



Journées Jeunes Talents de la Chimie en Ile-de-France 2022

Vendredi **21 octobre 2022** de 9h à 17h30

Amphi Charpak (campus Pierre et Marie Curie, Sorbonne Université)

<https://jtc2022idf.sciencesconf.org>

Le bureau SCF-IDF remettra quatre prix de thèse. Les lauréats de nos prix vont présenter leurs travaux au cours de cette journée.



Société Chimique de France



Prix d'excellence en Chimie Organique

Dr. Morgane de Robichon, BioCIS, Cergy-Paris Université

Directed C-H functionalization of pseudo-anomeric position of glycols substrates by metal-catalyzed processes

Current synthetic routes for C-arylglycosides involve multiple steps via prefunctionalized intermediates and frequently use strong bases. In recent years, C-H bond functionalization, which is an efficient transformation process, has become emerging in synthetic chemistry. To overcome the regioselectivity issues inherent in activating a specific C-H bond in complex substrates, the use of strategically placed directing groups (DG), has proven to be an effective strategy. However, examples of metal-catalyzed C-H functionalization (MCF) on sugars are still rare. MCF of Csp²-H bonds remains more developed in the literature examples than that of Csp³-H, thus making glycols (sugars possessing an intracyclic double bond) ideal partners to build C-C bonds at the anomeric position (position 1). Nevertheless, without DG, MCF on glycols occur almost exclusively at position 2 of the glycol. In order to direct the reactivity in position 1, it was considered in this PhD thesis project to place a DG at position 2 of the glycol. 8-Aminoquinoline (bidentate DG) is very popular in directed MCF examples and can be introduced in C2 via a pallado-catalyzed aminocarbonylation methodology previously developed in the laboratory. During this PhD thesis, a directed pallado-catalyzed C-H arylation in the pseudo-anomeric position was set up from these C2-amidoglycols. Through the use of different glycols and iodinated partners, various C-aryl/alkenylglycoside structures were synthesized. This allowed the synthesis of glycosylated amino acids and a Dapagliflozin analogue in excellent yields. Inspired by this arylation, a nickel-catalyzed C-H alkynylation reaction was performed on the same pseudo-anomeric position of the glycol, using the same DG. This alkynylation gives access to C-alkynylglycosides by using various glycols and alkyne bromides. Subsequently, a Huisgen cycloaddition reaction in the presence of copper could be performed, allowing the synthesis of various glycoconjugates in good yields. In particular, a lysine and a biotin derivative were introduced by this route.





Prix d'excellence en Chimie Organique

Dr. Thomas VARLET, ICSN, Université Paris Saclay

ENANTIOSELECTIVE AND DIASTEREODIVERGENT ACCESS TO SPIROCARBOCYCLIC INDOLENINES THROUGH CHIRAL PHOSPHORIC ACID-CATALYZED DEAROMATIC CYCLOADDITION

Faced with the current environmental challenges, chemists have been actively developing new tools to access more economic and less polluting processes. Asymmetric organocatalysis, which allows for the efficient synthesis of valuable chemical compounds, is one of these solutions. In this context, we have been developing, for several years, challenging new reactivities to access enantioenriched nitrogen containing small molecules. [1] We recently reported the asymmetric construction of spirocyclic indolenines, whose unique structural features make them attractive motifs, through intermolecular dearomatization of indoles.[2] Due to the consequent challenges in the generation and stereocontrol of quaternary carbon centres, few such examples have been reported so far. [3] The reaction between 2-substituted 3-indolylarylmethanols and dienecarbamates, in the presence of a chiral phosphoric acid, afforded highly substituted 6-membered carbocyclic spiroindolenines in good yields and with excellent enantioselectivities. This process proved to be highly diastereodivergent giving a selective access to two sets of diastereomers. DFT calculations revealed an unexpected mechanism at the origin of the stereocontrol. Finally, further transformations delivering attractive structures such as chiral 2,2-disubstituted spiroindolines and spirooxindoles, illustrate the large range of the synthetic possibilities offered by this methodology.



université
PARIS-SACLAY



Prix d'excellence en Chimie théorique, physique ou analytique

Romain Plais, Institut Lavoisier de Versailles - Université Paris-Saclay

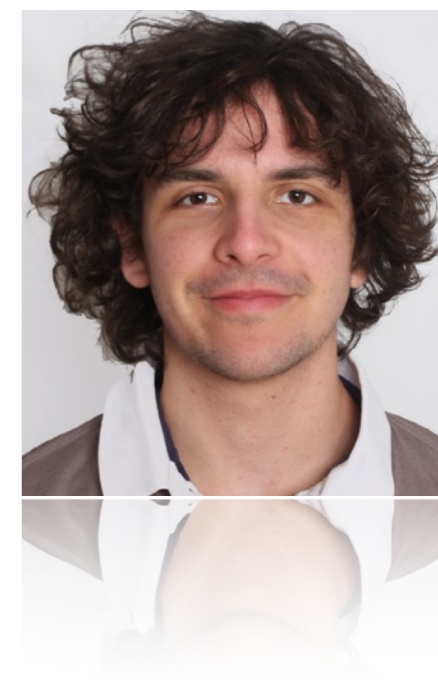
Understanding and Rationalizing Cooperativity Effects Between Non-Covalent Interactions/ Towards More Efficient Anion Receptor Platforms

Anions are widely spread in several areas such as biology, medicine, catalysis, or environment. Therefore, the molecular recognition of anions is a promising branch of supramolecular chemistry. However, unlike the extensive use of cation receptors, anion recognition is still in its infancy.

The development of receptors is based on the use of one or multiple weak interactions. Many of these interactions such as anion- π interaction, halogen or hydrogen bonding have been extensively studied independently. A combination of several weak interactions within a single polyfunctional molecular platform is likely to generate (anti)-cooperative effects on anion binding, but they remain difficult to highlight, predict and/or understand.

Based on these considerations, we recently focused on the emerging area of anion receptors combining hydrogen-bond donor groups and π -deficient heterocycles able to generate anion- π interactions. Only a few theoretical publications reported the study of cooperativity effects in such combination to date. Moreover, the accuracy between predicted properties and experimental results has to be improved.

In this communication, the combination of molecular modelling and analytical chemistry will be discussed to deliver some understanding of such complex effects. DFT calculations will provide some structural information on complexes formed. Correlation between calculated interaction energies and experiments will be assessed, enabling the establishment of a predictive model. Then, (anti)-cooperative effects between the different interactions will be evidenced and explained. As perspectives, the influence of small structural modulations on chloride binding will be highlighted.



 **ILV**
Institut Lavoisier
de Versailles

UVSQ 
UNIVERSITÉ PARIS-SACLAY



Prix d'excellence en Chimie inorganique, minérale et des matériaux



Dr. Imen Hnid, Université Paris Cité

Surfaces and photoactive molecular junctions: organizations, functionalizations and characterizations by STM and C-AFM

The first configuration is shedding a light on the use of methods and techniques for assembling and organizing photoactive molecules on surfaces. I studied with the scanning tunneling microscope (STM) the self-assembly and the photoswitch of two photochromic derivatives: An azobenzene derivative (AZO) and a diarylethene derivative (DAE). Both were functionalized with terminal bipyridine units (bpy) to give the systems (bpy-AZO-bpy) and (bpy- DAE-bpy). They were deposited by droplet deposition at the solid/liquid interface (s/l) and at a room temperature. A major observation, that has been noted, shows that 2D supramolecular structures can be generated and the constructed structures can be controlled using several external stimuli (solvent/pH and light irradiation). These stimuli provide us with high-level control between multiple stable molecular orders and reversible switching (at the single molecule level), by controlling the adsorption process of each isomer, which is rarely observed under ambient conditions.

Following this, I continued to use photoactive molecules on surfaces but this time by positioning them in a "vertical configuration" in order to generate new switches that can be used in metal/molecule/metal devices with molecular layers of $d = 3\text{nm}$ to 20nm thick. The thickness of the layer has an important influence on the transport according to the simplified theoretical equation of Simmons ($J = J_0 e^{-\beta d}$), where d is the thickness of the layer, J the current density and β is the attenuation factor). In addition, the control of the thicknesses will lead to the control of the transport regime, which will permit us to study the physical properties of the molecular junctions (MJs). We performed the metal/molecules/metal MJs by using gold surfaces, reducing diazonium salts to graft molecules with controlled thicknesses, and a tip of a conducting- Atomic Force Microscopy C- AFM to complete the MJs. First, we studied the behavior of MJs incorporating DAE oligomers with two different thicknesses. The junction formed by DAE 3nm gave an ON/OFF current ratio of 2-3, while the junction formed by DAE 9nm gave an ON/OFF ratio of 200-400. Secondly, we studied transport in bilayer molecular junctions made up of two different molecules (DAE/BTB) 9nm . ON/OFF ratios greater than 10 000 have been obtained reproducibly. The ratios were therefore further improved. This bilayer structure provides a novel way to fabricate switching systems and achieve high ON/OFF ratios rarely seen in photochromic based devices.

