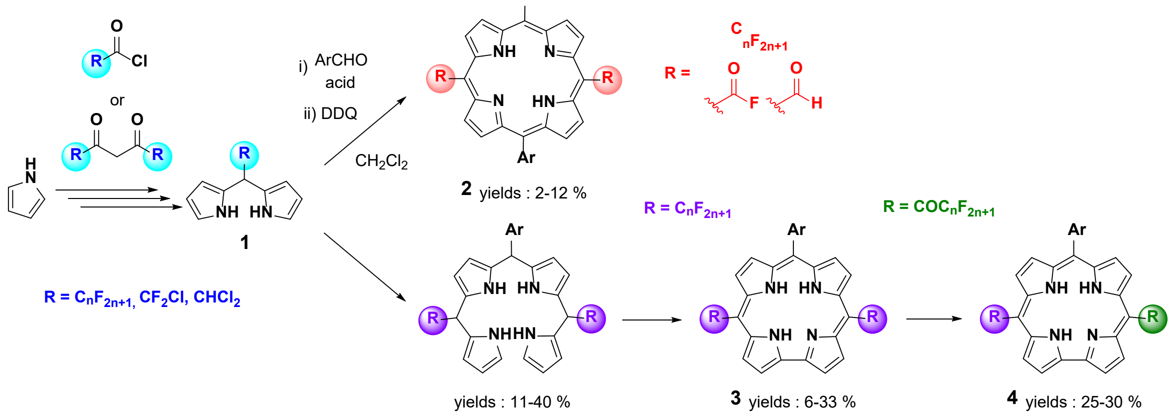

Figure 1: Synthetic pathways to meso-poly-halogeno-alkyl porphyrins, and their corroles counterparts

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Non-invasive analysis of late mediaeval goldsmith's materials: piedmontese reliquary busts in comparison

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In recent decades mediaeval reliquary busts of the Italo-French area have aroused considerable interest because of their importance as an independent artistic genre [1][2]. Nonetheless this study can not be based only on an artistic historical point of view, and it is desirable to expand research on the precious materials used in mediaeval goldsmithery including by means of materials analysis. The alloy and the gilding technique characterisation, the gem bezels or enamelled details composition identification, enable comparison among different manufacturing and give information about availability and supply of materials in a particular period. Furthermore, the large amount of data on various artefacts of mediaeval goldsmithing provide useful tools for dating or authentication of other similar artefacts.

This work concerns the study of the materials of ten masterpieces representative of religious goldsmith's art in Piedmont between XIV and XV centuries, never investigated before. They are generally stored in different places (usually churches), but were all exceptionally gathered in an exhibition held at Palazzo Madama in 2021, during which totally non-invasive analyses were performed by portable instrumentation [3].

Optical microscopy, UV-Vis-NIR diffuse reflectance spectrophotometry, and X-ray fluorescence spectrometry results provided useful information in order to define the materials and techniques employed by religious late mediaeval goldsmiths. Based on comparison of different objects, the studies allowed to deepen the piedmontese manufacturing of the 15th century, to identify the presence of possible later remakes and also to compare them with other goldsmiths' manufacturing. The outcomes offer a potential starting point for an inventory of European mediaeval metal busts able to collect useful interdisciplinary information for locating geographically and over time the productions.

Figure 1: San Giorgio Martire Reliquary [2]

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A versatile and straightforward process to turn plastics into antibacterial materials

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One possible solution to prevent bacterial contamination is to use inherently antibacterial materials.

The objective of this work is to propose an efficient, versatile and simple method to elaborate antibacterial polymeric materials based on the simple dispersion, in different common organic matrices, of a small amount of high molecular weight cationic amphiphilic methacrylic copolymers prepared by nitroxide-mediated controlled radical polymerization. Specifically, we demonstrated that less than 2 wt% of diblock copolymers based on butyl methacrylate and quaternized *N,N*-dimethylaminoethyl methacrylate dispersed by extrusion in conventional industrial polymer matrices conferred antibacterial activity to these initially inactive organic materials.[1-3] This approach, which does not require the usually costly modification of the material surface and which is not based on the dispersion of small molecules (e.g. antibiotics or silver nanoparticles that can migrate out of the material), also offers the advantage of providing materials that are active against different types of Gram + (*S. aureus*), Gram $^{-}$ (*E. coli*) or multi-resistant bacteria without loss of activity with time or use (Figure 1). This method could be of great interest to develop antibacterial food packaging.

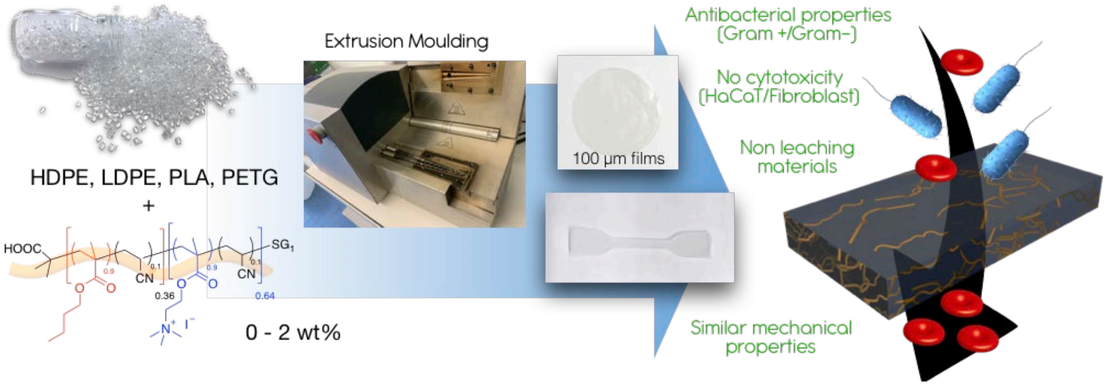

Figure 1 : Process for making antibacterial plastics by extrusion

[1 Benkhaled, B. T.; Hadiouch, S.; Olleik, H.; Perrier, J.; Ysacco, C.; Guillaneuf, Y.; Gigmes, D.; Maresca, M.; Lefay, C. *Polym. Chem*. **2018**, *9 (22),* pp. 3127-3141.

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The Stereochemistry of Isoprenoid Hydrocarbons as Molecular Fossils: Implications for the Search of Extinct Life on Mars

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Life on Earth is homochiral: in biology, amino acids are almost universally L-chiral while sugars are D-chiral. Less known, the chiral hydrocarbons in nature are also found in an enantiomerically pure form. In fact, homochirality is observed in all families of molecules used by life [1]. Of interest for us, due to their chemical inertia and thermal stability, hydrocarbons are expected to survive billions of years even in harsh environments, making them much better molecular fossils than the more reactive amino acids and fragile sugars when probing for very ancient life.

We focus on the most abundant chiral hydrocarbons found in primitive organisms: the isoprenoid alkanes pristane ($C_{19}H_{40}$) and phytane ($C_{20}H_{42}$). These are notably a major part of the cellular membrane of archaea [2], as well as the side chain of most chlorophylls (including those used by cyanobacteria) [3].

We now know that Mars most likely had oceans about 4.4 Gy ago [4], where it is believed that a lot of the conditions required for a potential Martian life to emerge were met [5]. The ExoMars space mission from ESA is set to land on the red planet in 2023 with the main scientific goal of looking for extinct or extant life. To do so, it contains the MOMA instrument: a gas chromatograph linked to a mass spectrometer for detailed in situ analysis of the Martian surface and subsurface [6].

Experiments are ongoing to test how well the instrument can separate the stereoisomers of pristane and phytane, but the first results are promising [7]. Then, if similar molecules are found on Mars, being able to distinguish between a racemic or homochiral sample will give enormous weight to a potential biological origin.

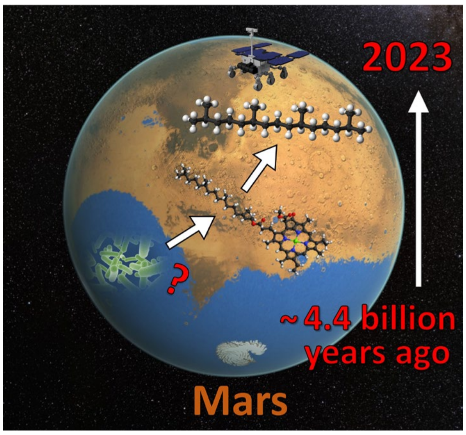

Figure 1 : Remnants of primitive lifeforms

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Novel organic-inorganic gold iodide perovskites: a new synthetic approach

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Among the class of organic-inorganic hybrid materials, halide organic perovskites have been thoroughly studied as light-harvesting materials for solar cells. Their general chemical formula is ABX_3, where A and B are monovalent and divalent cations respectively, and X is a halide. Organic-inorganic perovskites usually feature a metal divalent cation, such as Sn^{2+} or Pb^{2+}, and organic monovalent cations. Recently, gold iodide perovskites have gained some interest as active materials in solar cells [1]. They feature linear $[AuI_2]^-$, square planar $[AuI_4]^-$ and two monovalent organic cations, thus having the general formula $A_2[AuI_2][AuI_4]$.

The synthetic approach adopted so far consists in the reaction of $HAuCl_4$ (as an Au(III) source) with the desired organic salt in ethanol, and the subsequent addition of HI [2]. Besides granting chloride exchange in the final product, the iodide ions are also responsible for the Au(III)→Au(I) reduction, thus forming I_3^- as oxidation product. Depending on the size of the organic cation, I_3^- can be partially incorporated in the $[AuI_2]^-$ sites of the final perovskite structure.

To avoid the use of chlorides, we explored two alternative synthetic routes for gold iodide perovskites. The first strategy consists in the reaction of AuI and the organic cation in ethanol, the formation of Au(III) being ensured by the partial dismutation of $[AuI_2]^-$ into metallic gold and $[AuI_4]^-$. The second route consists in the reaction between $Au(OH)_3$ and the organic cation in ethanol, with the addition of HI. SC-XRD measurements allowed to assess the successful formation of $A_2[AuI_2][AuI_4]$ perovskites with NH_4I and Me_4NI salts with both synthetic routes, without any presence of vicariant I_3^-. Using bulkier alkylammonium salts such as Et_4NI and $n\text{-}Bu_4NI$ yielded the respective $[AuI_2]^-/I_3^-$ and $[AuI_4]^-$ salts, confirming that cation size plays a crucial role in obtaining organic gold perovskites.

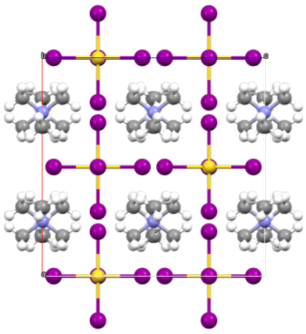

Figure 1 : View of $(Me_4N)_2[AuI_2][AuI_4]$ perovskite along b axis

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Synthesis and Structure-activity Relationship study of New antimicrobial peptides derived from Polistes gallicus hymenopteran venom.

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[3]*ISBST, BVBGR- LR11ES31, Univ. Manouba Biotechpole Sidi Thabet, 2020, Ariana, Tunisie* [4]*LATOXAN SAS, 845 Avenue Pierre Brossolette, 26800 Portes-lès-Valence, France*

The natural resistance of bacteria linked to the overuse of antibiotics in human and animal therapies and in various industries has led to the selection of pathogenic bacteria resistant to multiple drugs. Current classes of antibiotics face a constant threat from various bacterial resistance mechanisms. The bacteria Staphylococcus aureus, Pseudomonas aeruginosa belong to the group of most dangerous pathogens for immunocompromised patients as they are commonly isolated as drug resistant (DR) or MDR.

Natural products can be considered as promising antifungal agents. Animal venoms are a rich source of antifungal (AFP) and antimicrobial peptides (AMP). The first AMP from animal venoms was discovered in 1967. Melittin is the main active component of Apis mellifera bee venom with anti-Gram + and Gram- activity but also anti-fungal, anti-parasitic, anti-HIV and anti-cancer activity but is highly toxic to mammalian cells (Fennel et al., 1967). Since then, nearly 2900 AMPs have been identified to date, of which more than 2400 (83%) have antibacterial activity and more than 1300 are derived from animal venoms (Wang et al., 2004; 2009; 2016).

We have screened more than 180 venoms on microbial and fungal targets. We have identified, isolated, and characterized a peptide from Polistes gallicus hymenopteran venom with gram-acting antibacterial activity (Mabrouk et al., 2020; European patent EP19218273.1).

A structure-activity relationship study using synthetic peptides that resulted in a lead peptide with improved anti-microbial, antiinflammatory and antitumoral activity will be presented and discussed.

Fennell, J. F., Shipman, W. H. & Cole, L. J. Antibacterial action of a bee venom fraction (melittin) against a penicillin-resistant staphylococcus and other microorganisms. Res. Dev. Tech. Rep. 1–13 (1967).

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Wang, X. & Wang, G. (2016) Insights into Antimicrobial Peptides from Spiders and Scorpions. Protein Pept. Lett. 23, 707–721.

Mabrouk K., Maresca M., De Pomyers H., Gigmes D., 2020 brevet EP19218273.1.

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A lithium amide-promoted preparation of BINOL-derived carboxamides under bench-type aerobic conditions

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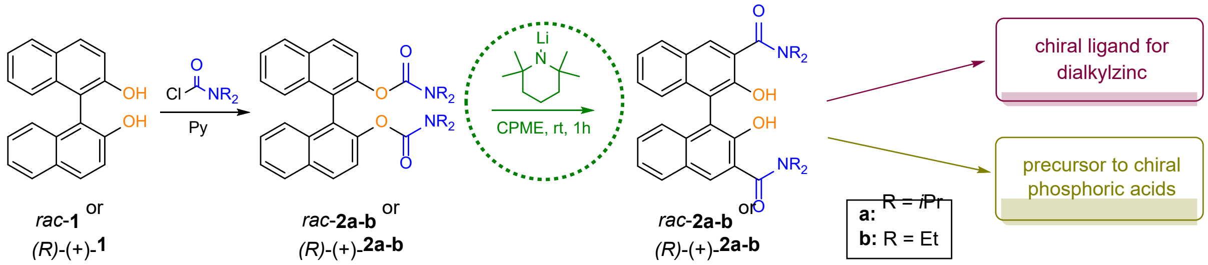
2,2′-Binaphthol (BINOL) is one of the most widely used chiral molecule as both organocatalyst and ligand in asymmetric synthesis.[1] In addition, its versatile backbone can be modified leading to the preparation of a wide variety of derivatives with different chemical, steric and electronic properties.[2] In this context, our investigations are currently devoted to the preparation of 3,3’-dicarboxamides derivatives of BINOL and their behaviour as chiral ligands/catalysts in enantioselective “green” transformations. The classical preparation of these compounds relies on the carboxylation of BINOL and subsequent treatment with thionyl chloride and an excess of dialkylamine.[3] We now propose a more sustainable synthesis of this class of potentially useful chiral scaffolds using a LiTMP-promoted Fries-rearrangement reaction on a series of BINOL-derived bis-carbamates as the key step, working under bench-type aerobic conditions (open-air, room temperature) and using cyclopentyl methyl ether (CPME) as a solvent. This synthetic procedure allowed the successful preparation of sterically hindered *N*,*N*-diisopropyl- and *N*,*N*-diethyl carboxamide BINOL derivatives in good yields both for racemic and chiral compounds. Their preparation, and their preliminary applications as chiral ligands in the asymmetric nucleophilic addition of dialkylzinc reagents to carbonyls under greener reaction conditions are presented.



Scheme 1: Sustainable synthesis of 3,3’-diamide derivatives of BINOLs by Fries rearrangement and their application in asymmetric reactions

[1] *Chem. Rev.* **2003,** *103,* 3155-3211;
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[3] (a) *Bull. Chem. Soc. Jpn.*, **1997**, *70*, 207-217; (b) *Chem. Lett.*, **1995**, *24*, 1113-1114

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Gold Catalysis: an Entry to Hedonic Materials for Fragrance Industry

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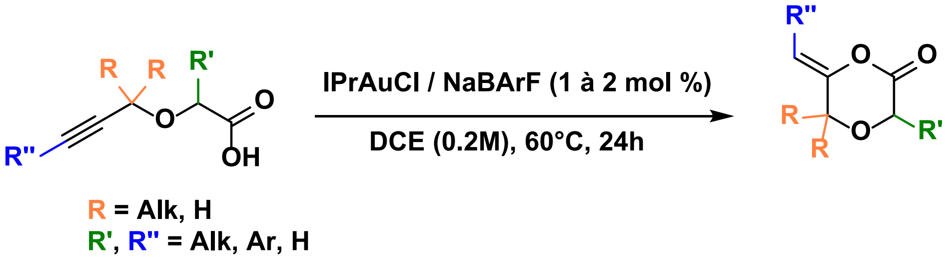
(2) *Expressions Parfumées, 136 chemin de St Marc, 06130 Grasse, France*

New olfactive molecules are always sought by fragrance industry to find new scents or improve properties of existing scents.[1] In addition, the regulatory policy is increasingly strict and main compounds of certain formulas may be banned each year (recently Lyral®). The consequence of these interdictions is a new demand of alternative odorant.[2]
As environmental concerns represent an integral part of modern industry, catalysis is proving to be an interesting tool to make new odorants. Following our interest in gold chemistry,[3] we have developed cycloisomerization of enynes leading to olfactory interesting bicyclic derivatives. We were also interested in novel methodologies to synthesize original volatile 1,4-dioxan-2-ones by cycloisomerization reactions of acetylenic acids.[4] These types of skeletons have been previously synthesized as dioxanones via Cu-catalyzed tandem isomerization/cyclization of α-allyloxy carboxylic acids or as intermediates in the synthesis of multi-ring heterocyclic products by Dixon's group.[5] Targets and intermediates have been submitted to perfumers for olfactive evaluation. Optimization of the reaction conditions as well as the unprecedented scope and limitations, and organoleptic properties will be presented.[6]



Gold-catalyzed formation of 1,4-dioxan-2-one

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Non-ambient structural and spectroscopic studies on different doped ceria systems for energy applications

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(2) *CNR-ICMATE, Via De Marini 6, 16149 Genova, Italy*
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Recently, RE-doped ceria systems (RE= rare earth) have been widely investigated to be used as solid electrolytes in Solid Oxides Cells (SOCs), due to their excellent ionic conductivity in the intermediate working temperature range (673 – 973 K).

Since pure ceria shows a cubic fluorite structure (F, space group *Fm*-3*m*), $Ce_{1-x}RE_xO_{2-x/2}$ systems typically retain a F-based structure up to a certain x_{max}, that mainly depends on the RE^{3+} ion considered [1]. In the mentioned compositional range, Ce^{4+} ions are randomly substituted by RE^{3+}, causing the occurrence of unassociated oxygen vacancies that are free to move through the F lattice: this phenomenon is responsible for the high ionic conductivity observed in these mixed oxides at low dopant amount. For $x>x_{max}$, due to the strong resemblance between the F structure and the one adopted by many RE^{3+} sesquioxides (named C, space group *Ia*-3), either a hybrid F/C phase (*e.g.,* for RE= Gd [2], Sm [3]), or a biphasic F+C region (*e.g.,* for RE= Lu [4]) may occur. In both cases, the growth of the C phase has a blocking effect on oxygen vacancies, thus decreasing the ionic conductivity of these systems. Moreover, Raman spectroscopic studies carried out on different systems by the present research group, thanks to the high sensitivity of the employed local technique, revealed that C phase nanoclusters are already growing within the fluorite region, thus clarifying why the maximum value of ionic conductivity in RE-doped ceria is always observed for $x<x_{max}$.

To date, structural and spectroscopic studies at non-ambient conditions on differently doped $Ce_{1-x}RE_xO_{2-x/2}$ systems are underway, with the aim of gaining as much structural information as possible on the present class of compounds, to evaluate the most promising systems to be used as electrolytes in SOCs and portable SOFCs (Solid Oxides Fuel Cells). In particular, high temperature μ-Raman, impedance spectroscopy, synchrotron X-ray diffraction (XRD) measurements, as well as high pressure XRD analyses were performed [6], and comparative results between different doped ceria systems will be discussed.

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An Original Donor-Acceptor Cyclopropane for the Thermal Synthesis of Carbocyclic Eight-Membered Rings

Kevin MASSON* (1), Jean-Luc PARRAIN (1), Laurent COMMEIRAS (1), Paola NAVA (1) and Gaëlle CHOURAQUI (1)

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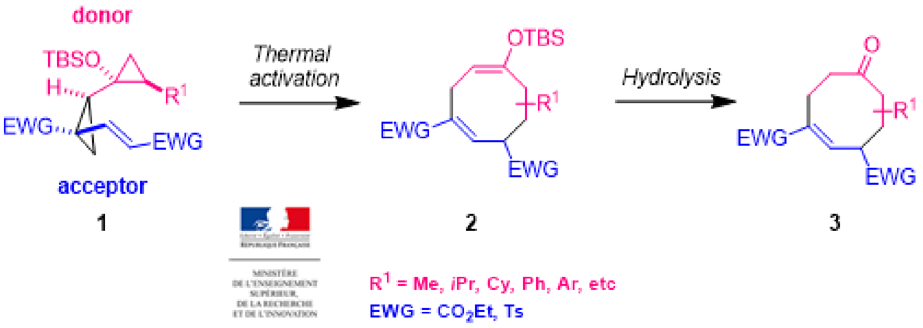
The development of efficient synthesis of eight-membered carbocyclic ring systems represents a particularly important area of research, given the number of biologically potent targets that incorporate such ring.[1] However, owing to ring strain and transannular interactions, the formation of eight-membered carbocyclic rings has sometime proven difficult.[2]

In this regard, the donor-acceptor cyclopropanes (DACs) represent a valuable class of intermediates for organic synthesis due to their high reactivity based on the inherent strain of the cyclopropane ring.[3] These molecules can easily undergo a ring opening reaction induced and oriented by the presence of the two antagonist groups. A valuable 1,3-dipole synthetic building block is thus delivered and has been used in plethora of reactions. Some of the resulting molecules have been used as advanced materials in the construction of biologically relevant materials.[4]

Quite recently, a new class of DACs **1** has been developed in our laboratory combining a silyl protected cyclopropanol with an α,β-unsaturated ester. Gratifyingly, we found out that DAC **1**, under purely thermal conditions, reacts intramolecularly to afford regio-and diastereselectively, a functionalized all carbon 8-membered ring **2** (Scheme 1). Furthermore, a mild acidic hydrolysis allows the preparation of cyclooctenones **3** with good overall yields.



Scheme 1: Thermal synthesis of carbocyclic eight membered rings

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Dextrin-based Nanosponges as an interesting material for drug delivery and bioapplications

Adrián Matencio*[1], Gjylije Hoti[1], Fabrizio Caldera[1], Claudio Cecone[1], Alberto Rubin Pedrazzo[1], Silvia Lucia Appleton[1], Yousef Khazaei Monfared[1], and Francesco Trotta[1]

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The global community is faced with various health concerns, including cancers, heart disease, neurodegenerative diseases, diabetes, obesity, osteoporosis, arthritis, and many others. Therefore, new approaches to develop more potent materials for the treatment of the aforementioned diseases to stabilize and deliver the drug in a proper way. One of the most promising nanocarriers between the wide range of materials is called cyclodextrin based nanosponges (CD-NSs), a type of dextrin-based nanosponges which is able to encapsulate, deliver and enhance the bioavailability and efficacy of drugs of different nature, without significant toxicity [1,2].

CD-NSs are chemically crosslinked polymers formed by cyclodextrins, which present many attractive features due to the cyclodextrin characteristics and modulable parameters, obtaining different applications in pharmacy, chemistry, gene delivery, biomedicine, and biotechnology, food, environment [2]. The CD-NSs synthesized by reacting cross-linkers such as carbonyl-diimidazole, diphenyl carbonate, and pyromellitic anhydride are considered the most effective delivery systems in several applications. Furthermore, in recent years novel greener processes such as the CD-NSs synthesis in natural deep eutectic solvents (NADES) and solvent-free CD-NSs synthesis have been developed to increase the possible applications.

This poster tries to summarize and introduce the extensive literature about the synthesis and characterization of the CD-NSs delivery systems and its application, that will further meet the challenges of the twenty-first century for improving drug administration and different application with lowering toxicity.

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SYNTHESIS OF COBALT-IRON NANO-STRUCTURED ALLOYS BY HYDROGEN ANNEALING OF SPINEL IRON OXIDE NANOPARTICLES

Jean-Pierre Miranda Murillo*(1), Maryam Abdolrahimi(2), Alexander Omelyanchik(1)(3), Pierfrancesco Maltoni(4), Fabio Michele Canepa(1), Diego Colombara(1) and Davide Peddis(1)(2)

(1) Dipartimento di Chimica e Tecnologie Chimiche, Via Dodecaneso 31, 16146, Italy
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(3) Immanuel Kant Baltic Federal University, 236016 Kaliningrad, Russian Federation
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Advanced energy processes such as thermal to electrical energy conversion can be improved by using magnetic fluids based on materials with high saturation magnetization (M_s) [1]. The FeCo system features compositions with an M_s up to ~240 Am^2/kg [2] that is among the highest reported values. Hence, Co_xFe_{1-x} alloys are appealing for the formulation of magnetic fluids, but are hardly synthesized homogeneously [3]. in this framework, the present communication represents a preliminary investigation of the M_s of Co_xFe_{1-x} alloys with 5 different compositions: 0, 33, 50, 67 and 100 at. % Co. five samples are obtained by combustion sol-gel ($Co_xFe_{3-x}O_4$) and subsequent hydrogen annealing (Co_xFe_{1-x}). The crystallinity and structure of the samples were determined by X-Ray diffraction (XRD), the composition was assessed by ICP-AES and the M_s was calculated from the registered hysteresis loop at 300 K via vibrating sample magnetometry (VSM). The study reveals the possibility of tuning this magnetic property as a function of the composition.

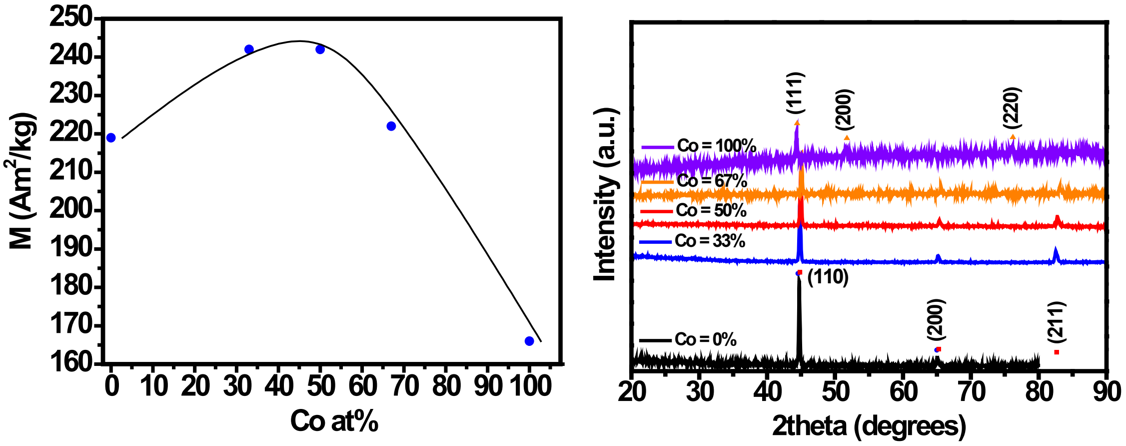

Figure 1: The saturation magnetization and the XRD pattern of CoFe alloys at 0, 33, 50, 67 and 100 at% Co.

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Novel bifunctional probes for oxidized proteins identification/localization

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Aix Marseille Univ, CNRS, ICR, UMR 7273, Sondes Moléculaires en Biologie et Stress Oxydant Faculté des Sciences de Saint Jérôme, Marseille, France

Oxidative stress defines pathological conditions by which uncontrolled excessive reactive oxygen species (ROS) such as superoxide and hydroxyl free radicals, and hydrogen peroxide may form in living organisms to trigger a series of detrimental effects on cells, tissues and organs. Hence, atmospheric pollution is a known example of oxidative stress where chronic inflammation is caused by inhalation of ultrafine particulate matter (e.g., containing metal catalysts) or pesticides aerosols. Carbonylated proteins (CPs) are considered precocious and relatively stable hallmarks of ROS formation [1]. Despite a wide array of assays in tissues is available there is still a need for improved CPs identification and localization probes.

Previously, a sensitive fluorometric and UV absorption assay for quantifying CPs in blood or animal tissues has been reported, based on the use of 7-hydrazino-4-nitrobenzo-2,1,3-oxadiazole (NBDH), an aromatic based hydrazine which specifically binds carbonyl groups of CP to yield strong fluorescent adducts [2].

In this study, a series of alkylated analogues of NBDH were synthesized as improved labels for CPs carbonyls, bearing a reactive tail that can covalently bind a cleavable resin by click chemistry. Cleavage of labeled CPs under mild conditions, followed by enzymatic digestion of the resulting enriched labeled CPs, would allow the oxidized amino acid sequences to be identified and/or localized by proteomic analysis.

The optimized synthetic NBDH modification and tail group will be presented, together with preliminary labeling assays of a series of relevant targets, such as small carbonylated derivatives, chemically oxidized aminoacids, and small peptides containing an oxidized residue. Experiments of labeling and proteomics analysis on tissues and organs from animal models exposed to pesticides using the most efficient of the new bifunctional CPs probes are underway.

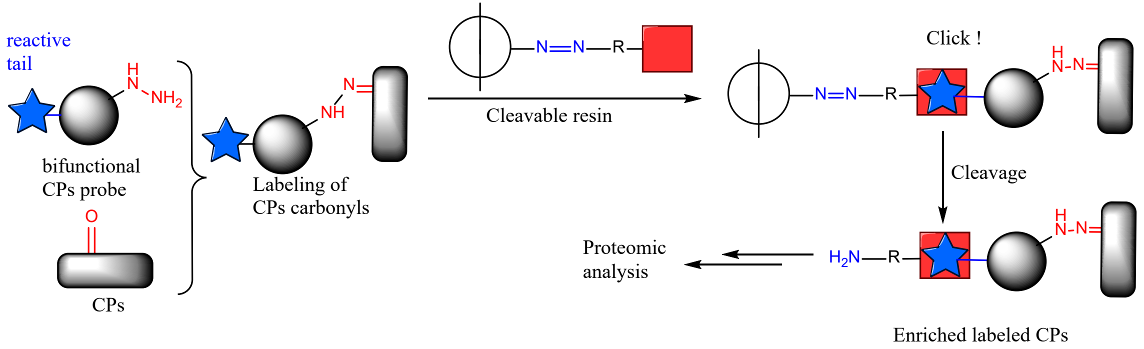

Figure 1: General principle of CPs probing using a bifunctional specific marker associated with a cleavable resin

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Coupling principle among polymethines

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Polymethines, often referred to as cyanines, are organic dyes with a charge delocalized between two heteroatoms over an odd number of carbon atoms. Upon molecular engineering (conjugation length or donor/acceptor strength), polymethines are capable of absorbing up to the Near-InfraRed region (NIR)[1] and are therefore used in multiple applications ranging from molecular electronics[2] to fluorescence or bio-imaging.[3,4]

According to a 1966 theoretical study reported by Dähne and Leupold, the coupling of two polymethines subunits linked by two single bonds would induce an enhancement of optical properties. However, dyes introducing multiple polymethine subunits have been scarcely reported so far,[5] seminal examples being the octamethyl-tetraaminobenzene dication and the benzoquinone imine zwitterion (Figure 1).[6,7] This coupling strategy would enable to further redshift the optical properties of polymethines.

With this aim, we recently developed coupled polymethines incorporating anionic oxonol and cationic heptamethine subunits (Figure 2) that gave rise to unprecedented DiSpiroPyran derivatives holding potential as pH- and photo-switches providing a wide span of absorption up to the NIR domain.

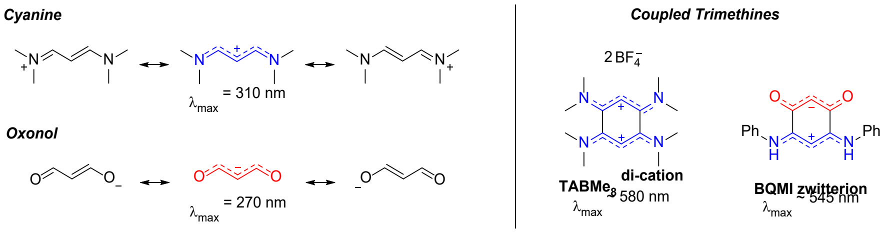

Figure 2: Comparison between regular trimethines and their coupled counterparts.

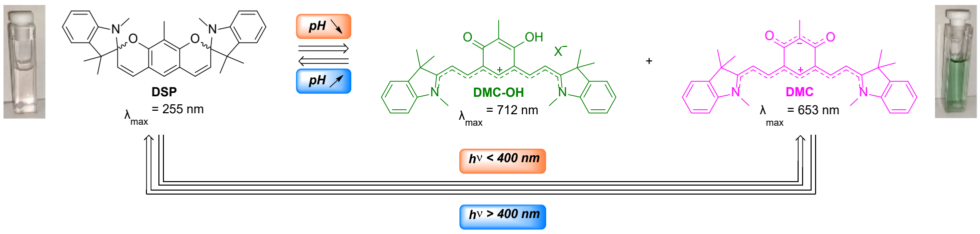

Figure 3: New DiSpiroPyran with acidochromic and photochromic properties.

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Phenazines chemistry: an unexpected synthetic route towards *N*- and *C*-substituted dyes

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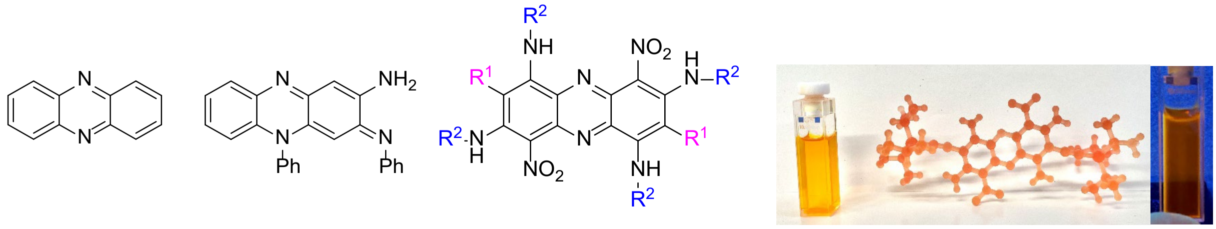
With applications ranging from biology[1,2] to optoelectronics,[3] phenazine derivatives are solidly established as a family of chromophores worth investigating, from the point of view of the synthetic routes[1,4]. The particular backbone structure consisting of two aromatic rings fused to a pyrazine core, resulting in a stable, planar and a fully conjugated aromatic π-system renders these molecules with highly attractive and easily tunable features.

In the field of phenazine chemistry, numerous synthetic methodologies have been already developed and are being currently investigated to control the nature and position of the functional group which is dictating the desired properties. Successfully combining various key features into a final structure requires adapting or even establishing of a new design strategy.

During our study, we have developed an unexpected and straightforward methodology that allows the efficient synthesis of nitrogen- and carbon-substituted phenazines, the nature of the substituents being easily tunable. The obtained derivatives present attractive absorption properties that could be further developed for organic electronics applications such as optical sensing or photovoltaics.



Phenazine

Induline

Figure 1: Phenazine structures and new substituted derivatives.

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Pharmacomodulations of antiplasmodial thienopyrimidinone hit with multi-stage activity

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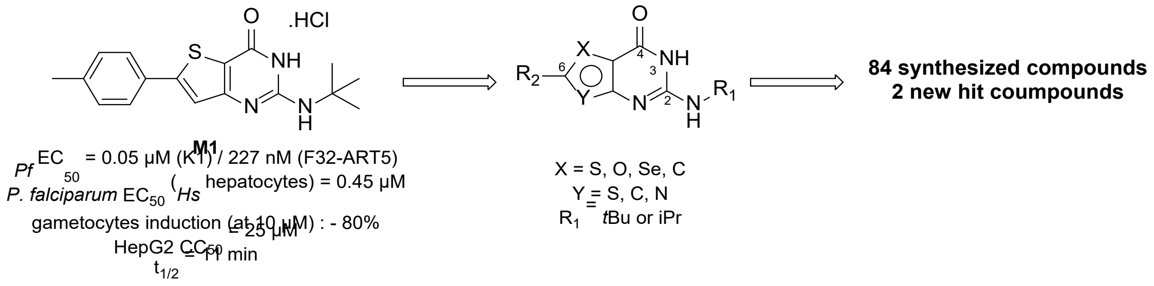
1. *Aix-Marseille Univ, CNRS, ICR UMR 7273, PCR, Faculté de Pharmacie, 13385 Marseille, France.*
2. *Aix Marseille Univ, IHU Méditerranée Infection, UMR VITROME, 13005 Marseille, France.*
3. *Sorbonne Université, CNRS/INSERM, CIMI, 75005 Paris, France.*
4. *Université Paul Sabatier, CNRS UPR 8241, LCC, 31077 Toulouse, France.*

Malaria is a parasitic infection caused by *Plasmodium* that affected 241 million people and killed about 627 000 in 2021, according to the WHO.[1] The discovery of new antimalarial compounds is necessary to tackle the spread of artemisinin-resistant *P. falciparum* strains.[2] In this context, we identified M1, a hit compound belonging to the 2-aminothieno[3,2-*d*]pyrimidinones series[3], showing *in vitro* multi-stage antiplasmodial activity associated with low cytotoxicity. Moreover, M1 is active against quiescent artemisinin-resistant *P. falciparum* strain. Unfortunately, M1 is quickly metabolized by mouse liver microsome into inactive derivatives ($t_{1/2}$ = 11 min), leading to weak *in vivo* activity on infected mouse model.

To improve M1 microsomal stability and to complete the structure-activity relationship (SAR) studies, position 6 of the thieno[3,2-*d*]pyrimidine scaffold was modulated and a scaffold hopping of the five-membered ring of the thienopyrimidine core was also investigated. All compounds were evaluated *in vitro* on the erythrocytic stage of *P. falciparum*. Best compounds were further assessed on the hepatic stage of *P. berghei* and *P. falciparum*, and their *in vitro* metabolic stability was determined. Pharmacomodulations allowed us to discover new molecules with improved metabolic stability while limiting the loss of activity. Interesting starting points for additional pharmacomodulations were also discovered. Synthetic routes and biological results will be presented in the communication.



Work supported by the "Fondation pour la Recherche Médicale" (FRM) – Project code DCM20181039565

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Monitoring of the lipid oxidation of dehydrated by-products coming from tuna processing

Turrini F. (1), **Grasso F.**[*] (1), Orlandi V. (1), Dondero L. (2), Grasselli E. (2) et Boggia R. (1)

(6) *Department of Pharmacy, University of Genoa, 16148, Genoa, Italy*
(7) *Department of Earth, Environmental and Life Sciences, University of Genoa, 16100, Genoa, Italy*

The increase in waste generated by the fish supply chain has a significant impact on environment and moreover it represents a big economic problem; in addition, it is necessary to consider the loss, within fish leftovers and their processing by-products [1], of precious compounds with high nutraceutical interest, with a view of a “zero waste economy”. University of Genoa is one of the 34 partners in EcoeFISHent, a European Union’s Horizon project (H2020-LC-GD-2020-3, https://cordis.europa.eu/project/id/101036428/it) implementing systemic solutions through multilevel circular value chains for an eco-sustainable valorization of fishing and fish industries side-streams.

By-products coming from canned tuna processing, made up of fillets scraps, fishbones, heads, once separated from viscera, have been dehydrated by a patented process in order to stabilize this highly perishable biomass and obtaining a powdered material with a residual humidity of about 5%. The bromatological analysis of the biomass before and after the dehydration step have been performed (humidity, protein, lipid, ash, and carbohydrates contents). Since lipid oxidation [2] may be considered one of the most dangerous modification in such an unsaturated food matrix, its monitoring seems mandatory in order to evaluate the possibility of further valorize these by-products. As far as fish oils are concerned, the analytical determinations suggested by Codex Alimentarius [3] are the Peroxide value (PV) and the Anisidine value (AV) to evaluate primary and secondary oxidation products respectively and combining them in the Total oxidation value (ToTox).

Looking for greener and more rapid approaches exploitable for the lipid oxidation monitoring of tuna by-products, the following determinations have been proposed:

- the Hara-Radin method to extract the lipid fraction has been proposed to replace the Folch method in order to avoid the use of halogenated solvents ;
- the spectrophotometric analyisis of the conjugated dienes was performed alternatively to PV test for the primary oxidation products evaluation ;
- the TBARS (Thiobarbituric Acid Reactive Substances) test [4] directly applied on the food samples, avoiding the lipid extraction step, has been proposed to evaluate the secondary oxidation products.

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Acknowledgements: EcoeFISHent project (Demonstrable and replicable cluster implementing systemic solutions through multilevel circular value chains for eco-efficient valorization of fishing and fish industries side-streams) Grant agreement ID: 101036428 has received funding from the European Union's Horizon 2020 EU.3.5. Green Deal, Call H2020-LC-GD-2020

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Design, synthesis and biological evaluation of new RNA ligands targeting miRNA-210: modulation of the circadian clock for cancer therapy

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(2) Molecular Medicine Research Line, Italian Institute of Technology (IIT), Genoa, Italy

Disruption of the circadian clock is associated with a variety of human pathologies, including cancer, and the expression of several clock genes is perturbed in many tumors[1]. The aberrant clock gene expression in tumors likely plays a causal role in the development of cancer and the survival of tumor cells. Recent observations suggest the hypothesis that pharmacological modulation of clock-related proteins may be an effective anticancer strategy.

Dr. Grimaldi reported the identification of a close connection between the circadian clock and MAX/MNT transcription networks. This study revealed a crucial role of the MAX transcriptional repressor (MNT) in regulating the activity of the molecular clock by repressing the expression of circadian genes. Notably, the expression of MNT under diverse conditions, such as hypoxia and cancer, appears regulated by miR-210[2]. The laboratory of Dr. Duca (ICN) has a successful experience in the design of multimodal small molecules targeting miRNAs, various series of compounds have been designed and synthesized to target oncogenic microRNAs precursors in a selective manner[3,4].

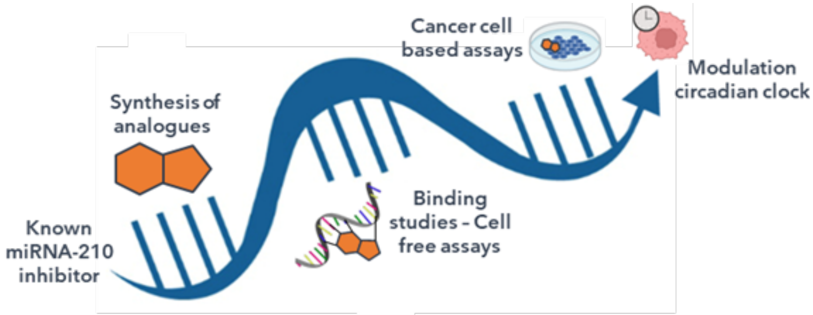

Figure 4 : Schematic view of the project

To this end, the main objective of this project is to identify a novel pharmacological approach that modulates the circadian activity through the targeting of the miR-210/MNT axis. On the one hand, the molecules generated will represent a valuable pharmacological tool for studying the role of miR-210 in circadian clock regulation. On the other hand, these molecules will provide suitable chemical scaffolds for the development of innovative clock modulators for treating circadian-related pathologies. Indeed, the anticancer activity of the miR-210 inhibitors will be also assessed.

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Chemistry Area :
☐ Material Chemistry or
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Synthesis and antileishmanial SAR study of new 5- and 7-substituted 3-nitroimidazo[1,2-*a*]pyridine using S_NAr and cross-coupling reactions

Paoli-Lombardo R. * (1), Primas N. (1), Hutter S. (2), Castera-Ducros C. (1), Bourgeade-Delmas S. (3), Sournia-Saquet A. (3), Valentin A. (3), Azas N. (2), Verhaeghe P. (3), Rathelot P. (1) and Vanelle P. (1)

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Leishmaniases are vector-borne parasitic diseases caused by several species of flagellated protozoa of the genus *Leishmania*. More than 1 billion people across 98 countries are at risk of infection by this neglected tropical disease (NTD), and nearly 1 million new cases occur annually. In humans, life-threatening visceral leishmaniasis is the most severe form, causing more than 20,000 deaths per year. Moreover, currently available treatments have major limitations.

In this context, our laboratory previously described three 3-nitroimidazo[1,2-*a*]pyridine lead compounds active *in vitro* against *Leishmania*[1] and *Trypanosoma*,[2][3] all substituted at position 6 and 8.

In the literature, positions 5 and 7 of the 3-nitroimidazo[1,2-*a*]pyridine ring have never been studied, so we decided to explore these positions. The synthesis of new compounds using S_NAr, Suzuki-Miyaura, Sonogashira and Buchwald-Hartwig reactions, as well as their antikinetoplastid activity, their selectivity and their physicochemical properties will be presented in the communication.

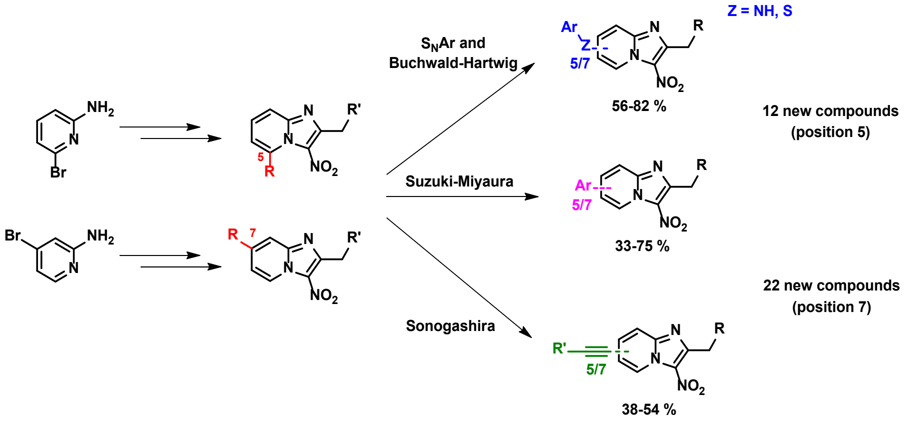

Figure 1: Synthesis of new 5- and 7-substituted 3-nitroimidazo[1,2-a]pyridine using S_NAr and cross-coupling reactions

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Chemistry Area :

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Magnetic Nanostructures: A smart platform for biomedical applications

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Single domain magnetic nanoparticles have attracted significant attention in nanomedicine as a promising material for theranostic applications[1,2]. Recently the possibility to assemble nanoparticles in ordered magnetic nanostructures open interesting new perspective in biomedical field. Accordingly, the aim of the work is to analyze the potential of magnetic nanostructures and their ideal characteristics for biomedical applications (i.e. to deliver and to harvest specific biomolecules; bio sensing, magnetic hyperthermia). This platform consists in spinel iron oxides ($MeFe_2O_4$; Me: Fe^{2+} and Co^{2+}) nanoparticles arranged in spherical structurally iso-oriented aggregates. The microstructure and morphology were studied by X-ray diffraction, transmission electron microscopy and N2-physisorption techniques. The primary nanocrystalline particles (~7 nm) assemble into spherical nanoporous aggregates with an average size of about 50-60 nm. Magnetization measurements show superparamagnetic behavior at room temperature. To optimize long-term, in-use colloidal stability, biocompatibility, and to provide specific sites for biological function grafting, MNPs were coated with 2,3-dimercaptosuccinnic acid (HOOC–CH(SH)–CH(SH)–COOH, DMSA) or citric acid ($HOC(CO_2H)(CH_2CO_2H)_2$). The investigation of the molecular coating has been carried out through Fourier Transform Infrared Spectroscopy (FTIR) and Thermogravimetric analysis (TGA). and the success of functionalization was investigated immobilizing neutravidin in lateral flow membrane strips (LFA assay). When the sample containing the particles flows along the membrane, the biotin captures the neutravidin attached to the MNPs, which are detected by the inductive sensor.

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Quinonediimine ligands for the design of oligomeric coordination complexes and molecular wires

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2,5-Diamino-1,4-benzoquinonediimine (QDI) stands as a versatile bis-bidentate and ditopic ligand for the preparation of coordination complexes featuring unusual optical or magnetic properties.[1] In solution, un/di-substituted QDIs allow to prepare extended and planar Ni(II) tapes whose absorption maxima directly depend on the length of the oligomers and can reach the near-infrared range for the longest complexes.[2]

Recently, on-surface synthesis of coordination polymers with QDIs under ultra-high vacuum conditions enabled the formation of flexible 1D π-d conjugated wires (M = Cr, Fe, Ni, Co, Cu) with lengths up to hundreds of nanometers.[3] This strategy also led to unprecedented hydrogen-bonded assemblies of QDIs that exhibit π-conjugation along the chain due to concerted proton transfer and can be easily manipulated on the surface.[4]

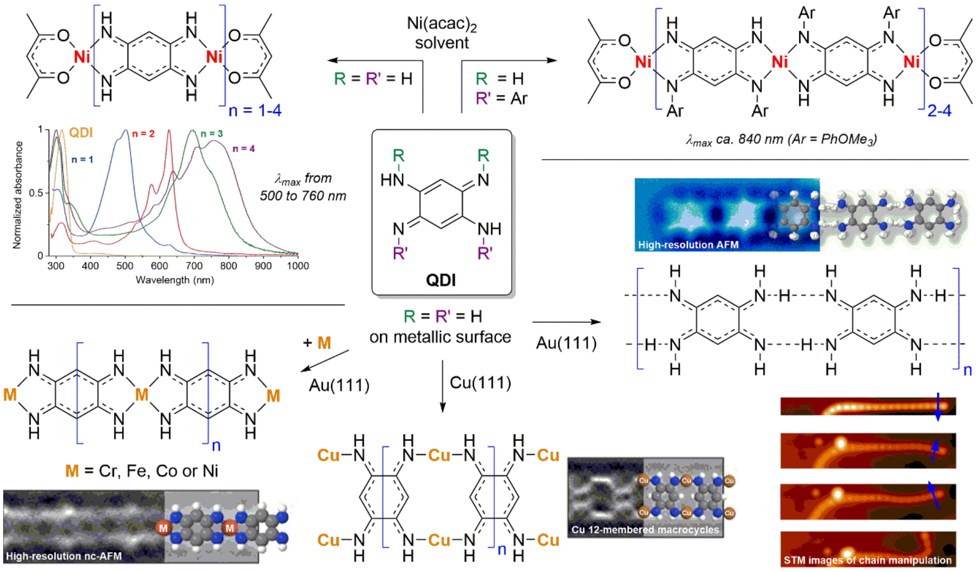

Figure 1: *Coordination chemistry of QDI in solution and on surfaces.*

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Chemistry Area :

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Ion - selective polymeric membranes for electrochemical devices

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During the last years, synthetic membranes have become widespread in laboratory or in industry as economically convenient and technically competitive separation solutions for different kinds of technologically advanced devices like filtration systems, fuel cells or redox - flow batteries (RFB). These membranes are usually obtained with functionalized organic polymers that are ion selective and can ensure good stability, duration and low cost of production. Basically centered on the development of membranes for electrochemical devices, our research aims to propose alternative membranes to the commercial ones (like Nafion®) able to reach the right compromise in term of good ionic conduction, stability and long life time to ensure high efficiency and a large number of charge - discharge cycles for these devices. We realized different types of membranes (Figure 1) based on stable functionalized aromatic polymers (PEEK, PSU). The main objective was to realize selective membranes able to exchange cations and anions. We thus introduced sulfonic groups on a PEEK backbone[1] to exchange protons or ammonium groups on PEEK and PSU to exchange anions[2]. Given the knowledge acquired on these two systems, we also realized amphoteric membranes able to exchange at the same time both kinds of ions, obtaining a versatile membrane for different applications. The continuous optimization of synthesis parameters, the choice of different polymers and/or functionalization groups and the improvement of casting procedures and treatments of membranes, led to good results in terms of ionic conductivity, selectivity and stability. The study of the main parameters of the synthesized membranes demonstrates a thermal stability above 200°C, a mechanical behavior characterized by a high elastic modulus and tensile strength and a relatively low ductility. Working on the degree of functionalization and the type of functionalizing groups, we obtained a tunable water uptake, an anionic conductivityup to $\simeq 3$ mS/cm and a very low .ion permeability (like vanadium ions for RFB applications) down to $\simeq 10^{-10}$ cm^2/min, which is much below typical literature data for cation- and anion separation membranes.

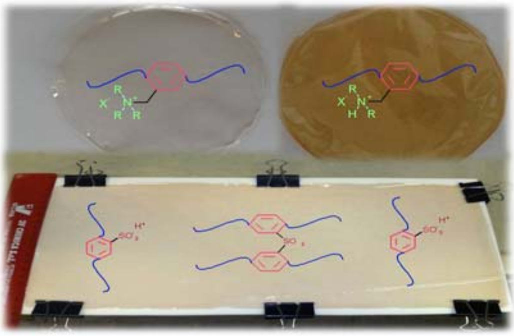

Figure 1 : Examples of studied anionic and cationic membranes

This work was supported by the Franco-italian University (Vinci program 2013).

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Chemistry Area :
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A study of modified Co/SiO_2 catalysts for CO_2 hydrogenation

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In the last decade, an increased attention has been given to the development of suitable heterogeneous catalytic systems for CO_2 hydrogenation to useful products among which both fuels and chemicals i.e., methane, CO, hydrocarbons, methanol, alcohols etc. [1]. Transition metal-based catalysts have been developed mainly relying on Ni and Ru for methane production [2-5], Co for methane, CO or hydrocarbons synthesis [6,7] and Cu when methanol is the desired product.

In previous works, Co/SiO_2 catalysts have been investigated by choosing different metal precursors and showing interesting activity in CO_2 hydrogenation to CH_4 and CO (reverse water gas shift product); their behavior has been also compared with the one obtained over unsupported Co based nanoparticles [7].

In the present work, Co/SiO_2 catalysts, modified with small amounts of K and Cu, have been characterized by means of XRD, FE-SEM, IR, UV-vis-NIR and tested for CO_2 hydrogenation at atmospheric pressure in the same conditions reported in [6,7].

Unmodified Co/SiO_2 catalyst achieved best performances showing the highest methane yield (75%) and small CO coproduction at 623-673 K. However, after exposure at the highest reaction temperature i.e., 773 K, a marked deactivation is observed by reducing catalytic activity and producing remarkable amounts of CO.

Modified K- and Cu- catalysts achieved lower performances and showed an enhanced deactivation for the proposed reaction. To shade light on this effect catalytic results have been compared with the forecasted thermodynamic equilibrium in the experimental conditions and deactivation has been investigated. For Co-catalysts, activity reduction might be ascribed both to a Co entrance in the catalyst matrix or to coke deposition over metallic particles.

A deep discussion on the role of the chosen modifiers on catalytic activity and deactivation will be presented by coupling a deep analysis and characterization of catalysts after reaction.

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Chemistry Area :

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Dihydrogen bioinspired photoproduction.

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Ladomenou, K.(2) Coutsolelos A. G. (2) Massin J. (1) Orio M. (1) Hardré R. (1)

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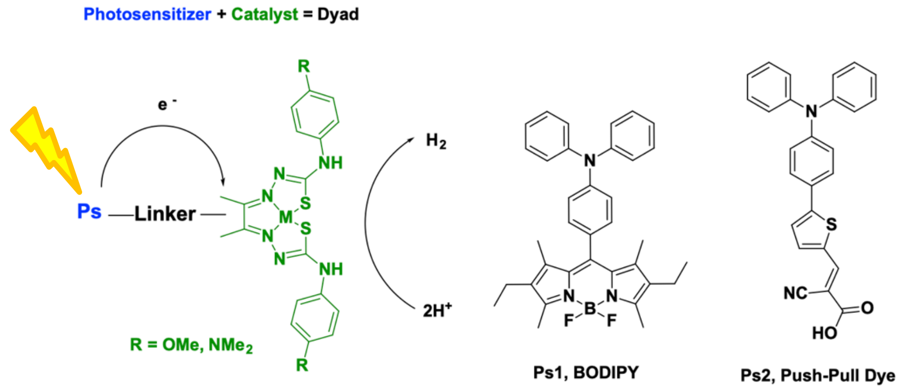
(3) *Co-funded by AMU (Aix Marseille University) and AID (Agence Innovation Défence).*

Dihydrogen is abundant and is considered an "ideal" fuel since only water vapors get released to the environment upon its combustion. In recent years, efforts have been made in developing new approaches to generate H_2 from renewable and sustainable resources, such as electrocatalytic and photocatalytic hydrogen evolution reactions (HER).[*]

Researchers have taken inspiration from Nature's through hydrogenase enzymes which contain inorganic cofactors that mediate the reversible conversion of protons and electrons into hydrogen.[†] Among all of the biomimetic and bioinspired catalysts that have emerged in the past years, transition metal ions such as cobalt or nickel, happened to be the building block for most efficient molecular catalyst for H_2 evolution. [‡]

Metal complexes with thiosemicarbazone ligands are emerging as a new class of electrocatalyst for HER. Recently, we reported the synthesis and characterization of a series of mononuclear nickel complexes (NiTSC) as efficient HER electrocatalysts.[§] Later on, we demonstrated that the parent complex (NiTSC-OMe) is an efficient photocatalyst when using an Iridium complex as a photosensitizer in a bimolecular process[**]. More recently, we showed that we can substitute the noble meta-photosensitizer by cheap and environmental-friendly NC-dots. [††] This has driven us to consider the design of dyads for photocatalytic HER by coupling our parent catalyst (NiTSC-OMe) with organic dyes using solar energy and protons to photoproduce H_2.



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Chemistry Area :

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Nanomaterials synthesis and assembling towards solution-processed elaboration of rectenna devices

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Rectenna devices have attracted increasing attention as potential candidates for next generation photovoltaic systems thanks to the exploitation of the wave nature of visible light and infrared radiations through a nano-antenna. These devices are composed of two different parts, one being an antenna matching the size of the wavelength to harvest, the other one being a rectifying material operating at the frequency of the same radiation. There are still many challenges in this field in order to use the visible and infrared wavelengths, as it requires the control of nanometer sized components, which is a difficult task still limiting the performances of rectifying antennas.

In this study, we start from a bottom-up approach based on colloidal metallic particles (silver or gold nanocubes), which can be fabricated on large scale at low cost. Nanocubes were synthesized and then assembled in a designed pattern, which was fabricated by electron beam lithography and then epitaxially connected at the atomic level by chemical growth in solution, to form monocrystalline nanopatterns on arbitrary substrates. The objective is therefore to control these antenna geometries by developing a solution-processed approach for the fabrication of the patch plasmonic nano-antennas. Another goal of the project is to develop a methodology allowing to electrically connect high frequency molecular diodes (or dielectric layers in a MIIM structure) and these patch plasmonic nanocubes in a rectenna design which allows improving the antenna/diode impedance matching. Further work on optical properties and conductivity measurements of the devices will be investigated.

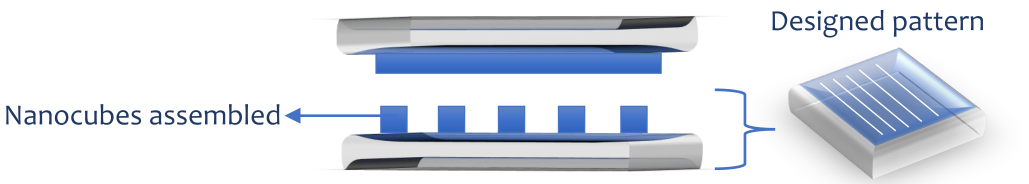

Figure 1: Finalized rectenna devices

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Engineering of Lytic Polysaccharide MonoOxygenases

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(3) European Synchrotron Radiation Facility, F-38043 Grenoble, France

Lytic Polysaccharide MonoOxygenases (LPMOs) are recently discovered mononuclear copper monooxygenases involved in recalcitrant polysaccharides degradation (cellulose, chitin) in synergy with glycosyl hydrolases [1]. From a mechanical point of view, the copper LPMOs active site hydroxylates the C-H glycosidic bond in the presence of oxygen or hydrogen peroxide and a reductant, leading to polysaccharide chains cleavage [1,2] (Fig 1a).

A very unusual metal coordination motif modulates the functionality of the copper active site. Known as "histidine brace", it consists of two fully conserved histidines, one of which is located at the N-terminus and binds copper by both its side chain imidazole and the free amino-terminal group [1,2] (Fig 1b). In the group, we investigate structure-reactivity relationships of the copper active site of LPMOs via an interdisciplinary approach from molecular biology to chemistry. Focusing our attention on the well-reported chitin-active LPMO *Sm*AA10, we created new-metal-binding motifs by site directed mutagenesis of first- and second-sphere residues. The new variants were characterized to evaluate how these substitutions affect the properties of the active site (copper binding affinity, geometry, redox properties) and its chitin degradation ability, emphasizing that this unusual coordination motif imparts unique features to the copper centre (Fig 1c).

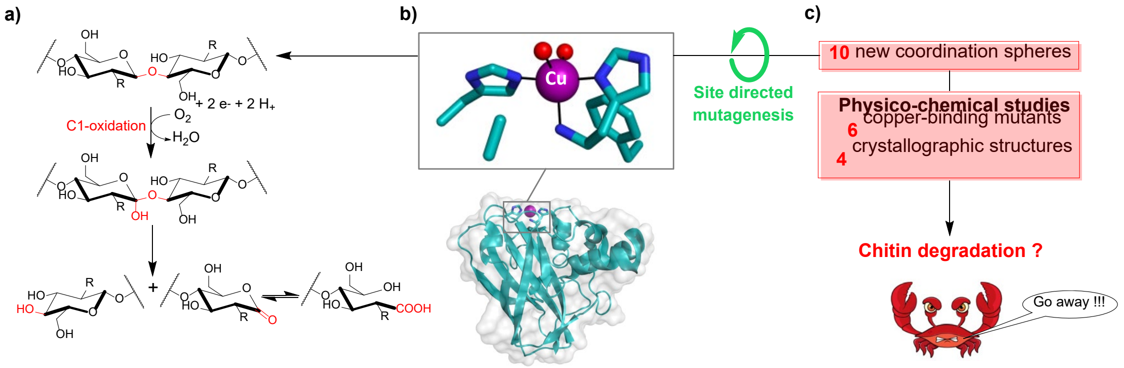

Figure 1: Engineering of SmAA10 LPMO: (a) Biopolymers oxidative degradation (b) LPMO active site (c) SmAA10 engineering and mutants' characterization

Project financed by the ANR (Projet Abiozyme ANR-18-CE07-0003)

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Fluorinated dendrimers as ^{19}F-MRI imaging probes

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Fluorine-19 Magnetic Resonance Imaging (^{19}F-MRI) is an emerging modality for molecular imaging, thanks to the high spatial resolution, deep-tissue penetration and no background ^{19}F-MRI signal in biological systems. However, designing an ideal ^{19}F-MRI imaging agent with high fluorine content, good water solubility and optimal MRI properties for biomedical imaging is challenging. In this perspective, we designed and synthesized fluorinated amphiphilic dendrimers, which have high fluorine content and suitable ^{19}F-MRI properties yet being highly soluble in water. They were able to self-assemble into small and stable nanomicelles and accumulate within tumor lesions via enhanced permeability and retention (EPR) effect for effective tumor imaging. Importantly, the formed nanomicelles also enabled encapsulation of anticancer drugs, offering both ^{19}F-MRI-based tumor detection and chemotherapy-based cancer treatment at the same time. They constitute therefore promising theranostics for cancer management. We are working actively in this direction.

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Bifunctional Iodoazolium Salts: Searching for Cooperation Between Halogen Bonding and Hydrogen Bonding

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Non-covalent interactions play an important role in all subfields of chemistry, including catalysis, where interactions of different natures can work together to improve reactivities and selectivities. Several families of molecules that incorporate both hydrogen bond (HB) and halogen bond (XB) donors[1] have already been studied. However, iodoazolium salts, which are very popular XB donors, have rarely combined with HB donors.[2] We share the synthesis of a library of iodoazolium salts bearing diverse HB donors (figure 1).

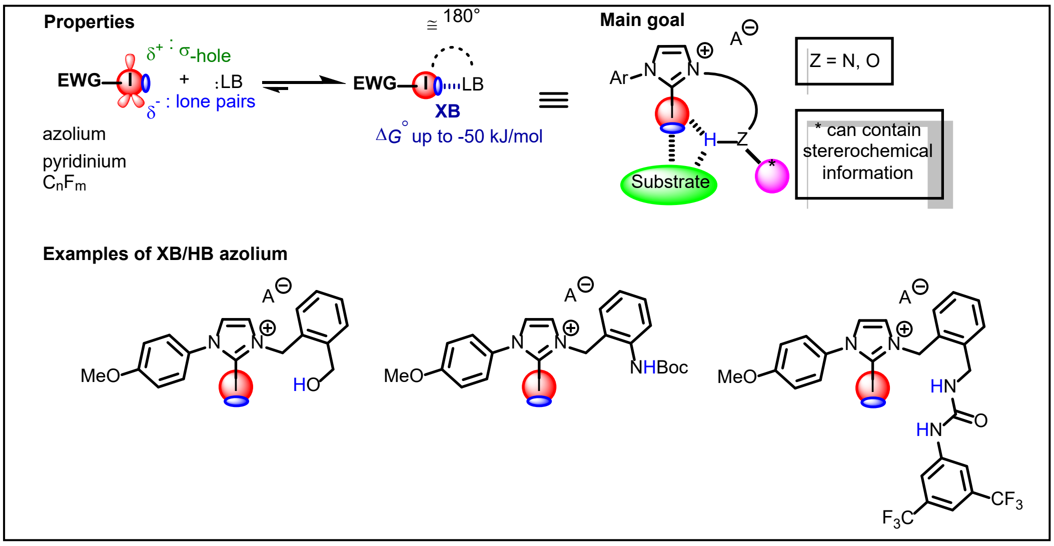

Figure 1: Properties and general structure of iodoazolium salts containing HB-assisted XB.

Along with a study of their physico-chemical properties using different technique (X-ray diffraction, ^{31}P NMR, ITC) their behaviour in catalysis was also evaluated in several reactions: (hetero-Diels-Alder reaction with *N*-arylimines and transformations of bromodiarylmethanes (Ritter-type solvolysis and Friedel-Crafts alkylation). Only limited evidence of cooperation between XB and HB could be obtained, presumably because of a too long spacer between both functionalities. However, our studies have provided experimental evidence for the real role of the iodoazolium salt in Friedel-Crafts alkylations with different classes of electron-rich (hetero)aromatic compounds.

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Bis-chalcone derivatives derived from natural products as promising near-UV/visible light sensitive photoinitiators of polymerization

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Photopolymerization is a process that rapidly transforms a liquid monomer into a solid material upon irradiation with light (e.g. ultraviolet light, visible light or even infrared). With the advantages of reacting rapidly at room temperature while requiring a minimum energy to be initiated, and being a relatively low-cost polymerization technique allowing a perfect temporal and spatial control, free radical photopolymerization is still of crucial interest in both the academic and the industrial communities. Due to their good biocompatibility and stability, photoinitiators derived from natural plants can be of great interest in various research fields ranging from imaging, radiation curing, and optics technologies to (bio)medicine, microelectronics, and materials science. After absorbing light of the appropriate wavelength, these compounds are promoted to an excited state that can interact with the additive through an electron (or energy) transfer reaction to produce reactive species (such as cations or free radicals) that can initiate the photopolymerization reaction.

Chalcones are a class of dyes that can be found in many natural plants and exhibit different light absorption properties and colors depending on the substituents as well as their positions on the chalcone backbone. Bis-chalcones have only been very scarcely studied in the literature as photoinitiators so that the mechanism involved in the photopolymerization process while using these bis-chalcone derivatives is still unclear.

In this work, a series of novel bis-chalcone compounds with a broad absorption extending over the near UV/visible range have been synthesized and examined for the first time as photoinitiators in combination with an amine and an iodonium salt for the free radical polymerization of acrylates and the cationic photopolymerization (CP) of EPOX. Interestingly, 3D patterns of high spatial resolution could be fabricated through the free radical polymerization of PEG-diacrylate, demonstrating the pertinence of the approach (See Figure 1).

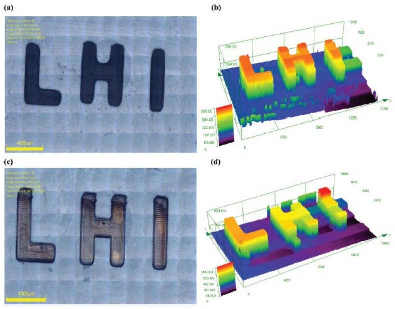

Figure 1: 3D pattern obtained by direct laser write.

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Synthesis of azonia polycylic aromatic atropisomers

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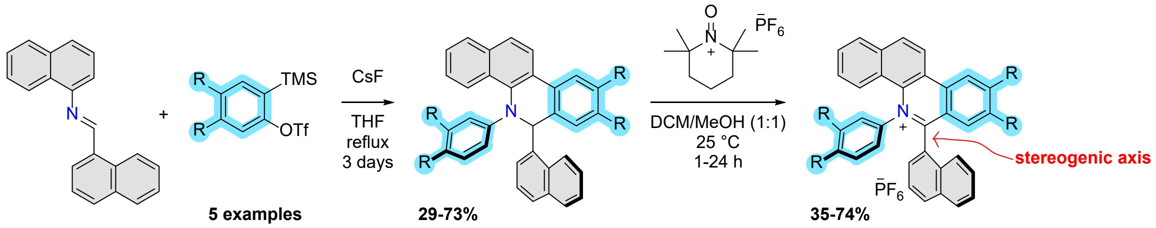
Cationic polycyclic aromatic compounds containing one or more nitrogen atom(s), also known as azonia polycyclic aromatic compounds, form a valuable class of molecules because of their fluorescent and/or medicinal properties. However, chiral azonia polycyclic aromatic compounds are scarce [1,2] and methods for their synthesis are highly desirable. The inclusion of π-electron-donating nitrogen atom (N-doping) is one of the most productive approach to modulate the electronics in π-conjugated networks. Nowadays, azonia polycyclic aromatic compounds are routinely synthesized from aza-dienes via rhodium-catalyzed annulative alkyne-insertion reactions involving a C–H bond activation [3]. Herein we propose a different approach.

Back to 2015, we have developed an aryne aza-Diels–Alder cycloaddition/*N*-arylation sequence for the synthesis of *N*-arylated hydroisoquinoline derivatives [4]. Recently, we examined the subsequent two-electron oxidation of these products to prepare some azonia polycylic aromatic atropisomers. Under optimized conditions, suitable 2-azadienes were reacted with an excess of aryne precursors, and the resulting products were oxidized with an oxoamonium hexafluorophosphate salt to afford the expected azonia polycylic aromatic atropisomers. The structural and optical properties of these molecules were determined, and their chirality ascertained by spectroscopic and computational methods.



Aryne aza-Diels–Alder cycloaddition / N-arylation / two-electron oxidation sequence for the synthesis of azonia polycylic aromatic atropisomers.

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Self-assembling supramolecular dendrimer nanosystems for tumor imaging

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2. *Aix-Marseille University, INSERM, INRA, Center de Recherche en Cardiovasculaire et Nutrition (C2VN), Marseille, France*
3. *Aix-Marseille University, Centre Européen de Recherche en Imagerie Médicale (CERIMED), Marseille*

Early tumor detection and precise diagnosis is the key for successful management of cancer. Bioimaging plays an important role in cancer diagnosis and treatment. However, imaging sensitivity and specificity still constitute key challenges. Nanotechnology-based imaging is particularly promising for overcoming these limitations because nanosized agents can specifically accumulate in tumors via the "enhanced permeability and retention" (EPR) effect, thus improving imaging sensitivity and specificity. We have developed innovative supramolecular dendrimer nanosystems for tumor imaging using positron emission tomography (PET) and single photon emission computed tomography (SPECT) [1-3]. These nanosystems were constructed via self-assembling of amphiphilic dendrimers bearing Ga^{3+} and In^{3+} radionuclides respectively, at the dendrimer terminals. They formed small, uniform and stable nanomicelles, which accumulated readily in tumor lesions for effective PET and SPECT imaging. Benefiting from the combined dendrimeric multivalence and EPR-mediated passive tumor targeting, these nanosystems demonstrate superior imaging compared to the clinical reference. Consequently, they constitute promising probes for early and efficient tumor detection. We are actively investigating the chemistry behind these nanosystems for their size, morphology, surface charge and self-assembling relating to biodistribution and imaging specificity.

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Synthesis of new broad-spectrum inhibitors for enterovirus

Roux H. (1), Khoumeri O. (1), Touret F. (2), Coluccia A. (3), Gattacecca F. (4), Fanciullino R. (4), Silvestri R. (3), Nougairede A. (2), Roche M. (1) et Vanelle P. (1)

(1) Aix-Marseille Université, CNRS, ICR UMR 7273, PCR, Faculté de Pharmacie, 13005 Marseille, France
(2) Aix-Marseille Université, Unité des Virus Émergents - (UVE) - IRD_190 - Inserm_1207 EFS - IRBA of Medical Research,Marseille, France
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(4) Aix-Marseille Université, Plate-forme SMARTc, CRCM--INSERM-1068, Marseille, France

Enterovirus (EVs) and rhinovirus (RVs) are responsible for several diseases with serious impact for some patients. Moreover, we have witnessed in recent years the emergence of new variants of EVs with more severe clinical consequences than those previously described. Finally, EVs became even more widespread during the SARS-COV2 pandemia [1].

Therefore, since 2014, the LPCR develops broad-spectrum and oral eligible drug candidates against EVs/RVs [2]. In 2019, three compounds were identified with either better activity or lower toxicity and a similar activity than reference drug against EVs (Vapendavir). In addition, their *in silico* pharmacokinetic evaluations are also better. Every drug targets and binds to an hydrophobic cavity of a viral capsid protein, which is similar for virus of pharmaceutical interest. The project is now dedicated to the optimization of the structure of drug candidates through sequential synthesis, structure-activity and structure-pharmacokinetic relationships (SAR / SPR). This optimization is conducted with 3 objectives: the discovery of new interactions to improve activity, the improvement of drug bioavailability by adding of new chemical groups, and the use of innovative synthesis strategies to achieve the larger number of modulations.

The presented poster will contain last results of the project.

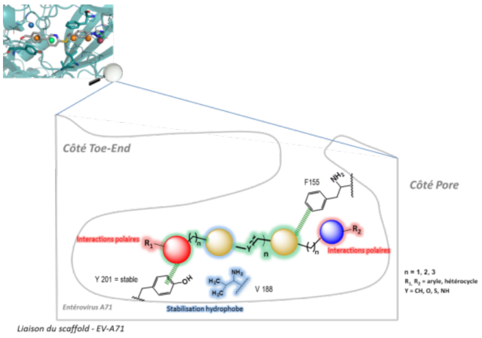

Figure 1:Broad-spectrum drug in the hydrophobic cavity of EV71

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Synthetic economies in 1,3-diols preparation

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(1) *Aix Marseille Université, Centrale Marseille, CNRS, iSm2, Marseille, France*

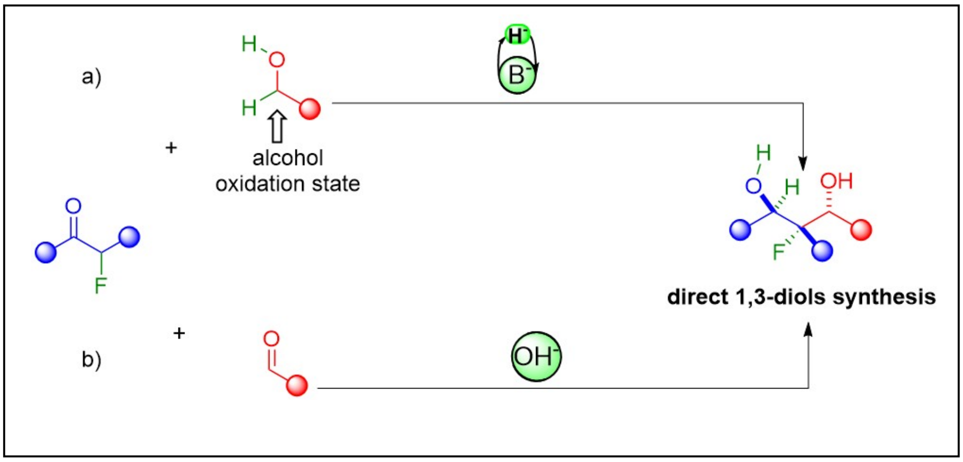
1,3-diols are ubiquitous in a broad range of natural products and drugs conferring excellent bioactivity to these organic molecules. As a result, discovering innovative methods with synthetic economies to rapidly prepare them is crucial. Unfortunately, most sequences available to prepare this key fragment are based on stepwise processes often involving numerous redox steps.[1]

In this context, we recently designed different eco-compatible cascades avoiding any unnecessary stoichiometric redox steps in their elaboration (figure 1). These condensations enable the direct elaboration of valuable fluorinated polyols directly either from the alcohol(a) or from the aldehyde(b) oxidation states.

From the alcohol, this redox-neutral aldolization cascade involves several Meerwein–Pondorf type hydride transfer from alcohols to carbonyl. As a result, the hydride coming from the alcohol is directly transferred to the final aldol product avoiding the use of stoichiometric redox reagents.[2]

In a complementary approach, using two equivalents of aldehydes, 1,3-diols featuring three contiguous stereogenic centers are generated with excellent yield and diastereocontrol (typically >99:1 dr) by a Tishchenko type aldolization.[3] Of interest, challenging fluorinated tetrasubstituted stereocenters are generated with perfect stereocontrol during this cascade.

Figure 1 :



Redox-neutral aldolization and Tishchenko type aldolization

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A study of Ni/SiO_2 catalysts for CO_2 hydrogenation

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Carbon dioxide hydrogenation, using renewable hydrogen, to methane through the so-called Sabatier reaction is recognised as a promising option. Ni-based catalysts represent a suitable choice for methanation reaction thanks to their high activity, the low cost of Ni and its remarkable natural abundance. In the literature, several supports have been tested i.e., Al_2O_3, SiO_2 [1], TiO_2, zeolites etc. [2]. However, many issues have been pointed out such as low activity at low temperature, low reducibility and dispersion of the active phase and, high deactivation manly due to particles sintering or coking.
In the present work, we investigated the catalytic activity of a prepared series of Ni/SiO_2 based catalysts [3] by incipient wetness impregnation (NiO loading 1-33 wt.%, commercial SiO_2 support) and we characterized both the fresh and the exhausted materials by means of XRD, FE-SEM with EDXS, H_2-TPR, IR, UV-vis, porosity and surface area measurements. Catalytic performances have been assessed in a laboratory scale plant [4] working at a GHSV=55000 h^{-1} and atmospheric pressure within the temperature range 523-773 K in ascending /descending mode and dilute conditions. In these conditions, the best catalyst results to be 33wt.%NiO achieving a methane yield of 74% at 723K nearby thermodynamic equilibrium. In Figure 1, it is possible to observe that the bright NiO particles, spherical or cubic in the fresh catalyst, appear in the exhaust catalyst as rounded particles, covered by a carbon veil.

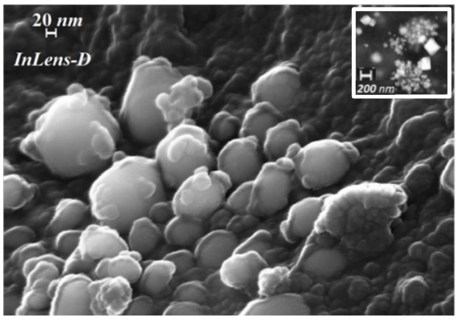

Figure 1: FE-SEM images of the exhausted Ni/SiO_2 catalyst (16.7 wt.% NiO) and of the fresh one (inset)

The obtained data will be discussed by looking at methane and CO production, insights on catalysts deactivation will also be also given.

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☐ Material Chemistry or

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One-pot synthesis of a bis-zwitterionic macrocycle *via* transamination reactions

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University POLITEHNICA of Bucharest, 1-7 Gh. Polizu Str., 011061 Bucharest, Romania.
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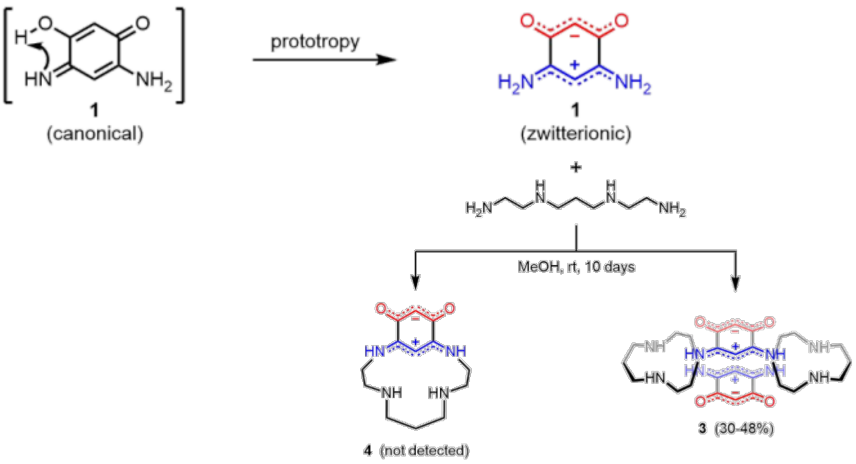
[d] Aix Marseille Univ, CNRS, Centrale Marseille, FSCM, Marseille, France
[e] Laboratoire CEISAM – UMR CNRS 6230, Nantes Université, 44322 Nantes, France.

Quinones represent an essential class of molecules that have shown their ability and versatility in various chemistry fields as oxidizing agents,[1,2] dyes and pigments[3,] and pharmaceuticals.[4] Particularly intriguing are the quinones derived from 2-hydroxy-5-amino-1,4-benzoquinonemonoimine (BQI) **1** which have never been obtained in their canonical form so far but were, instead, isolated in their zwitterionic form after a prototropic rearrangement (Scheme 1). This structural feature leads to a specific reactivity for a very efficient and versatile reaction: the transamination. This latter, taking place at the two nitrogen-bearing carbon atoms, arose as a powerful tool for fine-tuning the zwitterionic BQI properties by controlling the N– substituent nature (aryl vs alkyl).[5]



Scheme 1. Synthesis of macrocycle 3

Herein, following this line, we report the efficient and straightforward synthesis of a bis-zwitterionic macrocycle **3** (Scheme 1); that we discovered by serendipity using a polyamine instead of a monoamine. This novel route paves the way to the access of a new class of highly relevant flexible azamacrocycles featuring two confined donor cavities.

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Gold-Catalyzed One-Pot Cycloisomerization/Nucleophilic Addition /Rearrangement of Acenaphtylene Carbaldehyde.

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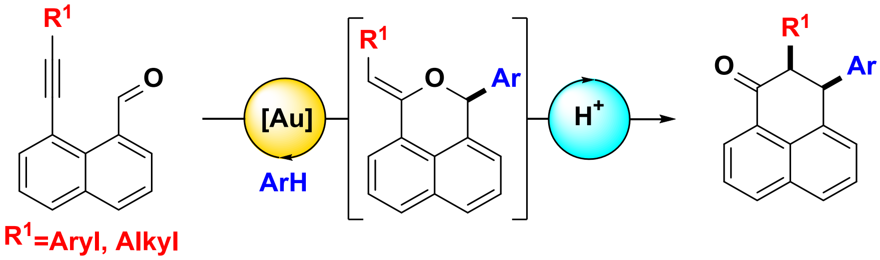
Gold catalysis has been recognized as a fascinating area in recent years to achieve the synthesis of complex core structure according to atom-economical and green processes. [*] Gold complexes are highly interesting tools due to their ability to activate unsaturated bonds, leading to nucleophilic additions. Regarding this characteristic, cycloisomerization and domino reactions of carbonyl-ynes could lead to polycyclic molecules.[2] Considering our continuous interest in gold-catalyzed cyclization and domino processes [3], we have been interested in the reactivity of acenaphtylene carbaldehyde. The group of Grela has described that reactivity in the presence of gold and alcohols as nucleophile.[4] We have studied the unprecedented gold-catalyzed domino reaction implying electron rich aromatic rings as nucleophile and leading to benzo[*de*]isochromenes derivatives.
We discovered a novel rearrangement leading to phenalen-1-one derivatives in presence of acid.[5]



One-pot gold-catalyzed formation of 2,3-dihydro-phenalen-1-one.

Optimization of the reaction conditions as well as the scope and limitations will be presented.

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[5] Truchon, A.; Dupeux, A.; Olivero S.; Michelet, V. unpublished results

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Combining voltammetric and mass spectrometric data to evaluate iron organic speciation in subsurface coastal seawater samples of the Ross Sea (Antarctica)

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Iron (Fe) is the most important trace element in the ocean, as it is required by phytoplankton for photosynthesis and nitrate assimilation [1]. Fe speciation is important to better understand the biogeochemical cycle and availability of this micronutrient, in particular in the Southern Ocean [2]. Dissolved Fe (dFe) concentration and speciation were determined in 24 coastal subsurface seawater samples collected in the western Ross Sea (Antarctica) during the austral summer 2017 as part of CELEBeR (CDW Effects on glacial mElting and on Bulk of Fe in the Western Ross sea) project. ICP-DRC-MS was used for dFe determination whereas CLE-AdSV was used to obtain the concentration of complexed and free dFe, of the ligands, and the values of the stability constants of the complexes. dFe values ranged from 0.30 to 2.50 nM and $\log K_{FeL}$ from 23 to 25, highlighting the presence of Fe-binding organic complexes of different stabilities. Principal Component Analysis (PCA) allowed us to explore the correlations among dFe, speciation parameters and the biogeochemistry of the area. A deep investigation on the nature of the organic ligands was carried out by HPLC-ESI-MS/MS. The results obtained by this analytical technique evidenced the presence of a heterogeneous class of siderophores in organic ligands pool.

[1] *E. Ibisanmi, S. G. Sander, P. W. Boyd, A. R. Bowie, and K. A. Hunter, "Vertical distributions of iron-(III) complexing ligands in the Southern Ocean," Deep. Res. Part II Top. Stud. Oceanogr., vol. 58, no. 21–22, pp. 2113–2125, 2011.*

[2] *M. Gledhill and K. N. Buck, "The organic complexation of iron in the marine environment: A review," Front. Microbiol., vol. 3, no. FEB, pp. 1–17, 2012.*

Chemistry Area :

☐ Material Chemistry or

☐Environmental and Analytical Chemistry or

■Organic and Bioorganic Chemistry or

☐Physical Chemistry

Heterohelicenes through 1,3-Dipolar Cycloaddition of Sydnones with Arynes

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Despite their fascinating structure and unique properties, the synthetic access to helicenes and heterohelicenes remains challenging and often requires multistep approaches. We reasoned that a late-stage formation of this helicoidal structure through sydnone 1,3-dipolar cycloadditions could allow a fast access to new Polycyclic Heteroaromatic Hydrocarbon (PHH). This process involves the design and synthesis of *ortho*-substituted polyaromatic sydnones, and highlights the first example of regioselective cycloaddition of such mesoionic dipoles with aryne derivatives. [1] The origins of this phenomena have been studied by DFT calculations in collaboration with Dr P.-A. Champagne (NJIT). [2] From the library of 24 hetero-helicenes synthesized, a pyridyl containing derivative displayed a reversible, red-shifted, pH-triggered chiroptical switching properties, with a rare CPL-sign reversal. [3]

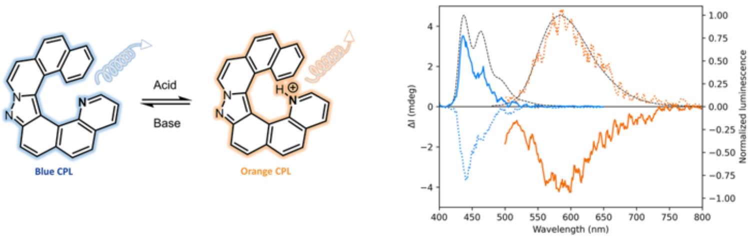

Figure 1 : CPL sign inversion upon protonation

[1] a) Nakazawa, S.; Kiyosawa, T.; Hirakawa, K.; Kato, H. *J. Chem. Soc., Perkin Trans. 1* **1974**, 621-621; b) Cheong, P. H.-Y.; Paton, R. S.; Bronner, S. M.; Im, G.-Y. J. Garg, N. K.; Houk, K. N. *J. Am. Chem. Soc.* **2010**, *132*, 1267–1269 c) Ikawa, T.; Masuda, S.; Takagi, A.; Akai S. *Chem. Sci*., **2016**, *7*, 5206-5211. (d) Ikawa, T.; Masuda, S.; Nakajima, H.; Akai, S. *J. Org. Chem.* **2017,** *82*, 4242-4253.

[2] Yen-Pon, E.; Champagne, P.-A.; Plougastel, L.; Gabillet, S.; Thuéry, P.; Johnson, M.; Muller, G.; Pieters, G.; Taran, F.; Houk, K. N.; Audisio, D.; *J. Am. Chem. Soc,* **2019,** 141, 1435–1440

[3] Yen-Pon, E.; Buttard, F.; Frederic, L.; Thuery, P.; Taran, F.; Pieters, G.; Champagne, P.-A.; Audisio, D, *JACS Au*, **2021**, 1, 807–818

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