BOOK OF ABSTRACTS

Journée de la Chimie
Sud-PACA
28 mars 2025 à Nice

UNIVERSITÉ CÔTE D'AZUR

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PROGRAMME

8h30 Accueil des participants

9h00 Ouverture *V. Michelet & Y. Coquerel*

9h10-9h50 C. NEVADO (Zürich University) ***Modératrice K. Plevova***

Metaloradical intermediates as a playground for structural complexity

Modératrice G. Chouraqui

9h50 (COM1) P. Guérin (AMU) Chiral biaryls: from axial to planar chirality using Kumada-Tamao-Corriu coupling

10h05 (COM2) K. Mao (UniCA) Reactivity of silver and ruthenium complexes in enynes' cyclizations: towards green and sustainable development

10h20 (COM3) S. Syahputra (AMU) Copper-doped Carbon Quantum Dots for Electrochemical CO_2 Reduction Reaction

10h35 (COM4) D. Lemire (UniCA) Speciation and mobility of natural radionuclides (U, Th, Ra) in the context of rare earth mining

10h50-11h35 Pause café – Session poster (Hall)

Modérateur O. Chuzel

11h35 (COM5) P. Merdy (UToulon) Marquage fluorescent de nanoplastiques de polyamide 6-6 pour une détection environnementale

11h50 (COM6) B. Samia (AMU) Atmospheric Fate of Pesticides: Heterogeneous Reactivity and Degradation Products

12h05 (COM7) E. Baubiat (UniCA) Synthesis and Oxidative Behavior of Gold(I) Catalysts

12h20 (COM8) N. Belkessa (UniCA) Molecular approach of uranium and neptunium accumulation in bivalve Mytilus galloprovincialis

12h35 (COM9) A. Gaucherand (AMU) Enantiospecific helical-to-central rearrangement and access to tunable dyes

12h50-14h10 Buffet déjeuner – Session affiches (Hall)

14h10-14h45 Olivier SIRI (Université Aix-Marseille, CINaM) ***Modérateur R. Melot***

Modérateur A. Kermagoret

14h45 (COM10) A. Lorenzo Reyes (AMU) Ground and excited state aromaticity in azulene-based helicenes

15h00 (COM11) A. Bonneau (UToulon) Green process for zinc oxide formation towards photocatalysis application

15h15 (COM12) C. Dubernet (UniCA) Évaluation de la qualité de l'eau dans les rivières de Nouvelle-Calédonie et impact sur la santé humaine

15h30 (COM13) A. Bourhis (AMU) Enantioselective Synthesis of Benzopyrane Atropisomers

15h45 (COM14) A. Reinbold (AMU) Enhancing the activity and the safety of ruminal Antimicrobial peptides using chemical diversity

16h00-16h40 Pause café – Session poster (Hall)

Modérateur H. Clavier

16h40 Remise du Prix de thèse 2024 SCF-Sud-PACA/NUVISAN Dr. Alexis Truchon

"Nouvelles réactivités de composés aldéhyde-ynes en catalyse organométallique"

Modérateur Y. Coquerel

17h00 Remise du Grand Prix 2025 de la SCF-Sud-PACA Dr. Maria Duca

17h00-17h45 Dr. Maria Duca "Innovative strategies to target non-coding RNAs with synthetic ligands"

18h00 Remise des prix de communications orales et posters - Clôture de la Journée

V. Michelet & Y. Coquerel

Comité Scientifique

Gaëlle Chouraqui

Hervé Clavier

Yoann Coquerel

Jade Dussart-Gautheret

Anthony Kermagoret

Philippe Marsal

Romain Melot

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CONFÉRENCES PLÉNIÈRES

PL-1

Metaloradical intermediates as a playground for structural complexity

Prof. Dr. Cristina Nevado Blazquez

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Our group has recently explored the reactivity of C and N centered radicals, in combination with transition metals, to streamline the functionalization of π-systems.

Here, we will present our efforts to generate and harvest these valuable intermediates in synthetically relevant contexts, including recent results towards their application in asymmetric transformations.[1]

Further, examples of Nickel catalyzed dicarbofunctionalizations of alkenes and alkynes in a chemo, regio- and stereoselective manner utilizing radicals as well as studies on the mechanistic features underlying these transformations will be presented in this lecture.[2]

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PL-2

A journey into the world of colors

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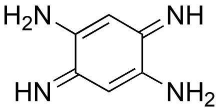
Colors are essential to our lives. They're so familiar that they even interfere with our emotions. But what lies behind this colorful life? What's going on at the very heart of color? What's going on at the molecular level? This presentation looks at color from different angles, from physics and biology (briefly) to chemistry (in details). A critical element in designing and fabricating dyes is the control and fine tuning of their color. An approach for controlling the color of dyes is to develop a family of modular chromophores and tune their photophysical characteristics at will. 2,5-Diamino-1,4-benzoquinonedimine **1** is a very long known molecule (1887) that has been poorly investigated owing to its low solubility and its instability in solution. We decided to revisit the chemistry of **1** in order to elaborate new dyes that are of major interest in many technological sectors. Our strategy is based on: 1) the use of **1** as ligand in coordination chemistry,[1] 2) the incorporation of **1** in extended pi-system,[2] and 3) the tuning of the molecular structure **1**.[3]



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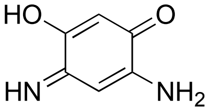

2

Herein, various emerging families of chromophores and fluorophores based on **1** with multiple and controlled colors will be presented. The different approaches and the key role of the quinoidal precursors will be described and discussed in the presentation. In addition, the related molecule **2** will be also reported in order to highlight the crucial influence of the heteroatoms in the construction of a wide range of dyes with tunable colors.[4]

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PL-3

Innovative strategies to target non-coding RNAs with synthetic ligands

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RNA is one of the most intriguing and promising biological targets for the discovery of innovative drugs in a large number of pathologies and various biologically relevant RNAs that could serve as drug targets have already been identified (1). Among the most important ones, it is worth to mention prokaryotic ribosomal RNA which is the target of a number of currently employed antibiotics, viral RNAs such as TAR, RRE and DIS RNA of HIV-1 or oncogenic microRNAs that are tightly involved in the development and progression of various cancers. However, difficulties in the rational design of strong and specific small-molecule ligands renders this kind of molecules relatively rare.

During the last fifteen years we devoted our research activities to the design, synthesis and evaluation of original small molecules as binders of non-coding RNAs for anticancer, antiviral and antimicrobial applications (2). This led us not only to the development of synthetic pathways to obtain new compounds selective for the biological target, but also to bioactive molecules able to induce the desired biological effect in cells (Figure 1). Results obtained in the field of targeting oncogenic microRNAs in cancer as well as the validation of new targets for antibiotic discovery will be presented illustrating the wide applications that the field of targeting RNAs with small molecules could have.

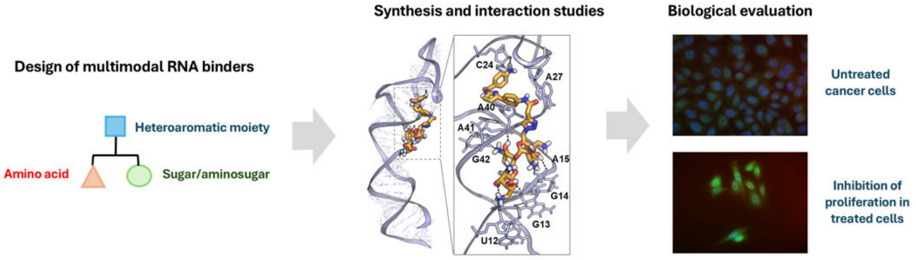

Figure 1. Workflow of the team strategies to target therapeutically relevant RNAs.

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COMMUNICATIONS ORALES

COM-1

Chiral biaryls: from axial to planar chirality using Kumada-Tamao-Corriu coupling

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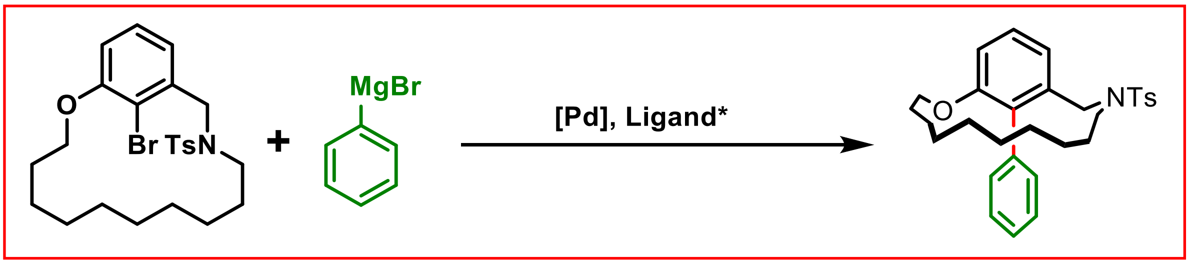
Palladium- or nickel-catalyzed Kumada-Tamao-Corriu couplings are widely used to synthetize biaryl compounds. Several ligands have been tested to develop enantioselective versions giving access to biaryls containing an axis of chirality.[1] Whereas good enantiomeric excesses can be obtained with including phosphorus-based chiral ligands, enantioinduction using chiral N-heterocyclic carbenes (NHC) is rather moderate, including with atropisomeric Pd-NHC complexes recently develop in our laboratory.[2,3] This led us to investigate this coupling reaction with peculiar substrates for which a planar chirality will be generated instead of an axial chirality: cyclophanes.

Cyclophanes are macrocycles composed from an aromatic ring and an *ansa* chain and can be found in many natural and pharmaceutical compounds.[4] Para- or metacyclophanes can display a planar chirality but methods to prepare them in an enantioenriched manner are limited, especially for metacyclophanes. In this work, it will be presented the synthesis of metacyclophanes, the study of their configurational stability and their uses in the Kumada-Tamao-Corriu coupling to generate enantioenriched planar chiral biaryls metacyclophanes with up to good ees (88% ee).



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COM-2

Reactivity of silver and ruthenium complexes in enynes' cyclizations: towards green and sustainable development

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In the context of the key principles of Green Chemistry,[1] the development of efficient, clean and mild strategies to access cyclized and functionalized molecules is highly important in the field of organic chemistry. We became interested in the reactivity of enynes in the presence of silver and ruthenium complexes. We investigate the cyclization of functionalized 1,6-enynes and showed that silver hexafluoroantimonate[2] catalyzed the intramolecular [4+2] cycloaddition reaction of amide-1,6-enynes, providing tricyclic and tetracyclic compounds. The effects of different catalysts (silver salts, gold and platinum complexes) on this reaction were also investigated, leading to a series of cyclic amides obtained in good yields.[3] In parallel, we developed a ruthenium-mediated ring-closing enyne metathesis transformation[4] of alkynyl B-anthranilamide (B(aam)) to prepare functionalized polycyclic azaborine skeletons. B(aam)-tethered enynes reacted with with Grubbs catalyst, affording the corresponding exo-cyclic compounds in good yields (25 examples, yields up to 89%).[5] This methodology was optimized and performed in dimethyl carbonate[6] as a green solvent, providing a direct and environmentally friendly access to functionalized azaborine scaffolds.

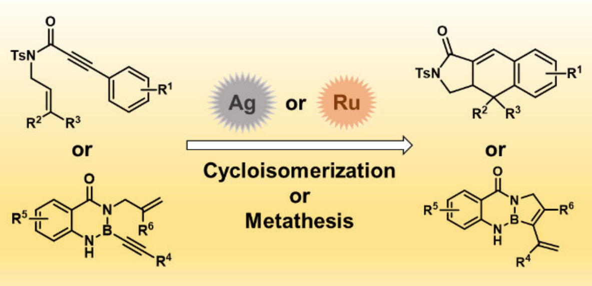

Figure 1: Silver and ruthenium-catalyzed cycloisomerization reaction of nitrogenated enynes

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COM-3

Copper-doped Carbon Quantum Dots for Electrochemical CO_2 Reduction Reaction

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The gradual increase of CO_2 emission amplifies the rate of global warming. Meanwhile, the value of CO_2 can be enhanced by transforming it to more useful products. One of the promising ways is through electrochemical CO_2 reduction reaction (eCO2RR). In this research, copper-doped carbon quantum dots (CQDs) were used to catalyze the eCO2RR. Two precursors of CQDs were used in this study: citric acid (CA) and glucosamine hydrochloride (GAH). In order to see the effect of the heteroatom doping, three different types of Cu-doped CQDs were synthesized with nitrogen or with nitrogen and sulfur: Cu,S,N-CQDs – CA, Cu,S,N-CQDs – GAH and Cu,N-CQDs – GAH. The eCO2RR was carried out in a conventional H-cell and with a rotating disk electrode (RDE). We focused on quantifying the products in solution using high performance liquid chromatography (HPLC) and hydrogen nuclear magnetic resonance (^{1}H-NMR).

An anion exchange polymer, poly(2,6-dimethyl-1,4-phenylene oxide) quarternized with trimethylamine grafted on long (pentyl) side chains (PPO-LC) was used to facilitate the mass transport of OH^- ions during the eCO2RR. PPO-LC was used as an ionomer for the oxygen reduction reaction in previous research of our group.[1-2] After applying linear sweep voltammetry (LSV) for these three electrocatalysts, Cu,S,N-CQDs – CA showed the best electrocatalytic performance (Figure 1(a)). Moreover, the product analysis with HPLC and H-NMR revealed that Cu,S,N-CQDs – GAH gave the highest Faradaic Efficiency (FE) of 31% for formate ions at 0 V/RHE whereas Cu,S,N-CQDs – CA showed the highest FE of 87% for acetate ions at -0.2 V/RHE as shown in Figures 1b and 1c. The further development of this study will use a flow cell which can mitigate the diffusion problem. The future study will also focus on gaseous products besides the products in solution.

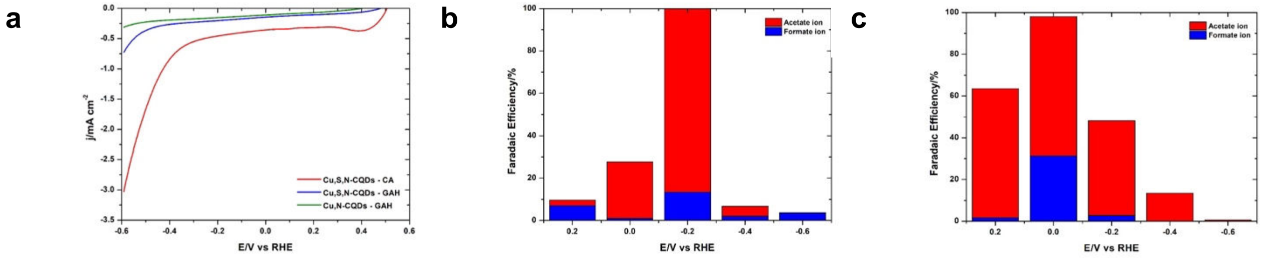

Figure 1. a) LSV curves; Faradaic Efficiency of **b)** Cu,S,N-CQDs – CA and **c)** Cu,S,N-CQDs – GAH with respect to the applied potential vs reversible hydrogen electrode (RHE) at 2500 RPM

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COM-4

Speciation and mobility of natural radionuclides (U, Th, Ra) in the context of rare earth mining

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The rare earth elements (REE) possess unique physicochemical properties which make them essential for the development of new technologies. The need of these metals leads to an explosion in demand, making their supply a strategic issue on a global scale. The REEs are however often found as geological resources in minerals containing other metals such as uranium and thorium.[1] The presence of naturally occurring radioactive materials (NORM) such as uranium, thorium and their descents (in particular radium Ra at ultra trace scale) is a major concern in the occupational and environmental radiation exposures during mining, milling, chemical processing and waste management of REE mine project.

Following the REE extraction, the fate of the non-desired NORM such as U, Th and Ra left in the mine site is poorly known. To answer this question, the mobility of the U, Th and Ra have been studied at the trace scale for U and Th and at ultra-trace scale for ^{226}Ra. Mobility is a key factor in determining the extent of the possible dispersion of contaminants in the environment. Moreover, it is strongly influenced by environmental parameters such as pH, temperature, redox-conditions and the presence of organic matter.[2]

Based on small bench top columns, a tailing model can be designed with *ad hoc* artificial weathering conditions.[3,4] Following the tailing of the contaminated soil, the distribution of radionuclides has been quantified by ICP-MS in the soil and leachate. On the other hand, *μ*-XRF imaging and SEM-EDX were used for the cartography of the uranium in the soil allowing to observe accumulation zones in specific compartments (figure 1). In parallel, the speciation of U and Th were monitored by EXAFS for a better understanding of the mechanisms that drive these two elements mobility (Ra speciation could not be monitored due to its presence at ultra-trace scale).

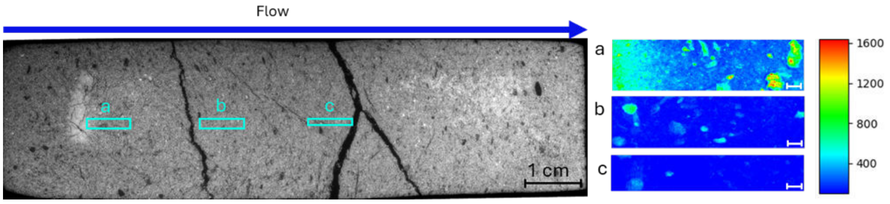

Figure 1. Slice of a contaminated column by SEM. a, b and c are cartography obtain by *μ*-XRF. scale bar of a=b=c=200 *μ*m, Intensity scale in counts

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COM-5

Marquage fluorescent de nanoplastiques de polyamide 6-6 pour une détection environnementale

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La pollution au plastique est une problématique environnementale majeure à laquelle tous les compartiments écologiques sont soumis comme les océans où un dixième du plastique mondial y est présent avec une quantité non négligeable de matériels de pêche tels que les filets composés en général de nylon (polyamide 6-6). Les phénomènes biotiques et abiotiques auxquels ces plastiques sont soumis, sont à l'origine de leur dégradation et fragmentation, donnant lieu à la formation de micro et nanoplastiques. Les études sur l'effet des nanoplastiques sont difficiles à réaliser car ils sont difficilement quantifiables en routine à l'aide des techniques analytiques actuelles. Un nouveau protocole de synthèse de nanoplastiques fluorescents est testé sur le polyamide 6-6.[1] Ce protocole permet d'incorporer le fluorophore choisi (rhodamine 6G et fluorescéine) directement dans le plastique lors de la production des nanoparticules. S'en suit une filtration membranaire permettant d'éliminer les fluorophores dissous, non fixés. L'objectif de cette étude est de pouvoir identifier spécifiquement les plastiques dans un échantillon prélevé sur le terrain mais aussi de pouvoir étudier leur toxicité en rendant visible les nanoplastiques dans les organismes. Des mesures de fluorescence moléculaire ont été réalisées à l'issue de la synthèse afin de s'assurer que le polyamide avait bien été marqué (Figure 1). Une analyse granulométrique au Nano Tracking Analysis a quant à elle permis de déterminer la répartition en taille des particules présentes dans les suspensions et leur concentration. Enfin, l'impact du nanoplastique fluorescent a ensuite été observé sur des rotifères marins. Les tests écotoxicologiques réalisés ont permis de déterminer le taux de mortalité chez ces organismes après 24h d'exposition puis après 48h. Il s'agissait également de s'assurer que le fluorophore fixé sur le polyamide n'induisait pas de mortalité supplémentaire par rapport au nanoplastique non marqué.

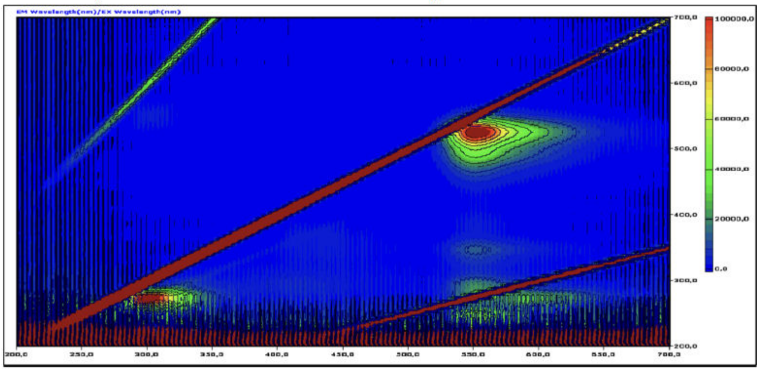

Fig.1. Spectre de fluorescence 3D du polyamide nanoparticulaire marqué à la Rhodamine

Références

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COM-6

Atmospheric Fate of Pesticides: Heterogeneous Reactivity and Degradation Products

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After application, 20 to 50% of pesticides can enter the atmosphere through spray drift, volatilization, or wind erosion, posing risks to ecosystems and human health. Once airborne, they can partition between the gas and particulate phases. However, regulatory assessments often overlook their slower degradation on particles, underestimating their persistence.[1]

This study investigates the atmospheric fate of nine pesticides commonly used in viticulture (Boscalid, Cypermethrin, Cyprodinil, Deltamethrin, Folpet, Pendimethalin, Spiroxamine, Tebuconazole, and Trifloxystrobin). Using a flow reactor, we exposed pesticide-coated silica particles to ozone and OH radicals, revealing atmospheric half-lives ranging from three days (Cyprodinil) to over a month (Folpet).

Furthermore, we identified degradation products on particles using LC-Orbitrap-MS/MS and GC-qMS and detected volatile degradation products in the gas phase using SRI-ToF-MS. Notably, the highly toxic phosgene (Cl_2CO) was identified as a degradation product of Folpet (as shown in Figure 1) and Cypermethrin.

These findings underscore the importance of integrating particulate-phase reactivity into risk assessments, as it significantly influences pesticide persistence, transport, and the formation of toxic byproducts.

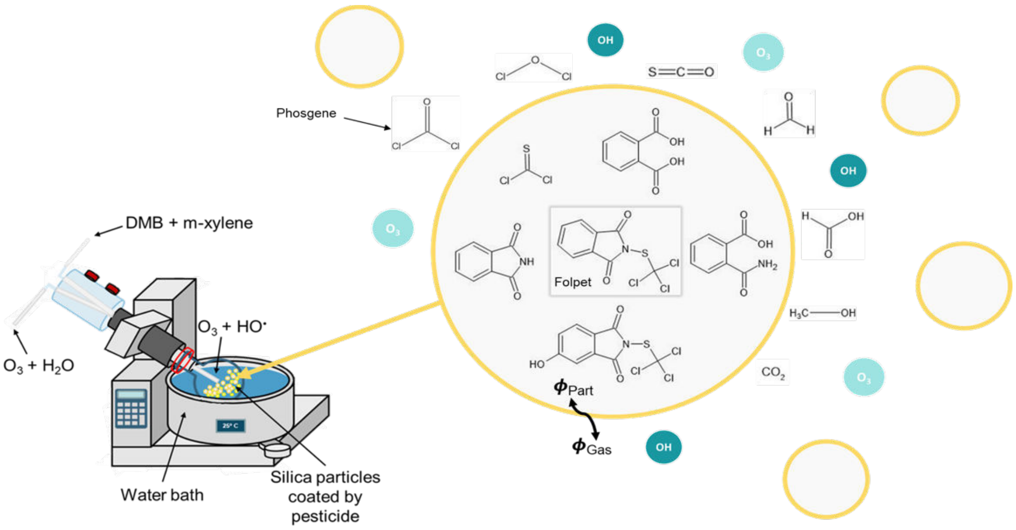

Figure 1: Degradation products of Folpet and their distribution between the particulate and gaseous phases.

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COM-7

Synthesis and Oxidative Behavior of Gold(I) Catalysts

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While the majority of gold-catalyzed reactions highlight the carbophilic Lewis acid character of gold(I),[1-4] several studies have shown over the last twenty years the feasibility of Au(I)/Au(III) catalytic systems through the use of external oxidants.[5] This development opens up new prospects in the field of gold-based catalysis. Simultaneously, electrosynthesis is experiencing a major upsurge in interest among the scientific community: the direct use of electricity offers an economical, sustainable and safer alternative to conventional oxidizing/reducing agents.[6] These methods are two powerful synthetic tools, both of which are undergoing a revival, and their combination could lead to new methodologies and new reactivities.[7]

In this context, a preliminary cyclic voltammetry study has been carried out on a range of gold complexes and ligands to determine their oxidation potentials. On the one hand, these data will potentially allow the *in situ* generation, the isolation and the characterization of gold(III) complexes. On the other hand, it will also enable the development of new catalytic processes under electrochemical conditions.

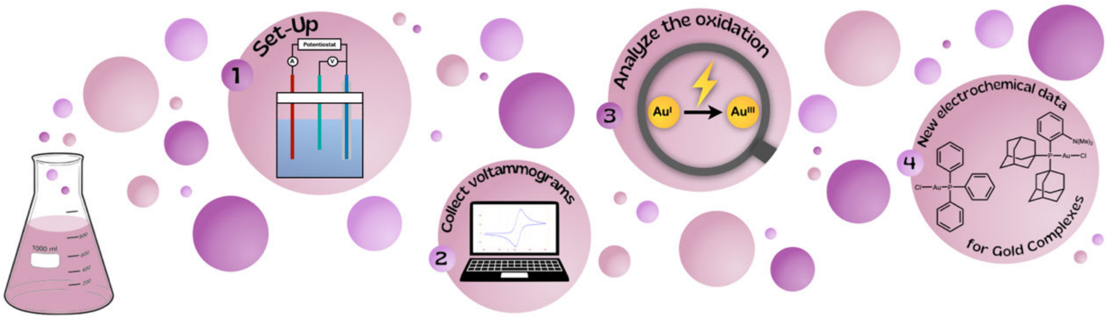

Figure: The different steps of the electrochemical study of gold complexes

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COM-8

Molecular approach of uranium and neptunium accumulation in bivalve *Mytilus galloprovincialis*

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Among the various environmental compartments that serve as outlets for different metal contaminants, seas and oceans can be considered as the ultimate receptacle for pollutants transported by rivers and watersheds. As a result, they function as long-term reservoirs for contaminants such as metals, gradually redistributing them through marine ecosystems. Indeed, the marine environment has often been monitored as a marker of pollution due to its role in the accumulation and dispersion of these contaminants. In the specific case of trace metallic radionuclides, such as uranium and plutonium (for which neptunium, less radioactive will be used as a surrogate), their origin in seawater is essentially anthropogenic, resulting from atmospheric nuclear testing, waste management, mining activities, accidental releases.

Most radioecological studies in marine ecosystems have focused on mapping and quantifying ultra-trace radionuclides, their propagation and accumulation areas in specific compartments such as water and marine organisms. The bioavailability of these pollutants plays a crucial role in their transfer to living organisms. In the marine system, bivalve mollusks, especially mussels, are widely used as bioindicators[1] due to their ability to filter large volumes of seawater and for their sedentary nature.

The objective of this study is to identify the main macromolecules in the mussel *Mytilus galloprovincialis* target organs upon contamination: hepatopancreas and byssus. *In vivo* exposure allowed to quantify uranium bioconcentration within the organs, using ICP-MS, and to determine its speciation after uptake, using EXAFS. This methodology is used to understand the interaction of each radionuclide within the biomolecules of the target organs. Metallothionein's (MTs) highly abundant metalloproteins in hepatopancreas are responsible of metals storage and detoxification processes[2] in mollusks, therefore they might have a role into actinide internalization within the organ. Mussel foot proteins (Mfp) are also favorable to metal complexes within the byssus due to their high concentration of metal-ligand sites[3], which make them good candidate for actinide complexation. For *in vitro* studies, MTs from *Mytilus galloprovincialis* was extracted and commercial Mfp was purchased (since this portein is difficult to extract). Both proteins were exposed to uranium(VI) and neptunium(V), then characterized using UV-vis absorption and EXAFS. This comparison between *in vivo* (target organs) and *in vitro* (purified proteins) approaches allows us to get a better insight into actinide internalization mechanisms. From a broader point of view, this research will provide basic bioinorganic information on uranium and neptunium (as a surrogate of plutonium) transfer processes to living organisms and their ecotoxicity.

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COM-9

Enantiospecific helical-to-central rearrangement and access to tunable dyes

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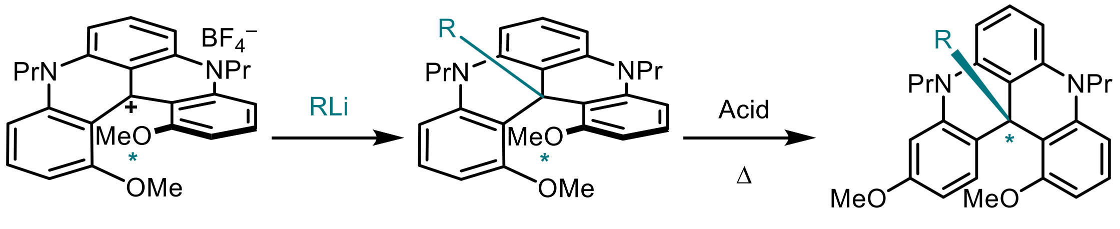
DiMethoxyQuinAcridinium (DMQA) is a helically chiral dye with potent chiroptical properties and wide applications.[1] In order to tune its properties, different post-functionalization reactions have been developed in the group, allowing the decoration of the outer rim of the helicenium.[2, 3, 4] Although a wide scope of chiroptical properties could be obtained, good regioselectivity was not achievable. Herein, we propose a two-step rearrangement of DMQA leading to the formation of a configurationally labile helicene, which underwent a series of regioselective S_NAr reactions. The acid-catalyzed rearrangement proved to be enantiospecific with a helical-to-central conversion of chirality and medium to good enantioretention, depending on the electronic character of the central adduct.



(M)-DMQA **(M)** **(S)**

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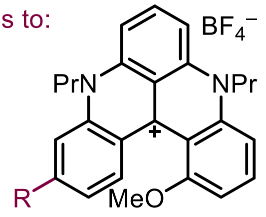

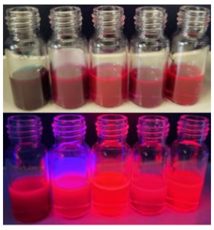

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COM-10

Ground and excited state aromaticity in azulene-based helicenes

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The introduction of the non-benzenoid like azulene units into nanographene and helicoidal structures has recently received particular attention due to the possibility to generate open-shell systems, which may lead to the realization of future spin filters, sensors, chiroptical switches or spintronic devices.[1] Recently, new modified azulene helical systems have been successfully synthesized.[2] At the same time, theoretical studies have shown how azulene-containing compounds can modulate the excited state properties.[3] However, the understanding of how the presence of five- and seven-membered rings influences the properties remains limited.

Our work aims to provide a comparative theoretical analysis of azulene-based [n]-helicene[1] ([n]-hel-azu, [n]-azu) compared to classical benzenoid helicene analogues ([n]-hel). After showing that the compounds we study can be synthesized, we focus on the analysis of the charge separation and dipolar moment induced by such modifications. We find that the incorporation of the azulene moiety introduces ionic and radical character into the wavefunction.

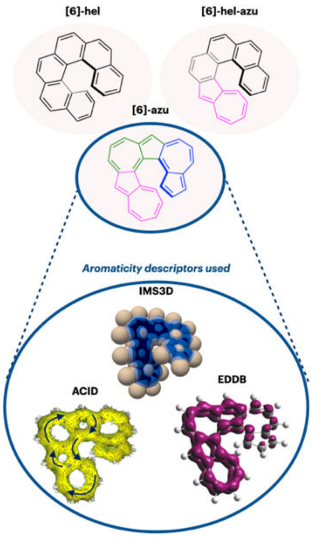

Figure 1. Example of azulene-based isoelectronic helicenes under study.

Subsequently, the aromaticity in terms of electrons delocalization is studied in the ground and first excited triplet state, using magnetically induced properties (3D Isotropic Magnetic Shielding (IMS3D) and Anisotropy of the Induced Current Density (AICD)) and electron decomposition method (Electron Density of Delocalized Bonds (EDDB)), Figure 1. For azulene-based helicenes larger than a critical size, that is more than six fused cycles, unexpected aromatic delocalization circuit appears. This feature is understood via the decomposition of the wavefunction into sets of carefully chosen local electronic structures.

We believe that this study will contribute to a deeper understanding of the electronic structure of modified helicenes and inspire further efforts to synthesize such compounds.[4]

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[1] n: total number of ortho-fused cycles in the helicenes, here for n =4,6,8.

COM-11

Green process for zinc oxide formation towards photocatalysis application

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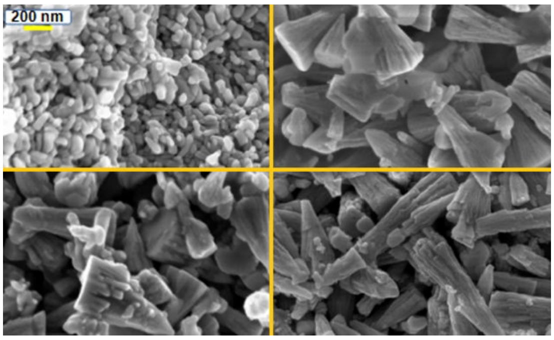
Zinc oxide is a semiconductor material with an interesting potential for photocatalysis of organic pollutants. It has been prepared according an eco-friendly green method, using five various plant extracts (banana, bitter orange, rosemary, olive tree and comfrey). Two different synthesis processes were tested: a hotplate synthesis and a hydrothermal method. Metal precursor used was zinc acetate. Plants present in the process allowed the formation and the self-assembling of ZnO during the crystal growth[1] thanks to the large chemical family of polyphenols which act as reductants.[2] Crystalline and organic matter-free compounds obtained after annealing were characterized with diffractive reflectance spectroscopy (DRS) to determine gap energies and confirm ZnO belonging to semiconductors, X-ray diffraction to verify the crystalline structure and its features, Fourier transform infrared spectroscopy (FTIR) to check the characteristic functional group and scanning electron microscopy (SEM) to reveal the self-assembling forms of ZnO.[3] Data about the shapes, dimensions and crystal planes of zinc oxide were regarded in the light of the plant and the synthesis method used.



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COM-12

Évaluation de la qualité de l'eau dans les rivières de Nouvelle-Calédonie et impact sur la santé humaine

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En Nouvelle-Calédonie, 1/3 du territoire est couvert par des formations géologiques ultramafiques (UM), naturellement enrichies en Ni, Cr, Mn et Co[1], tandis que les 2/3 restants par un substrat volcano-sédimentaire (VS). 61% des captages en eau potable proviennent des eaux de surface, vulnérables aux contaminations naturelles (lessivage des sols) et/ou anthropiques (pollutions minières, agricoles…). Cette étude vise à évaluer la qualité des eaux de rivière calédoniennes dans les deux types de substrat géologique, ce qui n'a jamais été réalisé dans le substrat VS. L'objectif est de mieux comprendre l'origine des contaminations et de déterminer les potentiels risques sanitaires. Plusieurs missions ont été réalisées entre 2021 et 2024, comprenant au total 191 échantillons dans des substrats UM et 97 dans des substrats VS. Les mesures in-situ des conditions physicochimiques ont révélé des eaux légèrement basiques ou neutres (pH_{UM} = 7.9 et pH_{VS} = 7.4), à une température oscillant entre 24 à 30°C, plutôt oxygénées (Eh_{UM} = 192 et Eh_{VS} = 182 mV), peu minéralisées ($\sigma < 150$ µS.cm^{-1}). Les compositions chimiques des eaux brutes et filtrées ont aussi été déterminées : les ions majeurs et les métaux. Les eaux sont de nature bi-carbonatée magnésique pour les substrats UM, tandis que la nature des eaux est variable en fonction des rivières pour les substrats VS. Les concentrations médianes de Cr et Ni sont plus élevées dans les substrats UM (17 et 15 µg.L^{-1}) que dans les substrats VS (5.2 et 1.7 µg.L^{-1}). Ces plus fortes concentrations de Cr et Ni dans l'eau sont supposées être liées aux concentrations importantes de Ni et Cr (dizaine de g.kg^{-1}) mesurés dans les sols, les sédiments ou les MES provenant des substrats UM. Les concentrations médianes de Fe et Mn sont plus élevées dans les eaux brutes des rivières drainant les substrats VS (295 et 21 µg.L^{-1}, respectivement) que dans celles des substrats UM (16 et 1.7 µg.L^{-1}) alors que les sols, les sédiments ou les MES provenant des substrats UM sont plus riches en Fe et Mn. Au vu des différences de pH et de potentiel redox, des transferts du solide vers eau de ces 2 éléments sont supposés être plus importants dans les eaux drainant les substrats VS.

Dans les deux substrats, les résultats montrent que le Fe et le Mn peuvent être présents sous forme particulaire dans l'eau (17-46%), tandis que le Ni et le Cr sont principalement sous forme dissoute (76-97%). Les espèces dissoutes sont plus biodisponibles et indique un risque sanitaire plus important pour Ni et Cr. Dans les substrats UM, les concentrations dissoutes de ces deux métaux dépassent souvent les limites françaises de qualité des eaux potables : soit 43% des échantillons pour le Ni (limite à 20 µg.L^{-1}), et 29% des échantillons pour le Cr (limite à 50 µg.L^{-1}). La spéciation du Cr a aussi révélé des concentrations en Cr(VI) au-delà de la limite (6 µg.L^{-1}) pour 87% des échantillons. Le niveau de risque sanitaire a donc été évalué grâce à deux indices : le quotient de danger (Hazard Quotient, HQ) et le risque de contracter cancer au cours de sa vie (Incremental Lifetime Cancer Risk, ILCR). Ils ont été calculés pour les adultes et les enfants, et en tenant compte de deux voies de contamination du Cr: le contact dermal et l'ingestion. Aucun risque sanitaire n'a été identifié dans les eaux drainant les substrats VS. Dans les substrats UM, les HQ sont supérieurs à 1 attestant ainsi d'un risque sanitaire pour les enfants ($HQ_{ingestion}$=3 ; HQ_{dermal}=2.3), et pour les adultes uniquement par ingestion ($HQ_{ingestion}$=2). Les ILCR sont de 10^{-3} pour les enfants et les adultes par ingestion, et de 10^{-5} par voie dermale pour les enfants. Ces valeurs soulignent donc un risque sanitaire important lié au Cr, et à des niveaux reconnus internationalement comme inacceptables.

COM-13

Enantioselective Synthesis of Benzopyrane Atropisomers

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Atropisomers are of utmost interest due to their prevalence in natural products,[1] but also for their biological relevance[2] and their numerous applications as chiral materials,[3] ligands[4] and organocatalysts.[5] Among them, biaryl and heterobiaryl atropisomers are the most common ones and many synthetic approaches are available.[6] Non-biaryl atropisomers constitutes another family of these axially chiral molecules with less synthetic approaches and consequently are less represented in the literature.[7] Within this family, the highly challenging enantioselective construction benzopyrane atropisomers still constitutes a daunting challenge of modern organic synthesis.[8] Enantioselective halogenation reaction is a useful reaction for the production of atropisomers in enantioenriched form, via a dynamic kinetic resolution (DKR) of substrates presenting low enantiomerization barriers.[9] Therefore, we propose to exploit this approach for the atroposelective synthesis of axially chiral benzopyranes. While non-catalyzed version of the reaction has allowed to produce several examples of chiral benzopyranes in racemic form, encouraging enantiomeric excesses have been obtained with the use of a chiral phosphoric acid derivative and further investigations are currently undergoing in our laboratory.

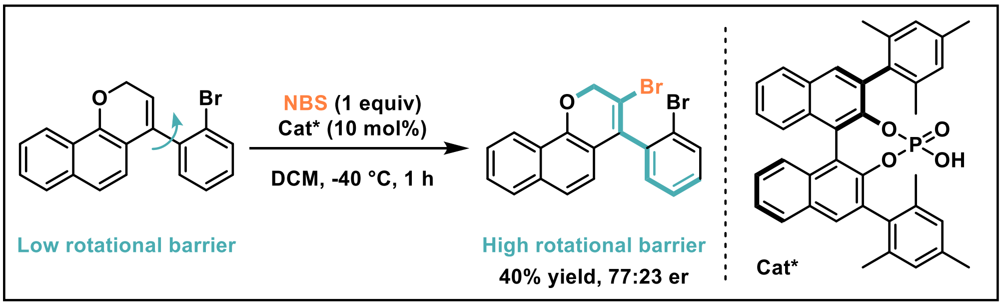

Figure 1: Bromination reaction scheme

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COM-14

Enhancing the activity and the safety of ruminal Antimicrobial peptides using chemical diversity

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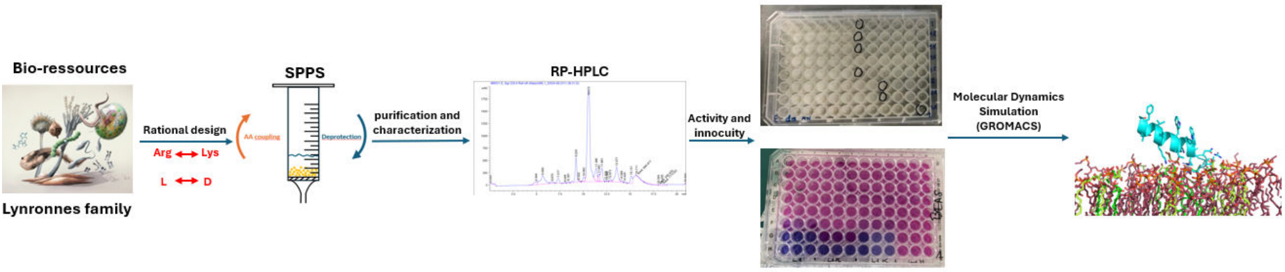
In the context of the threat of antimicrobial resistance, AMPs have proven to be good candidates. Among the many parameters that allow a peptide to be a good antimicrobial, two main ones are often cited in the literature, including the amphiphilic character and the cationic charge of these peptides, often positive charge allowing the targeting of bacterial cell membranes. In previous work, a family of antimicrobial peptides (Lynonne family) was identified and isolated via a metagenomic screening of a bacterial metagenomic library from the rumen. These peptides are good candidates both in terms of their antimicrobial activities and their low toxicity.[1]

The objective of our work is to modify the residues of this family of AMPs to further improve their antimicrobial activities while reducing their toxicity against human cells. For this and keeping in mind that the nature and number of cationic residues can impact the activity and/or toxicity, we designed, synthesized and purified Lynronne analogues containing the same number but different cationic residues. All-D analogues were also synthesized to study the impact of this class of amino acids. Currently, we are performing antimicrobial tests by the cascade dilution method (minimal inhibitory concentration (MIC) test) on ESKAPEE bacteria but also on yeasts and pathogenic fungi. Toxicity tests on human cells will also be performed to evaluate their therapeutic potential. Finally, the mechanism of action of these peptides will be evaluated via biophysical analysis but also by using molecular dynamics tools such as GROMACS to visualize the interaction of these peptides with membrane models.

The overall analysis of these results and the relationship with the primary amino acid sequence will allow a better understanding of the importance of the nature of the cationic residues or their D analogues on the AMPs of the Lynronne family.



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COM-15

Prix de thèse 2025 SCF-Sud-PACA/NUVISAN

New Reactivities of Aldehyde-Yne Compounds in Organometallic Catalysis

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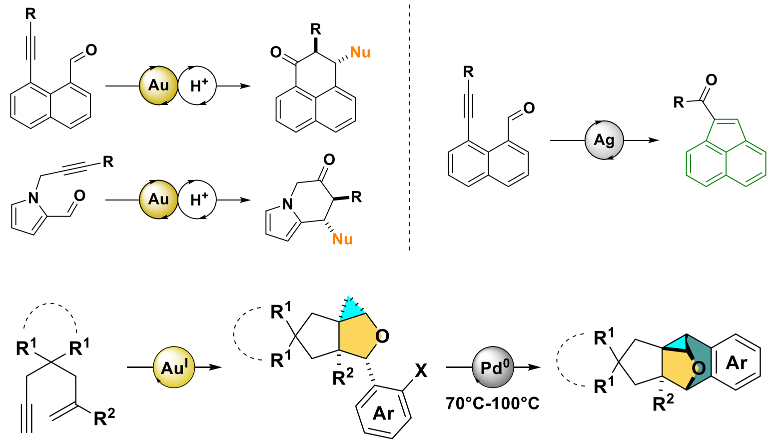
Over the past few decades, the use of aldehyde-yne compounds in intramolecular reactions has become increasingly prevalent.[1] As oxygenated analogs of enynes, these compounds have demonstrated significant interest through numerous methodologies and the synthesis of diverse frameworks. Moreover, these methodologies are highly valuable from an "efficiency and atom economy" perspective, enabling the formation of multiple C-C and C-O bonds in a single step.

This thesis work focuses on the design and development of reactions involving these compounds and organometallic complexes.[2] In the presence of gold and silver catalysts, aldehyde-yne compounds were engaged in an orthogonal tandem cyclization/nucleophilic addition/C-O rearrangement reaction. The hydrogen bond donor properties of HFIP were studied to highlight a combination between a gold complex and this solvent.[3] Also, a study on the reactivity of aldehyde-yne compounds with a naphthalene framework under silver catalysis is presented, aiming at the synthesis of fluoranthene-type derivatives of interest. Finally, a C-H activation reaction of cyclopropane was carried out using palladium catalysis, leading to the formation of novel polycyclic compounds.



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COMMUNICATIONS PAR AFFICHE

P-1

Gold(I)-Catalyzed Enantioselective Cycloisomerization of 1,6-Oxygenated Enynes

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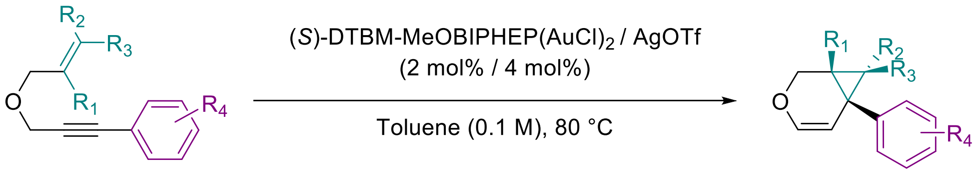
For several years, our group has focused on gold-catalyzed reactions[1-3] and more specifically on the gold-catalyzed cycloisomerization of 1,6-enynes in racemic conditions.[4] A novel synthetic methodology concerning the gold-catalyzed enantioselective cycloisomerization has been developed starting from readily available 1,6-oxygenated enynes precursors. The optimization of the reaction conditions allowed, in the presence of the chiral cationic Au(I) catalyst (*S*)-DTBM-MeOBIPHEP-$(AuCl)_2$ associated with AgOTf as co-catalyst, an efficient access to functionalized bicyclic adducts. Although this reaction has been studied by various groups, none has succeeded in obtaining excellent yields and excellent enantiomeric excesses for light molecules.[5,6] This efficient synthesis led to new volatile 3-oxabicyclo-[4.1.0]-hept-4-enes in excellent enantiomeric excesses ranging from 87–99 %. In addition to the olfactory applications of these compounds, whose odor depends on the major enantiomer, post-functionalizations have been carried out to further enhance their value.



Stereoselective and efficient cycloisomerization

Post-functionalization **Robust** **Olfactive compunds**

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P-2

Hits study and optimization for the targeting of MALAT1 long non-coding RNAs

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Long non-coding RNAs (lncRNAs) constitute the largest class of non-coding transcripts in the human genome and have been shown to play important functional roles in development and disease processes. Several of these large, diverse transcripts, which are greater than 200 nucleotides in length, have been proposed as therapeutic targets since they play a crucial role in various aspects of cancer progression such as the regulation of the expression of oncogenes. As these transcripts contain structured RNA elements, the approaches based on the use of small-molecule RNA ligands to probe the specific functions and interactions of these domains thus represents an exciting avenue toward the discovery of promising drug candidates as well as chemical biology tools for a better understanding of lncRNA biology.

In this work, we focused on the targeting of MALAT1 lncRNA (Figure 1A) since it is involved in the progression and metastasis of various cancers.[1] The role of this lncRNA is not completely elucidated yet and chemical probes are needed to allow for a detailed analysis of MALAT1 biological function. After the screening of 9,000 compounds and the identification of two hits bearing low micromolar affinity for MALAT1 and the ability to inhibit triple-helix formation characteristic of this lncRNA (Figure 1B). We developed the medicinal chemistry optimization of the hits in view of the description of structure activity relationships and the improvement of the biological activity. A small series of analogs has been synthesized and the biological assays, syntheses, docking are currently in progress.

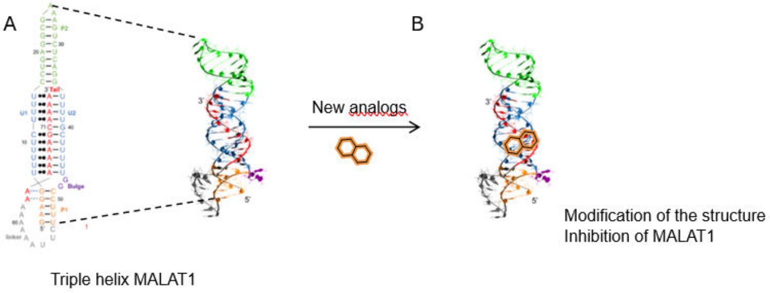

Figure 1 : A) Representation of triple-helix MALAT1. B) Potential inhibition of MALAT1 by small molecules.

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P-3

A Remarkable Catalyst-Free Photochemical Alkene Hydrophosphination with Bis(trimethylsilyl)phosphonite

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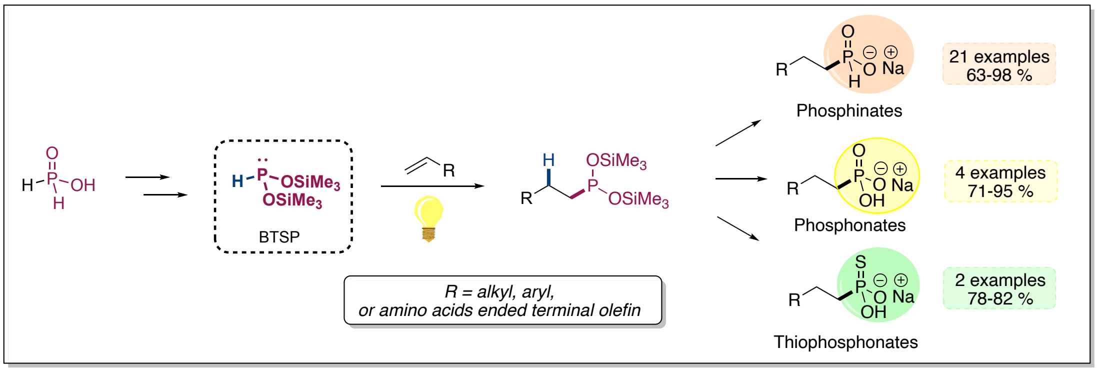
Organophosphorus compounds are well known for their various applications in chemistry, agriculture and biomedical science.[1,2]

However, only limited examples have been reported for a direct access to this class of compounds. Herein we reported an unprecedented route to phosphinates via hydrophosphination of alkenes, using silylated phosphonites as starting materials, generated *in situ*, under mild conditions and without photocatalyst. An unexpected and gratifying outcome emerged as our methodology demonstrated successful application to aromatic derivatives circumventing therefore the literature limitations.[3]

The regioselectivity as well as post-synthetic functionalization have also been studied, giving access to diversely functionalized organophosphorus class of compounds such as phosphonates and thiophosphonates known for their biomedical applications (Scheme 1).[4]

This methodology also has enabled the preparation of biologically relevant unnatural organophosphorus amino acids.



Scheme 1: Hydrophosphination, driven by irradiation, involving activated, inactivated, and amino acid-derived olefins

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P-4

New N3O quinoidal ligands for the selective formation of trinuclear complexes

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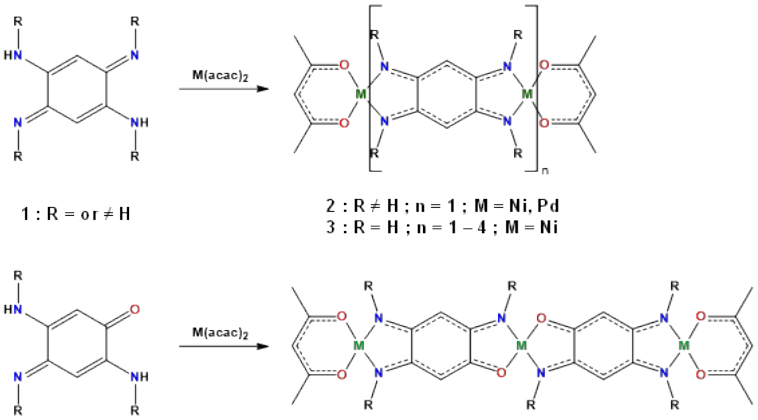
Tremendous interest was given to quinoidal molecules over the past decades thanks to their outstanding fundamental properties, as well as diverse applications in various fields. Among these, 2,5-diamino-1,4-benzoquinonediimines (QDIs) 1 are particularly interesting due to their unusual 12-π electron system distribution that can be considered as two nearly independent 6- π electrons sub-units, chemically linked by two C-C bonds, leading to remarkable optical properties.[1]

Extensive studies on QDIs enlightened their great versatility as ligands towards coordination species with a wide range of metals (M = Fe, Co, Ni, Cu, Zn, Ru, Pd, W, Re, Ir, Pt, Na, Li, B, Sn), exhibiting great technological value.[2] Steric hindrance of tetra-substituted QDIs lead to mono- or dinuclear coumpounds 2 while unsubstituted QDIs give rise to polynuclear species 3 with NIR absorption. However unsubstituted QDIs complexes experience dynamic exchange in solution towards longer insoluble oligomers.[3] Here, we show that substituting one nitrogen heteroatom by an oxygen 4 allow selective formation of unprecedented soluble trinuclear complexes 5 with promising physical properties.



1 : R = or ≠ H

2 : R ≠ H ; n = 1 ; M = Ni, Pd
3 : R = H ; n = 1 – 4 ; M = Ni

4 : R ≠ H

5 : R ≠ H ; M = Ni, Pd

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P-5

Synthesis of bio-based polymers from terpene epoxy derivatives

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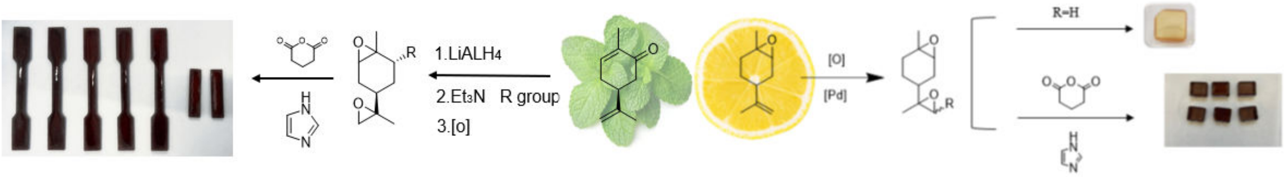
Worldwide demand for cleaner burning fuels and ‘clean or green’ chemicals has been increasing from the global issues of environmental concern and as fossil resources stocks will decrease in the next few decades.[1] Recent studies showed the use of monoterpenes as a versatile class of compounds, offering more than 1500 renewable molecules with potential biological and chemical use.[2] Some of these cyclic monoterpenes have great potential to be used as monomers and therefore to generate thermoplastic or thermosetting polymers.

Our laboratory has successfully converted limonene dioxide into thermosetting polymers.[3,4] In the presence of different anhydride allowing the challenging access to 100% bio-based polymer.[5,6] Considering the properties of such polymers, we envisaged to prepare some functionalized and reticulated ones. Therefore, we designed another method to obtain novel limonene derivatives (with a yield of up to 82%) through palladium-catalyzed synthesis.[7] At the same time, we also synthesized carvone derivatives,[8] and through oxidation and polymerization, we developed new polymer materials to meet the future demand for sustainable materials.[9]



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P-6

Atropisomeric Gold-NHC complexes for 1,6-enynes cycloisomerization

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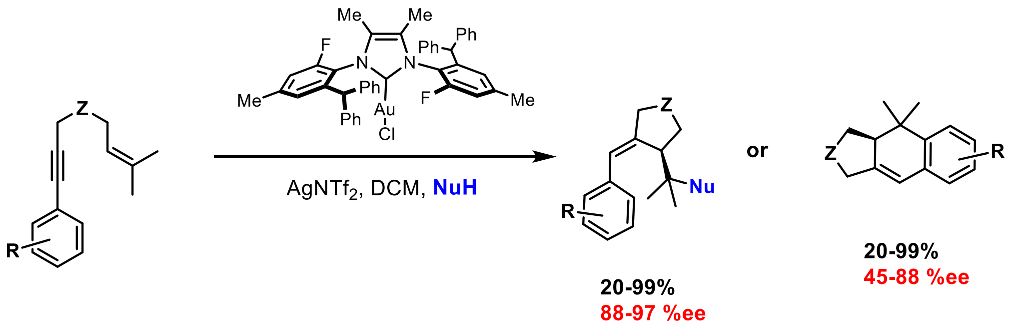
Gold(I) complexes are the most effective catalysts for the activation of multiple π-bonds in homogenic conditions.[1] One of the most common examples of gold-catalysed transformations is 1,6-enynes cycloisomerization. The gold(I)[2] complex, bearing phosphine or NHC ligand[2,3], selectively activate bonds, adopting the linear geometry.[4] Due to that, the high enantioselectivities in the asymmetric transformation are still challenging and just several good to excellent results were reported with phosphine and NHC ligands.[5]

Recently, the new design of chiral NHCs was developed in our team, which is based on restricted rotations along the N-aryl substituents.[6] The general concept was applied to the synthesis of gold complexes and the excellent chiral inductions (up to 97%) were obtained in 1,6-enynes cycloisomerization. The large scope and obtained results are going to be presented.



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P-7

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

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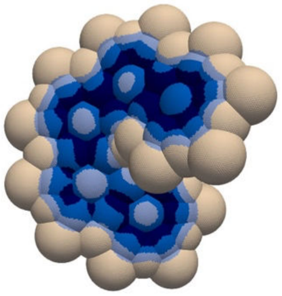
Meaningful interactive 3D contour maps of isotropic magnetic shielding (IMS, the negative of isotropic NICS) can be plotted around molecules using pseudo-van der Waals surfaces generated by overlapping spheres made of ghost atoms. 3D IMS maps are reminiscent of the Clar π-sextet model of aromaticity and provide an intuitive, yet detailed and quantitative evaluation of the aromatic, non-aromatic, and antiaromatic character in (highly) contorted polycyclic aromatic hydrocarbons (PAHs).[1] 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.



3D IMS maps

- ✓ ***3D interactive maps of electron delocalization***
- ✓ ***Suitable for contorted PAHs***
- ✓ ***Intuitive, detailed & quantitative***
- ✓ ***User friendly & open-source***

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P-8

2nd Generation Synthesis of a Selective Antagonist for *in-vivo* Assessment of The Melanin Concentrating Hormone System

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The Melanin-Concentrating Hormone system (MCH) is a regulator of energy balance in mammals[1,2] of the two receptor subtypes, the role of MCHR2 is poorly understood.

Following our interest in the synthesis of heterocycles and bioactive molecules,[3,4] we envisaged the synthesis of an identified MCHR2 antagonist[5] according to scalable and green chemistry principles. Installation of the key functional groups was envisaged via abundant transition-metal catalysis as well as the application of an efficient chiral resolution for isolation of an enantiomerically pure product. This compound and its derivatives can be used to help reduce the existing knowledge-gap in the understanding of the role of MCHR2 via in-vivo studies using an hMCHR2 mouse model developed by Nahon's team.

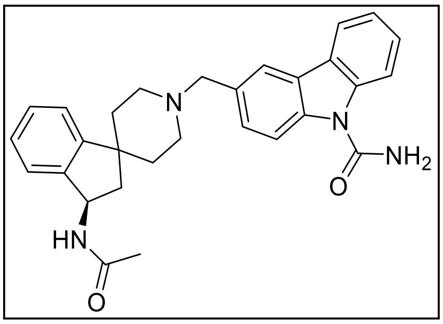

Figure 2: Selective MCHR2 Antagonist

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P-9

Influence des matières en suspension et des conditions environnementales sur la qualité de l'eau des rivières en Nouvelle-Calédonie

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En Nouvelle-Calédonie, 61 % des eaux de surface sont utilisées pour l'approvisionnement en eau potable, et 24 % des ressources en eau proviennent de formations géologiques ultramafiques. Dans ces massifs, l'altération naturelle et les activités anthropiques (exploitation minière, incendies et espèces invasives) intensifient l'érosion des sols et favorisent la production de matières en suspension (MES) riches en éléments potentiellement toxiques (EPT tels que Ni, Co, Cr) dans les rivières locales[1]. Cette étude examine la qualité de l'eau des rivières en aval des massifs ultramafiques, en mettant particulièrement l'accent sur le rôle des particules fines et des conditions environnementales sur la qualité de l'eau. Les fractions fines (< 100 µm) des sols issus des mines et des sédiments fluviaux ont été étudiées, car elles sont considérées comme représentatives des MES. La minéralogie et la composition chimique de ces échantillons ont été déterminées par DRX, ICP-AES et ICP-MS. La rétention des EPT au sein de ces particules fines a été estimée par des extractions séquentielles. Les sols et les sédiments sont principalement composés de serpentines, de quartz et d'oxydes/hydroxydes de Fe ou Mn. Ils contiennent des concentrations significatives de Fe, Mn, Ni, Co et Cr (quelques $g.kg^{-1}$), dépassant les seuils de qualité pour le Ni, Co et Cr établis en Europe et en Amérique du Nord. Cette étude révèle que des transferts potentiels d'EPT des particules vers la phase dissoute de l'eau peuvent se produire lors de modifications des conditions environnementales. Le Mn et le Co peuvent être transférés des MES vers la phase dissoute sous des conditions acides et réductrices (environ 37 % dans les sédiments, 60 % dans les sols). Ce processus est suggéré être associé à la dissolution des oxydes/hydroxydes de Fe et Mn. Le Fe, l'As, le Cr, le Ni, le Mn et le Co sont fortement retenus dans les phases solides, probablement dans des minéraux riches en Si tels que la serpentine et le quartz. Bien que la majorité des EPT restent fixés à la phase solide, les mécanismes de transfert ne sont pas négligeables en raison des concentrations totales élevées ($g.kg^{-1}$). Ces transferts peuvent conduire à des niveaux de Ni et Cr dans l'eau approchant les normes pour l'eau potable, voire dépassant la nouvelle norme pour le Cr (25 $\mu g.L^{-1}$ d'ici 2025). Cette étude souligne l'importance des MES dans l'évaluation de la qualité de l'eau.

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P-10

Domino Narasaka–Heck/C–H Activation and Amination: A Palladium-Catalyzed Approach to Spirocyclic Heterocycles

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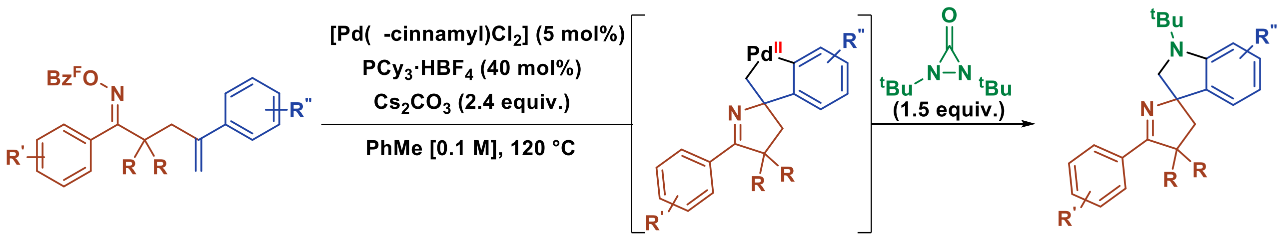
Heterocyclic spirocycles are key structural motifs in medicinal chemistry due to their rigidity and three-dimensional arrangement, which can enhance molecular interactions with biological targets.[1,2] Moreover, palladium-catalyzed domino reactions have long been recognized as a powerful strategy for streamlining the synthesis of complex molecular architectures.[3,4] We have developed a novel palladium-catalyzed strategy to access bis-heterocyclic spirocycles incorporating both pyrroline and indoline units.[5] This approach relies on a cascade reaction combining Narasaka–Heck coupling, C–H activation, and amination, using di-*tert*-butyldiaziridinone as a functionalizing reagent.

Optimization of the reaction conditions led to good yields with broad tolerance to aromatic substituents. The reaction is scalable to the millimole scale, and the resulting spirocycles exhibit strong potential for further modifications, including deprotection, reduction, and (3 + 2) cycloadditions. Mechanistic investigations, particularly kinetic isotope effect experiments, indicate that the C–H activation step is turnover-limiting in the catalytic cycle. This work highlights the efficiency of palladium-catalyzed domino reactions for the rapid construction of complex spirocyclic frameworks and opens new avenues for the design of bioactive molecules.



Novel Bis-Heterocyclic Spirocycles **3 C-N Bonds Formed** **Scalable** **Synthetically-Useful Products**

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P-11

Exploring New Chemical Space in Drug Libraries: A Divergent Synthesis of Hetero-Polycyclic Derivatives via Transition Metal Catalysis

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Drug Discovery is a complex and multi-faceted process which is confronted to several challenges, including increasing complex biological targets and antibiotic resistance, but also environmental concerns.[1] To respond to these issues, it is essential to push the boundaries of 'druggability', by enhancing the diversity of the molecular libraries. A crucial and challenging step in this direction is to increase the three-dimensional character of chemical structures.[2] However, synthesizing such original building blocks using an efficient and sustainable methodology remains a key challenge for an organic chemist. In this context, we focused on the development of a divergent and sustainable methodology based on transition metal catalysis, for the preparation of functionalized hexa-heterocyclic derivatives.[3] Starting from simple substrates, 1,6-enynes bearing an *ortho*-nitrophenyl moiety on the alkyne, we developed a cascade cycloisomerization/[3+2] cycloaddition leading to two different hexacyclic compounds with a pseudoindoxyl or benzoxazinone cores.[4] We succeeded to design selective and mild conditions for each of them, using respectively gold or silver complexes. These building blocks contain key units commonly found in various biologically active natural products,[5] making them privileged scaffolds in a search for increased molecular diversity for drug-candidate libraries.

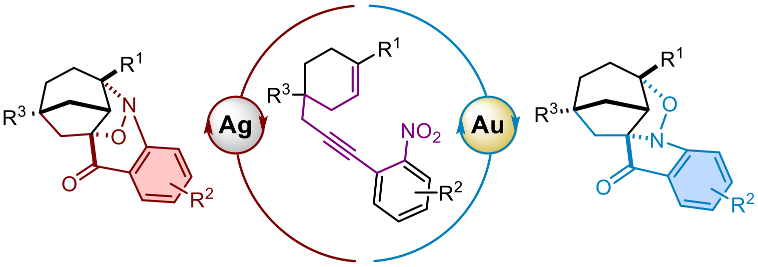

Figure 1: Divergent Synthesis of hexa-heterocyclic derivatives.

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P-12

Inhibition of the drug efflux activity of Ptch1 to overcome chemotherapy resistance

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Despite scientific advances, cancer remains one of the leading causes of death in developed countries and the search for new treatments a real challenge. In this context, chemotherapy resistance is one of the major obstacles in cancer treatment and is responsible for 90% of cancer deaths. Among the various mechanisms involved in chemotherapy resistance of cancer cells, the most prominent one is the overexpression of drug efflux pumps that decrease the drug concentration into cancer cells resulting in the ineffectiveness of treatment.

Our team identified the Hedgehog receptor Patched as a new and innovative drug efflux pump that participates in the resistance of cancer cells to chemotherapy.[1] Thanks to a screening program, Panicein A hydroquinone (PAH)[2], a natural compound purified from a marine sponge, was identified as an inhibitor of drug efflux activity of Patched. The synthesis of PAH allowed us to confirm that PAH increases the cytotoxic effect of several chemotherapeutic agents on melanoma cell lines in vitro and in vivo.[3] Recently, new original structures derived from our initial hit PAH have been identified to improve the efficacy and physicochemical properties of the molecule.

In this work, we focused on two complementary parts. On one hand, the synthesis of two chemical probes to get further comprehension of the mechanism of action via a fluorescent labeling, and the identification of the PAH binding site with photolabeling. On the other hand, the design of a new generation of analog and the realization of biological assay on them, such as IC50 in addition with chemotherapy on melanoma, breast cancer cell lines, and metabolic stability assay.

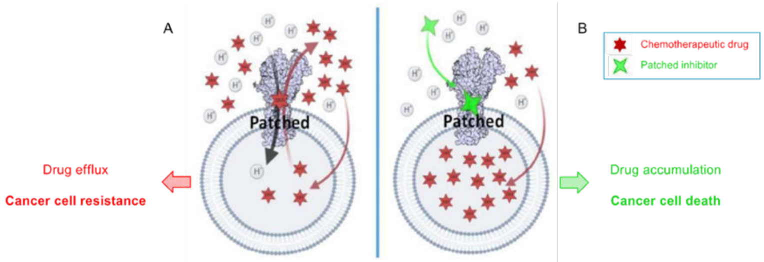

Fig 1 : Representation of (A) the drug efflux activity of Patched, (B) the potential inhibition of Patched by small molecules

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P-13

Synthesis of Ti(IV) complexes with $N_2O_2Cl_2$ coordination spheres towards combined coordination and radical polymerizations

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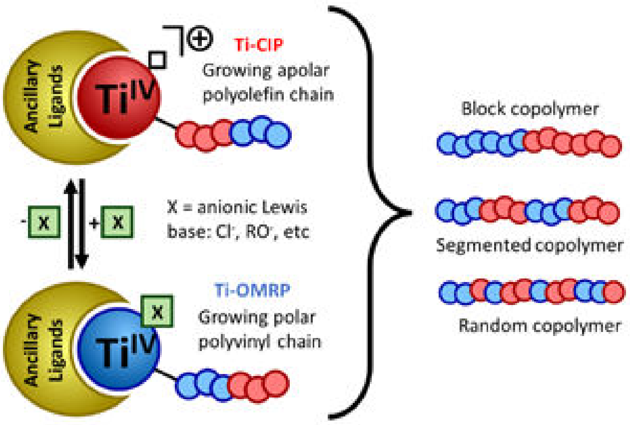
This work aims to perform the living copolymerization of olefins (ethylene and 1-alkenes) and vinyl polar monomers (VPM, e.g., acrylates or vinyl esters), leading to original, well-defined, linear copolymer structures.

Titanium complexes are active in both organometallic-mediated radical polymerization (OMRP, efficient at polymerizing VPM[1]) and coordination-insertion polymerization (CIP, efficient at polymerizing olefins[2]). Neutral titanium(III) complexes, active in radical reactions[3], initiate radical polymerization and are efficient radical trappers to control RP pathway[4]. On the other hand, cationic titanium(IV) complexes catalyze living CIP of 1-alkenes[5].

Finding a mechanism to switch between these neutral and cationic forms of titanium would lead to combine CIP-OMRP. As a first step towards this challenge, a computational (density functional theory) approach was used to predict the reactivity of the titanium complexes as RP controlling agents of various monomers, in particular to estimate the bond dissociation energy of Ti(IV) organometallic dormant species: $\text{Ti(III)} + R^{\bullet} \rightleftharpoons \text{Ti(IV)-R}$.

Then we evaluated the experimental performances of the most promising Ti complexes in polymerization processes.



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P-14

Évolution chimique et optique des aérosols de TITAN sous rayonnements énergétiques

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Titan, le plus grand satellite de Saturne, est le seul satellite du système solaire à posséder une atmosphère dense (1,5 bar) principalement composée de diazote et de quelques pourcents de méthane. Soumise à diverses sources d'irradiation, cette atmosphère constitue un milieu très réactif évoluant par croissance moléculaire et par production permanente d'aérosols. Parmi les molécules formées, les hydrocarbures (C_6H_6, C_4H_2, ...) et les nitriles (C_2H_3CN, HCN, ...) sont connus pour se condenser dans la basse stratosphère (Figure 1) et conduire à la formation de particules glacées et/ou de nuages. De précédentes études ont permis de proposer plusieurs molécules pour prétendre expliquer l'origine de nuages observés au niveau des pôles par comparaison avec les expériences réalisées en laboratoire.[1]

Durant leur séjour au niveau de la basse atmosphère (stratosphère et troposphère), ces particules ou nuages sont alors soumis aux photons UV solaires de longueur d'onde supérieure à 230 nm, à des électrons provenant de la magnétosphère de Saturne et vraisemblablement aux ions énergétiques GCR[2], et peuvent ainsi évoluer chimiquement. Le nuage HASP (High Altitude South Polar) observé par la mission Cassini-Huygens résulterait de la condensation simultanée du benzène (C_6H_6), du cyanure d'hydrogène (HCN) et de l'acrylonitrile (C_2H_3CN). Afin de mieux comprendre ces observations, la condensation et la photochimie de ces molécules, isolées, puis condensées simultanément et ce à différents ratios[3-5] a été préalablement réalisée en se focalisant sur l'impact des photons UV. Aujourd'hui, l'objectif est d'observer l'impact des électrons en le comparant à celui des photons UV et l'étude s'est pour l'instant centrée sur la glace pure de benzène (C_6H_6). Le dispositif expérimental (laboratoire PIIM) permet de suivre l'évolution de la phase solide par IR-TF lorsque ces glaces sont soumises aux photons UV de longueur d'onde supérieure à 230 nm ou à des bombardements électroniques. Ces résultats seront d'utilité dans l'interprétation des données de la mission spatiale Cassini-Huygens et de la future mission Dragonfly.

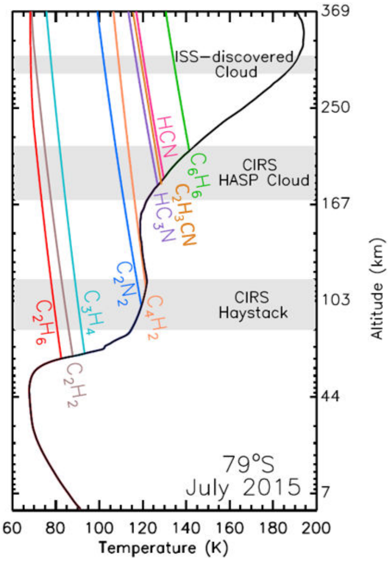

Figure 1 : Profil de condensation de différents composés organiques obtenu à partir d'un modèle de transfert radiatif et des mesures réalisées à 79°S, latitude de détection du nuage HASP par la mission Cassini-Huygens en juillet 2015, adapté d'Anderson et al.[1].

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P-15

Marquage fluorescent de nanoplastiques de polyamide 6-6 pour une détection environnementale

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La pollution au plastique est une problématique environnementale majeure à laquelle tous les compartiments écologiques sont soumis comme les océans où un dixième du plastique mondial y est présent avec une quantité non négligeable de matériels de pêche tels que les filets composés en général de nylon (polyamide 6-6). Les phénomènes biotiques et abiotiques auxquels ces plastiques sont soumis, sont à l'origine de leur dégradation et fragmentation, donnant lieu à la formation de micro et nanoplastiques. Les études sur l'effet des nanoplastiques sont difficiles à réaliser car ils sont difficilement quantifiables en routine à l'aide des techniques analytiques actuelles. Un nouveau protocole de synthèse de nanoplastiques fluorescents est testé sur le polyamide 6-6.[1] Ce protocole permet d'incorporer le fluorophore choisi (rhodamine 6G et fluorescéine) directement dans le plastique lors de la production des nanoparticules. S'en suit une filtration membranaire permettant d'éliminer les fluorophores dissous, non fixés. L'objectif de cette étude est de pouvoir identifier spécifiquement les plastiques dans un échantillon prélevé sur le terrain mais aussi de pouvoir étudier leur toxicité en rendant visible les nanoplastiques dans les organismes. Des mesures de fluorescence moléculaire ont été réalisées à l'issue de la synthèse afin de s'assurer que le polyamide avait bien été marqué (Figure 1). Une analyse granulométrique au Nano Tracking Analysis a quant à elle permis de déterminer la répartition en taille des particules présentes dans les suspensions et leur concentration. Enfin, l'impact du nanoplastique fluorescent a ensuite été observé sur des rotifères marins. Les tests écotoxicologiques réalisés ont permis de déterminer le taux de mortalité chez ces organismes après 24h d'exposition puis après 48h. Il s'agissait également de s'assurer que le fluorophore fixé sur le polyamide n'induisait pas de mortalité supplémentaire par rapport au nanoplastique non marqué.

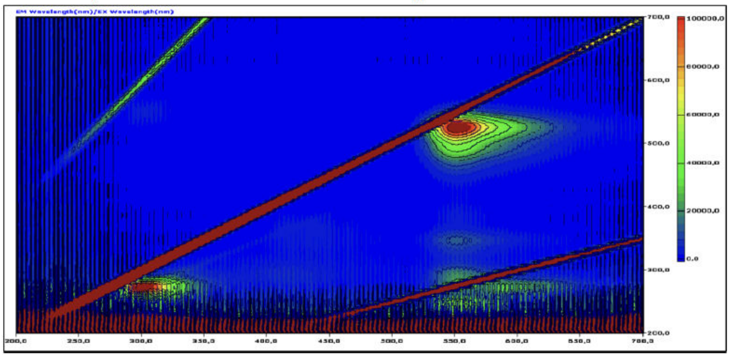

Fig.1. Spectre de fluorescence 3D du polyamide nanoparticulaire marqué à la Rhodamine

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P-16

From Coupling Principle to π-d Conjugation: Investigating Diamino- Benzoquinonediimine Ligands

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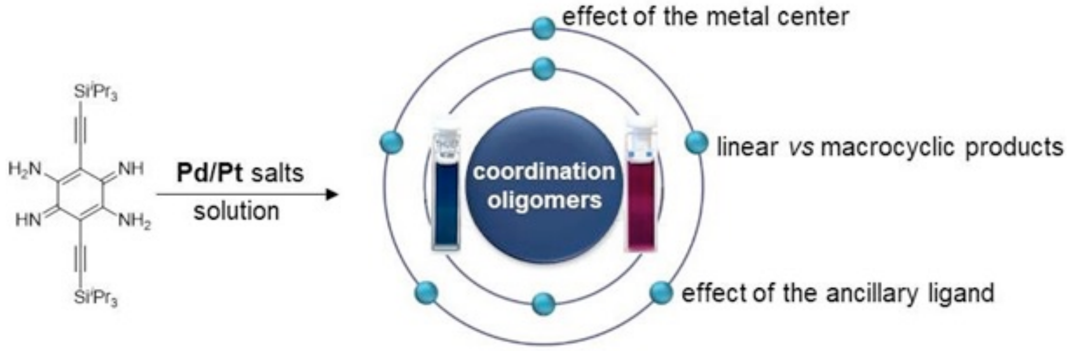
The development of near-infrared (NIR) dyes is at the heart of many of today's scientific challenges, given their high potential for applications in optoelectronics and biophotonics.[1-2] As part of the toolbox, coordination chemistry starts to gain territory due to innovative and unexplored potential, allowing to benefit from non-innocent ligands to build planar and extended architectures.[3-4] In this context, 2,5-diamino-1,4-benzoquinonediimine (BQDI) stands as versatile ditopic, bis-bidentate ligand for the preparation of coordination complexes with catalytic, optical or magnetic properties.[5]

The study of the BQDI alone brings to light curious results related to the chemistry of polymethine dyes,[6] while its metalation allows the isolation of stable mono-, di- or polynuclear oligomers with absorption up to the NIR region due to the extension of the π-d conjugation.[5-8] The N-substitution of BQDI plays an important role on the coordination properties of this building block but can notably be detrimental (steric effect) for the electronic delocalization between the metal centers.[3-7] Consequently, our present investigations takes the process one step further, by introducing C-substituents on the ligand and delving into the complexation mechanism and the optical properties of unprecedented palladium and platinum coordination oligomers.



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P-17

Development of new methodologies in the presence of gold(III) complexes

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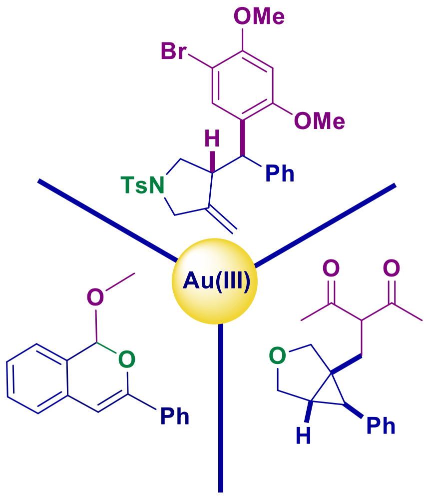
Developments in transition-metal catalysis, notably with gold, have dramatically transformed organic synthesis, pushing the limits of gold complex applications from apparent inertness to catalytically active roles.[1] Gold(I) and gold(III) complexes are characterized by their ability to facilitate a huge range of chemical transformations. Gold(I) complexes, renowned for their ability to activate π-C-C bonds, have played a key role in the development of gold catalysis. Despite extensive exploration of gold(I), the potential of gold(III) complexes has remained relatively untapped due to the challenges associated with obtaining stable, controllable reactivity. In 2015, Toste's group introduced a new method for stabilizing gold(III) complexes using biphenylene, leading to the development of a new gold(III) catalyst.[2] However, this catalyst has seen only limited application since its inception. Taking advantage of these developments and following our recent work on novel gold(I) complexes, we envisaged to use gold(III) complexes in domino cyclization of 1,6-enynes and aldehyde-yne reaction.[3,4] This approach has enabled the synthesis of complex cyclic molecules with high efficiency and precision. In this communication, we will present our preliminary results on gold(III) catalyzed transformations as well as scope and limitations of theses reactions.



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P-18

Exploring the Presence of Sugar in the Orgueil Meteorite

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The origin of life on Earth is intrinsically linked to the availability of essential biomolecules like amino acids and sugars. Understanding the abiotic processes that led to their formation will help constrain the emergence of life by clarifying which biomolecules were present and the environmental conditions in which life arose. In living organisms, sugars and amino acids exhibit homochirality, with D–sugars in DNA/RNA and L–amino acids in proteins. A leading hypothesis suggests that meteorite-delivered compounds not only supplied essential precursors for life but also directed the selection of biological handedness, supported by the detection of amino acids in carbonaceous chondrites enriched in the biological L–form.[1]

Experimental studies on interstellar[2] and Solar System ice analogs[3] have shown that sugars, like amino acids, can form in extraterrestrial environments. Recent analyses of the Murchison meteorite further confirm this hypothesis.[4] However, the enantiomeric composition of sugars in astrophysical samples remains largely unexplored due to significant analytical challenges. Abiotic synthesis of sugars is expected to produce a racemic mixture or slight enantioenrichment, so identifying either a racemic composition or slight enantiomeric excess would provide strong evidence of their extraterrestrial origin.

The most relevant objects for studying the extraterrestrial origin of sugars are asteroids, particularly the pristine samples from Ryugu and Bennu, returned by the Hayabusa2 and OSIRIS-REx missions. Unlike meteorites, which are prone to terrestrial contamination, the Ryugu and Bennu samples were carefully collected and preserved, making them invaluable for investigating extraterrestrial sugars. However, the availability of these samples is limited. To address this, the Orgueil meteorite, a CI chondrite with mineralogical and chemical similarities to Ryugu and Bennu[5], serves as a suitable analogue for preliminary studies on extraterrestrial sugars.

Our methodology combines ultrasonic extraction with high-sensitivity enantioseparation using two-dimensional gas chromatography coupled with time-of-flight mass spectrometry[6] to investigate sugar chirality in Orgueil. This approach allowed us to identify several sugars, including ribose, a key RNA component, and lyxose, a biologically rare sugar, both in near racemic form, supporting an extraterrestrial origin. Spiking experiments on the same meteorite matrix highlight challenges in extracting sugars, indicating that the mineral matrix significantly limits extraction efficiency. These results not only improve our understanding of extraction constraints but also emphasize the need for advanced techniques to study pristine asteroid samples, offering deeper insights into the emergence of life's building blocks.

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P-19

Towards Highly Selective Cu-doped Carbon Quantum Dots Catalysts for Electrochemical CO_2 Conversion to Formate and Acetate Ions

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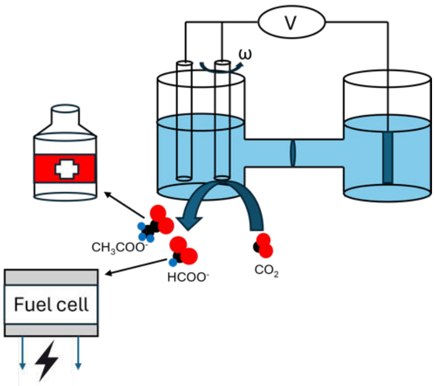
The gradual increase of CO_2 emission amplifies the rate of global warming. Meanwhile, the value of CO_2 can be enhanced by transforming it to more useful products. One of the promising ways is through electrochemical CO_2 reduction reaction (eCO2RR). In this research, copper-doped carbon quantum dots (CQDs) were used to catalyze the eCO2RR. Two precursors of CQDs were used in this study: citric acid (CA) and glucosamine hydrochloride (GAH). In order to see the effect of the heteroatom doping, three different types of Cu-doped CQDs were synthesized with nitrogen or with nitrogen and sulfur: Cu,S,N-CQDs – CA, Cu,S,N-CQDs – GAH and Cu,N-CQDs – GAH. The eCO2RR was carried out in a conventional H-cell and with a rotating disk electrode (RDE). We focused on quantifying the products in solution using high performance liquid chromatography (HPLC) and hydrogen nuclear magnetic resonance (^{1}H-NMR).



An anion exchange polymer, poly(2,6-dimethyl-1,4-phenylene oxide) quarternized with trimethylamine grafted on long (pentyl) side chains PPO-LC) was used to facilitate the mass transport of OH^- ions during the eCO2RR. PPO-LC was used as an ionomer for the oxygen reduction reaction in previous research of our group.[1-2] After applying linear sweep voltammetry (LSV) for these three electrocatalysts, Cu,S,N-CQDs – CA showed the best electrocatalytic performance. Moreover, the product analysis with HPLC and H-NMR revealed that Cu,S,N-CQDs – GAH gave the highest Faradaic Efficiency (FE) of 31% for formate ions at 0 V/RHE whereas Cu,S,N-CQDs – CA showed the highest FE of 87% for acetate ions at -0.2 V/RHE. The further development of this study will use a flow cell which can mitigate the diffusion problem. The future study will also focus on gaseous products besides the products in solution.

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P-20

Straightforward synthesis of α-alkoxyphosphonates diesters and their corresponding dealkylated analogs

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Phosphonates are widely used in both organic and medicinal chemistry. Their versatile physicochemical properties and their ability to mimic key biomolecules and transition states have drawn significant interest from medicinal chemists. Additionally, phosphonate provide better stability to drugs compared to phosphate moieties, thanks to the chemical and enzymatic stability of the P-C bond. However, phosphonic acids usually suffer from pharmacokinetic drawbacks and display poor bioavailability due to their negative charges at physiological pH.[1] For this reason, phosphonate diesters are a good compromise to improve drugs bioavailability. They can be used as prodrugs, as several diester derivatives enhance cell membrane permeability and can readily release the active phosphonic acid form in cellular media.[2] In the case of phosphonate alkyldiesters, the diester form has been shown to be stable in mammalian systems, highlighting their potential in the synthesis of more stable and lipophilic analogues of phosphonic acids.[2]

In this context, we have focused on the synthesis of α-alkoxyphosphonates, where we identified a lack of general and catalytic methods for their synthesis. Indeed, the reaction conditions described in the literature often required stoichiometric or even excess amounts of catalyst.[3,4] In this study, we describe a fast and versatile approach for the synthesis of α-alkoxyphosphonates from acetals and ketals, using a catalytic amount of a Lewis acid (Figure 1).

Figure 1: Synthesis of α-alkoxyphosphonates from phosphites and acetals or ketals

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P-21

Synthesis and Oxidative Behavior of Gold(I) Catalysts

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While the majority of gold-catalyzed reactions highlight the carbophilic Lewis acid character of gold(I),[1-4] several studies have shown over the last twenty years the feasibility of Au(I)/Au(III) catalytic systems through the use of external oxidants.[5] This development opens up new prospects in the field of gold-based catalysis. Simultaneously, electrosynthesis is experiencing a major upsurge in interest among the scientific community: the direct use of electricity offers an economical, sustainable and safer alternative to conventional oxidizing/reducing agents.[6] These methods are two powerful synthetic tools, both of which are undergoing a revival, and their combination could lead to new methodologies and new reactivities.[7]

In this context, a preliminary cyclic voltammetry study has been carried out on a range of gold complexes and ligands to determine their oxidation potentials. On the one hand, these data will potentially allow the *in situ* generation, the isolation and the characterization of gold(III) complexes. On the other hand, it will also enable the development of new catalytic processes under electrochemical conditions.

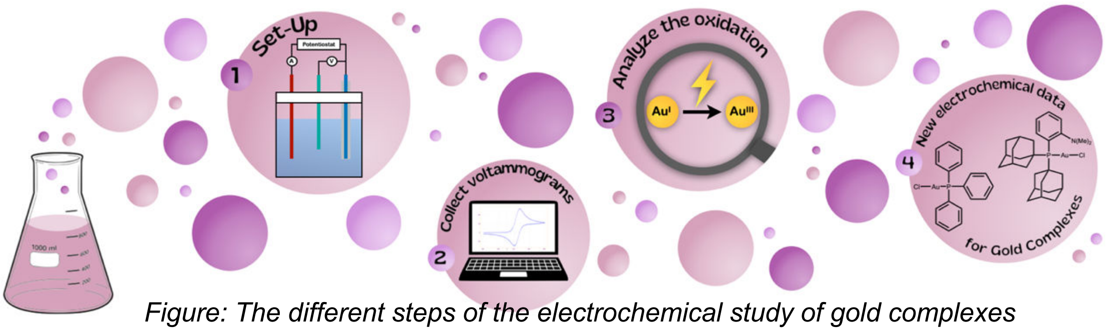

Figure: The different steps of the electrochemical study of gold complexes

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P-22

Reactivity of silver and ruthenium complexes in enynes' cyclizations: towards green and sustainable development

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In the context of the key principles of Green Chemistry,[1] the development of efficient, clean and mild strategies to access cyclized and functionalized molecules is highly important in the field of organic chemistry. We became interested in the reactivity of enynes in the presence of silver and ruthenium complexes. We investigate the cyclization of functionalized 1,6-enynes and showed that silver hexafluoroantimonate[2] catalyzed the intramolecular [4+2] cycloaddition reaction of amide-1,6-enynes, providing tricyclic and tetracyclic compounds. The effects of different catalysts (silver salts, gold and platinum complexes) on this reaction were also investigated, leading to a series of cyclic amides obtained in good yields.[3] In parallel, we developed a ruthenium-mediated ring-closing enyne metathesis transformation[4] of alkynyl B-anthranilamide (B(aam)) to prepare functionalized polycyclic azaborine skeletons. B(aam)-tethered enynes reacted with with Grubbs catalyst, affording the corresponding exo-cyclic compounds in good yields (25 examples, yields up to 89%).[5] This methodology was optimized and performed in dimethyl carbonate[6] as a green solvent, providing a direct and environmentally friendly access to functionalized azaborine scaffolds.

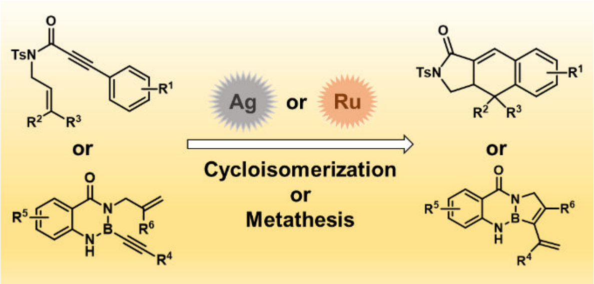

Figure 1: Silver and ruthenium-catalyzed cycloisomerization reaction of nitrogenated enynes

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