



## **– Journée de Rentrée de l'ED406 – promotion 2023 –**

Mercredi 6 mars 2024 à 9h00

*Amphithéâtre 25 – SU, Campus Pierre et Marie Curie*

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### **Livre des résumés**

**Roache ARULANANDAM**

**Biochemical study of UbiU-UbiV from *Escherichia coli*, two [4Fe-4S] enzymes involved in a prephenate-dependent anaerobic hydroxylation reaction**

*PhD advisors: Marc Fontecave, Murielle Lombard*

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Ubiquinone (UQ) is an essential small lipophilic molecule involved in electron transfer in the aerobic respiratory chain of all living organisms. Its aerobic biosynthesis involves a large number of proteins. Very recently, it was discovered that in anaerobic bacteria and in some facultative aerobes, this biosynthesis occurs even without oxygen and involves the [4Fe-4S] proteins, UbiU and UbiV. They are responsible for the hydroxylation reactions on the aromatic ring of the quinone, with prephenate serving as the source of the oxygen atom. The study of this newly discovered O<sub>2</sub>-independent ubiquinone biosynthetic pathway will allow us to unveil an unprecedented mechanism of anaerobic insertion of an O atom into a -CH bond, in a prephenate-dependent manner, and provide a new pathway to target within the scope of antimicrobial approaches. Indeed, the obtained mechanistic knowledge will be used to develop potential selective inhibitors of this anaerobic UQ biosynthetic pathway in pathogenic bacteria, using *Pseudomonas aeruginosa* as a model.

**Yan Zeng**

**Catalytic Metalation of C–H bonds with Main Group Element-Based Diazenes**

*PhD advisor: Louis Fensterbank and Clement Chauvier*

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The last twenty years have witnessed growing interest in the direct functionalization of C–H bonds. In particular, the direct silylation and borylation of C–H bonds are especially attractive transformations as they allow the expeditious preparation of stable organosilanes and organoboranes used in drug discovery, polymer synthesis or as advanced materials. Common approaches towards the silylation or borylation of C–H bonds either rely on the use of late transition metals-based catalysts or on stoichiometric procedures using potent metalation agents. Protocols relying on transition metal-free catalysts have also been reported, yet they lack generality in terms of substrate scope. As such, one of the main objectives of this PhD project consists in studying an emergent molecular platform, namely diazenes substituted by a silyl or a boryl group, able to generate under mild, transition metal-free conditions potent s-block metalation agents that could be catalytically regenerated upon silylation or borylation of a substrate C–H bond.

**Zhenhua CHEN**

## **Selective Tumor Delivery of Metal-based Photosensitizers for Photodynamic Therapy**

*PhD advisor: Kevin CARIOU & Gilles GASSER*

*Laboratory: Laboratory for Inorganic Chemical Biology, Chimie ParisTech, PSL University*

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Metal complexes are a promising source of anticancer drugs, yet they suffer from some drawbacks such as lack of selectivity. Herein, we wish to minimize unwanted side effects by double approaches of selectivity: precise activation by light and selective delivery to the tumor site. Developing long-wavelength absorbing metal-based photosensitizers is considered an appealing way to avoid interference of physical background and to decrease undesirable phototoxicity. Associating with biological targets, such as peptides and nucleic acid, we can realize specific delivery of highly efficient photosensitizers.

**Chonghuo Liu**

## **Synthesis of enantioenriched high value-added fluorinated building blocks through asymmetric transfer hydrogenation**

*PhD advisors: Dr. Virginie Vidal and Dr. Phannarath Phansavath*

*Laboratory: i-CLeHS, CSB2D Team, Chimie ParisTech-PSL, 11 rue Pierre et Marie Curie 75005 Paris*

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The doctoral research program aims at developing novel methods for synthetic efficiency and atom- and step-economical processes using transition metal-catalyzed reactions as they provide a direct and selective way toward the synthesis of highly valuable products. In this context, we will study the asymmetric transfer hydrogenation reaction of fluorinated and trifluoromethylated alkenes to access high value-added functionalized enantioenriched building blocks that can serve as key intermediates to access natural products and pharmaceutical drugs.

**Valisoa Niaina RABENANDRASANA**

## **Contribution to the design, synthesis and evaluation of peptides-based theranostic tools for cancer imaging and radiotherapy**

*PhD advisor: Pr. Philippe KAROYAN*

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Currently, the standard treatment for cancer includes surgery, external radiotherapy and chemo and/or immunotherapy. With the need to offer personalized treatments, tumor targeting strategies have emerged. Among these new approaches, internal radiotherapy allows a toxic dose of radioactivity to be delivered directly to the tumor cells, while preserving healthy tissues. Reaching this goal requires a compound that will selectively target the tumor cells to deliver the radioactivity. Among the possible vectors, peptides are powerful tools because they are accessible and can be easily engineered to construct radiopharmaceuticals selective of a cellular target. The aim of my thesis, supported by the ANR project PanCaIKS (Pan Cancer Imaging and Killing Strategy), is to develop a targeted radiotherapy agent based on a peptide (Peptide Receptor

RadioTherapy, PRRT) to treat cancers with poor prognosis. The project I will introduce here, gathers academic (DRUGLab, UBO, PARCC Inserm, CEM) and industrial (GUERBET,  $\gamma$ -PHARMA) teams.

### **Yagine BEN HADJ HAMMOUDA**

## **Metal-based antioxidants: evaluation for gut inflammation control**

*PhD advisor: Clotilde POLICAR – Philippe SEKSIK*

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Inflammatory Bowel Diseases are chronic disorders for which no curative therapy exists. Thus, new innovative strategies are urgently needed. Deeply intertwined with inflammation, oxidative stress is a well-recognized feature of IBD. In this context, low-molecular weight complexes with either organic or peptidic ligands mimicking enzymes antioxidant activity can be used as catalytic drugs. The objective of this project is to produce and select adequate mimics of antioxidants metalloproteins, assess their antioxidative and anti-inflammatory properties on cellular models before administrating them to murine model.

### **Hai Nam HA**

## **Lowering alkali cation in acidic CO<sub>2</sub> electroreduction into multicarbon products via surface modification of Cu-based catalysts or using high CO<sub>2</sub> pressure**

*PhD advisors: Prof. Marc Fontecave, Dr. Ngoc Huan Tran*

*Laboratoire de Chimie des Processus Biologiques, Collège de France, 11 pl. Marcelin Berthelot  
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This project is designed to lowering alkali cation in acidic CO<sub>2</sub> electroreduction into C<sub>2+</sub> products using Cu-based catalysts via the effect of surface modification. The modification of Cu-based electrode surface via crown ether-alkali cation complex immobilization. We anticipate that the presence of positively charged alkali cation on the electrode surface would inhibit hydrogen evolution and promote high selectivity of C<sub>2+</sub> products formation and, in addition, that the crown ether ligand would prevent the deleterious effect of electrolytes containing free alkali cations. With the study of immobilization of crown ether-alkali cation on Cu-based electrode, different type of electrolyzer, such as flow, MEA or high pressure electrolyzer could be used to test the catalytic activity of the modified electrode.

### **Duy Thai NGUYEN**

## **Molecular Modification of Copper Catalyst Surface for CO Electroreduction**

*PhD advisor: Prof. Marc Fontecave, Prof. Louis Fensterbank, Dr. Ngoc Huan Tran*

*Laboratory: Laboratoire de Chimie des Procédés Biologiques*

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The electrochemical reduction of CO<sub>2</sub> (CO<sub>2</sub>RR) using Cu catalysts holds immense promise for efficiently converting CO<sub>2</sub> into valuable C<sub>2+</sub> products. However, a challenge in CO<sub>2</sub> electroconversion is the formation of carbonates, which results in the loss of CO<sub>2</sub>. To circumvent this issue, a tandem approach can be employed, whereby CO<sub>2</sub> is first converted to CO and then CO is electroreduced to yield C<sub>2+</sub> products. In this study, we

propose an innovative strategy to enhance the efficiency and selectivity of CO electroreduction to C<sub>2+</sub> products by modifying the surface of copper catalysts with specific molecules. Utilizing molecular radical precursors, including iodonium and sulfonium compounds, as well as hypercoordinate bis-catecholato silicon compounds (silicates), we electrodeposited a molecular layer onto the Cu catalyst. This novel approach aims to finely tune the electrochemical properties of the catalyst, paving the way for improved CO electroreduction performance.

**Laura THIRION**

## **Broadening of Horizons in Transition-Metal Catalyzed C-H bond Functionalizations**

*PhD advisor: Prof. Jean-François Soulé*

*Institute of Chemistry for Life & Health Sciences, iCLeHS (Dir. C. Adamo) – Equipe CSB2D Chimie ParisTech/UMR CNRS, 11 rue Pierre et Marie Curie 75005 Paris*

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Transition-metal catalyzed C-H bond functionalization reactions have emerged as a powerful tool for the selective functionalization of C-H bonds and synthesis of complex organic molecules. However, most of the conditions require high temperatures and/or strong oxidants, which can limit their practicality, functional group tolerance and sustainability. In this project, we propose to investigate the Rh-catalyzed C-H bond functionalization reactions at room temperature as a sustainable approach to selective organic synthesis.

The aim of this Ph.D. are: i) Develop novel room temperature Rh-catalyzed C-H bond functionalization reactions. ii) Enhance reactivity by identifying Cp ligand design features thanks to mechanistic studies. iii) Evaluate the catalytic efficacy of the newly developed catalysts in enantioselective transformations or reactions with strict time constraints.

**Elise BOUDRY**

## **Synthèse one-pot de propane à partir de dioxyde de carbone**

*PhD advisor: Christophe THOMAS*

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La production d'hydrocarbures par valorisation du dioxyde de carbone (CO<sub>2</sub>) est essentielle pour la transition vers des sources d'énergie renouvelables et non basées sur les combustibles fossiles. Le marché du propane ne cesse de croître, les secteurs industriel et résidentiel étant les deux acteurs les plus importants. Dans les processus industriels, le propane est utilisé pour des applications à grande échelle telles que les fours et les appareils de chauffage. Dans le secteur résidentiel, le propane est utilisé pour la climatisation, le chauffage, et d'autres usages. Cependant, malgré l'importance de cet hydrocarbure, la formation de propane à partir de CO<sub>2</sub> a été à peine abordée dans la littérature. Nous nous concentrerons en priorité sur l'utilisation de catalyseurs homogènes connus pour la transformation du CO<sub>2</sub> en méthanol. Les systèmes les plus prometteurs seront ensuite évalués en combinaison one-pot avec les zéolithes. Nous envisageons que des catalyseurs zéolithes modifiés disponibles commercialement et peu onéreux pourraient servir de système catalytique efficace pour un accès direct et sélectif au propane à partir de méthanol. L'objectif principal de ce programme de recherche est de développer des procédés de catalyse one-pot efficaces pour obtenir du propane à partir de CO<sub>2</sub> de façon plus sélective que l'existant. L'utilisation de CO<sub>2</sub> pour produire du propane par ce type de séquence catalytique hybride inédite peut présenter à la fois des avantages économiques et environnementaux significatifs.

**Valentin POIRIER**

## **Hydrogenation and dehydrogenation studies of phenolic molecules from biomass.**

*PhD advisor : Dr. Marc Petit, Dr. Alexandre Pradal*

*Laboratory : Institut Parisien de Chimie Moléculaire (IPCM), 4 place Jussieu, 75005 Paris*

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Within a context of sustainable development, and renewal of habits in chemistry, this project aims at making use of biomass derivatives as platform molecules for hydrogen storage and industrial applications. Despite the efforts made towards the valorization of lignocellulosic biomass derivatives, lignin remains particularly underexplored and underexploited, owing to its inherent complexity. The core of the project consists in the hydrogenation and dehydrogenation of phenolic molecules, which can be obtained through lignin depolymerization. To tackle this challenge, it is envisioned to utilize first-row transition metals (e.g., cobalt, nickel, or iron) as catalysts, which are more abundant and less expensive than the commonly used noble transition metals (platinum, rhodium, palladium). By reducing the aromatic moieties under optimized conditions of pressure and temperature, platform molecules can be obtained, and could eventually store and carry hydrogen in a liquid state (liquid organic hydrogen carrier), thus bringing a contribution to the development of hydrogen-based technologies. The saturated molecules produced can also serve as useful bio-based synthons in organic chemistry.

**Nader BALBALI**

## **Peptidyl metal complexes for catalysis in water**

*PhD advisor: Nicolas Delsuc*

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Peptidyl metal complexes have been developed successfully as catalysts for reactions such as hydrogen transfer, oxidation, epoxidation, aldolisation and oxygenase-type transformations. Interestingly these reactions were performed in water and in some cases, good enantioselectivities could be reached thanks to the chirality of the peptidyl ligand. Peptidyl metal complexes mimicking antioxidant metalloenzymes have also been developed to reproduce the beneficial activities of the metalloenzymes. Owing to their good biocompatibility these complexes could be used in more relevant biological systems, namely in cellular models involving oxidative stress.

In this project, we will use a combinatorial strategy combined with activity-based assays to find efficient catalysts for reactions such as lytic oxidations or oxidative couplings involving CH activation. Also, mimics of nitrites reductases will be investigated. The selected complexes will be then studied in details to characterize their catalytic activities in solution, and when suitable in cells.

**Zeping ZHANG**

## **Luminescent Cycloplatinated Complexes Containing Organic Chromophores: Towards Panchromatic Emitters**

*PhD advisor: Hani Amouri*

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In this PhD research project we wish to design a novel family of panchromatic emitters. The target compounds contain organic chromophores, which are based on pyrenes. The latter are highly luminescent organic chromophores. In a judicious synthetic approach phosphorescent cycloplatinated-NHC moieties will be placed in close proximity to the organic chromophore. Thanks to the strong spin-orbit coupling of the metal center, this will facilitate the access to the triplet states of the organic chromophore and thus generating emissive complexes. Moreover the presence of strong  $\sigma$ -donor NHC-ligands should enhance the stability of the molecule and amplifies the luminescence properties of the target molecules as well.

**Dandan DI**

## **Understanding the Behaviors of Polymeric Nanomaterials in Biological Media: Focus on Intravenous and Oral Delivery**

*PhD advisor: Kawthar BOUCHEMAL*

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Over the past decade, nanomaterials (NMs) significantly impacted biomedical applications like imaging, diagnosis, drug delivery, and targeting. This prompted varied NM designs, but lack control or prediction of in vivo behavior. The challenge persists due to the unexpectedly complex interface between NMs and biological media. When a NM encounters biological barriers, it takes on a new identity, termed biological identity. Biomolecules (proteins, lipids, sugars) competitively bind to NM surface, forming a biomolecular corona. This corona-NM complex, not the pristine NM, interacts with biological machinery, influencing pharmacokinetics, biodistribution, cellular interaction, trafficking, targeting, biological activity, immunological reactions, and toxicity. Similar challenges arise with mucosal administration. Our goal is to comprehend polymeric nanomaterial behaviors with controlled synthetic identity towards the biomolecular corona and understand its impact on NM biological fate, with focus on intravenous and oral routes.

**Salomé LUCE**

## **Synthesis and characterization of silane-terminated polymers debondable on demand**

*PhD advisor: Amandine GUERINOT, Yvette TRAN*

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The aim of this thesis is to design and develop systems enabling the disassembly of cross-linked structures of silane-terminated polymers by the addition of a catalyst or the application of a different stimulus. The study will focus on a model cross-linked structure to which experimental conditions will be applied (e.g. excess alcohol and a catalyst) that would enable the inter-chain alkoxysilane bonds to be broken or the polymer to be

degraded. The range of monomers and cross-linking agents will lead to a variety of alkoxy-silane-functionalized polymers, and will provide a better understanding of the structure/adhesion/dis-adhesion relationship. In order to minimize the impact of the material, emphasis will be placed on the use of an ambivalent catalyst, capable of cross-linking in one experimental mode and disassembling under other conditions.

## Virgile ROUFFETEAU

### **ML-guided electrophotocatalytic multicomponent reactions**

*PhD advisors: Dr. L. Grimaud, Dr. M. Vitale*

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This PhD project aims to develop original multicomponent reactions leveraging the recent discoveries of electrophotocatalysis. The targeted multicomponent reactions are isocyanides based (named IMCR), as the team has a special interest in them. The project will start with electrocatalyzed IMCR, and photocatalyzed IMCR, such as carbamoylation of arenes. In order to develop more general methodologies, high potentials are needed. Since they are out of reach via classic electrocatalysis, electrophotocatalysis will be employed, as it is known to afford short-lived species with very high potential, unlocking new transformations. Each original transformation will be optimised with the help of Bayesian methods of machine learning, fed with a succinct screening of the conditions.

## Emilien BEUDY

### **Cooperative Silicates in Organometallic Catalysis**

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Following the principles of green chemistry, metal-catalyzed cross-coupling and metathesis reactions, recognized by Nobel Prizes, in addition to metal-catalyzed cycloisomerization reactions have witnessed intense developments since they allow access to molecular complexity, a key concept in lead discovery. In parallel, homogenous **gold catalysis** has opened new venues in organometallic catalysis due to the high  $\pi$ -Lewis acidity of gold complexes toward various unsaturations such as alkynes, allenes and alkenes. A lot of Au(I)-catalyzed processes rely on LAuCl complexes that are activated via halide scavenging in order to be catalytically active. This is generally achieved by anion metathesis using silver salts to generate [LAu+][Y-] active species, Y- being a weakly coordinating anion (WCA). This activation step being under equilibrium is rarely complete and yields various metallic species with potentially competing catalytic activities that can alter reaction outcomes. This "silver effect"<sup>2</sup> is well-documented and so far no general alternative has been proposed. The activation of metal halide species through the addition of non metallic reagents remains largely under developed. The project aims to fill this gap by introducing neutral silicon Lewis acids into organometallic catalysis and initially in Au(I) catalysis by activating LAuCl species and exploiting the concomitantly *in situ* generated hypercoordinate silicon anionic species, referred to as silicates.



**Abdourahim HAMMANI**

## **Integration of polyoxometallates in molecular spintronics devices**

*PhD advisor: Florence VOLATRON*

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The stages of the thesis will be organised as follows: 1) the synthesis of new families of POMs adapted to the final devices (so as to isolate the POM film from the device's lower and upper electrodes); 2) the development of their deposition on a magnetic substrate in the form of a monolayer (handling will take place in a controlled atmosphere, so prior deposition on an inert gold substrate will be necessary to determine the best deposition conditions); 3) structural characterisation of the substrates using conventional surface characterisation techniques as well as advanced synchrotron techniques; 4) study of the electrical behaviour of the POM monolayer (its conductivity, the voltage to be applied to charge the POMs) using conductive atomic force microscopy and 5) integration into a magnetic tunnel junction for magnetoresistance measurements.

**Serah NJOROGÉ**

## **Multi-Parametric Biosensors Designed by Surface Modification based on Metallic and Organic Nano-Platforms for the Detection of Emerging Pollutants.**

*PhD advisors: Sophie Griveau (Chimie ParisTech-PSL), Cyrine Slim (Chimie ParisTech-PSL), Laura Trapiella (Chimie ParisTech-PSL), Immaculate Michira (University of Nairobi) & Peterson Guto (University of Nairobi)*  
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The rapid increase in anthropogenic activities and industrial growth means the release of various pollutants into the environment. Most of these compounds were unknown a few years ago but have recently been discovered as new pollutants that could potentially endanger the ecosystem, the so-called emerging pollutants. They are difficult to degrade with harmful effects even at trace concentrations. Thus, it's crucial to develop analytical diagnostic tools to allow the monitoring of such compounds. In this project, the final aim will be to prepare a portable multi-detection device for the in-situ analysis of several trace-level emerging pollutants in real water samples. To this end, the conception of electrochemical biosensors will be privileged, due to their good analytical performances, simple use, easy miniaturization, and simple integration with electronics. The first step will be to develop new electrode surface modification via electrochemical means based on metallic nanomaterials and polymeric networks.

**Manon WITTWER**

## **Development of Dual-Input chemogenetic probes for metal cations (Ca<sup>2+</sup> and Zn<sup>2+</sup>)**

*PhD advisors: Blaise Dumat, Jean-Maurice Mallet*

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Despite the wide range of fluorescent organic dyes available that possess excellent photophysical properties and sensing capabilities, fluorescent proteins (FPs) appear to dominate the field of biological imaging due to their unmatched selectivity through genetic encoding. Recently, a new type of reporter called hybrid chemogenetic reporters has emerged. These reporters combine a genetically encoded self-labeling protein (SLP) tag with a small molecular fluorophore. This combination benefits from the precise targeting of recombinant proteins through genetics, as well as the structural diversity and versatility of organic chromophores. However, it may encounter common issues associated with molecular probes, such as off-target binding, yielding non-specific signal, and the need to remove excess dye. To address these challenges, advanced chemogenetic reporters are constructed using fluorogenic probes that only emit fluorescence when bound to specific protein tags. The objective is to develop locally-activatable fluorescent probes for targeted sensing of metal cations (Ca<sup>2+</sup> and Zn<sup>2+</sup>). These probes will be activated by reacting with the SLP tag called HaloTag, and their emission will be responsive to the presence of metal cations. The development of dual-input probes for Ca<sup>2+</sup> and Zn<sup>2+</sup> will facilitate the study of their roles and regulation in genetically-defined cell types or organelles with high specificity.

**Sarah CHAPUIS**

## **Enantioselective Catalysis through Activation of Grignard and Organozinc Reagents by Chiral non-Racemic Immobilized Carbenes**

*PhD advisors: Olivier Jackowski and Myriam Roy*

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Thanks to a Lewis-base activation, we aim to develop a new methodology of enantioselective 1,4 addition of organometallic reagent such as Grignard and organozinc halides. Using a family of chiral bidentate NHC carbene as Lewis base we envision to overcome the need of transition metal for achieving the creation of one to two new stereogenic centers starting from various Michael acceptors. In parallel, another target is the adaptation in flow chemistry, as well as in homogeneous and heterogeneous catalysis. For the later, NHC ligand would be anchored onto solid support like silica or polystyrene which could represents an interesting procedure for industries.

**Julian David PORRAS ARGUELLO**

## **Biodegradable polymeric nanomaterials for oral vaccination.**

*PhD advisor: Kawthar Bouchemal, Christophe Thomas*

*Laboratory: Chimie Organométallique et Catalyse de Polymérisation (COCP)*

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Mucosal vaccination is very promising for preventing infectious diseases, leveraging the effectiveness of local immune responses. Currently, only a few vaccines use this route, primarily live attenuated ones. The aim of the PhD is to create non-spherical, biodegradable nanomaterials mimicking microorganisms, enhancing mucosal vaccination. However, designing these materials with specific shapes, softness, and mucosal antigens poses a challenge. Robust technological tools are essential for producing nanomaterials with controlled properties, considering dimensions, softness, and surface characteristics. This approach sheds light on key parameters in oral vaccination, facilitating the precise design of the next generation of vaccines.

**Sophia BEN AHMED**

## **Molecular, bioinspired and heterogenized catalysts for CO<sub>2</sub> reduction**

*PhD advisor: Marc FONTECAVE, Yun XU-LI*

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In the current context of environmental crisis, sustainable methods are sought to accelerate the energy transition. In that respect, valorisation of the abundant feedstock of CO<sub>2</sub> is a promising strategy to afford a sustainable carbon source and for chemical storage of energy, yet hindered still by the high stability of the molecule. This project focuses on the development of molecular catalysts based on organometallic complexes mimicking the active sites of enzymes for the electroreduction of CO<sub>2</sub> to CO, which can readily be converted in hydrocarbons or in small molecules of industrial interest. The most promising catalysts are functionalized to allow their grafting onto heterogeneous electrode materials to make the electroreduction process more suitable for an implementation at industrial scale.

**Lei ZHOU**

## **Towards the Discovery of New Photodynamic Therapy Photosensitizers Based on Bioavailable Metals**

*PhD advisor: Prof. Gilles Gasser & Dr. Kevin Cariou*

*Laboratory: Laboratory for Inorganic Chemical Biology, 11, Rue Pierre et Marie Curie*

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In recent times, photodynamic therapy (PDT) has emerged as a promising avenue for highly efficient, low-side-effect, and long-term cancer treatments. However, the majority of presented photosensitizers rely on heavy and rare metals such as Ruthenium, Platinum, Iridium, which are both expensive and highly toxic. In contrast, first-row transition metals, including Mn, Fe, Co, Cu, and Zn, are more abundant on Earth and hold potential advantages. Utilizing first-row transition metal complexes not only offers cost-effectiveness but also contributes to reducing the dark toxicity of prodrugs. Hence, there is a compelling need to explore and develop new photosensitizers based on economically viable and less toxic first-row transition metals. The weak ligand

field in first-row complexes presents a significant challenge to develop complexes with long-lived charge-transfer excited states due to rapid deactivation via metal-centered (MC) states. Through the introduction of N-heterocyclic carbenes (NHC) and other strong  $\sigma$ -donor ligands, we improve the optical properties of first-row transition metals and design and synthesize new bioavailable photosensitizers.

## **Lucas FERREIRA DE CASTRO**

### **Gut microbiome-on-a-chip: Genomic, transcriptomic and proteomic a global insight**

*PhD advisor: Anne Varenne<sup>1</sup> et Yann Verdier<sup>2</sup>*

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The gut microbiome plays a crucial role in human health and disease and is associated with various physiological processes. To characterize these systems, complementary approaches including genomic, transcriptomic and proteomic are required, which are sometimes difficult to implement for small-volume samples. Thus herein, the idea is to develop a lab-on-a-chip device that enables cell lysis, nucleic acids and protein preparation for sequencing.

First, a microchannel with two electrodes will be used to carry out electrochemical cell lysis. The advantage of using this lysis principle is that it is suitable for different types of microorganisms, without the need for reagents that are incompatible with subsequent analyses. After that, at the end of the microchannel, a membrane will retain the DNA and RNA materials as well as proteins. Proteins will undergo enzymatic and/or electrochemical digestion, and the resulting peptides, which can pass through the membrane, will be recovered and analysed by mass spectrometry. Then, DNA and RNA will be driven to a chamber and recovered for analysis by PCR or by NGS sequencing. This developed device should therefore be able to carry out multi-omics analyses on low-volume samples.

## **Corentin LUDWIG**

### **Development of organometallic anti-leishmanial drug candidates**

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The aim of the project is to develop anti-parasitic organometallic compounds focusing not only on an improved biological effectiveness under different clinically relevant conditions, but also on the reduction of side-effects compared to existing drugs. The organometallic moiety would be introduced in pre-existing anti-infective scaffolds to capitalize on the benefits of organometallic derivatization of drugs. The results of this project may constitute the basis for a new generation of powerful and selective anti-parasitic chemotherapeutics.

**Olivia SOUFFLET**

## **Targeting CD47 with agonist peptides to address cancer with bad prognosis**

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CD47 is a transmembrane protein which functions as a marker of “self” by inhibiting phagocytosis of autologous cells through interaction with SIRP $\alpha$  expressed by macrophages. The overexpression of CD47 by cancer cells is one of the mechanisms of immuno-surveillance evasion for tumors associated with a bad prognosis. These findings led to the development of monoclonal antibodies (mAbs) approaches, **acting as antagonists**, to block the CD47/SIRP $\alpha$  interaction. However, in clinical studies, these strategies suffered from poor efficacy and severe side effects. **Novel therapeutic tools targeting CD47 with less adverse effects still need to be developed.** Academic efforts spearheaded by the DRUGLab led to the discovery of CD47 **agonist** peptides derived from the C-terminal domain of glycoprotein TSP1, able to induce selective death of cancer cells with an original mechanism of action. This project, a partnership between the academic DRUGLAB and the Biotech Pepkon, aims at optimizing the pharmacological profile of these peptides.

**Bhramar Biswas**

## **Reactivity of oxamate ligands in solvothermal and microwave synthetic conditions: preparing MOFs for molecule sensing or ion mobility**

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Coordination networks made of oxamate ligands have various applications, including water remediation, sieving, sensing, catalysis, and magnetism. Oxamate ligands have successfully led to the design of porous magnets thanks to spin topology and spin polarization. The main goal of this thesis is, with the help of new phenyloxamate ligand derivatives, the extension of our synthetic approach to prepare new coordination networks toward two important fields of study in MOF chemistry: ion mobility and molecule sensing. Apart from the classical solvothermal synthesis, we will also use microwave synthetic conditions to prepare neutral frameworks and increase the reactivity of the oxamate ligands.

**Margaux HANARD**

## **Enantioselective Coupling Reactions by Dual Catalysis**

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Artificial metalloenzymes represent a new class of catalysts, which combine the properties of proteins and metal complexes. Such hybrid species associate the main advantages of biocatalysis (highly chemo-, regio-

and stereoselective reactions under environmentally benign conditions) and of homogeneous catalysis (a plethora of chemical transformations involve transition metal-catalyzed reactions). In the past ten years, several artificial metalloenzymes have been developed for epoxidation, hydrogenation, oxidation reactions, C-H activation and olefin metathesis... However, until now, no metalloenzyme has been described for enantioselective photoredox reactions. Within this ANR program, we aim at developing new hybrid catalysts involving copper metal complexes for these yet challenging enantioselective reactions in homogeneous catalysis.

## **Cédric PECOU**

### **Magnetic Dendrimers**

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Developed in the 1980s, dendrimer chemistry has opened up new perspectives in fields as diverse as catalysis, molecular electronics and artificial photosynthesis. Surprisingly, however, magnetic dendrimers are not common in the literature due to puzzling difficulties in their synthesis and characterization. The aim of this doctorate is to synthesize and characterize coordination dendrimers, and ultimately study their magnetic properties. Using a supramolecular “complex as ligand” approach, combining a core with other complementary complexes serving as branching units, we have already succeeded in getting the first magnetic dendrimers, CrLn<sub>3</sub>Co<sub>6</sub> and ZrLn<sub>4</sub>Co<sub>8</sub>, fully characterized by X-ray diffraction. The magnetic properties of the dendrimer can be modulated by choosing carefully the core and the branching units, resulting in different magnetic behaviors (single-molecule magnets, high-spin molecules, magneto-calorific effect, photomagnetism...).

## **Chengjun WU**

### **Synthesis and Application of Novel Fe(II) and Zn(II) Catalysts**

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Polymers are significant materials to improve people's quality of life and accelerate social progress, while energy consumption and environmental pollution have forced scientific research to develop in the direction of renewable raw materials and sustainable products. During this process, the cornerstone of polymerization reaction that cannot be ignored is metal catalysts. In general, Ruthenium catalysts, Palladium catalysts and Platinum catalysts exhibit good catalytic efficiency, but the high price and patent restrictions of these transition metals limits their application in industrial mass production, which may also be shortcomings in the sustainable development of polymers. Based on these considerations, we hope to develop new cost-effective and inexpensive metal catalysts to accelerate the research of green chemistry. Preferentially, we tried iron and zinc catalysts. There is no doubt that the core metal of iron and zinc complexes has the advantages of abundant reserves, suitable price, especially its excellent catalytic polymerization ability, making it a significant research project.

**Eleni KOVANI**

## **Polyoxometalate-based Artificial Photosynthesis**

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Energy policies in developed nations are pressing. Solar energy, abundant on Earth, could meet global demands if efficiently harnessed. Storing intermittent solar energy is a challenge. An attractive option, however challenging, is to store this energy into chemical bonds, for example (photo)reducing proton into H<sub>2</sub> or carbon dioxide into C1 chemicals. Our group has recently shown that, upon irradiation with visible light, mixed V-W Dawson derivatives functionalized with a Cu-complex can store up to three electrons, and the latter have been used for reductive catalytic applications. Merging this electron accumulation ability with our previous work on CO<sub>2</sub> (photo)electroreduction with POM derivatives, the aim of this project is to activate by light the catalytic properties of a grafted complex known for its ability to electro-reduce protons or CO<sub>2</sub>. This will be done by replacing the Cu-Dipyridyl moiety by a Co-complex and its Fe- or Ni-analogues, and to test the photo-/electro-catalytic properties of these new hybrids.

**Wenqing XU**

## **High-throughput and large-scale IM-MS approach for the characterization of oligosaccharides in breast milks**

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Breast milk, being the primary source of nutrition for newborns, necessitates thorough characterization, particularly concerning human milk oligosaccharides (HMOs) due to their pivotal role in immune system development. Despite advancements, the structural diversity and isomeric complexity of HMOs pose significant analytical challenges. My PhD project aims to address these challenges by developing a large-scale and high-throughput approach for comprehensive HMO detection using ion mobility spectrometry, tandem mass spectrometry, and molecular network analysis. Ion mobility spectrometry offers rapid analysis and effective isomeric separation, while molecular networks facilitate the organization and interpretation of complex MS/MS data. The proposed methodology promises to advance the understanding of HMO diversity in breast milk, enhancing nutritional and immunological research in neonatal health.

**Mokhtar BEN GHANEM**

## **Design of transition metal systems bearing neutral ligands for oxidative reactions**

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Nickel, known for its cost advantages over palladium, offers a promising avenue for sustainable catalysis. This research will delve into the catalytic potential of nickel complexes with nitrogenated ligands, focusing on activating challenging electrophiles like Ar-OMe, Ar-F, or Ar-NO<sub>2</sub>. The study will systematically investigate the structure, stability, and reactivity of a diverse array of nickel complexes. Among various ligand types, phosphines remain a popular choice for traditional cross-coupling reactions, while nitrogenated ligands like bipyridines and phenanthrolines are commonly used in photo- and electrocatalytic processes, particularly for activating C-X bonds. Emphasis will lie on understanding oxidative addition reactions through electroanalytical methods, NMR, mechanochemistry and EPR. Kinetic measurements and multivariate linear regression models will provide insights into factors influencing reaction rates. The project will further explore product reactivity towards nucleophiles, aiming to optimize nickel-catalyzed couplings and expand late-stage functionalization possibilities, particularly targeting the prevalent aryl methyl ether motif.

**Sisi ZHU**

## **Instrumental and methodological developments for the on-line coupling of Microfluidic Capillary Electrophoresis to Surface Enhanced Raman Spectroscopy (MCE-SERS) applied to the separation and identification of submicro- and nanoplastics in water**

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This project will focus on the development of analytical electrokinetic methods for the physicochemical characterization of submicro(nano)plastics in environmental and consumable water samples. The resolving power of these methods should allow an initial sequencing depending on the size and chemical nature of these objects. Different couplings with spectroscopic detection methods (Fluorescence and Surface Enhanced Raman Scattering) are considered for structural and quantitative characterization of plastics. Development towards miniaturized analytical systems integrated on microfluidic chips will also be carried out for on-site analysis.



**Ruonan GAO**

## **Synthesis of Gd complexes and apply as MRI contrast**

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I major in organic chemistry. My work is synthesizing metal complexes and depending the different properties of different metals to apply in several fields. For instance, Gd has significant magnetism which can be used in magnetic resonance imaging (MRI). It is truly an effective way to diagnosis tumor. I also work with some Ru, Re and Os complexes, because their photochemical properties. Trying to combine more than two metals in one compound to achieve diagnosis and treatment at the same time.

**Tao MA**

## **Synthesis of chiral phosphines *via* asymmetric catalysis and their applications**

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Phosphine ligands' synthesis was a multi-step procedure that introduced the trivalent phosphorus at the end of the synthetic scheme. However, a revolutionary technique, pioneered by Hartwig in 2000, facilitated the modification of phosphine scaffolds through catalytic C–H bond functionalizations. Intriguingly, there has been no reported instance of preparing chiral phosphine using this catalytic method. This thesis delves into the relatively untapped domain of chiral phosphine preparation via varied catalytic enantioselective transformations. The research underscores the distinct advantages of the direct approach to phosphine synthesis, emphasizing its efficiency and the capability to incorporate chemically sensitive groups via late-stage functionalization strategy. While the primary focus in this field has traditionally been on monophosphines, this study advocates for the importance and potential of chiral diphosphines. Their critical role in producing high-value products when paired with transition metal complexes is a foundational aspect of this investigation.

## **Leyu TANG**

### **Synthesis of oligosaccharides for tumor imaging: aminoethyl glycoside of sialyl Lewis X**

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E-selectin is a cell adhesion protein that is expressed only in cytokine activated endothelial cells. Cancer cells are able to interact with E-selectin which is believed to be involved in the metastases invading process. Consequently E-selectin is expressed at the surface of tumoral endothelium, this property could be exploited for the diagnosis and targeted therapy of tumors. The tetrasaccharide sialyl Lewis X (sLeX) is known to bind with high affinity and selectivity with E-selectin. Our objective was to search a kind of molecular probe that is able to target E-selectin through sLeX moiety and recognize metastatic spot by imaging. My PhD project will focus on an efficient synthesis of the aminoethyl glycoside of sLeX, which would be a useful tool for grafting with the maleimidopropyl-lactose to synthesize a macromolecule for tumor imaging.

## **Grégoire BOIVIN**

## **Apollonia KALAMATIANOU**

### **Development of anti-infective organometallic drug candidates**

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Over the last decades, the incidence of fungal infections worldwide, as well as the associated mortality rates have constantly been increasing. Due to the ever-increasing resistance to conventional antimycotic treatment, fungal pathogens are now considered a global public health threat. This situation led the WHO to issue a list of fungi species that are classified as critical priority pathogens in October 2022. In particular, resistance to azoles, which are among the most widely used antifungal drugs, is particularly worrisome. Therefore, there is an urgent demand for novel, effective drugs to be used as alternative treatment against resistant pathogenic fungi. Organometallic complexes have found application in the field of medicinal chemistry, and metal-based drug derivatives have already been successfully employed to overcome resistance phenomena. Following this approach, in this project, we aim at derivatizing existing antifungal drugs such as azoles by incorporating organometallic moieties. Our objective is to obtain novel drugs that will be able to exert a broad-spectrum activity and bypass acquired resistance that threatens the efficacy of our therapeutic armamentarium.

**Théo Pierru**

## **New Cationic OrganoAcids for Applications in Synthesis**

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Organocatalysts have found applications in many transformations including Brønsted acid-mediated reactions and can be used in all areas of chemical sciences spanning from biochemical to industrial processes. Facing such enthusiasm, more acidic catalysts had to be developed to activate poorly reactive substrates. So far, only neutral and weakly to quite acidic catalysts have been reported. Within this ANR program, we aim at developing new super acidic cationic organocatalysts involving weakly coordinating anions for these yet challenging enantioselective reactions such as cycloisomerisations.

**YONGQIANG XU**

## **Cobalt-Catalyzed C4-Silylation by Hydroxyl-Directed C-H Activation of HMF Derivatives**

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Biomass, particularly agricultural wastes, is an alternative because they contain significant amounts of hemicellulose and cellulose. The acid hydrolysis of these carbohydrates provides two compounds in particular: *furfural* and 5-hydroxymethylfurfural (*HMF*).

For the functionalization of HMF, our *strategy* is to utilize the hydroxymethyl group of the HMF derivative. For instance, the *ortho-silylation* of aryl ketone, benzaldehyde, and benzyl alcohol derivatives has been developed, wherein a hydroxyl group formally serves as the directing element for Ir-catalyzed arene C–H bond activation.

However, considering the *high cost of Iridium catalysts*, we aim to develop innovative strategies for the selective C–H functionalization of the C4 position of the HMF. To this purpose, well-designed transient directing groups as these silylated compounds will be attached to the hydroxymethyl substituent of HMF. These groups will direct the C–H activation step at the C4 position. In order to move towards the most sustainable processes possible, the use of complexes based on cobalt, a first-rank transition metal which is cost-effective, abundant, and relatively environmentally benign, will be considered. This type of complex has indeed shown great promise in numerous C–H activation reactions.

**Tom Lacoma**

# Synthesis and biological activity of gold-based anticancer agents for targeted therapy

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Interest in gold (III) complexes as a new class of anticancer agents grew in the last decades, as they turn out to be promising isoelectronic and isostructural alternatives to platinum (II) complexes. However, despite being highly cytotoxic and fairly redox stable in cellular medium, they generally show a very low selectivity towards cancer cells, which is yet to be increased, by introducing complexes with new mechanisms of action. Accordingly, I investigate the synthesis and biological activity of a new generation of hemilabile complexes bearing both bisphenyl and bridged N-heterocyclic carbene-CH<sub>2</sub>-pyridine ligands, in which the pyridine can be either free or coordinated, which opens avenues to new modes of action. In parallel, specific enzyme inhibitors have emerged as efficient targeted treatments, thus decreasing the side effects associated with standard chemotherapy. Two suitable protein targets for such an approach are, on the one hand, the tyrosine kinase Bcr-Abl and, on the second hand, PARP-1, respectively associated with chronic myeloid leukaemia and BRCA-/- cancers. As part of my research project, I investigate the synthesis of Bcr-Abl (resp. PARP-1)-targeted gold(III) complexes by coupling enzyme inhibitors to gold (III) complexes. I also aim at determining their biological activity, their mode of action and their speciation *in cellulo*, with a particular attention to possible synergistic effects resulting from the combination of an inhibitor with a gold complex.

## **Tian ZENG**

### **Eco-Efficient Processes for the Synthesis of Sustainable Polymers**

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The development of new methods to transform biomass into resources suitable for polymer production remains a crucial obstacle on the way to a more sustainable chemical economy.<sup>1</sup> In this regard, the creation of renewable polymers through one-pot catalysis represents an important tool to support more sustainable plastics production.<sup>2,3</sup> In this project, hydrogen borrowing, a clean atom-economical technology, will be harnessed in a first step to synthesize lactones or lactames monomers from biosourced raw materials.<sup>4</sup> These will then be polymerized through stereoselective ring opening polymerization, providing novel polyesters or polyamides.<sup>5</sup> An intense emphasis will be placed on the design of new organometallic catalysts based on Earth-abundant metals, as well as on establishing the physicochemical properties of the polymers.