Société Chimique de France
Le réseau des chimistes

Journée de la Chimie SCF Sud-PACA 2023

31 mars 2023 - Palais du Pharo

Chères et chers ami(e)s,

C'est un plaisir et un honneur de vous accueillir à la Journée de la Chimie SCF Sud-PACA 2023 – JdlC2023, qui a lieu au Palais du Pharo à Marseille le 31 mars 2023.

La Journée de la Chimie SCF Sud-PACA est une manifestation scientifique organisée tous les 2 ans (années impaires) par le bureau de la section régionale Sud-PACA de la Société Chimique de France, en alternance avec les Journées Franco-Italiennes de Chimie co-organisées par la section régionale Sud-PACA de la Société Chimique de France et les sections régionales Piémont-Val d'Aoste et Ligurie de la Société Chimique Italienne (années paires).

L'organisation de ces rencontres scientifiques ne peux se faire sans le soutien financier d'institutions publiques et d'entreprises, sous forme de mécénat ou de participation comme exposant. La section régionale Sud-PACA de la SCF tient à exprimer sa profonde reconnaissance à nos partenaires, institutionnels et privés, pour leur engagement et leur confiance.

Pareillement, l'organisation de la JdlC2023 n'aurait pas pu se faire sans participants heureux de se retrouver pour échanger autour des dernières découvertes scientifiques, soyez toutes et tous remercié(e)s pour votre participation à cette manifestation.

Nous vous souhaitons une agréable journée riche de sciences et de rencontres. Bonne JdlC2023 !

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Programme

8h50		**Ouverture et introduction**	
9h00	Conférence plénière *Amphi Gastaut* *Modérateur: Cyril Bressy*	**CP1 | Prof. Mark Lautens (Univ Toronto)** ***Flipping the Switch: Reversibility in Catalysis***	
	Sessions parallèles de communications orales	Session 1 *Amphi Gastaut*	Session 2 *Amphi Touze*
9h45		CO-01 Florian Ferrer	CO-12 Yongxing Wang
10h00		CO-02 Samuel Cousin	CO-13 Sofiane Bourdillon
10h15		CO-03 Andrea Fasano	CO-14 Axel Bossavit
10h30	Pause-café	Session Poster *Salle des Voûtes*	
11h00		CO-04 Benjamin Mourot	CO-15 Paul Guérin
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12h00	Déjeuner buffet	Session Posters *Salle des Voûtes*	
13h30	Conférence plénière *Amphi Gastaut* *Modératrice: Patricia Merdy*	**CP2 | Dr. Isabelle Couturier-Tamburelli** ***Etude de l'évolution photochimique des aérosols de l'atmosphère de Titan***	
14h15		CO-08 Salma Bikerchalen	CO-19 Jingke Hou
14h30		CO-09 Micol Zerbini	CO-20 Arthur Gaucherand
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15h15	Pause-café	Session Posters *Salle des Voûtes*	
15h45	Conférence plénière *Amphi Gastaut* *Modérateur: Sylvain Marque*	**CP3 | Dr. Didier Gigmes - Grand prix régional 2023** **Alkoxyamines as valuable precursors for macromolecular engineering**	
16h30	*Amphi Gastaut*	Conclusion et clôture – Yoann Coquerel	

Programme détaillé Communications Orales - Session 1

	Session 1 ***Amphi Gastaut***
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10h00	CO-02 Samuel Cousin **Exploiting Solid-State Dynamic Nuclear Polarization NMR Spectroscopy to Establish the Spatial Distribution of Polymorphic Phases in a Solid Material**
10h15	CO-03 Andrea Fasano **Chimeric hydrogenase complexes: a new strategy to study structure function relationships**
11h00	CO-04 Benjamin Mourot **Synthesis and Spectroscopic study of new Coupled Polymethines as NIR absorbing dyes**
11h15	CO-05 Brahim Akhassi **Novel Z-scheme heterojunction oxyhalide photocatalyst for photodegradation of sulfadiazine antibiotic under visible light**
11h30	CO-06 Amélie Frison **An innovative solvent-free polymer sample preparation method for DNP SSNMR**
11h45	CO-07 Blanche Krieguer **Etude RPE du polypropylène et du polyéthylène irradiés par des rayons gamma et des rayons X**
14h15	CO-08 Salma Bikerchalen **Photocatalytic degradation of recalcitrant organic pollutants by non-typical stoichiometric oxygen-rich bismuth oxychloride $Bi_xO_yCl_z$ photocatalyst under UV and Visible light irradiation.**
14h30	CO-09 Micol Zerbini **Uranium in seawater, accumulation by brown algae Ascophyllum nodosum**
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15h00	CO-011 Floriane Delpy **Fluorescent labeling of nano/microplastics and application for ecotoxicity tests**

Programme détaillé Communications Orales – Session 2

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14h30	CO-20 Arthur Gaucherand **Simultaneous Control of Central and Helical Stereogenic Elements on Small Molecules**
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15h00	CO-22 Ange Wilfrid Embo-Ibouanga **Synthesis of smart alkoxyamines: theranostic against cancer**

Conférences Plénières

CP-1

Flipping the Switch: Reversibility in Catalysis

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A 1997 report by Catellani outlining a novel C-H functionalization reaction stimulated our interest in reversible reactions, since a key step is reversible carbopalladation with norbornene (1). We subsequently explored improved reaction conditions, and the synthetic potential of the Catellani reaction, including its application in the synthesis of natural products (2-4).

This lecture will discuss how our research program evolved to explore other metal catalyzed reversible reactions, including forming and breaking C-C and C-X bonds (5-7).

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CP-2

Etude de l'évolution photochimique des aérosols de l'atmosphère de Titan

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Titan, la plus grande lune de Saturne, est le seul satellite du système solaire à posséder une atmosphère dense (avec une pression en surface de 1,5 bars). Ses deux composants atmosphériques majoritaires à savoir, le diazote et le méthane, sont connus pour être photodissociés à haute altitude sous l'action d'électrons provenant de la magnétosphère de Saturne, d'ions énergétiques et de photons UV solaires [1]. Ces processus conduisent dès la haute atmosphère, à la formation de molécules organiques complexes (nitriles et hydrocarbures). Considérant à la fois le profil de température de Titan et ses variations saisonnières atmosphériques, certaines molécules peuvent se condenser dans la stratosphère conduisant à la formation de particules glacées ou de nuages, soumis à des photons UV solaires moins énergétiques (λ>230nm) à ces altitudes (Figure 1). Plusieurs molécules ont ainsi été proposées comme pouvant être à l'origine de nuages observés au niveau des pôles par comparaison avec les expériences réalisées en laboratoire [2].

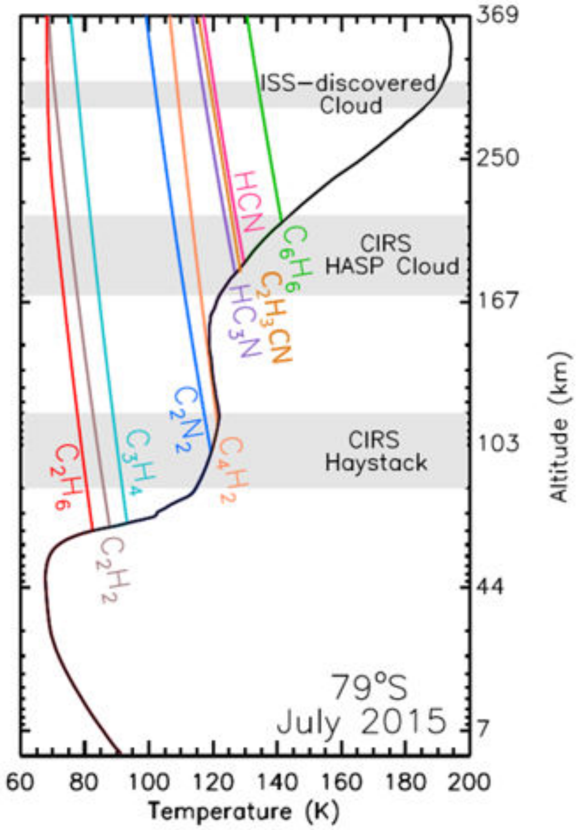

Figure 1: Profil de condensation de différentes espèces détectées en phase gazeuse dans l'atmosphère de Titan [2]

Le dernier nuage observé par la mission Cassini-Huygens, dénommé nuage HASP (High Altitude South Polar) résulterait de la condensation simultanée du benzène, C_6H_6, du cyanure d'hydrogène, HCN et probablement d'acrylonitrile, C_2H_3CN [3]. Afin de mieux comprendre ces observations, nous simulons expérimentalement la condensation et la photochimie de ces molécules, isolées, dans un premier temps, puis condensées simultanément avec différents ratios [4-6]. Le dispositif expérimental conçu dans notre laboratoire nous permet de suivre l'évolution de la phase solide par IR-TF. Ces résultats sont d'utilité dans l'interprétation des données de la mission spatiale Cassini-Huygens et de la future mission Dragonfly.

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CP-3

Alkoxyamines as valuable precursors for macromolecular engineering

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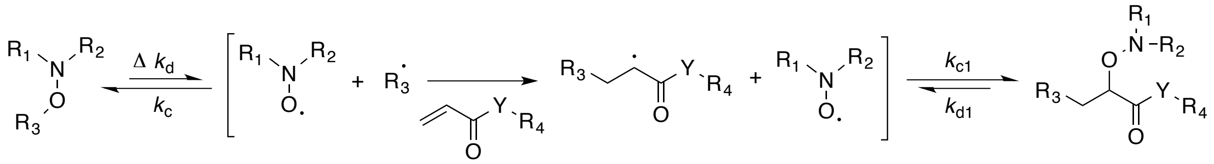
Alkoxyamines are labile molecules that can undergo homolysis of the C–ON bond under, heating or irradiation, to release the corresponding nitroxide and alkyl radical (Scheme 1). Due to this property, alkoxyamines are widely used in Nitroxide Mediated Polymerization (NMP) as initiator/controller agents,[1] but find also valuable applications in radical organic chemistry as a source of alkyl radicals[2] and even as possible therasnotic agents.[3] Moreover, according to their low cleavage temperature, highly labile alkoxyamines can participate in clean intermolecular radical 1,2-addition (IRA) onto various activated olefins in mild condition reactions.[4,5] In this lecture we will focus on the potential of this strategy as a key reaction for the preparation of various block copolymers finding advanced applications as solid polymer electrolytes for lithium metal battery technology[6,7] and as bioimplants for the central nervous system repair.[6]



Scheme 1. Principle of intermolecular radical 1,2-addition of alkoxyamines onto olefins.

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Communications Orales

CO-1

Polarization Amplification by Solubilizing Traditional Ionic Salts (PASTIS)

Florian Ferrer, Samuel Cousin, Pierre Thureau, Giulia Mollica, Ribal Jabbour, Marie Juramy, Fabio Ziarelli, and Stéphane Viel*

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The improvement of sensitivity is a major challenge in the field of Nuclear Magnetic Resonance (NMR) to overcome the low intrinsic sensitivity of this technique. In order to achieve this goal, Dynamic Nuclear Polarization (DNP) is a hyperpolarization technique already widely used where radicals like AMUPOL[1,2] are added to the solution to be analyzed at 100K. The behavior of this solution is important to consider at this very low temperature. Thus, the sample preparation is a key element in DNP. Indeed, at this temperature, the solvent must be in a glassy state to allow a homogeneous distribution of the radicals in the solution[3]. This vitreous state is usually obtained using cryoprotectants and in particular deuterated glycerol. By using glycerol, the ^{13}C carbon spectrum will be polluted with the glycerol signal and this could sometime lead to overlapping signals, let alone the expensive cost of using deuterated glycerol in DNP preparations. A promising alternative method is the use of salts as cryoprotectants[4] to replace glycerol. In this work, we used several different salts by varying their concentrations as well as the radical concentrations to determine which was the optimal DNP preparation. Our results show that the use of salts makes it possible to obtain gains in sensitivity close to those obtained with deuterated glycerol and these gains make it possible to work on concrete cases such as the analysis of scalar couplings between the carbons of nicotinamide.

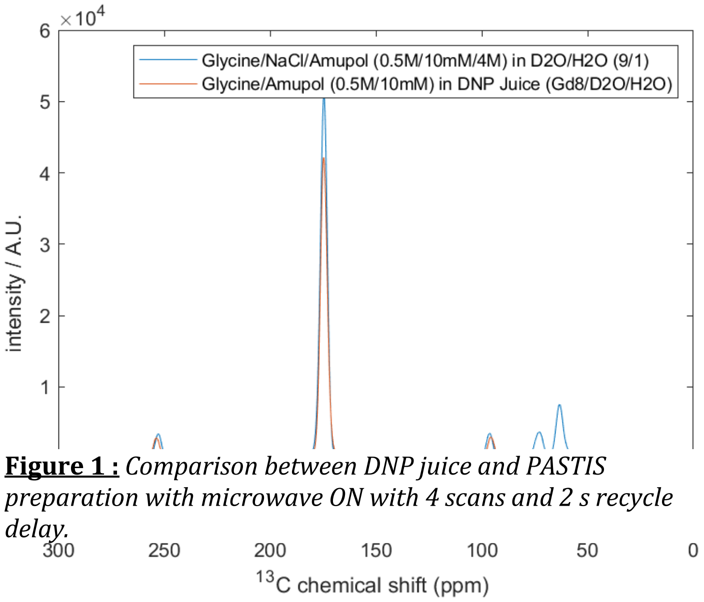

Figure 1 : *Comparison between DNP juice and PASTIS preparation with microwave ON with 4 scans and 2 s recycle delay.*

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CO-2

Exploiting Solid-State Dynamic Nuclear Polarization NMR Spectroscopy to Establish the Spatial Distribution of Polymorphic Phases in a Solid Material

Samuel F. Cousin, Colan E. Hugues, Fabio Ziarelli, Stéphane Viel, Giulia Mollica, Kenneth D.M. Harris, Arthur C. Pinon* and Pierre Thureau*

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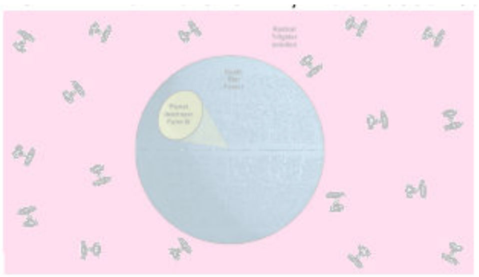
In the context of organic molecular materials, the phenomenon of polymorphism arises when a given type of molecule can form two or more solid phases with different crystal structures. In the context of pharmacology, sample formulation can be the key of the posology and toxicity of a chemical compound and have to be understood. In particular: is a polymorphic form stable? Does it transform to another form? How does this transformation take place, and can we avoid it? Nuclear Magnetic Resonance can very efficiently determine which polymorph is present in a given sample, since two polymorphs have different chemical physical properties and nuclear spin environments. However, conventional solid-state NMR methods are impacted by two main roadblocks. First, NMR is an insensitive technic that struggles to detect low abundance forms. Second, solid-state NMR average the information over the all sample, and is general not in capacity to determine the localization of a given polymorph within the NMR sample.

In this study, we use a peculiar form of NMR called "Dynamic Nuclear Polarization Magic Angle Spinning" (a.k.a. DNP-MAS)[1] to kill two birds with one stone. First, this technique can be used to amplify drastically solid-state NMR signal by one or two orders of magnitude, allowing an increase by 2 or 4 orders of magnitude the time needed to perform an NMR experiment. Second, this technique can be used to gain spatial resolution in NMR and allow to localize the spectroscopic information within the sample. We applied this technique to the 3-Aminobenzoic acid, also known as meta-aminobenzoic acid or MABA).[2] Indeed, this molecule is known to possess several polymorphs, with the polymorphic Form I hard to characterize by PXRD. By applying our methodology to this compound, we manage to determine that what is believed to be Form I is a mixture between form I and III, with form III almost undetectable to the PXRD spectrum of form I. A geometrical model of the form III within the form I has been determined with a death star-shaped geometry.



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CO-3

Chimeric hydrogenase complexes: a new strategy to study structure function relationships

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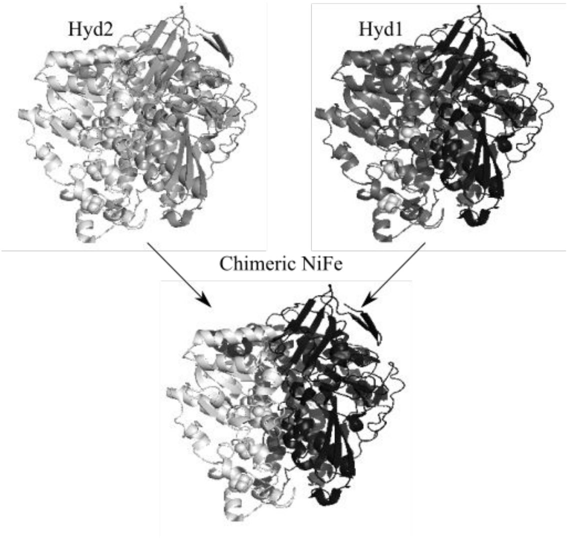

NiFe hydrogenase enzymes are very efficient molecular catalysts of hydrogen oxidation and production. They are composed of two subunits, the large one contains a bimetallic active site, where the reaction takes place, and the small one contains additional inorganic cofactors that mediate electron-transfer to the active site. Homologous NiFe hydrogenases have different properties, in terms of catalytic directionality and reversibility, resistance to small inhibitors (i.e., O_2 and CO), redox-driven (in)activation. Understanding which subunit confers specific properties to the enzyme is needed for the design of equally efficient artificial catalysts of hydrogen oxidation and production.

Protein Film Electrochemistry (PFE) is a powerful technique to investigate the catalytic response of redox enzymes[1] and learn about their catalytic properties[2].

To investigate the roles of the two subunits of NiFe hydrogenases, we employed an original strategy: we have designed and produced a chimeric enzyme dimer, made by assembling two subunits of two homologous NiFe hydrogenases. We characterized the chimeric NiFe hydrogenase by PFE and we compared the results with those of the native (wild-type) enzymes. This allowed a precise assignment of the catalytic properties of each enzyme to a specific subunit. In particular, we obtained new insights about O_2 resistance, questioning the belief that it is entirely conferred by a particular cofactor in the small subunit[3].

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CO-4

Synthesis and Spectroscopic study of new Coupled Polymethines as NIR absorbing dyes

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Polymethine dyes, often referred to cyanines, are organic chromophores with an even number of π electrons delocalized between two terminal heteroatoms over an odd number of unsaturated carbon atoms. Upon molecular engineering (extremities, conjugation length…), polymethines are capable of absorbing up to the near-infrared (NIR) region and are therefore used in multiple applications ranging from molecular electronics[1] to bio-imaging [2] and nonlinear optics.[3]

According to a theoretical study by Dähne and Leupold published in 1966, the coupling of two polymethines subunits linked by two sigma bonds would induce an enhancement of optical properties.[4] So far, dyes introducing multiple polymethine subunits have been scarcely reported, the most recent examples being red-absorbing zwitterions based on benzoquinone monoimine (BQMI)[5] and diaminobenzoquinone diimine (DABQDI).[6]

With the aim to use the coupling strategy to develop new families of dyes, we recently synthesized coupled polymethines incorporating anionic oxonol and cationic heptamethine subunits that gave rise to unprecedented derivatives holding potential as pH- and photo-switches, providing a wide span of absorption up to the NIR domain.

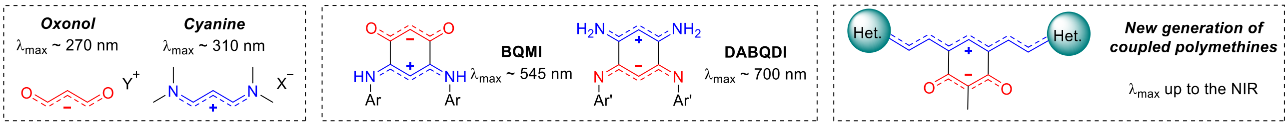

Figure 2. Examples of respectively: trimethines, coupled trimethines and new generation of coupled trimethine and heptamethine.

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CO-5

Novel Z-scheme heterojunction oxyhalide photocatalyst for photodegradation of sulfadiazine antibiotic under visible light

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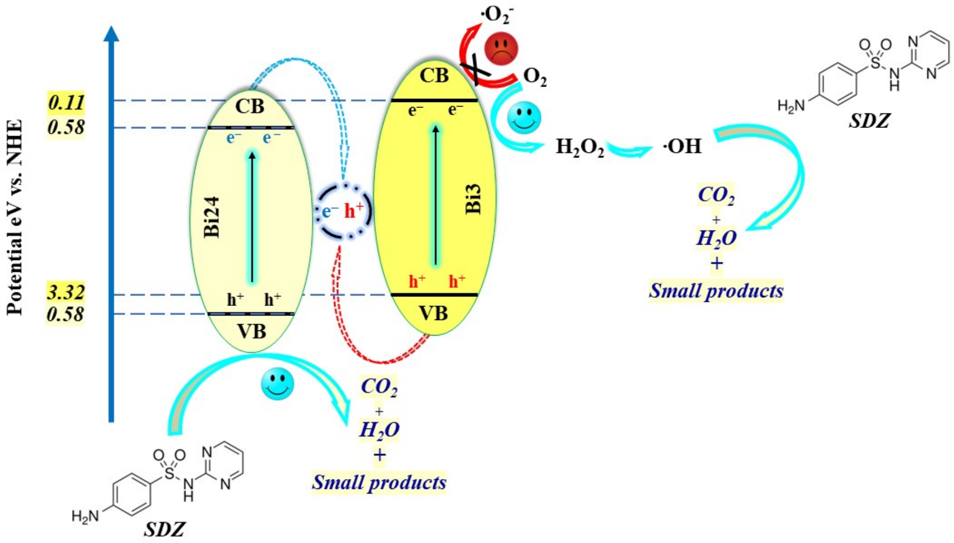
In this work, novel efficient visible−light driven Z−scheme heterojunction Bi3/Bi24 is developed by a simple and eco-friendly solid-state approach using a single Bi_2O_3 precursor. The resulting photocatalysts were characterized by X-ray diffraction, scanning electron microscopy, high-resolution transmission electron microscopy, Raman and Fourier transform infrared spectroscopies to explore the formed heterostructure between the pristine semiconductors [1]. Furthermore, the gap energy of the semiconductors is determined experimentally and theoretically by UV-vis diffuse reflectance and density function theory, respectively. The photocatalysis assays revealed enhanced photocatalytic activity for the decontamination of the antibiotic sulfadiazine (SDZ) in significant amounts. Finally, an improved degradation mechanism is proposed based on photoluminescence analysis and reactive oxidative species scavenging tests.



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CO-6

An innovative solvent-free polymer sample preparation method for DNP SSNMR

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Solid-state NMR (SSNMR) is highly suitable for analyzing polymers but has low sensitivity. This limitation can be overcome using dynamic nuclear polarization (DNP), a technique that enhances NMR sensitivity by transferring the electronic spin polarization of polarizing agents to surrounding nuclei[1]. However, mainly soluble polymers can be analyzed by DNP SSNMR because efficient methods for preparing the samples for DNP usually require initial polymer solubilization[2]. In this work, we will present an innovative solvent-free sample preparation method based on the use of supercritical CO2 technology. More precisely, supercritical CO2 is used as a plasticizing agent to lower the polymer glass transition/melting points, allowing thus an efficient mixing of polarizing agents within the resulting soften/molten polymer matrix and therefore a homogeneous and in-depth loading, similarly to a conventional polymer extrusion process but at moderate temperatures. This method was applied to incorporate either TEKPol[3] or AMUPol[4] as polarizing agents within different polymers. The resulting samples were characterized by CW EPR and DNP SSNMR. The results were compared to conventional polymer sample preparation methods (Fig.1) highlighting the potential of the proposed process as a new and efficient method to prepare polymer samples for DNP.

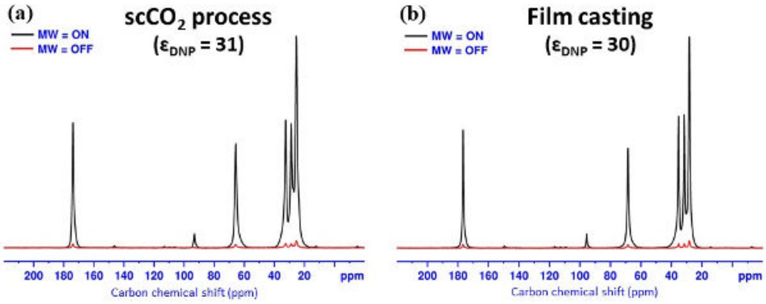

Fig.1. 13C CPMAS DNP SSNMR spectra of a polycaprolactone sample obtained by (a) supercritical preparation method, (b) film casting preparation method

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CO-7

Etude RPE du polypropylène et du polyéthylène irradiés par des rayons gamma et des rayons X

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Parmi les différentes technologies de stérilisation des dispositifs médicaux et biopharmaceutiques, le rayonnement reste l'une des techniques les plus répandues et notamment l'utilisation de l'irradiation gamma. Selon le contexte sanitaire actuel entrainant une forte croissance de fabrication de produits destinés à l'industrie pharmaceutique et à l'innovation de ces derniers toujours grandissante, des questions concernant la capacité de stérilisation se posent. Ainsi, pour garantir la continuité des activités de production de ces systèmes, des méthodes alternatives de stérilisation par rayonnement doivent être développées ; la stérilisation par rayons X est considérée comme une technologie prometteuse. Dans cette étude, les effets des rayons gamma et des rayons X sont étudiés sur 22 matériaux constitués de polypropylène (PP), de polyéthylène (HDPE, LDPE, LLDPE) et d'élastomère thermoplastique (TPE) composé de mélanges de polypropylène. Des analyses RPE ont été effectuées sur chaque matériau sur une période de 380 jours. L'objectif est d'identifier et de quantifier les radicaux générés après les deux irradiations sur chaque classe de polymères.
Les deux groupes de polymères étudiés génèrent des radicaux caractéristiques indépendamment des technologies d'irradiation. Pour tous les échantillons de PP, un signal RPE similaire a été observé et attribué à un radical peroxyle[2]. Une analyse de résolution de courbe (SIMPLISMA)[1] permet d'identifier les radicaux. Contrairement au LDPE et au LLDPE, les échantillons de HDPE présentent un fort signal RPE après irradiation gamma et rayons X, lié à leur densité et à leur cristallinité. Pour tous les échantillons de HDPE, des radicaux alkyle, allyle et polyényle sont observés[3], et différenciés par leurs constantes de couplage (figure 1). Parmi les 22 matériaux étudiés, aucune différence significative des signaux RPE n'a été observée entre l'irradiation gamma et l'irradiation aux rayons X. L'équivalence des signaux RPE, de la cinétique et de la concentration en radicaux pour les deux classes de polymères étudiés permettent de mettre en évidence une interaction de rayonnement-matière similaire.

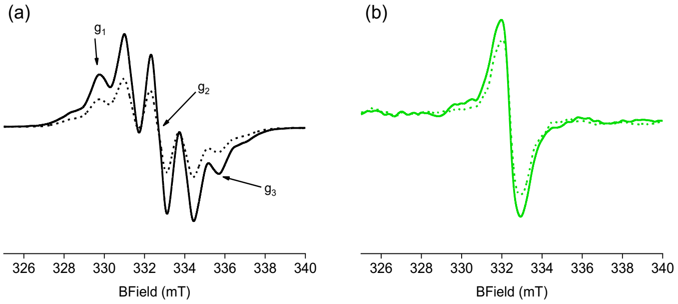

Figure 3:(a) Signal of HDPE sample 9 days after gamma (solid line) and X-rays (dotted line) irradiation corresponding to a mixture of allyl and alkyl radicals. (b) Signal of HDPE 60 days after gamma and X-rays irradiation corresponding to a polyenyl radicals.

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CO-8

Photocatalytic degradation of recalcitrant organic pollutants by non-typical stoichiometric oxygen-rich bismuth oxychloride $Bi_xO_yCl_z$ photocatalyst under UV and Visible light irradiation.

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In this study, an oxygen-rich bismuth oxychloride $Bi_xCl_yO_z$ was successfully prepared by solid-state method. The physicochemical and morphological properties of as-synthesized sample was characterized by X-ray diffraction (XRD), Scanning electronic microscopy (SEM), Energy dispersive X-ray Spectroscopy (EDXs), Raman Spectroscopy and UV–Vis pectroscopy. The results of XRD analysis confirmed the pure monoclinic P2/c oxygen-rich bismuth oxychloride $Bi_xCl_yO_z$ phase was obtained.

The photocatalytic activity of the photocatalyst was evaluated by degradation of Rhodamine B (RhB) under UV and visible light irradiation. the UV–visible spectrometry was used to analyze the evolution of dye degradation. Moreover, the catalyst has excellent photocatalytic activity, the decomposition rate of RhB solution is about 99% after 90 min under UV light irradiation and 180 min under visible light.

The $Bi_xCl_yO_z$ photocatalyst has excellent stability and repeated cycle performance. Basing on the results of the trapping experiments, it is proposed that the main active substance of the catalyst for degrading dyes is $^{\cdot}O^{2-}$ significant roles in the degradation process.

CO-9

Uranium in seawater, accumulation by brown algae Ascophyllum nodosum

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Uranium is naturally present at trace levels on the earth surface but the recent growing use of nuclear energy and the possible accidental release of nuclear material have brought increasing possibilities of dispersion in the environment [1]. As seawater is the major recipient of human pollutants, its ecosystem is considered at risk and in recent years important research has been done to understand the impact of the radionuclides in the marine environment [2].

Ascophyllum nodosum is a brown alga that lives along the coast of the Atlantic Ocean in Nord Europe and Nord America and is widely studied as a bioindicator for metal ion pollution due to its high tolerance to chemical toxicity and high metal CFs (Concentration Factor) [3].

Uranium is known not to have no role in organism life but it can be accumulated in tissue and become a toxic heavy metal due to its chemical toxicity (its radiotoxicity is considered negligible). However, its chemical behavior (solubility, migration and bioavailability) strongly depends on its speciation related to the environmental characteristic such as pH, ionic strength and content of organic matter. For this reason, a single determination of the accumulation rate is not sufficient to identify the risk of the contamination, but a speciation study is required.

We present here a multi-scale investigation of *Ascophyllum nodosum*, aiming at understanding the impact of uranium accumulation in the algae tissues at molecular level and describing the uptake mechanism. Contamination of *A. nodosum* specimens in closed aquaria was pursued with 10^{-5} M natural uranium, whose main speciation in seawater is $CaU(VI)O_2(CO_3)_3$ [4].

The algal uptake has been quantified by ICP-MS and a localization study at tissue level was obtained by combining microscopy imaging (SEM) and micro-XAS spectroscopy. The experimental results indicate that the brown alga can bioaccumulate U(VI) through an active mechanism with a specific compartmentalization ability showing higher concentration in the receptacles, the reproductive part of the algae. A preliminary analysis of the *in vivo* speciation suggests that the alginate polymer, the main polysaccharides present in algae tissue, is not involved in the radionuclide uptake. Instead, we identified a distinct uranium speciation according to the algae specimens' gender.

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CO-10

Langmuir-Blodgett nanocube assembly technique for the fabrication of complex nanostructures

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Metal nanocubes behave as individual optical resonators, that can be coupled to metallic films to obtain robust plasmonic nanocavities displaying strong field confinement. They are also interesting as building blocks for supercrystalline structures exhibiting improved coupling with external electromagnetic field[1], and also as building blocks to realise monocrystalline nanostructure[2,3]. Complex nanopatterns, such as plasmonic metasurfaces, are still difficult to achieve due to intrinsic limitations of conventional self-assembly approaches. Here we lift this barrier by introducing a new methodology to assemble nanocubes in predefined nanoscale patterns of arbitrary geometry. This methodology relies on directed assembly of floating nanocube films obtained via Langmuir-Blodgett technique. We demonstrate the fabrication of various complex nanopatterns, such as U-shape, L-shape, +-shape, S-shape and also split-ring resonators on PDMS, that cannot be obtained with conventional assembly techniques. We will also present preliminary results of nanocube epitaxy to transform the assembly into continuous metallic nanostructures. This strategy potentially offers an alternative to a bottom-up fabrication for metal nanostructuring which then can be applied to optical, nanoplasmonic, or photoelectrochemical devices.

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CO-11

Fluorescent labeling of nano/microplastics and application for ecotoxicity tests

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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.

Nano/microspheres of plastics (PS, PE-HD, PE-LD, PP, PVC and PET) were first produced following the protocol developed by Merdy et al. (2023), and then labeled with fluorescent dyes. This fluorescent labeling technique was used for understanding the interactions between the plastic particles and some marine organisms. Microalgae and rotifers were put in contact with labeled plastics. The plastic particles were adsorbed at the surface of phytoplanktonic cells, whereas they were identified inside the digestive system of zooplankton proving their ingestion (Figure 1). These insights should help assessing the impact of nano/microplastics on such organisms.

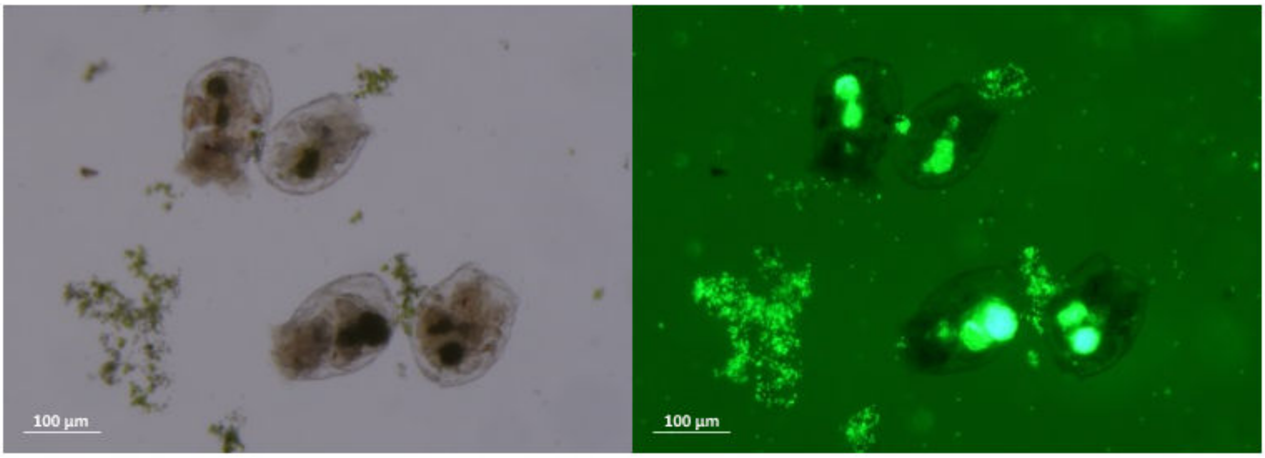

Figure 1. Ingestion test of a cocktail of the microalga *Chlorella vulgaris* (5-10 µm) and fluorescent polystyrene microspheres (2 µm) by the rotifer *Brachionus plicatilis*.

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CO-12

Bioinspired mono-copper complexes: synthesis, activity and mechanism

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In the context of challenging substrate oxidations by copper-containing enzymes, Lytic Polysaccharide Mono-Oxygenase (LPMO) is an important biological example of a catalyst capable of activating strong C−H bonds of polysaccharides using dioxygen (and electrons) or hydrogen peroxide as co-substrate.[1, 2] Among possible Cu/O_2 species, **high-valent copper oxygen adducts (e.g. $[CuO]^+$ or $[CuOH]^{2+}$)[3] have been proposed as key oxidizing intermediates. (Figure 1)**

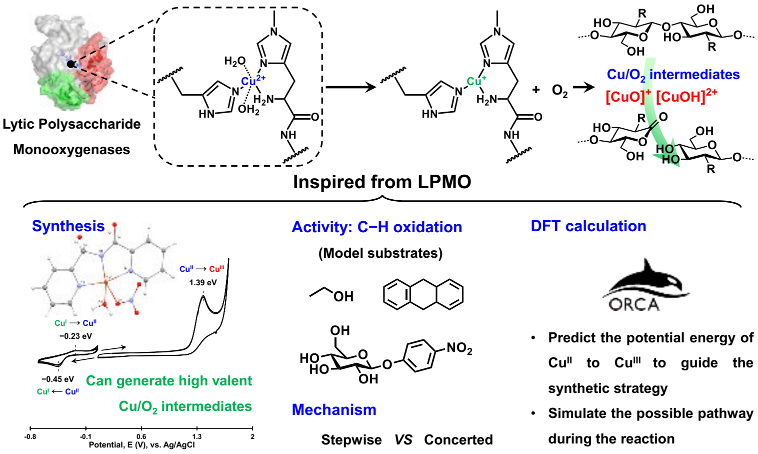

Figure 1. Proposed active site of lytic polysaccharide monooxygenase (LPMO) for strong C−H bond oxidation (up); Research strategy of mono-copper complexes that inspired from LPMO (down).

Bioinspired from LPMO, we have prepared and characterized new mono-copper complexes that can stabilize high valent Cu/O_2 species. Their properties (e.g. XRD, EPR, UV-Vis, electrochemistry) and reactivity towards various substrates have been investigated. Our experimental data, combined with DFT calculations will be presented.

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CO-13

Host-Guest interactions between cyclodextrins and β-phosphorylated nitroxides

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The design of new supramolecular systems is one the next steps 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. In fact, supramolecular Host (CD)-Guest (nitroxides) 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, new β-phosphorylated nitroxides were 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 nitroxide (**1**) exhibits 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.

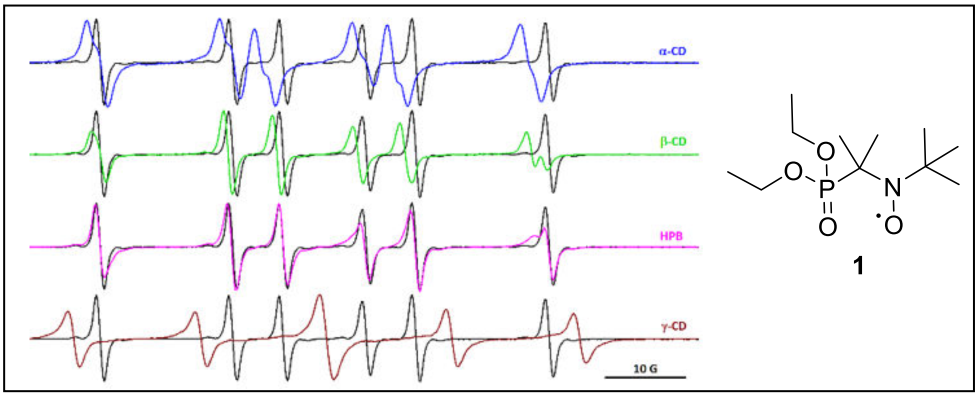

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Figure 1: EPR signals between Nitroxide-Cyclodextrins and free nitroxide, in black, for comparison

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CO-14

Complexes organotitanes pour la copolymérisation des monomères vinyliques polaires et des α-oléfines

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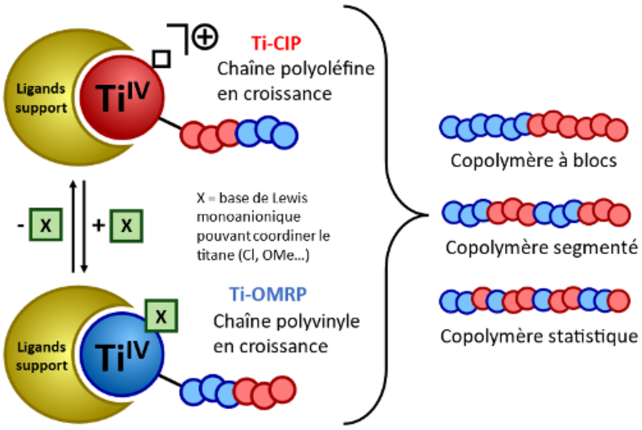
Nos recherches ont pour but la copolymérisation vivante des α-oléfines (éthylène, 1-alcènes) avec les monomères vinyliques polaires (vinyl polar monomers, VPM : (méth)acrylates, acétate de vinyle…), pour obtenir des copolymères linéaires originaux de structures bien définies.

La CIP (coordination-insertion polymerization) est efficace pour la polymérisation vivante des oléfines[1], et la CRP (controlled radical polymerization) est efficace pour la polymérisation vivante des VPM[2] : nous développons donc une méthode basée sur ces deux modes de polymérisation. Le titane est actif à la fois en CRP et en CIP : d'une part, des complexes neutres de titane(IV) produisent diverses réactions radicalaires[3], certaines pouvant initier des polymérisations, puis les contrôler selon un mécanisme OMRP (organometallic-mediated radical polymerization)[4]. D'autre part, des complexes cationiques de titane(IV) catalysent la CIP vivante des oléfines[5].

La découverte d'une méthode pour passer d'une forme (cationique ou neutre) de titane à l'autre conduirait à une CIP-OMRP combinée. Dans ce but, nous avons d'abord évalué l'activité du chlorure de titanocène(III) (Cp_2TiCl) comme agent de contrôle OMRP de différents VPM, reposant sur des espèces dormantes titane-alkyle : $Ti(III) + R^{\bullet} \rightleftharpoons Ti(IV)\text{-}R$.

En OMRP, la concentration d'espèces radicalaires dépend de la rupture homolytique de la liaison titane-carbone. Ainsi, nous utilisons la modélisation moléculaire (DFT) pour évaluer l'énergie de dissociation de divers complexes comportant une liaison titane-carbone.

D'autres complexes de titane, connus et originaux, sont en cours de préparation, et seront testés en OMRP et en CIP.



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CO-15

Kumada-Tamao-Corriu Coupling catalyzed by Pd-NHC complexes to generate axial chirality

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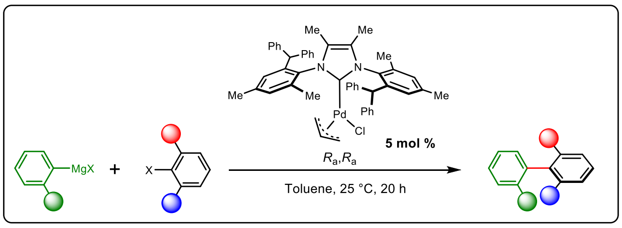
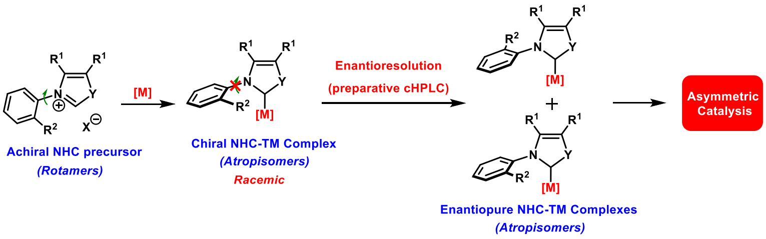
Asymmetric catalysis is a useful pathway to produce enantioenriched compounds, in which chiral organometallic complexes play an important role. Some of these complexes, bearing an N-heterocarbenic ligand (NHC), form a group of catalysts widely studied.[1] These very stable complexes allow to catalyze a large variety of reactions (Suzuki-Miyaura,[2] hydrogenation,[3] α-arylation[4]…). At the iSm2, within the Chirosciences team, were developed several atropoisomeric Pd-NHC complexes[5], for which we are currently looking for new applications. As the Kumada-Tamao-Corriu coupling has not been thoroughly studied for Pd-NHC complexes,[6] we chose to test this reaction with our atropoisomeric Pd-NHC complexes to generate axially chiral products.

First, we will present the results obtained on a benchmark reaction using different Pd-NHC complexes developed in our laboratory to evaluate their catalytic activity and enantioinduction. These complexes bear different types of chirality (atropisomerism, chirality on the backbone of the NHC, on the N-substituents; or on bicylic hindered type of structures). The best catalyst was found to give a yield of **99%** and an enantiomeric excess of **35%**.

We will also discuss the scope on this Kumada-Tamao-Corriu coupling using our best catalyst to generate biaryles and binaphtyles compounds, which are axially chiral. Recently, we were able to obtain a binaphtyle with a remarkable enantiomeric excess of **63%**, paving the way to substantial improvements for the preparation of enantioenriched binapthyles.





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CO-16

Ynamides in Radical Reactions: A Route to Original Persubstituted 2-Aminofurans

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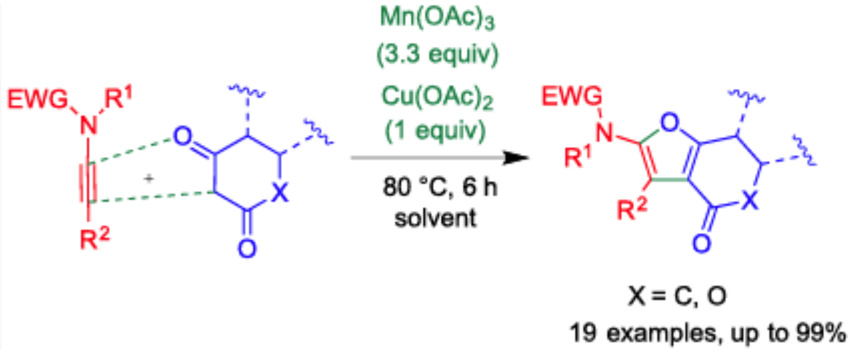
$Mn(OAc)_3$ $Cu(OAc)_2$-mediated reaction between ynamides, derived from oxazolidone or 3-methylindole carboxylate, and cyclic α-dicarbonyl radicals led to the one-pot synthesis of 2-aminofurans. The transformation involves addition of the α-dicarbonyl radical to ynamide, oxidation to ketene-iminium, and polar cyclization steps to provide original persubstituted 2-aminofurans in good to excellent yields. This work represents the first radical route for the synthesis of furans from ynamides[1].



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CO-17

Photoinduced intramolecular electron and energy transfer in a ruthenium-modified laccase system

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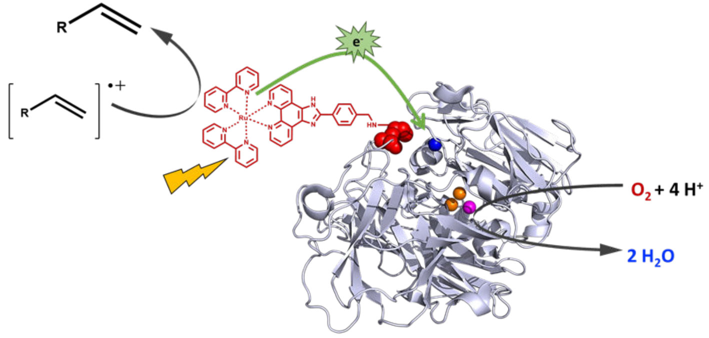
Electron transfer (ET) reactions are essential in biological processes like photosynthesis. Understanding how electrons are transported in these systems can lead to the discovery of new tools to perform multielectronic chemical transformations. It is a major interest to design photocatalytic systems that use light energy to drive enzymes to perform both oxidation and reduction reactions.[1] The multicopper oxidase laccase couples the substrate mono-electronic oxidation (at a T1 surface located Cu^{2+} center) to the 4-electron reduction of O_2 into H_2O (at an embedded tri-nuclear Cu^{2+} center TNC) via successive intramolecular ETs. Here, a strategy is presented for achieving a controlled orientation of a ruthenium-polypyridyl photosensitizer graft at the surface of a fungal laccase. Laccase variants are engineered by site-directed mutagenesis with unique surface-accessible lysine residues (designated UNIKs) located at a desired position on the enzymes' surface. Ruthenium-polypyridyl-modified UNIKs are obtained by reductive alkylation of lysine residues,[2] allowing to trigger and probe both fluorescence resonance energy transfer (FRET) and photoinduced ET processes from discrete surface grafting points relative to the redox-centers (both T1 and TNC). In none of these Ru-UNIK hybrids the presence of the graft compromises the oxidation and reduction activities of the enzyme. Under constant white light irradiation, the Ru-UNIK hybrids undergo photoreduction, in which both rate and extend of reduction seems to be intrinsically dependent on the grafting location. In addition, under these experimental conditions, electrons can be directly injected in the TNC to be, subsequently, transferred to the T1 center in a reverse intra-molecular ET process. The same effect is observed for O_2 reduction, the catalytic efficiency of each hybrid is improved under continuous irradiation depending on the grafting position. On the other hand, under laser flash irradiation – within the lifetime of ruthenium triplet excited state (~ 1 µs) – most of the interaction with laccase is related to FRET events that are dependent on the photosensitizer position regarding the copper centers. This approach is useful to study intramolecular energy and electron transfer processes, showing that Ruthenium-polypyridyl photosensitizers are amenable to deliver multiple electrons to buried active sites and sustain photocatalytic activity upon visible light excitation.



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CO-18

Orthogonal Tandem Gold-Catalyzed Cycloisomerization/Nucleophilic Addition/Rearrangement of Acenaphthylene Carbaldehyde Derivatives

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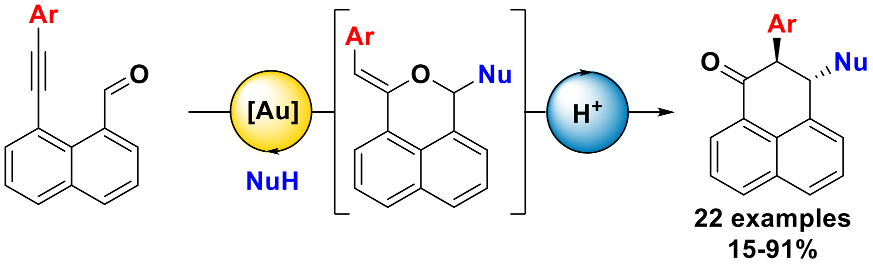
Gold catalysis has been recognized as a fascinating area in recent years to achieve the synthesis of complex core structure according to atom-economical and green processes.[1] On the other hand, HFIP emerged recently as a new tool notably for its Lewis-acid properties due to its hydrogen donor bond ability.[2]

Merging these two trendy areas, and following our wide program on gold catalysis,[3] we developed a methodology involving a cycloisomerization/nucleophilic addition and a C→O rearrangement, starting from aldehyde-ynes derivatives. Inspired by the work from Grela's and Harrity's[4] groups we decided to engage in a new program based on the association of HFIP and gold complex.

A large range of acenaphthylene carbaldehyde has been prepared and engaged in this process coupling gold catalysis and Lewis-acid behavior of HFIP and led to cyclic ketones with yields ranging from 15 to 91%. The mechanism of this tandem process was investigated will be presented. The interest of such transformation was also demonstrated by performing it on a gram-scale and a post-functionalization bromination.

This communication will present the optimization as well as scope and limitations.[5]



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CO-19

Physical Separation of Enantiomeric Products by Compartmentalized Parallel Kinetic Resolution

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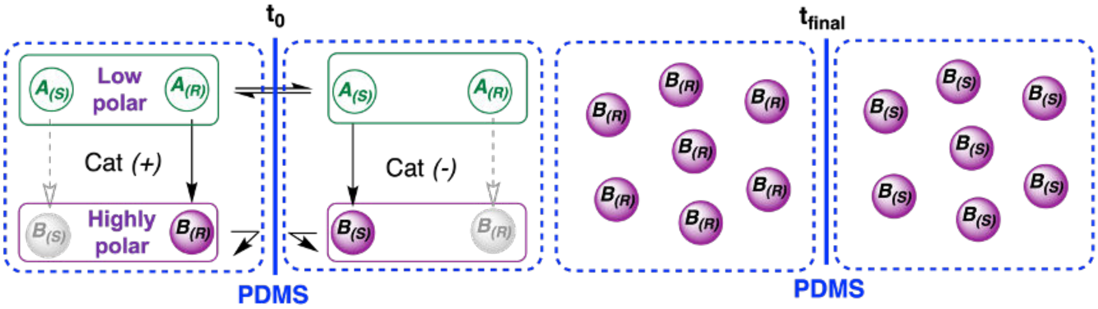
Parallel **K**inetic **R**esolution[1] (**PKR**) is a powerful strategy to form two non-enantiomeric products starting from a racemic substrate through completely different reaction pathways. In this study, a **C**ompartmentalized **P**arallel **K**inetic **R**esolution (**CPKR**) system is described combining a simultaneous production of enantiomers using chiral catalysts and a physical membrane separation starting from a racemic mixture. In this process, a double reactor separated by a polydimethylsiloxane (PDMS) membrane isolates two catalysts with opposite configuration (Cat (+) and Cat (-)). The racemic substrates **A** with a low polarity can cross the membrane while each enantiomeric product **B** is sequestrated in one compartment due to their higher polarity.[2] This unprecedented system was successfully applied to the simultaneously preparation of both enantiomers of chiral 1,2-diols starting from racemic epoxides using Jacobsen's hydrolytic kinetic resolution[3] (HKR) in parallel.[4]



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CO-20

Simultaneous Control of Central and Helical Stereogenic Elements on Small Molecules

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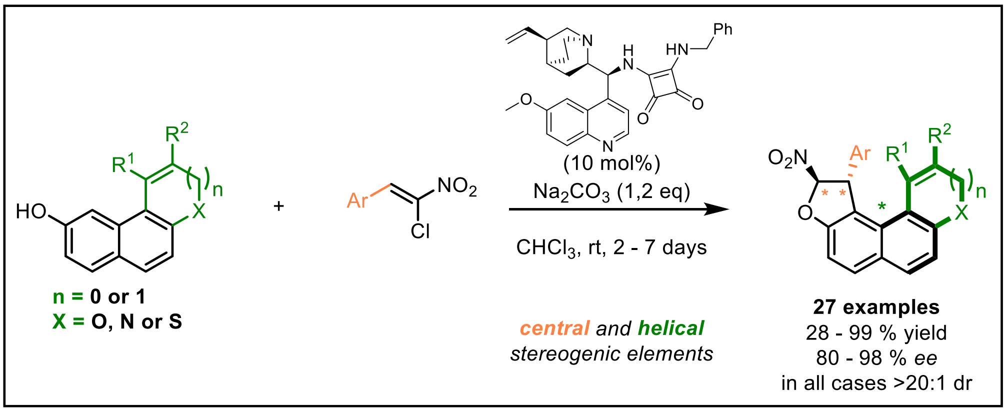
Small molecules featuring different types of stereogenic elements are very challenging synthetic targets, especially when displaying configurationally labile helical chirality. Previously, we developed a method to access enantiomerically enriched atropoisomers[1] and dioxa[6]helicenes[2] via centrally 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.



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CO-21

Synthèse de nouveaux composés hétérocycliques et évaluation de leur activité antimicrobienne

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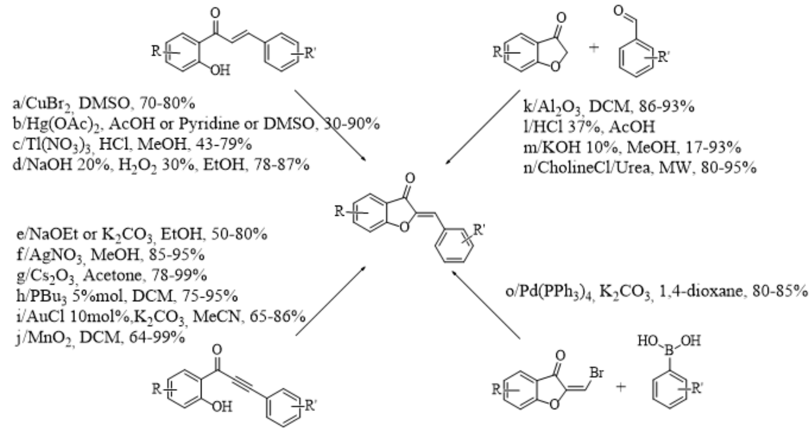
Les aurones sont des molécules relativement peu étudiées de la famille des flavonoïdes. On les retrouve parmi les membres les plus évolués des astéracées comme le muflier ou le dahlia[1]. Elles recouvrent plusieurs rôles clés au sein de la plante, le premier et principal étant celui d'attracteur des polinisateurs par le biais de motifs chromatiques dans le spectre UV. Elles présentent également de très bonne propriétés antioxydante, et ont dernièrement été décrites comme pouvant avoir une activité intéressante sur certaines souches bactériennes notamment Gram négative, ainsi que sur des virus et des champignons[1,2]. C'est sur ces derniers types d'activités que se sont concentré nos recherches.

La plupart des aurones naturelles sont relativement peu variées et très riches en groupement hydroxy sur les deux cycles A et B. Ces substituants présentent un intérêt certain dans le cadre d'une activité antioxydante mais sont peu intéressant à visée antibactérienne. Nous avons donc synthétisé de nouveaux dérivés 5'-aminoaurone et 5'-acétamidoaurones sur lesquels nous avons fait varier les subsistants du cycle B[3]. Ces nouvelles molécules ont été testées sur plusieurs souches pathogènes de bactéries, virus et champignons.

Des résultats prometteurs ont été obtenus sur plusieurs lignées bactérienne d'intérêt thérapeutique comme *A. baumannii*, *S. aureus* résistant*, C. difficile* ainsi que sur plusieurs membres de la famille des *Burkholderia*. Des résultats intéressants ont également été obtenu sur SARS-COV-2.



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CO-22

Synthesis of smart alkoxyamines: theranostic against cancer

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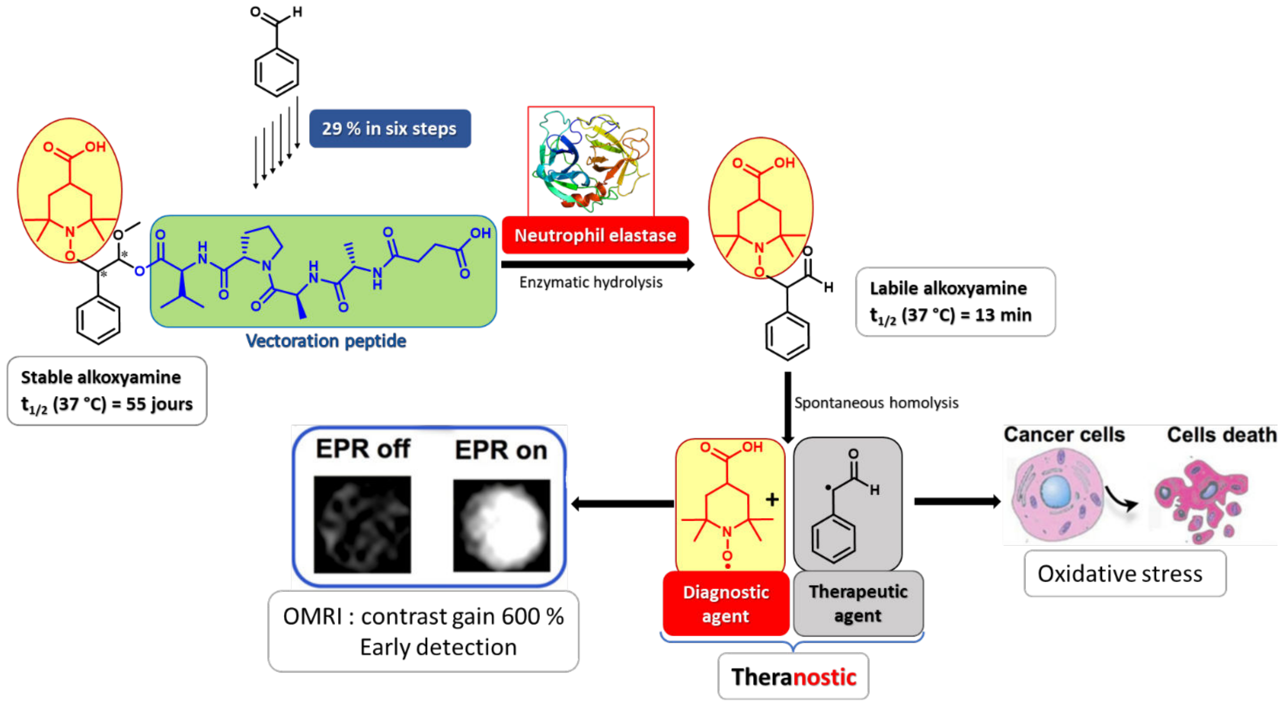
Cancer, an uncontrolled proliferation of cells, is one of the leading causes of death worldwide. According to the World Health Organization (WHO), in 2020, it was responsible for 10 million deaths. That's more than 27,000 deaths a day. Faced with this major public health problem, several chemotherapy treatments are used : methotrexate and paclitaxel for example. However, it still faces the problems of its difficult early detection and the low selectivity of anticancer drugs (heavy side effects). Therefore, the search for a means of early detection and more selective substances is a major challenge for the fight against cancer.

During our project, we are developing an intelligent alkoxyamine able to produce, locally, a cytotoxic radical and a contrast agent (nitroxide) for Overhauser magnetic resonance imaging for a better diagnosis : theranostic.[1] We turned our interest to the enzymatic activation of HO-Succ-Ala-Ala-Pro-Val-alkoxyamine prodrugs. It is an alkoxyamine based on an acetal function linked to a tetrapeptide targeting neutrophil elastase, an overexpressed protease in lung cancer.

The synthesis of this alkoxyamine was realized in 6 steps with an overall yield of 29%. Tests have shown that, in vitro, in the presence of target protease, radicals are formed. This confirms the enzymatic targeting and the mode of action written on the diagram below. In vivo tests are underway, and they could be as promising as in vitro tests. **This result is very encouraging for exploring more carefully this approach.**



Scheme : target's synthesis and concept

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Communications par affiche

P-1

Electron deficient cages harnessing anion-π interactions

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Supramolecular chemistry is a field that focuses on harnessing non-covalent interactions for a variety of purposes. One of its key aspects is molecular recognition, which refers to the selective binding of a target molecule by a host molecule. The goal is then to mimic the highly efficient host-guest chemistry observed in biological systems such as enzymes.

Among the numerous existing interactions, our focus is on anion-π interactions. They can be defined as the interaction between an anion and an electron deficient π-system and were first described in 2002.[1] Since then, they have received a growing interest owing to both the crucial role of anions in many biological and chemical processes, and the involvement of π-aromatic systems in ions transport and molecular recognition.[2] However, when using anion-π interactions, the strength of the interaction is limited by the instability of highly electron deficient surfaces.[3]

To tackle this issue, our strategy is to design and synthesize supramolecular cages combining several electron deficient surfaces, to increase their π-acidity through synergy.

Among the different supramolecular hosts already described, we have chosen to use cryptophanes. This class of cages is based on two C_3 cyclotriveratrylene units connected by linkers. Cryptophanes are already known for their selectivity in the molecular recognition of small molecules and ions and exhibit interesting chiral properties which are relevant for our purpose.[4]

Hence, we will present the synthesis and characterization of a cryptophane possessing three electron deficient naphthalenediimides linkers. The chirality and molecular recognition properties of this cage will also be discussed together with DFT calculations.

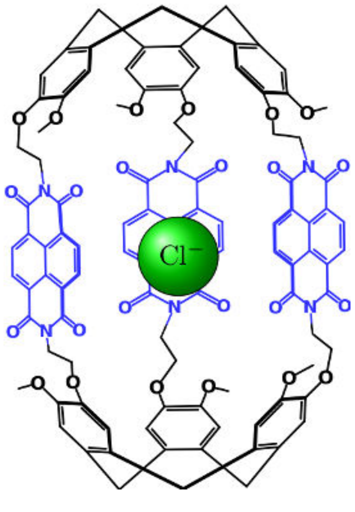

Figure 1: Schematic representation of encapsulated chlorine ion within a cryptophane with electron deficient arms.

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P-2

Simultaneous oxidative and reductive transformations by parallel catalysis with *N*-Heterocyclic Carbenes

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The last decade, a multitude of organocatalyzed transformations of carbonyl derivatives took advantage of the oxidation of Breslow intermediates, arising from the reaction of these carbonyl substrates with stable N-Heterocyclic Carbenes (NHCs). However, valorization of the electrons lost during these oxidative transformations had not been addressed until recently. In 2021, Ohmiya and Bertrand independently demonstrated that these Breslow intermediates can also be used as formal reductants.[1,2] NHC-organocatalyzed arylacylations of diverse alkenes were thus performed upon reduction of iodoaryl derivatives into radical species. In their reaction, the aldehyde used to generate the Breslow enaminol was also integrated in the final addition product.

Our goal was to develop a system enabling the use of aldehydes as sources of potent Organic Electron Donors (OEDs)[3,4] for reductive transformations in organic chemistry. Our strategy allows the coexistence of two distinct and interdependent catalytic cycles where the Breslow enolate catalyst both serves as an electron source for reduction reactions and as key intermediate for the valorization of aldehydes through oxidative transformations. Imidazolylidene-based enaminols proved to be powerful organic donors for the single-electron transfer reduction of various challenging substrates. The generated radical intermediates were further exploited in arylations of alkenes while the sacrificial aldehydes were valorized through oxidation reactions.

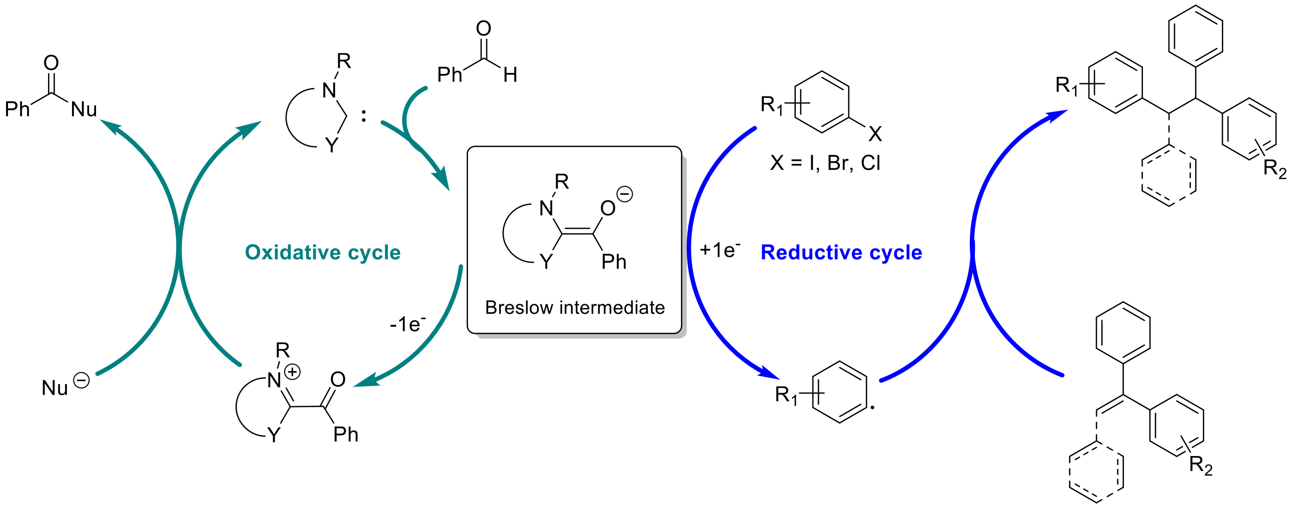

Figure 4 - Proposed mechanism for the concomitant oxidative and reductive transformations

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P-3

Insights Into the Anticancer Therapeutic Properties of Cu(II) Complexes of Phenanthroline and Histidine Containing Ligands

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Cancer is the second cause of death worldwide. Due to this, the scientific community has been exploring for many years different kinds of possible treatments for this disease, among them anticancer metallodrugs. The best-known anticancer metallodrug is Cisplatin, a planar Pt^{2+} complex approved by the FDA in 1978. Since the discovery of the anticancer effect of Cisplatin, the community of bioinorganic chemistry has intensified the research on anticancer therapy in order to overcome the different drawbacks of Cisplatin and the rest of platinum based metallodrugs, being the main one their high toxicity, which leads to undesired side-effects. [1] Copper has become a real alternative to complexes of platinum and the rest of metals of its group as anticancer drugs. [2,3,4] This is due to the versatility of this biometal, which can bind to different donor atoms forming complexes with very diverse features like different geometries and distinct redox properties.

Two copper complexes which are based on phenanthroline and histidine containing ligands were synthesized and characterized by different methods such as potentiometry, spectroscopy, mass spectrometry, electrochemistry and DFT calculations. [5] They show high stability in aqueous solution and are redox active (Cu^{2+}/Cu^{+}). DNA cleave studies reveal low redox based nuclease activity and the cytotoxic studies using MCF7 and A2780 cancer cell lines reveal moderate IC_{50} values. To further understand their properties and optimize their cytotoxic effect, Cu uptake, DNA interaction and production of reactive oxygen species inside the cancer cells were analysed. These data will be presented and correlated with the cytotoxic activity against different cancer cell lines.

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P-4

Aryne atropisomers: enantioselective generation and synthetic applications

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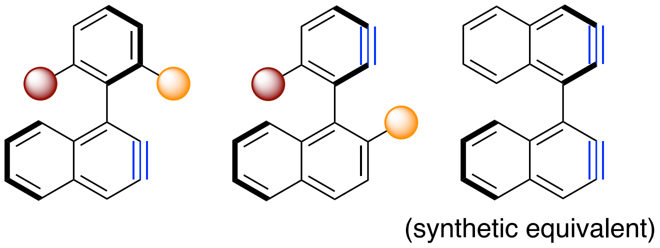
Arynes are strained short-lived species that must be generated in situ, most commonly through the *ortho*-elimination of suitable aromatic precursors.[1] Arynes are generally planar molecules, but enantioenriched aryne atropisomers having a biaryl stereogenic axis vicinal to the reactive triple bond 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.[4] 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.[5]



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P-5

Revision of the Titanium surface for successful implantation using anodization treatments

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Abstract.

Artificial hip implants and dental implants are widely used to restore the functionality of bones [1]. Some criteria of Titanium and its alloys characterize their biocompatibility that allow them to be used as materials to manufacture biomedical implants [2], by modifying their surface as soon as the adhesion of cells on the surface of this type of materials is generally not good [3]. The formation of a nanotube layer is preferred via anodic oxidation in electrolytes containing fluorine ions [4], whose the nanotubes have higher tendency to bone cell growth and never cause chronic inflammation or fibrous encapsulation [5]. This participation was supported by an electrochemical modification on the surface of Titanium recording corrosion, mechanical adhesion, topographic and structural measurements.

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P-6

Development of original catalysts without transition metals designed for hydrogenation reactions

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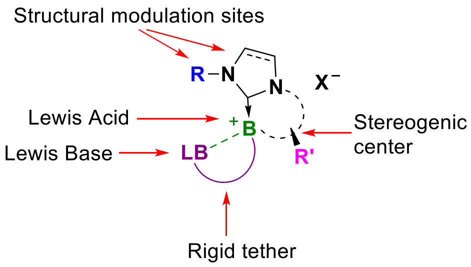
To answer the current societal issues, chemistry must imply a responsible approach by limiting its environmental impact, and by promoting green chemistry. This is one of the current challenges of chemists, and among the twelve principles of green chemistry; the field of catalysis holds a major place.

This project involves the development of modern tools for homogeneous catalysis based on original structures including a Lewis base and a Lewis acid. These platforms will be used in organic catalysis as Frustrated Lewis Pair (FLP) catalysts and their ability to activate small molecules.

Herein, we wish to disclose our efforts directed towards the synthesis of small molecules which will be used for the development, in a few steps, of a library of bifunctional and ambiphilic chiral main-group catalysts (see ***Scheme***). The design of these structures is based on one hand, on a NHC skeleton previously developed in our group[5] and, on the other hand, on scaffold known in the literature to split the dihydrogen molecule.[6,7]



***Scheme:** Design of new original ambiphilic catalysts based on scaffolds known to split the dihydrogen molecule by a FLP-type process.*

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P-7

Synthesis of Polycyclic Derivatives Towards Gold-Catalyzed Cycloisomerisation of 1,6-Enynes

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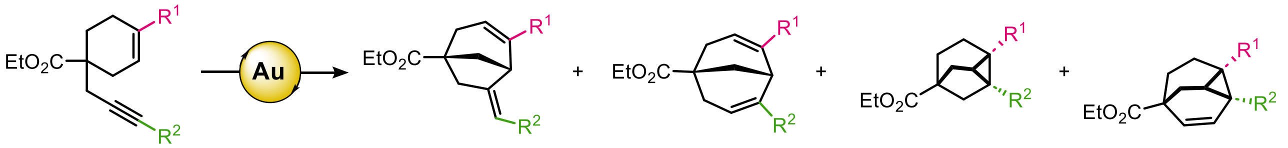
Recently, in an effort to increase the molecular diversity in drug libraries, a particular attention has been devoted to chemical structures with a three-dimensionality character.[1,2] However, synthesizing these new and original building blocks using a fast and efficient methodology remains a key challenge for an organic chemist. Gold catalysis is a powerful tool for the synthesis of complex core structures according to atom-economical and green processes. Indeed, gold complexes possess a specific reactivity able to activate π-systems towards nucleophilic additions.[3,4] It offers new possibilities to enhance the molecular complexity, by reaching various carbocyclic or heterocyclic scaffolds, starting from simple substrates. In this context, we developed an efficient and mild synthetic route for the preparation of functionalized bi- and tricyclic derivatives via gold-mediated cycloisomerization of 1,6-enynes.[5,6] Depending on the substrate and the reaction conditions, the process occurred under a 5-*exo* or a 6-*endo* pathway and these different mechanistic routes allowed the formation of four different polycyclic derivatives.[7] These building blocks represent privileged scaffolds in a search for increased molecular diversity of drug-candidate libraries.



A
***exo* derivative**

B
***endo* derivative**

C
tricyclic derivative rearrangement of the *exo*-form

D
tricyclic derivative rearrangement of the *endo*-form

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P-8

Bioinspired constrained peptides: versatile ligands to evolve copper catalysts for sustainable oxidation reactions

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Peptide frameworks constitute a very attractive and versatile platform for the development of metal catalysts because they can provide multiple donor atoms in a single molecule and in a chiral environment. In addition, they have structural and chemical diversity (possibility of using both proteinogenic and non-proteinogenic amino acids and peptide backbone modifications), accessible chemical synthesis by well-established solid-phase methodologies and water solubility.

Inspired by copper-containing enzymes that participate in a variety of O_2-processing reactions acting either as oxygenases or as oxidases [1], we have been developing a family of constrained His-containing peptides capable of coordinating copper(II) [2-4]. We have shown how the introduction of different degrees of conformational constrains in the peptide backbone and amide methylation [4], have a drastic effect on the formation and properties of the copper(II) species. In this communication, we will present the rationale of our designs and the recent data in the catalytic sulfoxidation of different substrates using H_2O_2 as oxidant and aqueous media.

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P-9

Design of supported catalysts for hydrogen production

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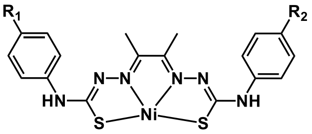
Numerous challenges for the upcoming decades arise from the worldwide reliance on fossil fuels as energy carriers and raw materials for industrial products. The reserve of these source are finite, which make the interest of the research community to find an alternative source.

Hydrogen is regarded as an "ideal" fuel due to its abundance and the environmental side since it only emits water vapors during combustion. The new challenge is to generate hydrogen from renewable and sustainable resources, such as electrocatalytic and photocatalytic hydrogen evolution reactions (HER).[1]

In previous work, we reported on the use of nickel bis-thiosemicarbazone complexes (NiTSC-R) and their use as electrocatalysts in HER (Figure 1). A series of chemical substituents -R placed on the para position of the ligand phenyl groups were chosen to display various electronic properties (Figure 2). Our study included the methoxy $-OCH_3$, thiomethyl $-SCH_3$, dimethylamino $-N(CH_3)_2$ and cyano -CN groups. The resulting catalysts provided interesting results with the thiomethyl derivative giving the optimum results with respect to the TOF and overpotential requierement . These results indicate that the chemical nature of the substituent in the para position of the ligand indeed influences the electrochemical and catalytic behaviour of the system.[2]



NiTSC-R

$R_1 = R_2 =$ -OMe, $-NMe_2$, -SMe, -CN
$R_1 =$ -CN $R_2 = -NMe_2$

Figure 1. Chemical Structure of Nickel complexes.

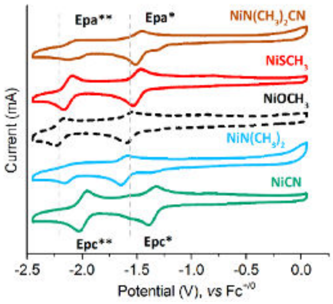


Figure 2. Cyclic voltammograms of Nickel complexes.

To pursue our investigations on the substituent effect on electrocatalytic hydrogen evolution, we are designing a new series of catalysts based on ligands bearing fluorine groups such as -R = OCF_3, C_6F_5, …etc). Our strategy aims at studying the electronic properties, the electrochemical behavior as well as the capability of the complexes to mediate protons reduction to evaluate the impact of the presence of these electron-withdrawing groups.

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P-10

Design and optimization of ALD of NiO with novel precursors

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NiO thin films have attracted tremendous attention owing to their outstanding chemical stability, good magnetic and catalytic properties[1]. NiO is considered a wonderful electrocatalyst for water oxidation, and it is a native p-type semiconductor with optical transparency due to its wide bandgap of 3.6 eV. Furthermore, NiO films can control between high and low conductive states under an external electric field, which is very useful for developing resistance switching random access memory devices[2].

Until now, NiO films have been prepared by different deposition techniques, including sputtering, sol-gel, pulsed laser deposition, spray pyrolysis, and chemical vapor deposition (CVD), atomic layer deposition (ALD). Among these, ALD is a powerful technique to grow thin conformal films with fine tuning of both composition and thickness.

The commonly used nickel precursors for ALD process are $\mathrm{Ni(Cp)_2}$, $\mathrm{Ni(MeCp)_2}$, $\mathrm{Ni(EtCp)_2}$, $\mathrm{Ni(dmamp)_2}$, $\mathrm{Ni(dmamb)_2}$, $\mathrm{Ni(acac)_2}$, $\mathrm{Ni(apo)_2}$, $\mathrm{Ni(dmg)_2}$, $\mathrm{Ni(thd)_2}$, and $\mathrm{Ni(amd)_2}$ in combination with ozone, water, hydrogen peroxide, or oxygen plasma[1]. However, ALD of NiO is not well developed yet. The major disadvantages associated with these nickel precursors are low volatility, thermal instability, and less reactivity. Some of these precursors are expensive or very difficult to synthesize. The aforementioned situations indicate that developing a new ALD recipe for the NiO film with new precursors is pertinent.

In this work, we propose a reliable recipe to grow high-quality NiO films with highest deposition rate by using novel precursors such as Ni-ketoiminates, $\mathrm{Ni(ipki)_2}$ and $\mathrm{Ni(eeki)_2}$, synthesize by Univ. Bochum[3] or Alanis patented by Air Liquide[4]. Here, we have optimized the ALD of NiO by using Alanis precursor, giving an excellent GPC of 1.2 Å/cy with ozone as a co-reactant, it also gave some interesting results with H_2O and H_2O_2 as co-reactants. And now we are focusing on the optimization of ALD recipes with ketoiminate precursors.

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P-11

Molecular machine activated by silver coordination

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The construction of molecular machines is a high scientific challenge of the supramolecular chemistry.[1] In this context, we explored the translocation of a the cucurbit[n]uril macrocycle[2] on a rigid and linear multi-station viologen−phenylene−imidazole molecular axle.[3,4] We exploited the Lewis-base properties of the imidazole moiety and of the carbonyl groups of cucurbit[n]uril to induce the dynamic macrocycle switch from the viologen station to the phenylene (Figure 1). While a large series of metal cations has been tested, only silver cations were able to activate this molecular machine.[5] NMR, UV−vis spectroscopy, mass spectrometry, ITC, and modeling were combined to show that ring translocation or uptake along a molecular thread is possible in water by Ag^+ as a metal stimulus.

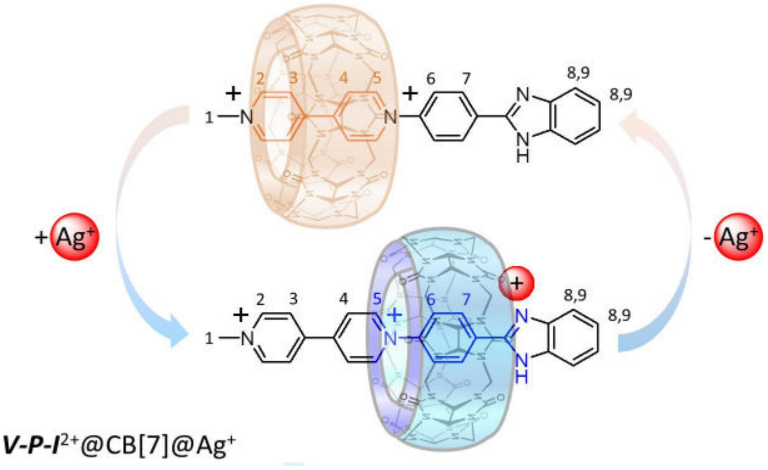

Figure 1: Metal-actuated supramolecular switch.

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P-12

Metabolomics of natural resins for archaeological and cultural purposes: Isolation and structural characterization of taxonomic chemomarkers from Pinaceae and Cupressaceae

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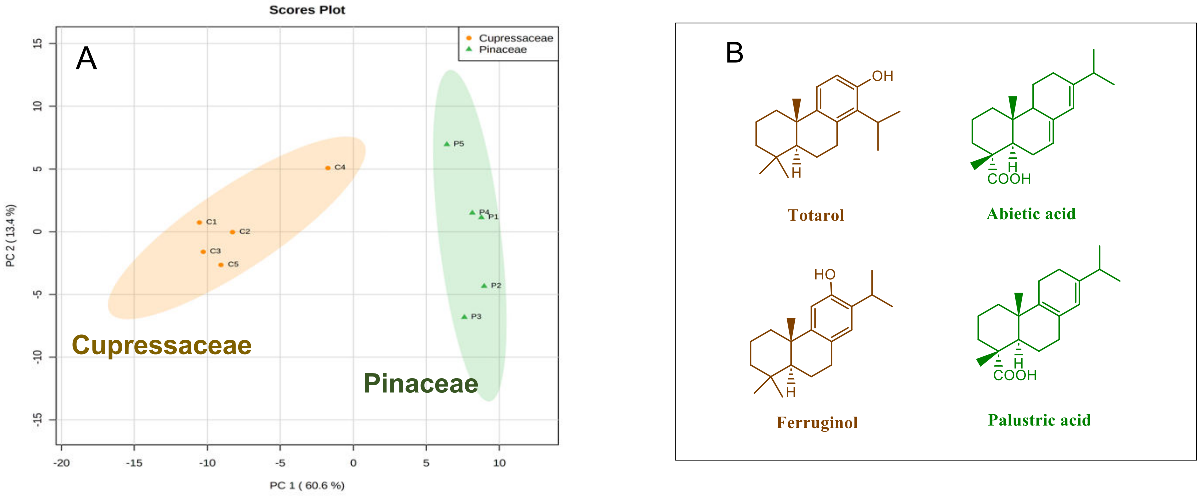
Archaeological materials are remnants of the past that may contain well-preserved organic chemical markers. In some cases, these chemical markers can be used to trace the botanical origin of natural resins used for practical or ritual purposes. More broadly they can provide information on about the various and complex ancestral practices related to such raw materials [1].

This study reports the phytochemical analysis of certified plant resins produced by trees and shrubs belonging to Pinaceae and Cupressaceae, in order to find taxonomic chemomarkers specific to each of these two botanical families. For that purpose, an untargeted metabolomic approach was performed by gas chromatography-mass spectrometry (GC-MS) on taxonomically well-defined natural resins. This study was carried out on four species of Pinaceae and four of Cupressaceae as well as on commercial resins such as colophony obtained from Pinaceae and sandarac from Cupressaceae. Following the chromatographic profiles of all these resins, more than 200 metabolites were detected. Supervised multivariate statistical analysis (principal component analysis, PCA) and unsupervised analysis (partial least squares discriminant analysis, PLS-DA) were used to identify specific chemomarkers to each of these two families.



(A) PCA score plot built using the GC-MS dataset of the resins, (B) Chemical structures of the main chemomarkers.

The relevance of this method was validated by the fact that, well-known chemomarkers, such as abietic and palustric acids for Pinaceae resins or totarol and ferruginol for Cupressaceae resins, were detected among these molecules [2]. In addition, several other chemomarkers not listed as such in the literature are being isolated (flash chromatography, semi-preparative high-performance liquid chromatography) and structurally characterized (1D and 2D NMR, HR-MS) by a phytochemical approach conducted on commercial resin samples.

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P-13

Ligand Redox Non-Innocence in Low-Valent Octahedral Molybdenum Complexes: A DFT Study

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Two octahedral molybdenum complexes containing a bidentate ligand, a β-Diketonate substituted with dipiavaloylmethanate (dpm) or dibenzoylmethanate (dbm), have been synthesized to catalyze the CO_2 carboxylation reaction. Our work aims at characterizing the electronic structure of the complexes after successive reductions and oxidations to evaluate the possible role of the ligand during the electrochemical processes. DFT calculations were employed making use of the crystallographic structures of the series of complexes to determine the molecular orbital diagrams and the spin states of the species. Our results suggest that the dbm ligand is involved during the second and third reductions that are best described as ligand-based processes. Thus, we can support that the dbm-substituted β-Diketonatee ligand is non-innocent which will have direct implications for catalysis especially regarding the decarboxilation reactions.

P-14

Natural and synthetic antibacterial polymers: Comparison of antimicrobial peptides and copolymers.

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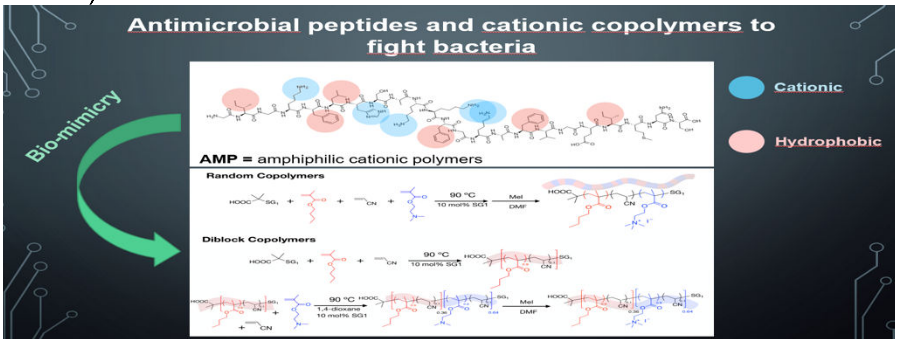
Resistance to conventional antibiotics used in medicine is dangerously rising worldwide [1]. New types of antibacterial molecules have to be developed and be i) nontoxic to humans, ii) active against bacteria already resistant to conventional antibiotics, iii) not able or less prompt to cause resistance. In that context, antimicrobial peptides (AMPs) and antibacterial cationic copolymers stage a come-back thanks to novel approaches/understandings in peptide research/development and because of the discovery of unexplored while interesting new candidates. Their particular mechanism of action relying on a fast and selective insertion into the bacterial membrane (pore-forming activity) makes them very promising as alternative to conventional antibiotics [2-5]. In addition, their anti-inflammatory activity makes them able to fight both the bacterial infection and the inflammation related to it. This presentation will discuss the advantages and limitations of cationic copolymers, peptidomimetics bioinspired from AMPs, and natural AMPs in term of activity, innocuity, sensitivity to physiological factors (such as proteases, salts, or human serum), and production (time, price, scale..).



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P-15

Gold Catalysis: an Entry to Original Scaffolds for Fragrance Industry

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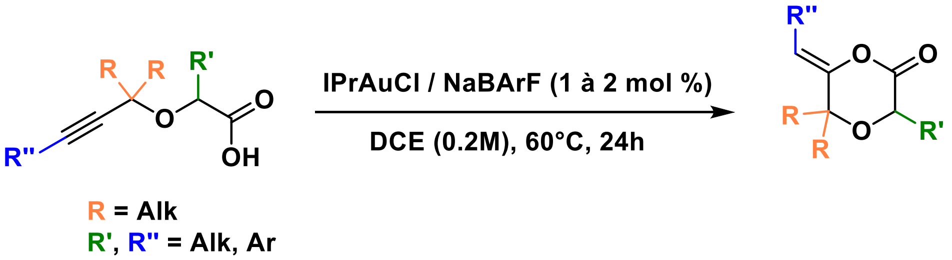
New olfactive molecules are always sought by fragrance industry to find new scents or improve properties of existing scents.[1] In addition, the regulatory policy is increasingly strict and main compounds of certain formulas may be banned each year (recently Lyral®). The consequence of these interdictions 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 been interested in cycloisomerization of enynes leading to olfactory interesting bicyclic derivatives.[4] We developped novel methodologies to synthesize original volatile 1,4-dioxan-2-ones by cycloisomerization reactions of acetylenic acids.[5] These types of skeletons have been previously synthesized as intermediates in the synthesis of multi-ring heterocyclic products by D-J. Dixon.[6] 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.



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

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P-16

Unusual interactions in confined space

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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.[1] 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.[2]

Molecular cages are attracting considerable attention in modern supramolecular chemistry due to their possible applications in molecular recognition, catalysis, drug delivery, biosensing, separation and storage. Hemicryptophanes are heteroditopic host compounds built from a cyclotriveratrylene (CTV) unit with another C3-symmetrical moiety. They are able to recognize various charged or neutral guests, such as ion pairs, zwitterions, ammoniums, carbohydrates and fullerenes.[3]

We have developed a series of chiral molecular cages based on electron-deficient units in order to encapsulate anionic, zwitterionic and ion pairs species. A drastic modulation of the recognition properties was achieved demonstrating the selectivity of our systems.
The synthesis of hemicryptophanes, their special conformational isomerism with a switch of chirality depending on the solvent and the study of their molecular recognition properties will be highlighted.

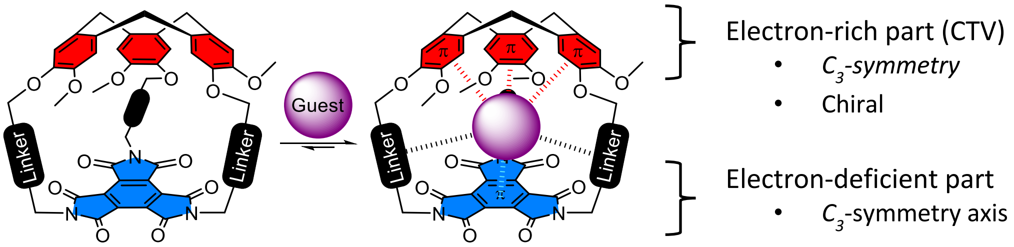

Figure 1: Host guest equilibrium and the possible interactions between the host and the guest

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P-17

Bioinspired hydrogen photoproduction

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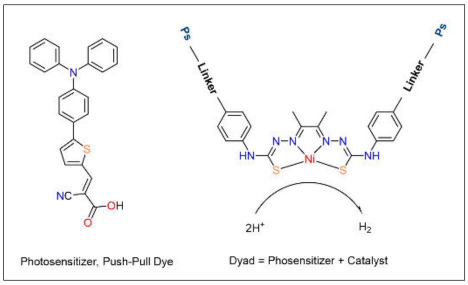
Hydrogen is abundant and is considered an "ideal" fuel since only water vapors get released to the environment upon its combustion. In recent years, efforts have been made in developing new approaches to generate H_2 from renewable and sustainable resources, such as electrocatalytic and photocatalytic hydrogen evolution reactions (HER).[8]

Scientists have taken inspiration from Nature's through hydrogenase enzymes which contain inorganic cofactors that mediate the reversible conversion of protons and electrons into hydrogen.[9] 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 the most efficient molecular H_2 evolution catalyst. [10]

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.[11] 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[12]. More recently, we showed that we can substitute the noble meta-photosensitizer by cheap and environmental-friendly nitrogen doped-carbon dots. [13] This has driven us to consider the design of dyads for photocatalytic HER by coupling our parent catalyst (NiTSC) with organic dyes using solar energy and protons to photoproduce H_2.



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P-18

The influence of gap spacing and antenna size in gap plasmon resonance spectra of Individual Ag nanocubes

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Plasmonic nanocavities can trap light in ultrasmall volumes and can be obtained with a simple fabrication process. As a result, they receive increasing attention in the nanophotonics and nanoelectronics communities due to the potential applications in optoelectronics, quantum optics, and novel nanophotonic and plasmonic-circuit devices.

In this study, we have systematically investigated the gap plasmon resonance of monodisperse silver nanocubes (AgNCs) separated from a supporting gold film by a thin dielectric layer such as aluminum oxide film (Al_2O_3) or titanium dioxide film (TiO_2). Scattering and absorption measurements were performed on individual plasmonic cavities for various nanocube size and dielectric thickness. Correlative SEM analysis enables to precisely interpret experimental data and characterise the optical properties of the dielectric layer (refractive index, thickness) via numerical simulations. This work will enable the development of high-performance tuneable optical nanodevices or active tuning applications and rectennas devices by controlling light absorption, scattering, or emission.

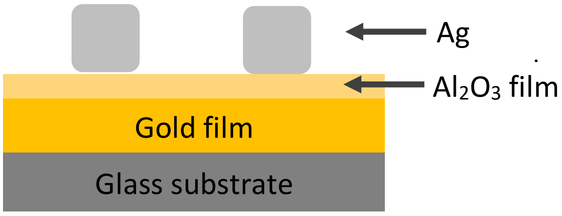

Figure 1: The diagram of the silver nanocubes on a gold substrate, separated by the dileclectric layer

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P-19

Electrodeposition of ionomer on zinc anodes for zinc-air batteries

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Abstract

Among all metal-air batteries, zinc air batteries (ZAB) represent a safe, environmentally benign, and affordable. The cyclability and overall battery efficiency of zinc air batteries (ZAB) can be enhanced by protecting the zinc metal anodes. In addition, it can also reduce the corrosion and inhibit the zinc dendrite formation. In this research, the protection of the zinc anodes was done by electrodepositing poly(N-vinylbenzyl N,N,N trimethylammonium) chloride (PVBTMA) ionomer thin films on Zn by using cyclic voltammetry. The deposition of PVBTMA on zinc anodes was observed by scanning electron microscopy and the wettability of the ionomer-coated zinc surface was investigated by contact angle measurement. The open circuit voltage was measured both in alkaline electrolyte and in solid-state configuration. The results of open circuit voltage measurements showed that the zinc with PVBTMA protection performed better in comparison to bare zinc without PVBTMA protection which shows low cyclability and low open circuit voltage. Cycling tests were also done to see the discharge capacity of ZAB in liquid electrolyte and in solid-state configuration.

Keywords: metal-air batteries; solid-state batteries; oxygen reduction reaction; anion exchange membranes; electropolymerization

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ZIARELLI	Fabio	Aix Marseille Université	CO1 CO2 CO6

8h50		**Ouverture et introduction**	
9h00	Conférence plénière *Amphi Gastaut* *Modérateur: Cyril Bressy*	**CP1 | Prof. Mark Lautens (Univ Toronto)** ***Flipping the Switch: Reversibility in Catalysis***	
	Sessions parallèles de communications orales	Session 1 *Amphi Gastaut*	Session 2 *Amphi Touze*
9h45		CO-01 Florian Ferrer	CO-12 Yongxing Wang
10h00		CO-02 Samuel Cousin	CO-13 Sofiane Bourdillon
10h15		CO-03 Andrea Fasano	CO-14 Axel Bossavit
10h30	Pause-café	Session Poster *Salle des Voûtes*	
11h00		CO-04 Benjamin Mourot	CO-15 Paul Guérin
11h15		CO-05 Brahim Akhassi	CO-16 Aurélien Galibert-Guijarro
11h30		CO-06 Amélie Frison	CO-17 Iago A. Modenez
11h45		CO-07 Blanche Krieguer	CO-18 Alexis Truchon
12h00	Déjeuner buffet	Session Posters *Salle des Voûtes*	
13h30	Conférence plénière *Amphi Gastaut* *Modératrice: Patricia Merdy*	**CP2 | Dr. Isabelle Couturier-Tamburelli** ***Etude de l'évolution photochimique des aérosols de l'atmosphère de Titan***	
14h15		CO-08 Salma Bikerchalen	CO-19 Jingke Hou
14h30		CO-09 Micol Zerbini	CO-20 Arthur Gaucherand
14h45		CO-010 Muhammad Luthfi Fajri	CO-21 Attilio Di Maio
15h00		CO-011 Floriane Delpy	CO-22 Ange Wilfrid Embo-Ibouanga
15h15	Pause-café	Session Posters *Salle des Voûtes*	
15h45	Conférence plénière *Amphi Gastaut* *Modérateur: Sylvain Marque*	**CP3 | Dr. Didier Gigmes - Grand prix régional 2023** **Alkoxyamines as valuable precursors for macromolecular engineering**	
16h30	*Amphi Gastaut*	Conclusion et clôture – Yoann Coquerel	