1-2 FEBRUARY 2024 BORDEAUX, IECB

JOURNÉES GRAND SUD-OUEST

SOCIÉTÉ CHIMIQUE DE FRANCE

Programme & Book of abstracts

Bienvenue

Nous avons le plaisir de vous accueillir à l'Institut Européen de Chimie et Biologie pour les journées Grand Sud-Ouest 2024 de la Société Chimique de France.

Ces journées ont pour objectif de réunir le plus grand nombre de doctorants et de jeunes chercheurs afin de favoriser les échanges dans une zone géographique représentant un quart du territoire français. Elles visent à rassembler la communauté des chimistes des régions Occitanie et Nouvelle Aquitaine, dans un esprit de transversalité thématique.

Le programme scientifique a été préparé conjointement par les 3 sections régionales (Aquitaine, Occitanie Pyrénées et Occitanie Méditerrannée) s'associant à l'organisation de ces journées, avec des conférencières et conférenciers de renom dans des domaines tels que la méthodologie de synthèse, la catalyse, la chimie théorique, la chimie physique, la chimie bioorganique, la chimie du solide, la chimie supramoléculaire et les polymères. Nous aurons aussi le plaisir de recevoir Alexandre Pons, chercheur à l'Institut des Sciences de la Vigne et du Vin lors d'une conférence Grand Public intitulée : *Signature moléculaire et marché expérimental. De Bordeaux à la Napa Valley, l'arôme des vins à l'épreuve du changement climatique*.

Le programme comprendra également 36 communications orales pour offrir aux doctorants, post-doctorants et chercheurs l'occasion de présenter leurs travaux dans le cadre de sessions thématiques. Les sessions posters organisées simultanément aux pauses donneront à tous les participants l'occasion d'échanger plus librement dans un climat convivial. Pour optimiser leur visibilité, les posters feront l'objet de flash-communications avant ces sessions. En outre, grâce notamment à la générosité des sponsors, 4 prix seront décernés: 2 prix pour des communications orales et 2 prix pour des posters, et un ouvrage scientifique sera offert à chaque lauréat et lauréate. Huit exposants seront également présents sur site.

Nous sommes très reconnaissants à l'IECB de nous accueillir et nous remercions également tous les sponsors industriels et académiques pour leur générosité et leur soutien.

Nous espérons que ces journées favoriseront votre ouverture à de nouveaux domaines de la chimie, mais aussi l'échange d'idées en vue de collaborations et de développements futurs.

Le comité d'organisation des Journées Grand Sud-Ouest 2024 de la SCF

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RÉGION Nouvelle-Aquitaine

	Jeudi 1 Février (IECB)	
10:30	Accueil et Introduction (Amphi IECB) – **Laurent Chabaud**	
10:45	**Conférence Plénière 1** (Amphi IECB) – **Laure Monconduit**	
11:30	Présentation sponsors (5 min x8) + flash comm. 1 min x 20 (Amphi IECB)	
12:30	Repas & session Poster (La Vague, Hall)	
	Session 1 (Amphi IECB)	**Session 2** (Salle Haut-Brion)
14:00	**OC1 –Naveen Gupta**	**OC6 – Karine Abou Ezze**
14:15	**OC2 – Morgan Wloch**	**OC7 – Yuhan Huang**
14:30	**OC3 – Tiejun Li**	**OC8 –Hani Farhat**
14:45	**OC4 – Kevin Peyraud-Vicré**	**OC9 –Robin Hess**
15:00	**OC5 – Sandee Mummadi**	**OC10 –Yaidel Toledo-Gonzalez**
15:15	**Conférence Plénière 3** (Amphi IECB) – **Sylvain Caillol**	
16:00	Pause-café (La Vague, Hall)	
16:30	**Conférence Plénière 3** (Amphi IECB) – **Claire Kammerer**	
	Session 1 (Amphi IECB)	**Session 2** (Salle Haut-Brion)
17:15	**OC11 – Yu Zou**	**OC15 – Gary Cooney**
17:30	**OC12 – Jordan Lehoux**	**OC16 –Vivien Willems**
17:45	**OC13 – Oussama Fayafrou**	**OC17 – Kamolchanok Sarisuta**
18:00	**OC14 – Chloé Courdurié**	**OC18- Ruben De Barros**
18:15	**Conférence Grand Public** (Amphi 1, ENSMAC) – **Alexandre PONS**	
19:15- 21:15	Wine and Cheese, Session poster (La Vague, Hall)	

	Vendredi 2 Février (IECB)	
09:00	**Conférence Plénière 4** (Amphi IECB) – **Sami Lakhdar**	
	Session 1 (Amphi IECB)	**Session 2** (Salle Haut-Brion)
09:45	**OC19 – Etienne Bequet-Ermoy**	**OC23 – Romain Hello**
10:00	**OC20 – Naoual Bakhrou**	**OC24 – Nicolas Martin**
10:15	**OC21 – Guillaume Compain**	**OC25 – Benoit Odaert**
10:30	**OC22 – Ilan Garcin**	**OC26 – Jorge Juan Cabrera-Trujillo**
10:45	Pause café (La Vague, Hall)	
11:15	**Conférence Plénière 5** (Amphi IECB) – **Danielle Laurencin**	
12:00	Repas & session Poster (La Vague, Hall)	
13:30	**Conférence Plénière 6** (Amphi IECB) – **Sébastien Bontemps**	
	Session 1 (Amphi IECB)	**Session 2** (Salle Haut-Brion)
14:15	**OC27 – Mattéo Cayla**	**OC32 –Guillaume Gimenez**
14:30	**OC28 – Romain Larrieu**	**OC33 – Ambreen Ambreen**
14:45	**OC29 – Arthur Lamouroux**	**OC34 – Alexis Maillard**
15:00	**OC30 – Khaled Al Yaman**	**OC35 – Simon Colanges**
15:15	**OC31 – Luc Soliman**	**OC36 – Grégoire Boé**
15:30	Pause café (La Vague, Hall)	
16:00	**Conférence Plénière 7** (Amphi IECB) – **Karinne Miqueu**	
16:45	**Conférence Plénière 8** (Amphi IECB) – **Frédéric Friscourt**	
17:30-17:45	Remise des prix - Conclusion (Amphi IECB) – **Laurent Chabaud**	

INVITED CONFERENCES

Jeudi 1er Février

Laure Monconduit, ICGM, Montpellier
Du lithium, au sodium puis potassium pour les batteries ??

Sylvain Caillol, ICGM, Montpellier
From Biobased Phenols to Sustainable Polymers: A Platform Approach

Claire Kammerer, CEMES, Toulouse
Design and synthesis of molecular machines for mechanical studies at the single-molecule scale

Alexandre Pons, ISVV, Bordeaux
Signature moléculaire et marché experimental - De Bordeaux à la Napa Valley, l’arôme des vins à l’épreuve du changement climatique

Vendredi 2 Février

Sami Lakhdar, LHFA, Toulouse
New Polar and Radical Methods for the Formation of Carbon-Phosphorus Bonds : A Mechanistically-Driven Approach

Danielle Laurencin, ICGM, Montpellier
New roadmaps for ^{17}O NMR

Sébastien Bontemps, LCC, Toulouse
Bis(boryl)acetal as key intermediates to use CO_2 as a C_n source

Karinne Miqueu, IPREM, Pau
New insights in gold chemistry. Contribution of the computational chemistry to the understanding of mechanisms and the description of new bonding situations.

Frédéric Friscourt, IECB/ISM, Bordeaux
Exploiting Bioorthogonal Reporters for Controlling the Processing of Sialosides by Glyco-enzymes in Living cells

Journées Grand Sud-Ouest de la Société Chimique de France
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Du lithium, au sodium puis potassium pour les batteries ??

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Aujourd'hui, près de 30 ans après sa commercialisation, la technologie Li-ion semble atteindre une valeur limite de densité d'énergie.[1] En parallèle le marché des batteries Li-ion (LIB) a décuplé au cours des deux dernières décennies avec le développement des smartphones et des véhicules électriques, et les ressources des matériaux d'électrode des LIBs s'épuisent. L'urgence est donc au développement de moyens de stockage électrochimique de l'énergie alternatifs aux LIBs. Dans ce contexte, de nouvelles technologies de batteries sont attendues, et certaines émergent déjà, comme les batteries Na-ion (NIB).[2] Au regard de la classification périodique, le sodium apparait comme le candidat le plus proche pour remplacer le lithium. Bien que présentant de nombreuses similitudes, le sodium est trois fois plus lourd que le lithium, possède un rayon ionique plus important et un potentiel du couple Na^+/Na plus élevé que celui de Li^+/Li. Par conséquent, les densités d'énergie théoriques des NIBs sont inférieures à celles des LIBs. Par contre le sodium est beaucoup plus abondant, et les prix des précurseurs sodés très avantageux ; dès lors le plus faible coût de revient de ces systèmes pourrait être un avantage pour leur utilisation, notamment pour du stockage stationnaire de l'énergie. Si de nombreuses similitudes ont été observées entre les LIBs et NIBs, des différences notoires apparaissent également, par exemple le graphite, électrode négative phare des LIBs, présente une activité électrochimique réduite dans les NIBs. Ainsi le carbone dur (hard carbon, HC) est devenu l'électrode négative la plus employée dans les NIBs, et les matériaux d'alliages présentent également des performances très intéressantes. Consécutivement à ces succès, les sociétés comme Natron Energy, Faradion, Hina Battery, CATL ou encore la start-up française Tiamat commencent aujourd'hui à commercialiser les NIBs.

Plus récemment, l'intérêt pour un autre élément proche de Li et Na est apparu dans la littérature des batteries : le potassium. En plus de son abondance, le potassium, comme le sodium, présente l'avantage de pouvoir utiliser des collecteurs de courant en aluminium, beaucoup moins onéreux que ceux en cuivre, utilisés pour les LIBs. Le très bas potentiel standard du couple K^+/K (-2,9 V vs ESH), ainsi que ses propriétés de solvatation dans les électrolytes à base de solvants organiques (couramment utilisés dans les batteries) sont de réels avantages pour le fonctionnement à fortes densités de courant.

De récents résultats sur ces nouvelles batteries NIBs[3,4,5,6] et KIBs,[7,8,9] avec un focus particulier sur les électrodes négatives, seront décrits, tant au niveau de leur performances que des mécanismes électrochimiques mis en jeux.

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From Biobased Phenols to Sustainable Polymers: A Platform Approach

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Recent years have witnessed an increasing demand on renewable resource-derived polymers owing to increasing environmental concern and restricted availability of petrochemical re-sources. Thus, a great deal of attention was paid to renewable resources-derived polymers and to thermosetting materials especially, since they are crosslinked polymers and thus cannot be recycled. Also, most of thermosetting materials contain aromatic monomers, able to confer high mechanical and thermal properties to the network. Therefore, the access to biobased, non-harmful, and available aromatic monomers is one of the main challenges of the years to come. Starting from phenols available in large volumes from renewable resources, our team designed platforms of chemicals usable for the synthesis of various polymers. Hence, we studied, tanins, lignin-derived vanillin, eugenol or cardanol. Various aromatic building blocks bearing polymerizable functions were synthesized: epoxy, amine, acid, carbonate, alcohol, (meth)acrylates... for obtaining corresponding polymers for various applications. At the end of the life of these materials, the recycling is also investigated.

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Design and synthesis of molecular machines for mechanical studies at the single-molecule scale

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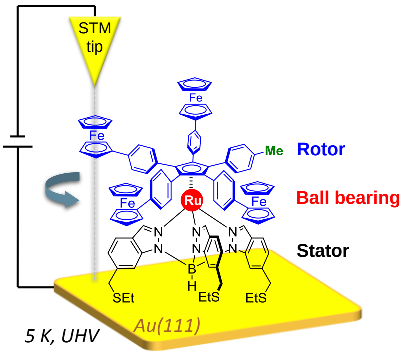
In a context of ultimate miniaturization, obtaining nanometer-sized devices and mastering their controlled motion triggered by an external stimulus is highly desirable.

Following a bottom-up approach, our group has designed and synthesized electron-fueled molecular motors, to be studied on surface at the single-molecule scale by Scanning Tunneling Microscopy (STM). One of these ruthenium-based organometallic motors, featuring a dissymmetric rotating subunit, has been shown to undergo unidirectional rotary motion upon excitation, with a direction of rotation governed by the location of the STM tip.[1]



Unidirectional and reversible rotation

The next milestone is now to master the assembly of several individual molecular machines into complex functional nanoscale machineries. In this regard, gear systems appear as essential elementary units to propagate the motive power delivered by a motor,[2] and we thus initiated a project to investigate the mechanical transfer of rotary motion between neighboring molecules.

In this presentation, our efforts towards on-surface molecular gearing will be detailed, with a special emphasis on the design and synthesis of star-shaped molecules, geometrically analogous to cogwheels, displaying diameters up to 5 nm.[3]

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Signature moléculaire et marché expérimental

De Bordeaux à la Napa Valley, l'arôme des vins à l'épreuve du changement climatique

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L'œnologie est une science relativement récente dont le sujet d'étude est la transformation du raisin en vin, sa stabilisation et son vieillissement. Elle est à la croisée de la chimie, de la biochimie, de la microbiologie et de la génétique. L'application des connaissances propres à chacune de ces disciplines a permis au fil des décennies, de mieux comprendre pour mieux maitriser les différentes étapes jalonnant l'élaboration des vins de qualité qu'ils soient blancs, rouges ou rosés. Ces acquisitions concernent par exemple la maitrise des fermentations alcooliques et malolactiques, l'extraction et la stabilisation de la couleur et des polyphénols ou encore la révélation du potentiel aromatique des raisins….Un des axes de recherches visant à améliorer la qualité des vins porte sur la compréhension des phénomènes chimiques et biochimiques impliqués dans la formation des tonalités aromatiques fruitées des vins rouges. Selon le niveau de maturité des raisins, les vins développent une large palette aromatique rappelant l'odeur de l'herbe coupée, le poivron, la fraise, le cassis ou encore le pruneau et la figue sèche, dont le travail de caractérisation moléculaire a permis d'identifier des principales molécules odorantes associées à chacun de ces descripteurs. Aujourd'hui, le changement climatique impacte fortement la physiologie de la vigne et par conséquent la maturité du fruit, sa composition et celle du vin.

Après un bref rappel des bases de la vinification nous présenterons les derniers résultats relatifs à l'étude de l'impact du changement climatique sur l'équilibre aromatique des vins rouges et de leur évaluation par les consommateurs. Une analyse comparative de l'évolution au cours du temps des vins de la Napa Valley et ceux de Bordeaux viendra étayer ces observations. Tout au long de cette présentation une attention particulière sera portée aux contributions respectives de la chimie analytique et de la chimie organique à la maitrise de la qualité olfactive des vins.

New Polar and Radical Methods for the Formation of Carbon-Phosphorus Bonds : A Mechanistically-Driven Approach

Sami Lakhdar

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Organophosphorus compounds are important scaffolds that have gained tremendous attention owing to their prevalence in various areas ranging from agriculture to medicine. Although there are many effective synthetic methods for forming carbon-phosphorus bonds, some of them are prone to the use of harsh reaction conditions.

The lecture will cover recent developments from our group that aim to provide practically simple methods for synthesizing organophosphorus scaffolds from readily available phosphorus sources. It will also underline the importance of physical organic tools in understanding the reaction mechanisms and the design of new transformations.

The concluding segment of the presentation will explore the photochemical activation of robust chemical bonds.

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Journées Grand Sud-Ouest de la Société Chimique de France
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New roadmaps for ^{17}O NMR

Danielle Laurencin,[a] Ieva Goldberga,[a,b] Jessica Špačková,[a] Rishit Yadav,[a] Adam Nelson,[a,b] Sébastien Mittelette,[a,b]
Nicolas Fabregue,[a] Philippe Gaveau,[a] Dorothée Berthomieu,[a] Thomas-Xavier Métro,[a] César Leroy,[a]
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Oxygen is everywhere. It is present in the vast majority of molecules and materials, forming covalent, ionic, coordination or hydrogen bonds with neighbouring atoms. Being able to finely identify oxygen bonding environments is thus important, in order to be able to rationalize and optimize the structure and properties of different systems. Because it is a *local* analytical probe, NMR spectroscopy naturally appears as ideally suited for this purpose. However, it intrinsically suffers from a very poor sensitivity, the natural abundance of the only NMR active isotope, oxygen-17, being only 0.04%. This implies that ^{17}O-labeling is most-often necessary to perform high resolution analyses.

Up until recently, the most-widely used ^{17}O-labeling protocols suffered from various drawbacks, including (very) high costs, long reaction times, and/or constraining chemical reactions or experimental set-ups. In 2017, our group in Montpellier demonstrated for the first time that synthetic procedures based on mechanochemistry are highly attractive for the ^{17}O-enrichment of a variety of organic and inorganic compounds, in a cost-effective and user-friendly way.[1] In this presentation, our most recent progress in this field will be presented, with examples showing that ^{17}O NMR can be key in solving the structure and dynamics within complex materials, including calcified biominerals such as those found in bone and kidney stones. [2]

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Journées Grand Sud-Ouest de la Société Chimique de France
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Bis(boryl)acetal as key intermediates to use CO_2 as a C_n source

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Photosynthesis is a major process enabling living organisms to use CO_2 as an energy carrier and a source of carbon. In this natural process, CO_2 is transformed into glyceraldehyde-3-phosphate, a C3 carbohydrate.[1] For chemists, such transformation is a great synthetic challenge, implying the unprecedented formation of polyol chain and of asymmetric carbon atom from CO_2 as the only source of carbon.

Few years ago, we started to study the hydroboration of CO_2[2] and notably reported its controlled 4 electron reduction to synthesize a large variety of products featuring new C-N, C-O and C-C bonds in using CO_2 as a C1 source.[3]

We report now that the selective hydroboration of CO_2 is a key step toward the use of CO_2 as a Cn source eventually leading to the first cell-free enantioselective transformation of CO_2.[4]

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Journées Grand Sud-Ouest de la Société Chimique de France
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New insights in gold chemistry.
Contribution of the computational chemistry to the understanding of mechanisms and the description of new bonding situations.

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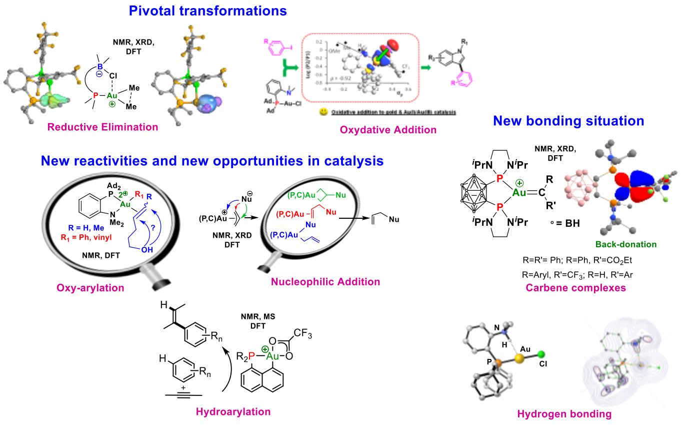
Long considered as a noble element, too inert and therefore useless in catalysis, the status of gold changed completely in the 1990s when interesting reactivities were discovered and applied in several reactions of industrial importance. Initially, the carbophilic properties of gold were widely explored for the activation of π-systems leading to the synthesis of highly functionalized molecules. More recently, new gold catalysts relevant to homogeneous catalysis were synthesized, extending the field of applications in organic synthesis.



With the aim to open new avenues in gold chemistry, in close collaboration with the team of D. Bourissou, we explore in depth the structures and reactivity of new gold complexes by combining experimental studies and DFT calculations. Thanks to rationale ligand design, pivotal transformations in many processes, such as oxidative addition or challenging Csp^3-Csp^3 reductive elimination, were made possible with this metal.[1]

These ligands opened up novel reactivities and new possibilities for catalysis. Recent and representative examples[2] are : i) the oxy-arylation of alkenes *via* Au(I)/Au(III) catalysis using hemilabile (P,N) ligand; ii) the hydroarylation of alkynes catalyzed by (P,C)-Au(III) complexes; iii) the nucleophilic addition of β-diketo enolates to π-allyl (P,C)-Au(III) complexes. Special interest has also been devoted to the in-depth description of unusual bonding situation[3] such as hydrogen bonding, carbenic complexes… In this oral presentation, the fruitful interplay between theory and experiments will be illustrated. The focus will be on the contribution of computational chemistry to these various topics.

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Exploiting Bioorthogonal Reporters for Controlling the Processing of Sialosides by Glyco-enzymes in Living cells

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Sialic acids are anionic carbohydrates generally found as terminal sugars of mammalian cell-surface glycoproteins and glycolipids. Sialo-glycoconjugates (also known as sialosides) are often key mediators of physiological and pathological events, including cell adhesion, host–pathogen interactions, and cancer progression.[1]

The bioorthogonal chemical reporter strategy, pioneered by C. Bertozzi (2022 Nobel Prize in Chemistry) which elegantly combines the use of metabolically labeled azido-sugars and highly reactive cyclooctyne probes, is emerging as a versatile technology for labeling and visualizing sialosides.[2] This strategy relies on the fact that bioorthogonal chemical reporters are highly reactive species while being biologically noninvasive.

During this talk, I will present our recent efforts to show that chemical bioorthogonal reporters may actually impact sialosides processing enzymes activity,[3] providing us with novel, more selective, chemical biology tools for studying the biological roles of cell-surface sialosides.

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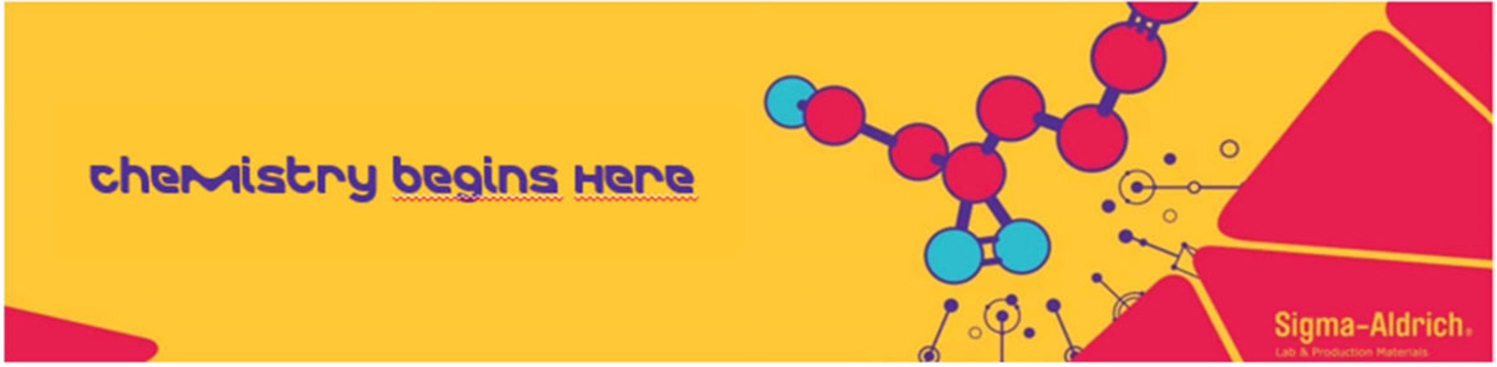

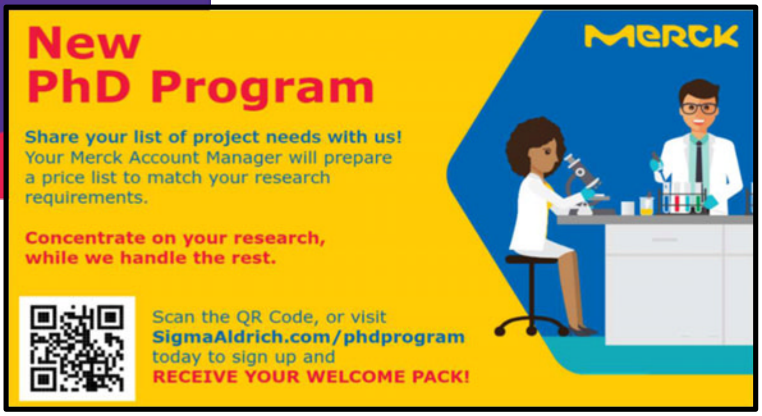


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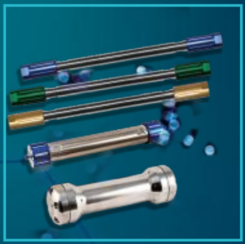

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ORAL COMMUNICATIONS

Session 1 (Amphi IECB)	Session 2 (Salle Haut-Brion)
Jeudi 1er février – 14h00 - 15h00	
OC1 –Naveen Gupta	OC6 – Karine Abou Ezze
OC2 – Morgan Wloch	OC7 – Yuhan Huang
OC3 – Tiejun Li	OC8 –Hani Farhat
OC4 – Kevin Peyraud-Vicré	OC9 –Robin Hess
OC5 – Sandee Mummadi	OC10 –Yaidel Toledo-Gonzalez
Jeudi 1er février – 17h15 - 18h15	
OC11 – Yu Zou	OC15 – Gary Cooney
OC12 – Jordan Lehoux	OC16 –Vivien Willems
OC13 – Oussama Fayafrou	OC17 – Kamolchanok Sarisuta
OC14 – Chloé Courdurié	OC18- Ruben De Barros
Vendredi 2 février – 9h45 - 10h45	
OC19 – Etienne Bequet-Ermoy	OC23 – Romain Hello
OC20 – Naoual Bakhrou	OC24 – Nicolas Martin
OC21 – Guillaume Compain	OC25 – Benoit Odaert
OC22 – Ilan Garcin	OC26 – Jorge Juan Cabrera-Trujillo
Vendredi 2 février – 14h15 - 15h30	
OC27 – Mattéo Cayla	OC32 –Guillaume Gimenez
OC28 – Romain Larrieu	OC33 – Ambreen Ambreen
OC29 – Arthur Lamouroux	OC34 – Alexis Maillard
OC30 – Khaled Al Yaman	OC35 – Simon Colanges
OC31 – Luc Soliman	OC36 – Grégoire Boé

Investigating Sequence-Structure-Activity Relationship and New Substrate Scope in Foldamer Catalysis

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The ability to synthesize artificial sequence-based oligomers that fold with high fidelity (i.e. foldamers) raises new prospects for developing strategies in asymmetric catalysis.[1] Preorganization of multifunctional catalysts through folding may enhance catalysis efficiency through cooperative substrate binding and minimization of the entropic cost of transition-state binding. In a previous account, we have shown that enantiopure foldamers can be used as H-bond donor organocatalysts in enantioselective C-C bond transformations.[2] In particular, we demonstrated that a catalytic system consisting of a chiral urea-based foldamer (H-bond donor component) and a simple tertiary amine (Brønsted base component) was able to promote the Michael reaction between enolizable carbonyl compounds and nitroolefins with excellent enantioselectivities, even at very low (up to 1/10000) chiral catalyst/substrate molar ratio. Compared to common bifunctional catalysts used for dual activation of nucleophile and electrophile, this synergistic system differs by allowing low chiral H-bond donor catalyst loading as well as high tunability to optimize the achiral Brønsted base for activation of pronucleophiles. These results were recently rationalized by DFT studies, which provided a first insight into the origin of enantioselectivity and synergistic activation at the two available catalytic NH sites (see Fig. 1).[3] In this work, we have further explored the interplay between sequence, structure and catalytic activity (both in terms of conversion and enantiocontrol) by introducing subtle variations at the first two urea positions to fine tune the catalytic site (geometry, acidity of NHs). To expand substrate scope, we have investigated the foldamer catalysts in Mannich reaction and addition of diphenyl phosphite to nitroolefins with satisfactory to good enantioselectivity and yields.

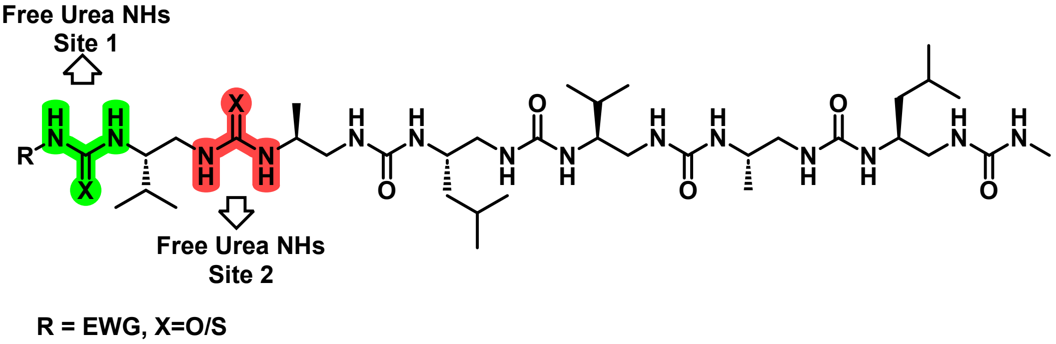

Figure 1

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Journées Grand Sud-Ouest de la Société Chimique de France
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Total synthesis of (+)-strepantibin A via hydroxylative phenol dearomatization mediated by chiral iodyl compounds

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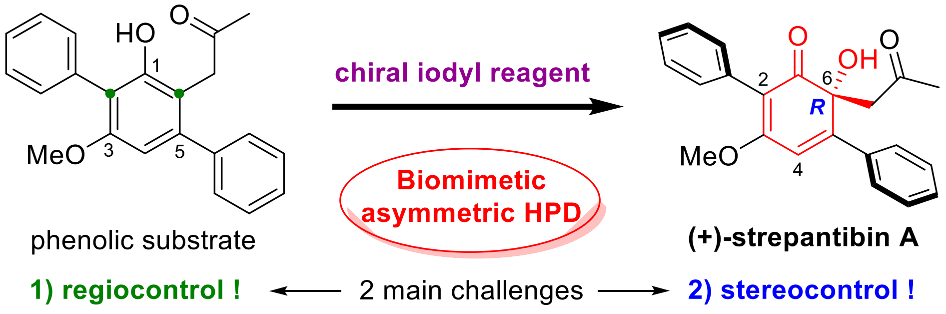
ortho-Quinols (*i.e.*, 6-alkyl-6-hydroxycyclohexa-2,4-dienone derivatives) are valuable intermediates in the biosynthesis of numerous natural products, and their versatile chemical reactivity allows for reaching complex structural architectures.[1] Strepantibin A is a non-dimerizing *ortho*-quinol, which was recently isolated from *Streptomyces* sp. associated with the larvae of the mud dauber wasp *Sceliphron madraspatanum.*[2] Promising *in vitro* inhibitory activity of this natural *ortho*-quinol was found against hexokinase 2, an enzyme responsible for tumor growth. Among many existing chemical transformations that allow the generation of *ortho*-quinols,[1] Hydroxylative Phenol Dearomatization (HPD) promoted by chiral hypervalent iodine (V) compounds, referred to as λ^5-iodanes or iodyl reagents, is a biomimetic reaction that we have been developing in our laboratory. A dearomative oxygen-transfer performed on an *ortho*-substituted phenol, produces *ortho*-quinols in a fairly well regio- and stereocontrolled manner. We thus relied on a HPD reaction as a key biomimetic transformation to achieve the first total synthesis of (+)-strepantibin A. The first challenge of our work was to set up an efficient way to access the *p*-terphenylic structure of the phenolic precursor of strepantibin A and analogues thereof. Previously reported home-made chiral λ^5-iodanes,[3] and new chiral iodyl reagents were synthesized and further evaluated on those phenolic substrates with the aim of promoting a regio- and stereocontrolled HPD reaction.



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Journées Grand Sud-Ouest de la Société Chimique de France
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Modular gold complexes: synthesis and catalytic properties

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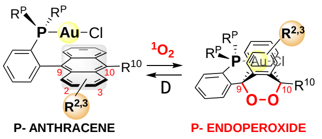
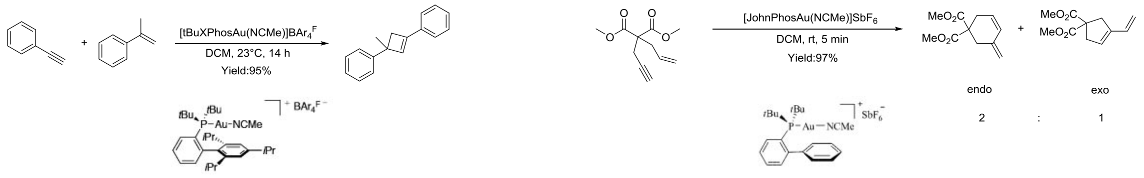
During the past decade, gold complexes have flourished as the most attractive catalysts for the electrophilic activation of unsaturated C-C bonds toward a large variety of nucleophiles[1]. While only three main approaches are developed in the field of switchable gold catalyst, light stimulus, redox stimulus and encapsulation[2].

To develop the switchable gold catalyst, we proposed a new type of gold complex with an anthracene core that can be added by singlet oxygen, as a chemical stimulus, to form an endoperoxide[3], showing changes of conformation and electron density.

We optimized the synthetic methods of the anthranyl and endoperoxide catalysts and studied the catalytic reactivity of the Ant/Endo pairs in benchmark reactions such as [2+2] cycloaddition of alkynes with alkenes and cycloisomerization of 1,6-enyne.

Proposal





Benchmark reactions

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Bio-inspired NHC-organocatalyzed reactions in aqueous droplets: towards a new chemistry of Life

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The formation of C-C bonds in water and in the absence of enzymes is a crucial step for the prebiotic synthesis of Life's biomolecules. Bio-inspired *N*-Heterocyclic carbenes (NHC) have recently been shown to catalyze C-C bond formation in water.[1] To go further, we aim in this work at demonstrating such a reaction within model protocells (rudimentary forms of compartments that could have played a role in the origin of Life) called "coacervates". Coacervates are micrometer-sized aqueous droplets readily formed in water by liquid-liquid phase separation (LLPS) when mixing two oppositely charged polyelectrolytes. These membrane-free droplets have the ability to spontaneously accumulate organic molecules[2], promote simple reactions such as polycondensation[3] and have been hypothesized to be viable protocell models. We show here that coacervates are a compatible reaction medium that can improve the efficiency of an organic reaction. Overall, by rationalizing the impact of coacervates on the selectivity and the efficiency of a model C-C bond forming reaction, our studies should provide new hypothesis for the emergence of complex molecules in simple protocells.

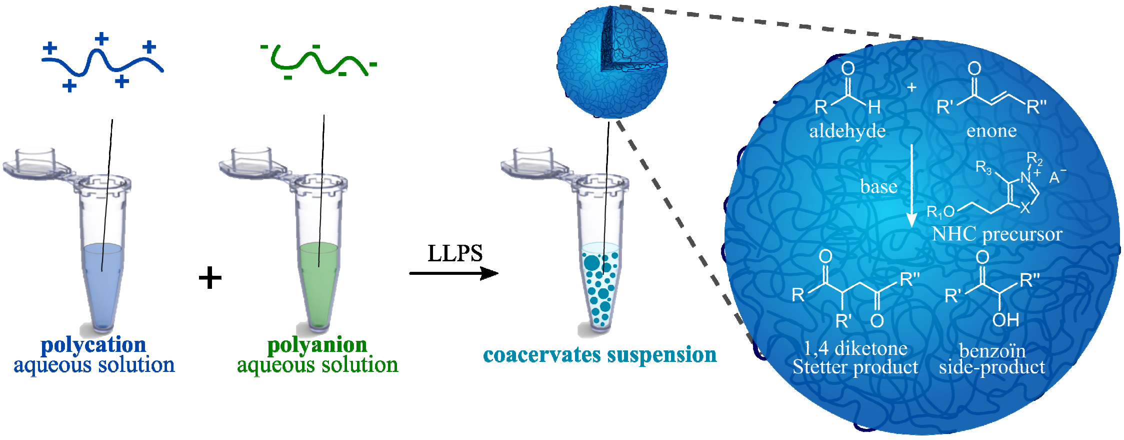

Figure: General strategy of our work

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STEREOSELECTIVE SYNTHESIS OF HEXA-, PENTA- AND TRIFLUORO LEUCINE

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Keywords: Stereoselective synthesis; fluorinated amino acids

Summary: Fluorinated amino acids are privileged structural motifs in various fields such as medicinal chemistry, chemical biology and supramolecular chemistry.[1–3] The hydrophobic properties of fluorine and its small Van der Waals radius are interesting features for modulating the lipophilicity[4] of amino acids while retaining their structural morphology.[3] Amino acids with polyfluorinated side chain have emerged as promising building blocks to modulate the properties of bioactive peptides.[1] In addition, fluorinated versions of proteinogenic hydrophobic residues have proved particularly well-suited to study the structure and function of proteins using ^{19}F NMR.[5] Among hydrophobic amino acids, leucine is the most frequently found in the hydrophobic core of proteins, within hydrophobic binding hot spots, or in contact with the lipid component of membranes. This amino acid is also found in many therapeutic peptides. In this respect, polyfluorinated leucines thus represent very useful tools. Although the enantiopure syntheses of several polyfluoroleucines were reported in the literature, some synthetic pathways have disadvantages, e.g. the number of steps, the use of expensive or gaseous reagents, and several derivatives were not reported so far.[5,6]

To address these current limitations, we recently developed a straightforward route to synthesize both (*S*)- and (*R*)-5,5,5,5',5',5'-hexafluoroleucine based on a stereoselective fluoroalkylation using a liquid and affordable hexafluorinated reagent.[7,8] We showed that changing the reaction conditions provides access to original (2*S*,4*S*)-5,5,5,5',5'-penta- and (2*S*,4*R*)-5,5,5-tri-fluoroleucine with excellent control of both chiral centers (Fig. 1).[9]

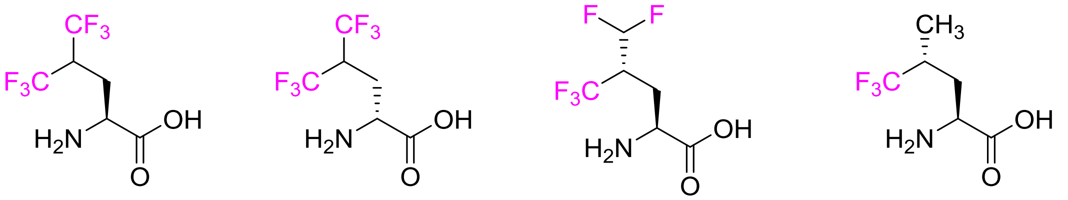

Fig. 1 Structures of (2*S*)- and (2*R*)-5,5,5,5',5',5'-hexa-, (2*S*,4*S*)-5,5,5,5',5'-penta and (2*S*,4*R*)-5,5,5-trifluoroleucine

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N-Heterocylic Carbene dimers as cross-linking points for recyclable functional polymer networks

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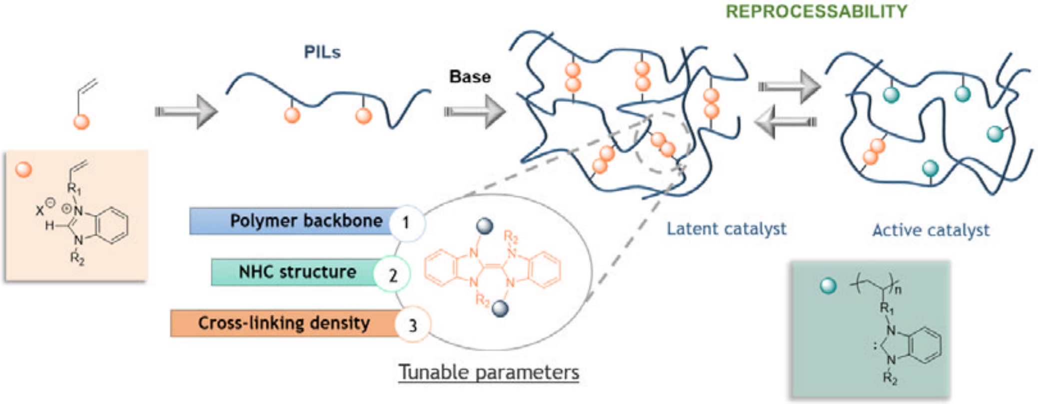
Polymer networks find widespread applications in a variety of areas, ranging from engineering polymers, to task-specific functional materials, such as biomaterials, sensors or heterogeneous catalysts. To solve their recyclability issue, the introduction of reversible chemical cross-links, which are dynamic by stimulation, attracted increasing attention over the past decade. Under specific stimuli, these cross-links can exchange each other, enabling the material to be reprocessed. The introduction of novel chemistries as dynamic cross-linking points is of high interest to broaden the scope of functional recyclable materials. N-Heterocyclic carbenes (NHCs) enable to achieve breakthrough in molecular synthesis, being used both as organocatalysts and powerful ligands. Their versatility has also been proven in polymer science. For instance, in 2006, Bielawski dimerized bis-NHC to form thermoreversible polymers. This thermoreversibility was provided by the carbene/dimer equilibrium, which can be modulated by temperature.[1] [2] The aim of this project is to introduce NHC dimers as dynamic cross-linking point for the production of reprocessable functional materials.

For this purpose, the optimal conditions to prepare NHC dimers by deprotonation of benzimidazolium salts have been investigated on small molecular analogues. To study their dynamic exchange, a cross-over reaction between two dimers featuring different substituents was performed. The successful results proven by NMR spectroscopy and mass spectrometry, granted us the ability to shift to the macromolecular scale. Following the same methodology, poly(ionic liquids) (PILs) bearing benzimidazolium pendant functions were deprotonated in the presence of a base to generate poly(NHC)s. Upon this reaction, the NHCs dimerized to yield a cross-linked polymer. Their thermo-mechanical propertie of the networks, as well as their self-healing ability, provided by the dimer metathesis reaction, were investigated. Additionally, the catalytic activity of the polymer networks was studied. Indeed, upon thermal stimulus, the NHC dimers dissociated to form NHCs, which are interesting organocatalysts, for instance in the benzoin condensation reactions.[3] Thus, the synthesized polymer networks meet requirements of modern applications, such as self-healing capacity and catalytic activity.



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Journées Grand Sud-Ouest de la Société Chimique de France
1-2 Février 2024, Bordeaux

Gold-coated AFM-based TERS Tips via Electrochemical Fabrication: From Air to Liquid Applications

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Nanoscale analysis remains an essential challenge for areas such as molecular electronics, materials, biophysics, and biology. Tip-enhanced Raman spectroscopy (TERS) has gained considerable interest due to its nanoscale spatial resolution, high sensitivity, and ability of simultaneous topographic and spectroscopic imaging.[1] By using a sharp metallic nanotip to confine and enhance the light field near the tip apex, a single hot-spot is excited and nanoscale chemical imaging is achieved.[2] Several physico-chemical methods have been developed to fabricate modified AFM-based TERS tips such as vacuum evaporation, chemical deposition, nanoparticle attachment, and microfabrication methods.

TERS active AFM-based TERS tips were fabricated by gold electrodeposition methods, by controlling the applied potential and time.[3] Depending on the thickness of the gold layer, the TERS tips exhibited various radii of curvature at their apexes and different plasmonic properties. These tips demonstrated promising performances for amplifying the Raman signal of carbon nanomaterials (such as carbon nanotubes and graphene) in air and biomolecules (such as $A\beta_{1-42}$ amyloid fibrils) in an aqueous medium, at relatively low cost. TERS measurements in liquid are technically more complex than their homologues in air, but they reduce the risk of sample damage due to the more efficient dissipation of the laser-induced thermal heating in liquid compared to air. Moreover, they are mandatory to explore in a more realistic manner interactions between biological systems. Here, we will show that our gold-electrodeposited tips can be convenient for TERS imaging of $A\beta_{1-42}$ amyloid fibrils in a liquid environment, and thus to obtain colocalized chemical, structural and morphological information on these biomolecules with nanoscale spatial resolution.

These results show that our electrochemical methods can constitute easy and powerful tools to fabricate metallic coated AFM-based TERS tips for applications in air and in liquid, and especially to characterize protein and peptide structures, such as amyloid aggregates. In the future, our methods will be further optimized and tested on other biological samples (e.g. membranes and cells).

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Journées Grand Sud-Ouest de la Société Chimique de France
1-2 Février 2024, Bordeaux

Advanced Surface Shielding: Atomic Layer Fluorination for Cathode Material Protection in Lithium-ion Batteries

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High-voltage Lithium Nickel Manganese Oxide (LNMO : $LiNi_{0.5}Mn_{1.5}O_4$) has attracted widespread attention as a promising cathode material for the next generation LIBs[1] due to its numerous advantages such as a three-dimensional spinel structure that improves the flow of lithium ions with open Li^+ sites[1], high operating voltage (~4.7 V vs. Li/Li^+), and energy density[1], with a theoretical capacity of 147 $mAh.g^{-1}$. However, the use of LNMO in batteries still faces several obstacles that hinder its widespread adoption. These obstacles include reactions with electrolytes at high voltages, leading to the loss of active Li^+ ions and the dissolution of the LNMO cations. These issues result in capacity fading over time during long-term battery cycling. Despite these challenges, efforts are being made to improve the practical applications of LNMO[2]. Surface coating with fluorine atoms proves to be an effective solution to mitigate the issues hindering its practical applications. This can be achieved through a simple process using xenon difluoride (XeF_2) as a fluorination agent and has been shown to enhance both high-rate cycling stability and long-term cycling stability[3].

In the GANDALF project, we achieved the surface fluorination of LNMO through an innovative *atomic-layer fluorination* process using XeF_2. A series of LNMO-Ft samples were prepared by decomposition of XeF_2 using different fluorination times (Ft) ($30 \text{ min} \leq Ft \leq 210 \text{ min}$). The preservation of the spinel structure after fluorination was confirmed by X-ray diffraction (XRD). The XPS analyzes were carried out on bare and fluorinated particles with the aim of precisely characterizing the electronic structure of their surfaces, the fluorination mode and its impact on the LNMO materials surfaces. The analysis revealed the formation of the Li-F bond for $Ft \geqslant 60$ min. After fluorination ($Ft \geqslant 60$ min) a partial change of the Mn environment was confirmed by the Mn3p spectra and shows the coexistence of $Mn^{3+}/Mn^{4+}/MnO_xF_y$ on the surface and the energy shift in Ni3p suggested the presence of NiO_xF_y bond. The investigation of the fluorine diffusion in depth and its spatial distribution, using AES (Auger Electron Spectroscopy) and SAM (Scanning Auger Microscopy) analyses were conducted on the highest fluorinated LNMO particles both before and after cross-sectioning (cp). The results highlight the exclusive presence of fluorine at the periphery of the particle, forming a shell-like fluorinated layer.

Analyzing the nonfluorinated LNMO electrode at the open circuit voltage and again after a charge/discharge cycle allowed investigation of the chemical composition of the *cathode-electrolyte interphase layer* (CEI). A comparison between the pristine LNMO electrode with the fluorinated one at Ft = 210 min revealed the impact of the fluorination layer on the final chemical composition of the SEI.

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Journées Grand Sud-Ouest de la Société Chimique de France
1-2 Février 2024, Bordeaux

Orchestrated Motions of Macrocycle and Helix in a Foldarotaxane Molecular Machine

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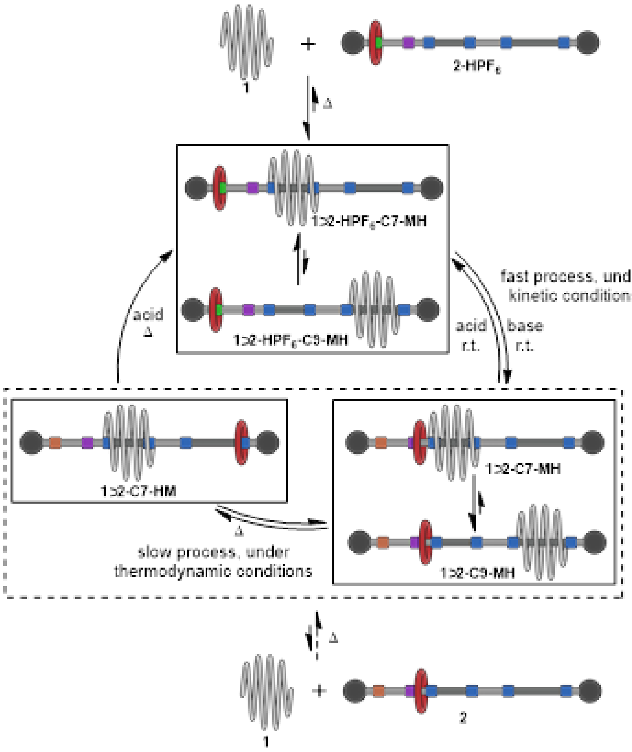
Pseudo-rotaxanes and kinetically unstable rotaxanes such as foldarotaxanes provide important insight into fields like molecular machines, nanoscience and nanotechnology. They are formed by dynamic self-assembly, meaning that they are not irreversibly interlocked and their associated components can be replaced.[1] Foldarotaxanes may have a long lifetime, as the winding and unwinding of the helix around the axle of the rotaxane has to overcome a kinetic barrier. Therefore, well-defined molecular motion is possible before dissociation of the components occurs.[2] Recently, it has been shown that the winding and the compartmentalisation of a helix and a ring, can be influenced by each other.[3]

Herein, the synthesis of a foldarotaxane and its operation as a two cascading triggers-based molecular machine were performed. The pH-dependent localization of the macrocycle along the thread was utilized to modulate the association between the foldamer and its sites of interaction belonging to the rotaxane axle. Under kinetic control, the pH-responsive translation of the macrocycle along the encircled thread triggered the displacement of the helix through gliding process. Under thermodynamic control, when unfolding and refolding of the helix around the rotaxane's axle was accelerated, system relaxed toward the equilibrium state upon variation of pH, along with the helix acting as a supramolecular kinetic barrier that may trap the macrocycle over a thread region for which it has less affinity. To resume, under kinetic control, the macrocycle enforces the preferential position of the helix along the axle, while, conversely, under thermodynamic control, the high affinity of the helix for its station enforces the partial position of the macrocycle away from its best site of interaction.



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Journées Grand Sud-Ouest de la Société Chimique de France
1-2 Février 2024, Bordeaux

Urea-based foldamer catalyst for C-C bond forming in asymmetric Michael reaction: a DFT investigation

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Bioinspired urea-based oligomers that fold with high fidelity (foldamers (**F**)) have been proven as robust alternatives to metal based asymmetric catalysis, able to catalyze challenging C-C bond forming reactions with high enantioselectivity, and loadings as low as 1:10000 chiral catalyst/substrates molar ratios (see Figure 1).[1] Yet, studies developed at the atomistic level are necessary to understand the characteristics and function of the foldamers as catalysts. A DFT based Global Optimization procedure has been performed here to find the low-lying molecular arrangements in the conjugate addition of dimethylmalonate (**M**) to (1E)-3-methyl-1-nitrobut-1-ene (**N**), followed by the characterization of the reaction energetic profile. It was found that **N** prefer the second site of the foldamer as H-bond donor, and **M** the first site. Therefore, the H-bond donor capabilities of the first two ureas were characterized by estimating their pKa.[3] In general, the interactions stabilizing the system are electrostatic and noncovalent, with a set of Van der Waals interactions well defined between **N** and the phenyl group in **F**. The energetic profile revealed that enantiomer R was predominant over the enantiomer S, which is in agreement with the experimental observations. The enantiocontrol was then identified to be related with specific geometrical parameters of the catalyst. These results rationalize the structure-properties relationship of the catalyst, and present for the first time a conclusive identification of its function. Further improvements to the catalytic properties of **F**-like foldamers are now possible.

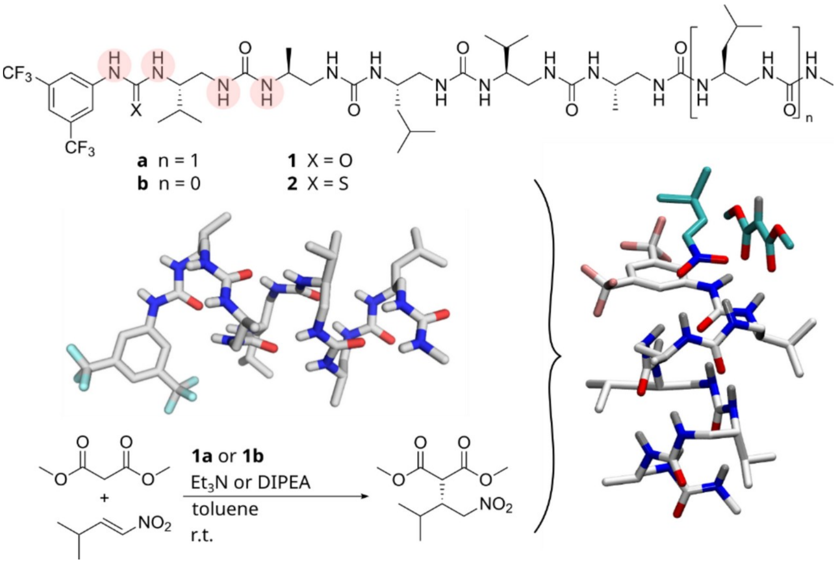

Figure 1. Formulae of helical foldamers 1 and 2, X-ray structure of 1a and their use as hydrogen-bond donor chiral catalyst in the enantioselective conjugate addition of dimethylmalonate to (1E)-3-methyl-1-nitrobut-1-ene.[1,2]

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Journées Grand Sud-Ouest de la Société Chimique de France
1-2 Février 2024, Bordeaux

Which Dendrimer to Attain the Desired Properties
Focus on Some of Their Applications

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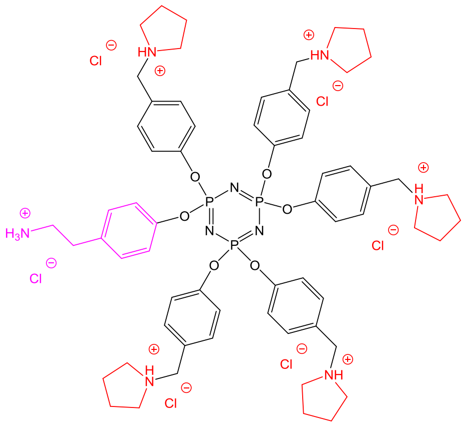
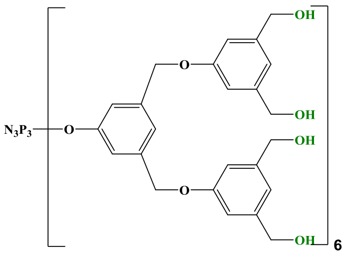
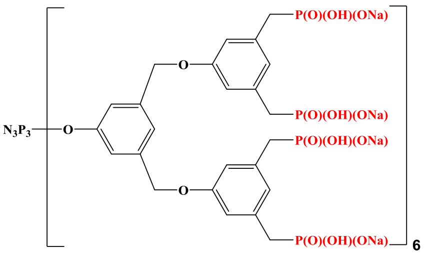
Dendrimers - ubiquitous types of precisely defined polymers and specially phosphorus dendrimers or dendrons are attracting a large interest due to the possibilities to use them for many applications in different fields ranging from biology, nanomedicine, catalysis or nanoscience in general, playing with their size, topology, molecular weight, nature of their branches or their surface, solubilities etc…Many applications were developed with phosphorus dendrimers of high generation alone or in combination with for example drugs in contrast with those obtained with low generation dendrimers.

The purpose of the presentation is to illustrate some unprecedented properties and applications of new cationic, neutral or anionic phosphorus dendrimers of generation 0 or 1. As an example the synthesis of water soluble unsymmetrical cationic phosphorus dendron as a non-viral vector to transfer microRNA inhibitor for breast cancer will be presented.[1] Indeed the corresponding complexes dendrimers/miR-30d show in vivo a significant effect in inhibiting 4T1 tumor cell proliferation.[2]

Original synthesis of new neutral or anionic phosphorus dendrimers were also reported and preliminary results concerning their properties investigated.







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Journées Grand Sud-Ouest de la Société Chimique de France
1-2 Février 2024, Bordeaux

Multi-step total synthesis of phenolic phytoprostanes

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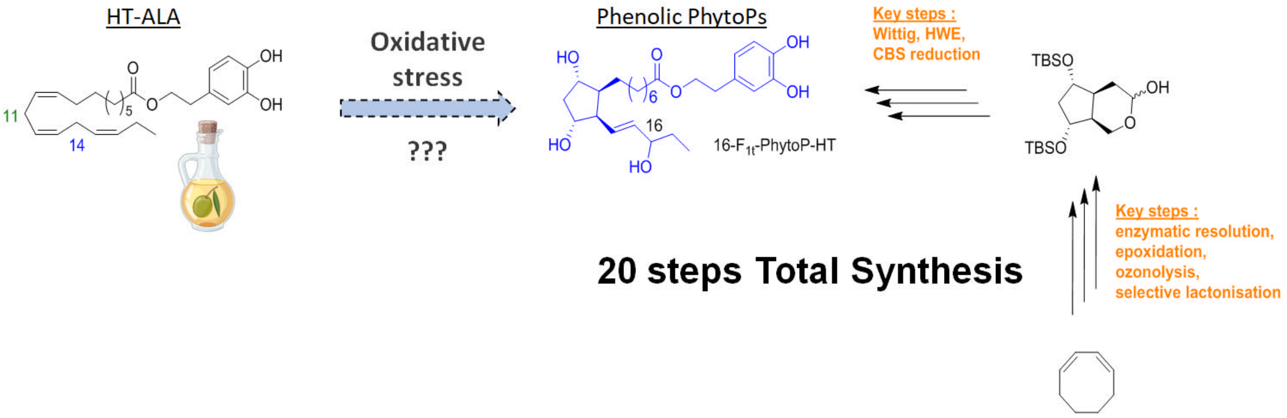
Lipophenols, polyphenolic compounds acylated by a fatty acid, have recently been identified in food matrices naturally rich in both polyphenols and fatty acids, making them natural derivatives present in human diet. The identification of natural lipophenols is particularly relevant to understand their pharmacological actions, metabolism or to use them as analytical standards.

As an example, hydroxytyrosol (HT) linked to polyunsaturated fatty acids (PUFA) is naturally present in extra virgin olive oil (EVOO)[1] and should participate to its antioxidant properties. As a preliminary work, the chemical synthesis of HT lipophenols allowed UHPLC-MS/MS quantitative study in EVOO during a 12 months period, mimicking both commercial and inappropriate conditions of storage. The results highlighted HT-OA as a relevant marker for the monitoring of oil storage conditions and quality.[2] Based on this study, an emphasis was put on HT-ALA, exhibiting a different analysis pattern than its analogues. This result might be due to oxidation of this compound to form **phenolic phytoprostanes**. Phytoprostanes (PhytoPs) are non-enzymatic lipid peroxidation products coming from ALA, biomarkers of oxidative stress in plants.

This hypothesis was strengthened by the literature, showing that phytoprostanes coming from ALA were present in some vegetal oils,[3] as well as preliminary oxidation studies on HT-ALA in flask.
The first stereoselective total synthesis of phenolic PhytoPs as analytical standards was therefore performed in 20 steps with a 3% global yield (84% average yield by step) from commercially available 1,3-cylooctadiene. The lactol key intermediate was synthesized in 11 steps with controlled stereochemistry, which then allowed the introduction of the two side chains using Wittig and HWE reactions.



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Journées Grand Sud-Ouest de la Société Chimique de France
1-2 Février 2024, Bordeaux

Ruthenium(II) Bipyridyl Complexes with Phosphonium Ylide Ligands

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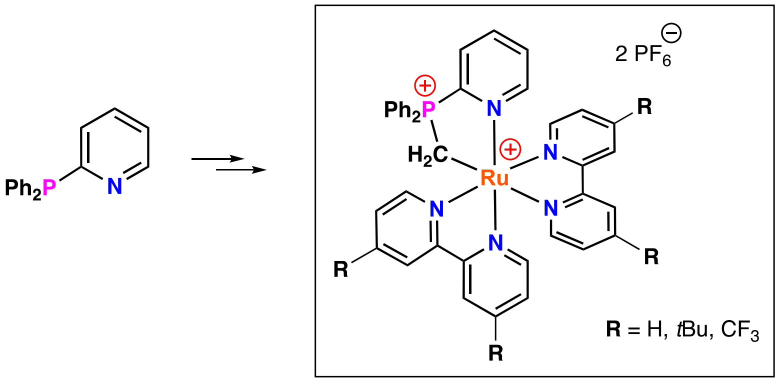
Taking advantage of their high chemical stability and the relative ease of modifying the nature of their ligands, ruthenium(II) bipyridyl complexes have been extensively studied for their unique redox and photophysical properties.[1] Given the beneficial effect of introducing electron-rich σ-donating N-heterocyclic carbene ligands (NHCs) such as the destabilization of ^{3}MC states with longer excited state lifetimes,[2] we considered the incorporation of phosphonium ylides in these octahedral metallic architectures, as another class of neutral carbon ligands characterized by superior σ-electron donating ability compared to NHCs.[3]

In this contribution, we report thus the straightforward preparation of the first ruthenium(II) bipyridyl complexes with the general formula $[Ru(C^\wedge N)(bpy\text{-}R)_2](PF_6)_2$ (R = H, *t*bu, CF_3) containing *C,N*-chelating pyridine-phosphonium ylide ligands from readily available 2-(diphenylphosphino)pyridine. Structural, spectroscopic, electrochemical and photophysical properties will be detailed. Application of these phosphonium ylide-based Ru(II) complexes in visible-light photoredox catalysis for the formation of C−C bonds through the Aza-Henry reaction will be also discussed.[4]



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Photoresponsive Self-Assembled Monolayers for data storage devices

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One of the challenges of our current time is to face the amount of information produced with new high density data-storage devices. One of the key to face it would be storing information at the molecular level. In this context, the project aims at designing photo-responsive Self-Assembled Monolayers (SAMs), functionalized with non-linear optical (NLO) photoswitches, as new data storage devices. Photoswitches, which commute reversibly from one structure to another under irradiation, can constitute a binary code and the difference between the non-linear optical responses of the two forms will allow to read the information by a non-destructive process. Selected as molecular bits, azobenzenes (AZO)[1] and Donor-Acceptor Stenhouse Adducts (DASA)[2] derivatives have been synthesized with an alkyne end, allowing their covalent grafting on an azide SAM platform. These two families were chosen because they have orthogonal photoswitching that allows independent control of both types of chromophores on the surface.[3] Once the best performing compounds from each family have been identified, SAMs mixing two types of photochromes will be developed to address the challenge of multi-encoding.

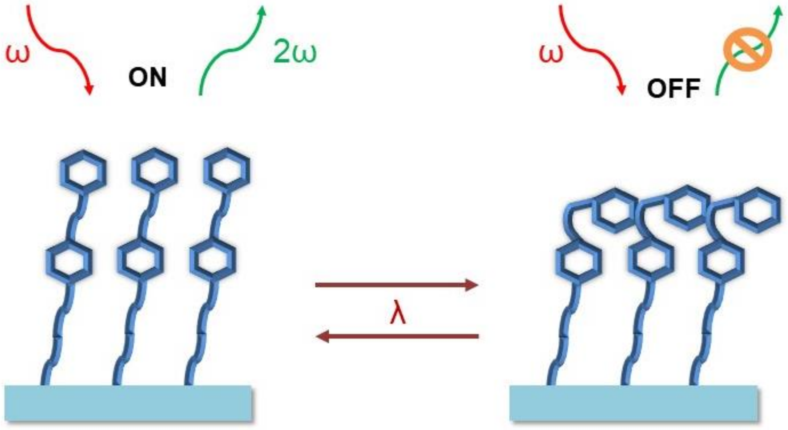

Figure 1 : Schematic representation of photoswitches grafted on a surface and able to switch between two forms with different NLO responses by irradiation.

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Journées Grand Sud-Ouest de la Société Chimique de France
1-2 Février 2024, Bordeaux

Nanoscale chemical imaging of biomolecules and biomaterials using tip-enhanced Raman spectroscopy

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Tip-enhanced Raman scattering (TERS) spectroscopy has unprecedented potential to provide nanoscale structural and chemical characterization of biomolecules compared to traditional diffraction-limited vibrational spectroscopies. An intense and confined electromagnetic field is generated at the metallised atomic force microscopy (AFM) tip apex by the excitation of the localised surface plasmon resonance (LSPR). This results in the high enhancement of the Raman signal of probed molecules in close proximity to the tip. The advent of total-internal reflection (TIR-) TERS geometry allows for electromagnetic enhancement factors higher than in traditional bottom-illumination TERS, all the while giving lower far-field signals of samples, high lateral spatial resolution, and facilitating tip-laser alignment.[1]

In my work, I used TIR-TERS to characterize amyloid fibrils formed by aggregation of microtubule associated protein Tau, which is an intrinsically disordered protein associated with several tauopathies such as Alzheimer's disease. The formation of pathogenic Tau fibrils is still poorly understood with little known about the exact nature of incorporation of negatively charged cofactors such as heparin, lipids, or RNA. [2] Fibrils formed from the disease-associated mutation of P301L of the full-length Tau with polyadenosine (polyA) cofactor were studied under 561 nm laser excitation using Ag-coated AFM silicon tips. PolyA incorporation into the fibril structure was observed by correlation of the protein amide I bands with the characteristic ring breathing mode of adenine. Positively charged amino acids lysine, arginine, and histidine that are hypothesized in cofactor binding were also shown to correlate with polyA and core β-sheet domains.[3]

In the prospect to characterize amyloid species interacting with biological membranes using TERS, the development of TERS in liquid media is mandatory. To date, most TERS experiments of biomolecules have been performed in dry conditions. Liquid applications remain challenging due to delamination of metal-coated TERS tips, optimisation of the photon excitation and collection, and the laser focalisation on the tip end through a specialised liquid cell.[1] I will present our preliminary works to investigate self-assembled phospholipid monolayers using our liquid-adapted TIR-TERS system and how we overcame the inherent challenges of working in liquid media.

Journées Grand Sud-Ouest de la Société Chimique de France
1-2 Février 2024, Bordeaux

Phase-separation dependent active motion of Janus lipid vesicles

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Active colloidal particles serve as model systems to mimic the dynamical behaviour of biological microswimmers. These artificial microswimmers are capable of self-propulsion and directed motion driven by an external energy source, such as electric fields or chemical gradients. Despite efforts to include responsive materials to tailor the swimming behaviour of active colloids[1], the architecture of solid colloidal particles limits the versatility and functionality of these artificial microswimmers. Thus, there is a growing interest in soft artificial microswimmers that mimic the properties and the architecture of cell membranes.

Here we present the fabrication and actuation of Janus lipid vesicles as artificial microswimmers with reconfigurable dynamics, actuated with AC electric fields[2]. We fabricate phase-separating giant unilamellar vesicles (GUVs) from a ternary lipid mixture exhibiting phase separation at room temperature[3], leading to a Janus-like asymmetry of the GUVs. Upon application of an AC electric field between parallel electrodes the Janus vesicles exhibit self-propulsion via induced charge electroosmosis. We characterize the behaviour of these Janus GUVs over a range of AC field conditions and find rich dynamical behaviour not observed in hard Janus colloids. Remarkably, the fluid nature of the lipid membrane affected by the electric field leads to asymmetry-symmetry transient states resulting in run-and-tumble events supported by structure domain analysis. The tumble events lead to an enhanced reorientation of the vesicles motion, decoupled from thermal rotational diffusivity. Finally, we demonstrate that this system is viable for applications involving cargo transport and release due to its compartmentalized architecture. These simple, cell-inspired artificial microswimmers provide an alternative route towards creating motile artificial cells and soft microdevices.

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Journées Grand Sud-Ouest de la Société Chimique de France
1-2 Février 2024, Bordeaux

5-Methylene-1,3-Dioxane-2-One: A First Choice Comonomer for Trimethylene Carbonate and Functionalized via Thiol-ene Reaction for Tunable Degradation

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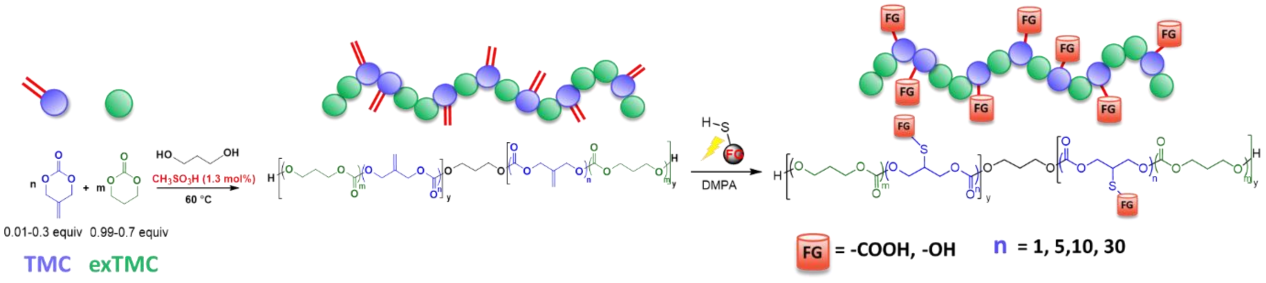
Aliphatic polycarbonates are attracting considerable attention not only in the medical field, due to their biodegradable character, but also for, packaging and other commodity applications, thanks to additional suitable physical properties.[1] Further developments in these areas require reliable access to a broad range of polycarbonates with different and well-controlled structures. One method to achieve this goal is the ring-opening (co)polymerization (ROP) of functionalized cyclic carbonates, which permits to tune the polymer properties by introducing lateral groups.[2] For instance, functionalized PTMC derivatives were reported as carrier for drug delivery thanks to their neutral degradation, low toxicity residues, and facile side chain modification in order to tune degradability.[3] Nevertheless, conventional syntheses of functionalized trimethylene carbonates (TMC) monomers require using toxic reagents and protection/deprotection reaction.[4]

To overcome this limitation, the 5-methylene-1,3-dioxane-2-one (exTMC, a six-membered ring cyclic carbonate bearing an exocyclic methylene group) was developed by our team using CO_2 as raw material in one-step reaction.[5] exTMC was then investigated as comonomer for TMC with the aim to prepare polycarbonates bearing unsaturated CC bond for further click thiol-ene functionalization. Methane sulfonic acid (MSA) was chosen as ROP organocatalyst to promote the copolymeriation of exTMC & TMC in a controlled manner leading to copolymers of adjusted composition and high randomness (reactivity ratios of 0.95-0.98 and 1.00-1.06 for exTMC and TMC, respectively). The post-modification on the exomethylene group by thio-ene reaction with functionalized thiols bearing non-protected hydrophilic functions improves the hydrophilicity and enable controlling the polymer degradation. The exTMC monomer avoids thus protection/ deprotection reaction and enables easy post-modification by numerous thiol derivatives which allow adjusting degradability properties.[5]



Scheme 1. Syntheses of PTMC-*co*-PexTMC and functionalization of PTMC-*co*-PexTMC *via* thiol-ene reaction

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α-GeO$_2$; un matériau piézoélectrique utilisable à très hautes températures pour des capteurs SAW passifs

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Le développement de nouveaux matériaux résistants à de très hautes températures (jusqu’à 1000 °C) pour les capteurs à ondes élastiques de surface (SAW) est aujourd'hui un domaine de recherche intensif. En effet, les secteurs industriels de l’automobile, du nucléaire et de l’aérospatiale sont fortement demandeurs de capteurs et d’actionneurs intégrés fonctionnant sur une plage étendue de températures qui implique de déporter l’électronique d’acquisition pour éviter de l’exposer à des températures rédhibitoires.

Dans le cadre du projet ANR OVERHEAT, l’étude, la conception et l’évaluation d’un capteur de température piézoélectrique SAW miniaturisé, opérant sans fils ni batterie, exploitable dans une gamme de très hautes températures (600–1000 °C) et dans des atmosphères oxydantes et/ou sous irradiation, sont en cours de réalisation. Ce capteur est basé sur le matériau piézoélectrique α-GeO$_2$ développé lors d’un précédent projet (ANR PIEMON). J’introduirai le matériau α-GeO$_2$, de structure α-quartz (groupe d’espace P3$_1$21 ou P3$_2$21), dont les constantes piézoélectriques à température ambiante sont parmi les plus élevées de la famille iso structurale du quartz. Puis, je détaillerai sa cristallogenèse par flux à haute température, l’étude des impuretés chimiques via la spectrométrie de masse à décharge luminescente, et sa stabilité structurale en température, étudiée par des mesures de diffraction neutronique en température jusqu’à 1000 °C (ILL, Grenoble). L’évolution des constantes piézoélectriques et des propriétés diélectriques jusqu’à 600 °C, mettant en évidence le potentiel de α-GeO$_2$ pour des applications dans des environnements sévères, seront présentées.

La conception d’un SAW nécessite de développer des des électrodes en peignes interdigités (IDT). Or, pour résister aux hautes températures, les électrodes en métal ne doivent pas se vaporiser, fondre ou diffuser. Le platine, déposé par épitaxie, limiterait ces effets qui induisent une dérive du signal piézoélectrique et donc, une instabilité du capteur. Nous avons donc initié une série de mesures (MEB, AFM, EDX et DRX) afin d’observer et caractériser la dégradation/tenue en atmosphère oxydante (air), à différentes hautes températures, d’un dépôt de Pt (différentes épaisseurs) sur substrat α-GeO$_2$. Ces résultats seront présentés couplés à ceux de l’effet d’un milieu radiatif (>1 MRad) sur la stabilité/dérive de la fréquence de vibration d'une lame orientée et métallisée (Pt) de α-GeO$_2$.

Je montrerai une première expérimentation, à températures modérées, de la propagation des ondes acoustiques de surface sur α-GeO$_2$ en utilisant des électrodes an aluminium qui valide le potentiel de ce matériau pour son intégration dans un capteur SAW passif.

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Metal free biaryls synthesis using boranes

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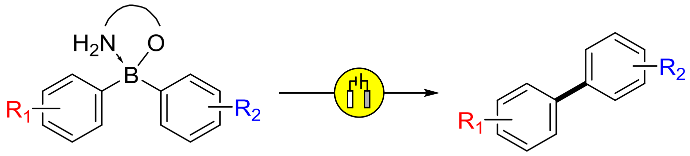
Cross-coupling reactions are ubiquitous in organic chemistry, thanks to their ability to form C–C bonds with broad scope using a transition metal catalyst. Expectedly, since their discovery in the 70s, extensive studies followed, leading to the Nobel Prize award (Heck, Negishi, Suzuki) in 2010.[1]

Nonetheless, with environmental concerns ever-growing, even established classics alternatives are worth looking into. The use of metal catalysts like palladium can lead to toxic waste generation. To address this issue, metal-free alternatives have been studied.[2] For instance, biaryls formation can be conducted under electrochemical conditions.[3] For example, the electrocoupling of tetrarylborate salts can lead to a variety of biaryls under transition metal-free conditions.[4] However, in this process two equivalents of aryl species are lost.

In collaboration with D. Didier's team, we looked for a greener alternative by replacing two of the aryl moieties of tetrarylborate salts by aminoalcohols. The reactivity of these organoborinates derivatives was investigated in homo- and hetero-electrocoupling conditions.



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Journées Grand Sud-Ouest de la Société Chimique de France
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Catalyseurs recyclables pour le clivage de liaisons C-O par transfert d'hydrogènes

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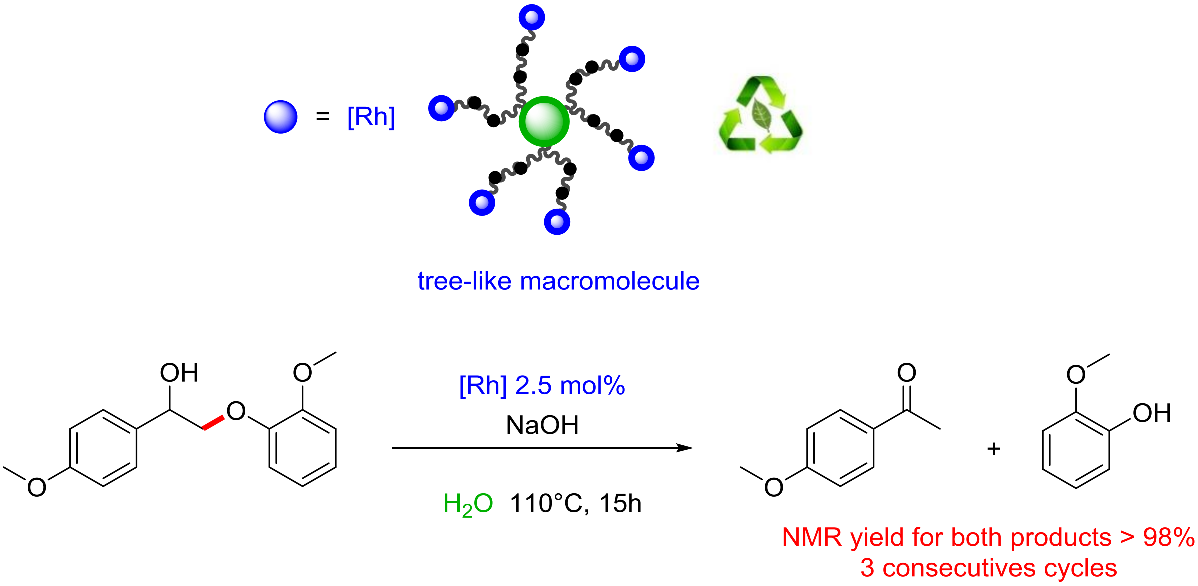
La lignine, biopolymère très abondant, constitue une source importante de noyaux aromatiques et une alternative aux ressources fossiles.[1] Dans ce domaine, l'un des verrous actuels consiste en la dépolymérisation efficace de cette lignine pour accéder à des molécules de faibles poids moléculaires.

Dans ce contexte, le but de ce projet consiste à découvrir des catalyseurs efficaces et innovants pour cliver des liaisons C-O, sur des molécules modèles de lignine. Les systèmes que nous avons étudiés sont à base de rhodium et procèdent par transfert d'hydrogènes. En outre, ils opèrent en conditions douces par rapport aux autres systèmes existants, qui requièrent souvent de fortes pressions d'hydrogène et des températures élevées.[2] Dans ce travail, nous proposons de greffer des complexes terpyridine-rhodium sur des macromolécules arborescentes. Le nanocatalyseur en résultant permet le transfert d'hydrogènes intramoléculaire à l'origine du clivage de la liaison C-O (Figure), avec une bonne activité et la possibilité de plusieurs recyclages sans perte d'activité.[3]



NMR yield for both products > 98%
3 consecutives cycles

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[3] publication en cours de rédaction

Covalent Peptide Inhibitors Targeting a His Residue: New Modalities to Block Protein-Protein Interactions

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Over the past decade, the development of covalent drugs has gained momentum with the approval of several Targeted Covalent Inhibitors (TCIs) in oncology and as antivirals.[1] Potential benefits of TCIs over non-covalent inhibitors are manifold. When forming an irreversible bond, the inhibitor is no longer in competition with natural binding proteins. Additionally, covalent inhibition can improve the inhibitory potency and selectivity, increase the duration of action, and reduce the emergence of resistance. Moreover, targeting extended protein-protein interaction interfaces with competitive small molecule inhibitors is not always achievable, and peptide-based inhibitors with an irreversible mode of action can be considered as emerging modalities for such targets. TCIs are generally targeted to cysteine, the most intrinsically reactive amino acid residue, yet the low abundance of free cysteine is a limitation to the development of covalent drugs. In contrast, there are only a handful of studies on the use of histidine as a nucleophile, as highlighted in a recent account,[2] its potential interest in drug discovery is largely overlooked. The fact that histidine is much less frequently targeted by covalent inhibitors compared to cysteine and even lysine may be attributed to its lower nucleophilicity, making it more challenging to target.

In recent years, our consortium has been exploring the potential of inhibiting the bacterial sliding clamp (SC),[3] an essential component of the bacterial replisome that has been identified as a relevant target for developing new antimicrobial agents. The *Escherichia coli* SC contains a histidine residue lining the binding site, largely conserved among Gram-negative and Gram-positive pathogens, which we thought could be exploited for covalent inhibition. In this work, we anticipated that the lower reactivity of histidine could also be counter-balanced by the precise positioning of mild electrophilic warheads proximal to the imidazole group of histidine using a structure-based design approach.[4] In this talk, I will present the latest results obtained in our lab.

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γ-Peptide foldamers for NHC organocatalysis

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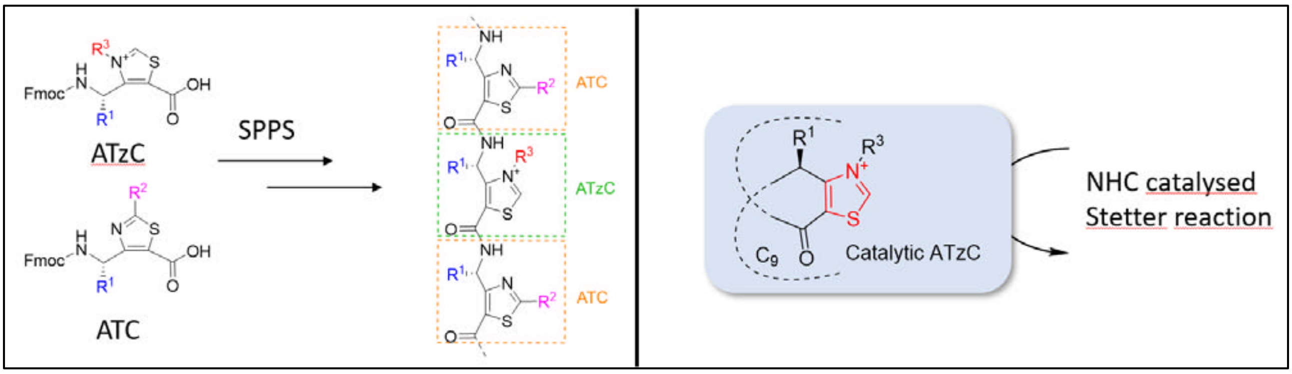
Foldamers were introduced by Gellman in 1998 as short oligomers that will able to fold in a predictable conformation in solution.[1] They can mimic the folding structure of short biomolecules, such as peptides. Recent research indicates that functional groups and catalytic sites can be attached to foldamers, making them a potentially promising class of organocatalysts. Over the past few years, Maillard's group has developed and optimized the synthesis of a type of foldamers built around a thiazole ring. These foldamers are made of monomers that are named ATC, which stands for 4-**A**mino(methyl)-1,3-**T**hiazole-5-**C**arboxylic acid. This kind of sequence adopts a well-defined 9-helix structure in solid state, organic solvents, and water.[2] Recently, Maillard's group and Campagne's group investigated the potential of ATC foldamers for enamine-type organocatalysis. They validated that they are promising tractable platforms for a nitro-Michael addition reaction.[3] In an effort to extend these results, it was intended to explore a new reactivity with ATC foldamers: NHC-type organocatalysis. To achieve this goal, a new monomer called ATzC, which is structured around a thiazolium ring was designed. The objective of this project is to develop a synthetic pathway to the newly designed ATzC monomer, build the ATC/ATzC foldamers by SPPS, and subsequently evaluate their performance as an organocatalyst in the Stetter type reactions.



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Development of electrostatic polymer complexes for the local and controlled release of actives.

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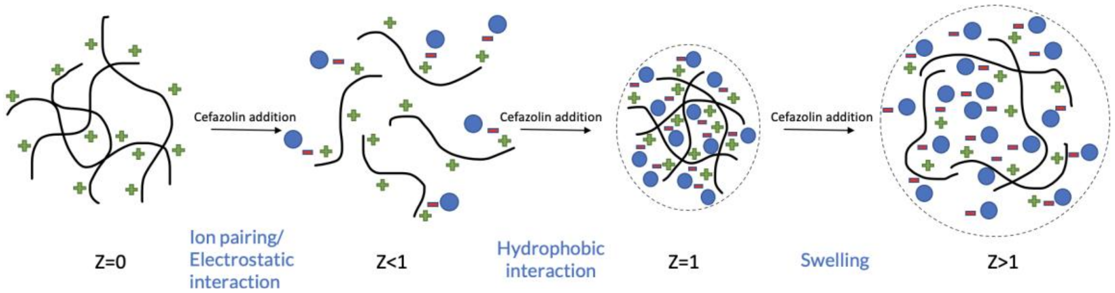
The topical route, used to obtain a local or systemic release of active agents, offers numerous advantages. It avoids the first metabolic barrier, acid pH and enzymes in the digestive tract, and offers greater surface availability. To prolong therapeutic efficacy, the topical route is generally presented in a galenic form such as patches, gels, lotions, creams, ointments, or sprays. The active molecules used in these types of devices range from anesthetics to hormones and antibodies[1, 2]. In this context, the design of a biodegradable polymer for the local controlled release of an antibiotic could lead to the development of a new technological platform meeting unmet needs.

The development of topical antibiotic delivery for prophylactic use could be a significant asset in the fight against infections and antibiotic resistance. To this end, cefazolin, a broad-spectrum cephalosporin antibiotic on the World Health Organization (WHO) Essential Medicine List, was chosen for further development. According to the WHO, antibiotic resistance is one of the greatest threats to global health, food security, and development today. Indeed, antibiotic resistance can affect anyone, at any age, in any country.

To stabilized and achieve sustained release of cefazolin, a negatively charged molecule at physiological pH, electrostatic complexes with a strong, synthetic and readily available cationic polyelectrolyte, poly diallydimethylammonium chloride (PDADMAC), were first investigated in aqueous media. Firstly, the complexation/self-assembly between cefazolin and PDADMAC was studied at different charge ratio, pH, salt concentration and temperature using complementary techniques based on different physical foundations (DLS/SLS, conductimetry, HPLC, SANS, ITC…). The kinetics of cefazolin release from the complexes was then evaluated. Finally, to strengthen the complexes, a strong polyanion, PSS (polystyrene sulfonate), was introduced into the formulation in an attempt to increase release time[3]. These results will be used to pursue our work on the development of bioresorbable and biocompatible formulations suitable for topical delivery.



Schematic representation of the complexation between PDADMAC and Cefazoline at different charge ratio Z

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Non-enzymatic oligonucleotide ligation in light-responsive coacervate droplets

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DNA contains the essential information to guide all the properties of cells, from their growth and division to their ability to adapt to their environment. Yet, the emergence of such a link between DNA and cellular properties at the origins of Life remains elusive. Coacervates are membrane-free microdroplets produced in water by associative liquid-liquid phase separation between oppositely charged polyions. These droplets represent viable models of protocells able to accumulate organic molecules and promote simple, non-enzymatic reactions.[1] [2] In a recent study, we have succeeded in demonstrating a coupling between the structure of coacervates and the non-enzymatic synthesis of polynucleotides.[3] Using chemically reactive oligonucleotides capable of end-stacking into long physical polymers and a molecular azobenzene cation, we have been able to produce three different coacervate phases that significantly enhance oligonucleotide polymerization, with a marked phase-dependent reaction efficiency. Dynamical modulation of coacervate assembly and dissolution via *trans-cis* azobenzene photoisomerisation is used to demonstrate cycles of light-actuated oligonucleotide ligation. Finally, changes in the length distribution of polynucleotides during polymerization induce phase transitions to produce multiphase coacervates via length-based DNA self-sorting. Overall, by combining a tight reaction-structure coupling and environmental responsiveness, our light-responsive reactive coacervates provide a novel general route to the non-enzymatic synthesis of polynucleotides, and pave the way to the emergence of a primitive genotype-phenotype coupling in membrane-free protocells.

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Urea-based Multivalent Agonist Peptides of the Death Receptor 5 drive Apoptosis of Cancer Cells by activating the TRAIL Pathway

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The extrinsic pathway of apoptosis can be used to fight cancer through the recognition, oligomerization and activation of Death Receptors (DRs) by the recombinant protein TRAIL (TNF-Related Apoptosis Ligand), monoclonal antibodies or synthetic ligands. At CBMN, we focus our attention on 16-mer agonist peptides of DR5 discovered by phage display, deprived of any homology with TRAIL, that not only induce apoptosis in cancer cell lines at the same level as TRAIL, without affecting the survival of normal ones, but also significantly reduce tumor volume in HCT116 colon cancer xenografts in mice[1]. In order to improve peptide stability against proteolytic cleavage for *in vivo* studies, amide bonds have been substituted by ureas to multimerize the peptides or to graft the peptides on a non canonical and chemically stable helix. Such a strategy not only allows to rationally control the degree of oligomerization, the spacing and the relative peptide orientation, but is expected to increase the half-life and duration of action *in vivo* of the therapeutic peptides. The aim of our project is to decipher the mechanism of DR5 activation by these multivalent agonist peptides at the molecular and structural levels, in order first to optimize their primary sequence for increasing their affinity to the DR5 receptor, but also to propose potential agonist peptides specific to the DR4 receptor. We have used a multidisciplinary approach combining molecular biology, biochemistry and biophysics. The Extra Cellular Domain (ECD) of DR5 was cloned, over-expressed and isotopically $^{13}C^{15}N$ labelled in *Escherichia coli* and produced in a cell-free system followed by optimized purification. Purified monomeric proteins were analyzed by SDS-PAGE, RP-HPLC, MS, SEC-MALS and heteronuclear Liquid State Nuclear Magnetic Resonance (NMR) Spectroscpy[2, 3]. Directed mutagenesis was performed at regions and residues, likely to be involved in complex formation, based on NMR titration data. The kinetics and binding affinities of wild-type and mutated proteins to the urea-based dimeric NO2-102 peptide were measured by Surface Plasmon Resonance (SPR) in the presence or absence of TRAIL. The results enabled us to identify the key residues and regions in the complex formation, as well as to validate the structural model of the complex obtained by molecular docking under restraints derived from NMR titration data as well as Binding Assay-Alanine scanning in the original peptide (Pattern WO 2009/002947 A2, Affymax Inc). We have shown that multivalent peptides dimerize DR5 by using SEC-MALS with a sub-nanomolar affinity measured by SPR, similar to that of TRAIL, in agreement with literature data. We have demonstrated that the natural and synthetic ligands do not compete for DR5 binding, but form a ternary complex with the receptor, as the peptides bind to the 40s and 60s loops, while TRAIL binds to the 50s and 90s loops. We have obtained the first crystals for elucidating the 3D structure of the ternary complex. Such results pave the way for the use, as a targeted bi-therapeutic strategy, of the recombinant human soluble TRAIL protein combined with multivalent synthetic peptides, to combat resistance in cancer cell lines and increase apoptotic activity, as we hypothesize the formation *in vivo* of a highly organized supramolecular network of ternary complexes at the membrane level. This targeted approach is original, innovative and complementary to conventional cancer therapies. The project is funded by the Ligue Contre le Cancer and Fondation Bordeaux Université.

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Journées Grand Sud-Ouest de la Société Chimique de France
1-2 Février 2024, Bordeaux

Computational-Experimental Study of Stable Acyclic (Amino) (haloaryl) carbenes: Evidence of Highly Ambiphilic "Push-Pull" Carbenes

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Since Bertrand's seminal report of the first isolated singlet phosphinosilylcarbene in 1988, closely succeeded by Arduengo's discovery of N-heterocyclic carbenes (NHCs) a few years later,[1] carbene chemistry has rapidly evolved, emerging as a powerful tool in chemistry with a myriad of applications.[2] In 2001, Bertrand reported several stable acyclic (amino)(aryl) carbenes (AAACs) where it was established that the presence of just an amino group is enough to stabilize the carbene system, while the aryl substituents were deemed as mere spectators (i.e. π-innocent).[3] Despite this significant milestone, reports on AAACs are very scarce, and the factors governing their stability remain poorly understood. This lack of understanding severely hampers the design, synthesis and further applications of this riveting family of carbenes.

In this study, we present the synthesis and reactivity of novel acyclic (amino)(haloaryl) carbenes (Figure 1A) along with experimental and computational studies of their unprecedented stability. Our results confirm the highly ambiphilic nature of these (amino)(haloaryl) carbenes which are among the most electrophilic stable carbenes reported to date. We also provide evidence that they can be described as "push-pull" systems where aryl groups play a crucial role by accepting electron density from the carbene center (Figure 1B). Finally, steric hindrance was computationally assessed and it was found that halogenated *ortho*-substituents play also a relevant role by providing steric protection, thus stabilizing the carbene as it hinders self-dimerization.

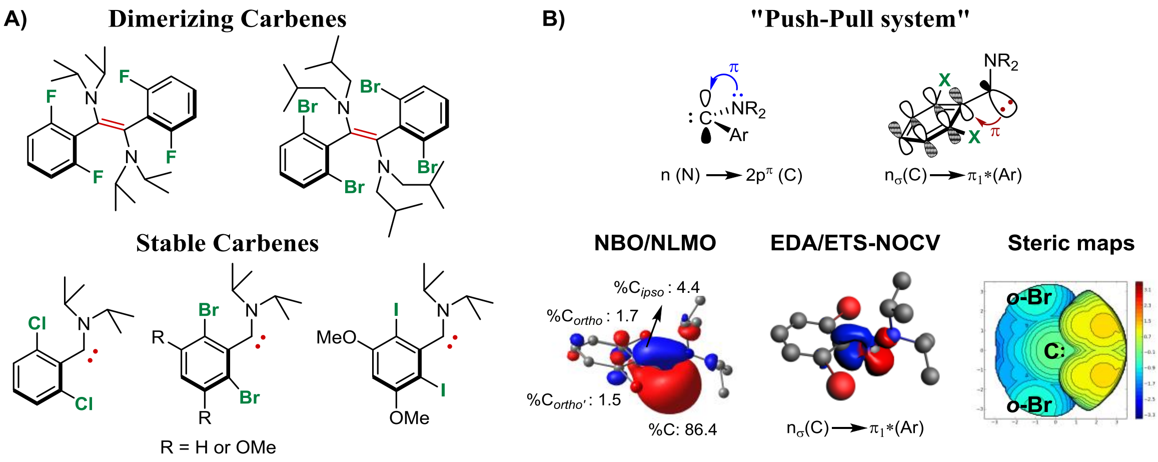

Figure 1. A) Dimerizing and stable carbenes reported in this study. B) Schematical representation of the "push-pull" carbene system along with orbital and steric analyses carried out in this work.

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Singlet Oxygen Modular Chiral Phosphoric Acid Asymmetric Organocatalysts

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Recently, modular 9,10-diphenylanthracene receptors were developed via a reversible singlet oxygen cycloaddition[1]. This [4+2] reversible reaction allows the dearomatization of the anthracene moiety inducing a change from a planar geometry to a concave one for the endoperoxyde product.

This modular anthracene/$^{1}O_2$ system has not been explored in modular catalysis, where stimuli are limited to physical (light), electrochemical or chemical (ion, molecule) ones[2].

We aim to develop a new modular organocatalyst, by modifying chiral phosphoric acids (CPA) based on *(R)*-BINOL which Brönsted acid activity have been well-explored and mechanisms were supported by extensive theoretical studies[3].

We will design customized modular catalysts by molecular modelling, synthesise them and study their catalytic activity in benchmark reactions such as the asymmetric ring-opening of oxetanes.

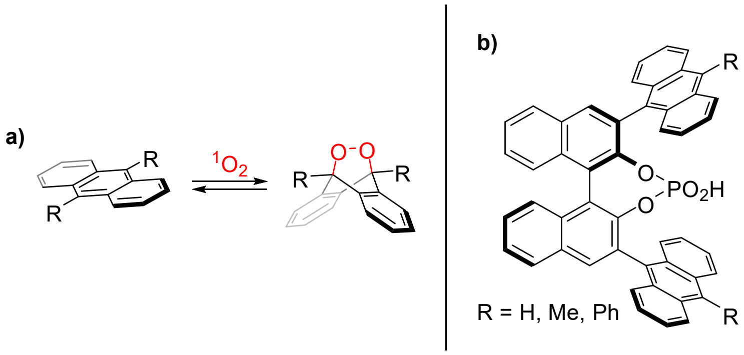

Figure 1 : a) singlet oxygen modular system with 9,10-diphenylanthracene ; b) CPA for modular catalysis

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Journées Grand Sud-Ouest de la Société Chimique de France
1-2 Février 2024, Bordeaux

TOWARD THE TOTAL SYNTHESIS OF VESCALAGIN, A BIOACTIVE NATURAL PRODUCT FROM THE *C*-GLUCOSIDIC ELLAGITANNIN FAMILY

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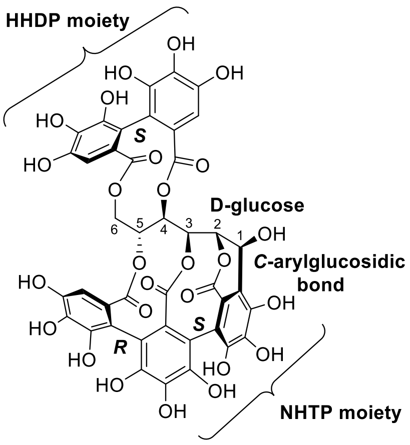
The *C*-glucosidic ellagitannins are natural polyphenols resulting from the specialized metabolism of certain plants.(1) (–)-Vescalagin, an emblematic member of this class of ellagitannins, is a water-soluble compound that can notably be extracted from oak (*Quercus*) or chestnut (*Castanea*) heartwood.(2)

From a structural point of view, vescalagin features two atropoisomerically-defined bi- and teraryl units made up of galloyl units: a 4,6-hexahydroxydiphenoyl unit (HHDP) and a 2,3,5-nonahydroxyterphenoyl unit (NHTP), which are esterified onto a D-glucose core. Its characteristic structural element is the presence of a *C*-arylglucosidic bond linking the NHTP unit to the carbon-1 center of the glucose core.



Vescalagin is known to express various biological activities. For example, it acts as a preferential catalytic inhibitor of the α-isoform of the human DNA topoisomerase II, an enzyme targeted by anti-cancer drugs.(2a,b) Vescalagin also acts as an anti-actin agent capable of disrupting filamentous actin in cells.(3a) We later found that vescalagin expresses an actin-dependent inhibition of bone resorption by osteoclastic cells, making it a valuable candidate for the treatment of osteoporosis.(3b)

These therapeutically-relevant biological effects and the complex chemical structure of vescalagin led us to engage in efforts towards its total synthesis, as well as that of analogues thereof, in the aim of further investigating its biological properties and its development as a pharmaceutical drug candidate.

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Structure-based design and synthesis of stapled ^{10}Panx1 analogs for use in cardiovascular inflammatory diseases

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Pannexin1 (Panx1) is an important transmembrane protein mediating cellular communication through formation of heptameric channels.[1] However, the disproportionate opening of these channels is known to be related to a wide range of pathologies – including cardiovascular inflammatory diseases – and therefore, Panx1 channel blockade may represent an innovative strategy for the treatment of these diseases.[2]

Following a rational design, a series of macrocyclic (‘stapled’) peptidomimetics of ^{10}Panx1, the most established peptide inhibitor of Panx1 channels, were developed and synthesized. Two macrocyclic analogs outperformed the linear native peptide. During *in vitro* ATP release and Yo-Pro-1 uptake assays in a Panx1-expressing tumor cell line, both compounds revealed to be promising bidirectional inhibitors of Panx1 channel function, able to induce a two-fold inhibition, as compared to the native ^{10}Panx1 sequence. The introduction of triazole-based crosslinks within the peptide backbones increased helical content and enhanced *in vitro* proteolytic stability in human plasma (>30-fold longer half-lives, compared to ^{10}Panx1). In adhesion assays, a ‘double stapled’ peptide inhibited ATP release from endothelial cells, thereby efficiently reducing THP-1 monocyte adhesion to an TNF-α-activated endothelial monolayer,[3] and making it a promising candidate for future *in vivo* investigations in animal models of cardiovascular inflammatory disease.

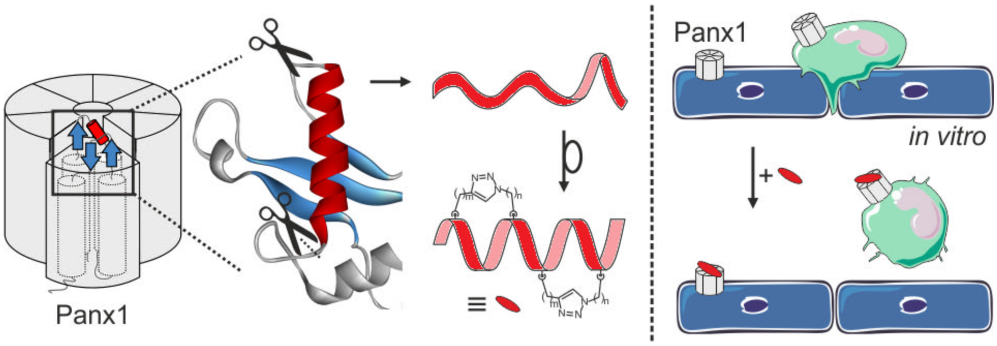

Figure 1. Schematic representation of the heptameric assembly of Panx1 where extracellular α-helix and β-strands are colored in red and blue, respectively (*left*). The lead peptide sequence of interest is represented as a red ribbon which leads to an optimized bicyclic peptidomimetic able to efficiently reduce monocyte adhesion to an activated endothelial monolayer (*right*).

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Journées Grand Sud-Ouest de la Société Chimique de France
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Design, Synthesis and Physico-Chemical Properties of a New Generation of Amphiphiles for Sustained Release Drug Delivery Systems

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The early discovery of archaea microorganisms revealed an exceptional chemical and mechanical stability and lower permeability of their cellular membranes. This is due to an original structure of the phospholipids composing such membranes, called bola-amphiphiles (1). Inspired by such natural molecules, several groups tried to design artificial bolas for drug delivery applications (2,3). Our group is also interested in the development of sustained release drug delivery systems. One approach was to design new bola derivatives (Figure 1) by creating a covalent link between two natural phospholipids. Using coarse-grained molecular dynamics, this type of derivatives was shown to self-assemble into spherical nanoparticles. Their subsequent synthesis and formulation validated the molecular modeling results: liposomes (small unilamellar vesicles) were obtained when such bolas were used alone during the formulation steps, or in a mixture with other natural phospholipids.

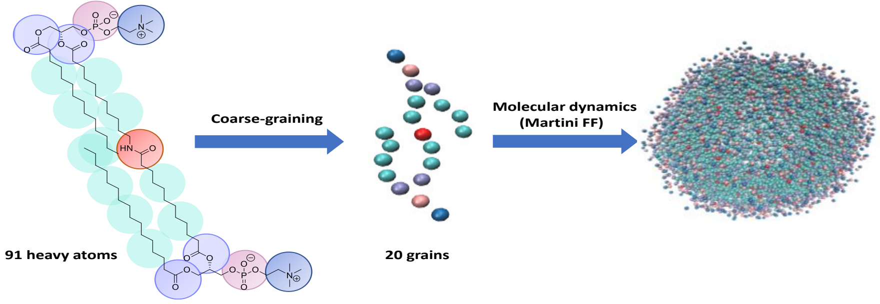

Figure 1: *In silico* designing of bolaphospholipid with an amide linker in the lipidic interface

The synthesis of a chemical library of amide-based bola-amphiphiles from the commercially available lyso-phosphatidylcholines will be detailed (Figure 2), along with the preliminary physico-chemical characterization of the nanoparticles induced from such bola derivatives.

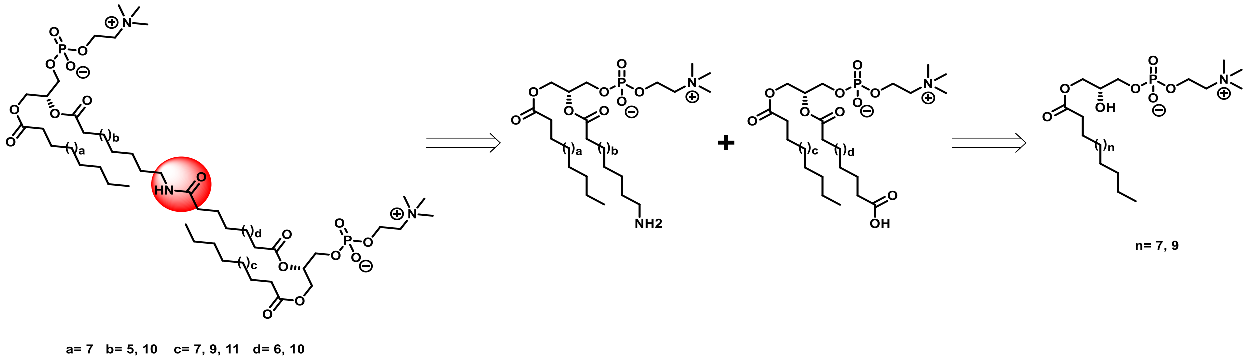

Figure 2: Retrosynthesis of target bolaamphiphiles

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Journées Grand Sud-Ouest de la Société Chimique de France
1-2 Février 2024, Bordeaux

Microcycles :
Easily accessible achiral and chiral phenanthrocyclophanes

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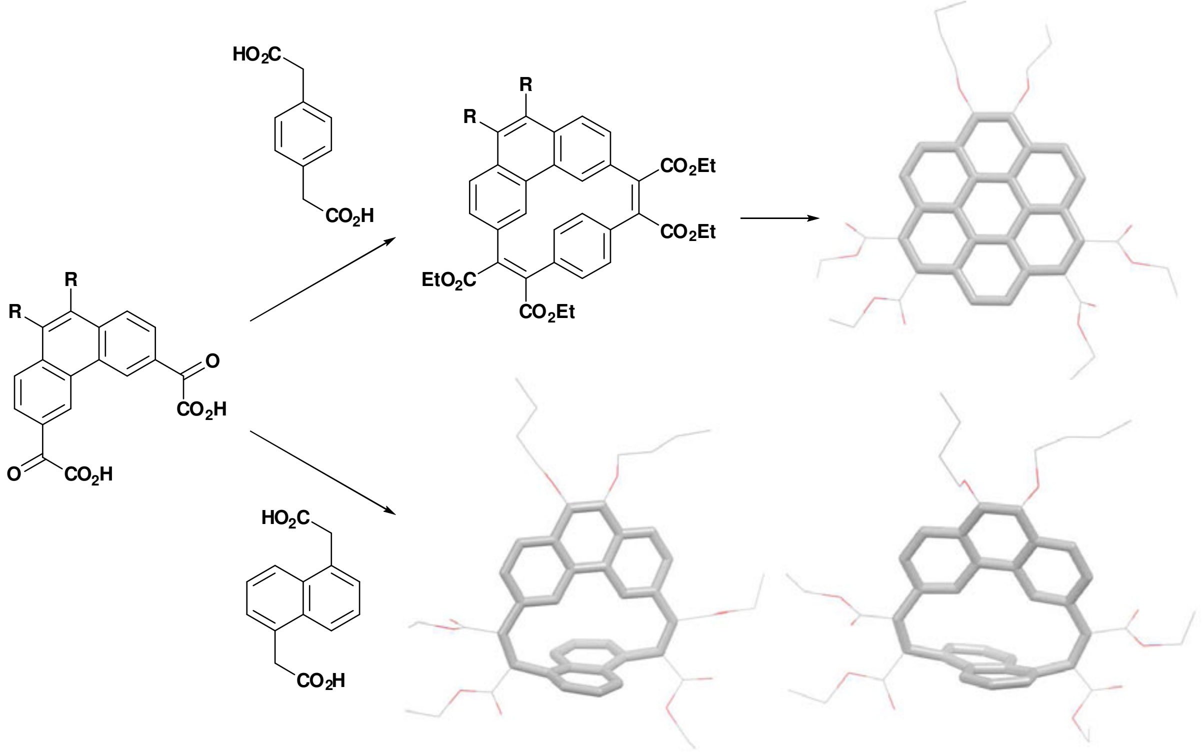
The synthesis of conjugated macrocycles from polycyclic aromatic fragments has been a subject of extensive research the last decades because of their unusual structures and physical properties.[1] Our team developed a synthetic pathway for the formation of new carboxy-substituted polycyclic aromatic compounds based on a modified version of the historic Perkin reaction.[2] This strategy allows the formation of large variety of conjugated molecules, linear or branched, flat or twisted, and has even been proved to be highly efficient for the formation of macrocyclic compounds.[3] Using bifunctionnalized phenanthrene building blocks and commercially available phenylene diacetic acid, macrocycles resulting of [1+1] macrocyclization reactions were isolated. The tense macrocycles obtained proved to be ideal precursors for functionnalized coronenes. When using a naphthalene instead of a phenylene, racemic mixtures of enantiostable macrocycles are obtained. The enantiomers were separated by chiral HPLC and their photophysical and chiroptical properties were studied.



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Biomimetic mussel adhesive-inspired made by self-coacervation of polyampholytes

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Living organisms have always been a source of inspiration for the design of molecular systems with interesting properties. Mussels have adhesive properties that enable them to adhere to a surface and resist the forces to which they may be subjected. This adhesion property of mussels comes from a protein secreted by an organ called the "foot"[1]. The secreted protein forms coacervates in a saline environment thanks to various interactions between its residues[2]. Coacervates are spherical micrometric structures that result from a phase separation of two aqueous phases driven by polymer assembly. This phase separation, called "coacervation", resulting in a polymer-rich phase and a polymer-poor phase is usually driven by the complexation of oppositely-charged polyelectrolytes. In this project, the process of "self-coacervation" is investigated by using a single polymer to form the coacervates[3]. This polymer was synthesized by functionalizing polyacrylic acid (PAA) chains with N,N'-dimethylethylenediamine and 4-aminobenzoic acid. At certain pH and ionic strength conditions, electrostatic interactions between amine and carboxyl groups and π-π interactions between aromatic groups on the PAA chains lead to self-coacervation for different functionalization rates of amine and aromatic groups. Furthermore, at certain functionalization rates, coacervate aggregates can be obtained to form an adhesive. Probe-tack tests and rheological measurements were carried out to investigate their adhesive properties. The aim of this project is to formulate coacervates capable of mimicking the adhesive properties of mussels for underwater adhesives.

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Journées Grand Sud-Ouest de la Société Chimique de France
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AgNW Network as Transparent Electrodes for Electrochromic Films

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The global energy demand accounts for 30-40% of the total energy for the building sector. This energy is used for heating, cooling, lighting, and other purposes in residential and commercial buildings. Electrochromic smart windows are one of the promising solutions to minimize energy consumption in buildings and improve the indoor comfort of inhabitants[1]. Electrochromism refers to the ability of materials to change their optical properties, under an applied voltage. Electrochromic devices (ECDs), typically consist of multiple layers stacked together as two outer transparent conducting layers, an electrochromic layer, and a counter electrode separated by an electrolyte. Indium tin oxide (ITO) is used extensively as a transparent electrode for electrochromic devices due to its high transparency, electrical conductivity, and chemical stability. However, some main limitations are its relatively high cost, scarcity, and brittleness, limiting its use in some applications. Silver nanowire (AgNW) networks appear as a promising alternative thanks to their high optical transparency, excellent electrical properties, and mechanical flexibility. AgNWs have indeed gained much attention in the last few years. However, the stability of AgNWs under electrical, thermal, and environmental stress remains a key issue for the applications.

The present work aims to prepare ITO-free electrochromic films using AgNW networks as a transparent electrode. The AgNW networks are deposited through spray-coating on transparent glass substrates, afterward, the electrochromic material is deposited using radio frequency magnetron sputtering. Bare AgNWs undergo degradation in sputtering conditions. To avoid such degradation, the AgNW networks are coated with a thin conformal protective oxide layer, ZnO and SnO_2, using atmospheric pressure spatial atomic layer deposition (AP-SALD)[2]. The performance of different electrochromic materials, like V_2O_5[3] and WO_3 deposited on AgNWs are investigated through cyclic voltammetry and chronoamperometry. The switching kinetics of AgNWs-based electrochromic films are studied by *in-situ* optical measurement and compared with the ITO-based films.

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Plasma assisted micro poling of glassy surfaces: a new tool to achieve liquid crystal multi-domain alignments

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We propose an innovative approach to program the alignment of liquid crystal (LC) assemblies allowing for the formation of multi-domain alignments whose orientation axis and sizes are controlled at the micrometer scale by an electrically patterned glass surface. The glass surface preparation is based on a thermo-electrical imprinting process to induce localized space charge implantations in the glass matrix just below its anode surface. To demonstrate this new approach, a commercial soda-lime glass slide has been polarized using as anode a simple micrometric nickel grid. Characterizing the polarized glass surface by second harmonic generation polarized microscopy; we show an accurate control of both location and spatial components of frozen static fields embedded in the glass as a function of the electrode patterns. The polarized glassy surface is then used in the conception of a LC cell in which homeotropic or planar alignments can be controlled following the electrical pattern induced on the glass surface. This study also points out the importance of plasma discharges spatially controlled along the electrode pattern during the process in order to promote the in-plane electrical polarization effects, which are essential for the programming of the in-plane LC alignment on the polarized glass surface.

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Journées Grand Sud-Ouest de la Société Chimique de France
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Reconfigurable soft acoustic material

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Key words: Polymer, Photochemistry, Porous, Acoustic

Abstract: The purpose of this project concerns the development of new reconfigurable, self-healing and recyclable materials for acoustics.

In earlier studies[1] it was shown that soft porous polymer materials (i.e. with a glass transition temperature much smaller than room temperature) exhibit an acoustic velocity that strongly depend on the materials porosity value. Using this property, gradient-index acoustic lenses were obtained by spatially assembling pieces of materials with different porosity values[2]. In this study, we now aim at locally changing the value of the acoustic velocity by controlling the crosslinking of the soft porous polymer matrix through the application of a UV stimulus of tuneable intensity. To do so, we grafted some UV-sensitive chemical functions (namely cinnamoyl groups[3]) onto different polymer backbones and measured the evolution of the mechanical properties as a function oft he UV illumination time. We also investigated the chemical properties of the obtained grafted polymers. Our results show that the materials mechanical properties can be significantly changed by the application of this stimulus. We present and discuss some results obtained with two backbones polymer chains, namely polybutadiene and polydimethylsiloxane. The obtained results confirms the validity of our approach and opens the way to soft reconfigurable acoustic devices.

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Journées Grand Sud-Ouest de la Société Chimique de France
1-2 Février 2024, Bordeaux

Understanding the phase equilibrium in deep sea fluids: A co-localized IR-Raman setup for high pressure - high temperature mixtures studies

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Hydrothermal smokers present unique physico-chemical conditions, suspected of having contributed to the emergence of life on Earth(1). Those deep-sea environments, under high pressure, are formed by the gush of water and hot gas emitted by magmatic pockets, subjected to a brutal temperature gradient when they arrive at the seabed. We present here the development of a high-pressure, high-temperature reactor and the associated innovative quantitative analysis method. Sapphire and silica windows allow the application of Raman and infrared spectroscopies, and thus in-situ real-time monitoring of the evolution of the system, composed of various compounds under gaseous, liquid, and/or supercritical phases. Reliable experimental results are particularly interesting in the study of complex gas mixture under pressure, given the few experimental data available to confirm modeling(2,3).

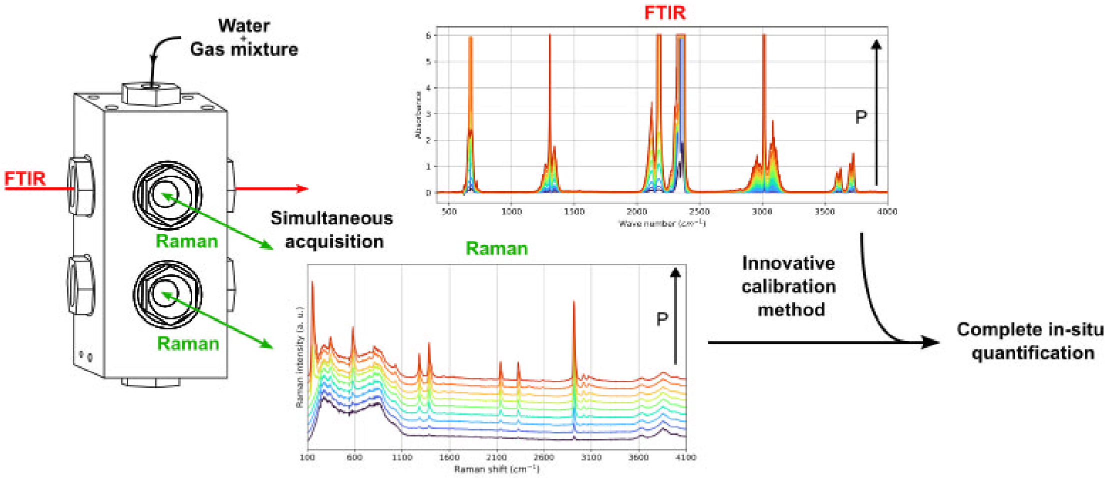

Figure 1: Windowed high-pressure high-temperature experimental cell coupled with IR and Raman spectrometer for the co-localized in situ investigation of complex fluid mixtures.

The understanding of the compounds repartition and availability of the different compounds is required to understand the mineral/fluid interaction in the hydrothermal fields, and thus the particular weathering of the minerals occurring in these environments.

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Journées Grand Sud-Ouest de la Société Chimique de France
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Improving the Stability of Liposomes for Sustained Drug Delivery

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Liposomes have been receiving much attention in pharmaceutical area as drug carriers, however, one of the longstanding problems is how to improve their stability in order to prevent drug leakage before delivery to the target site [1]. The membrane of certain species of Archaea, such as Thermoacidophiles, is composed of a special class of lipid molecules, known as bolalipids, that contributes to their exceptional stability against severe environmental conditions [2]. Inspired by these natural lipids, our lab designed a new class of bola-lipids composed of two natural phospholipids unified through a polar linker (Figure).

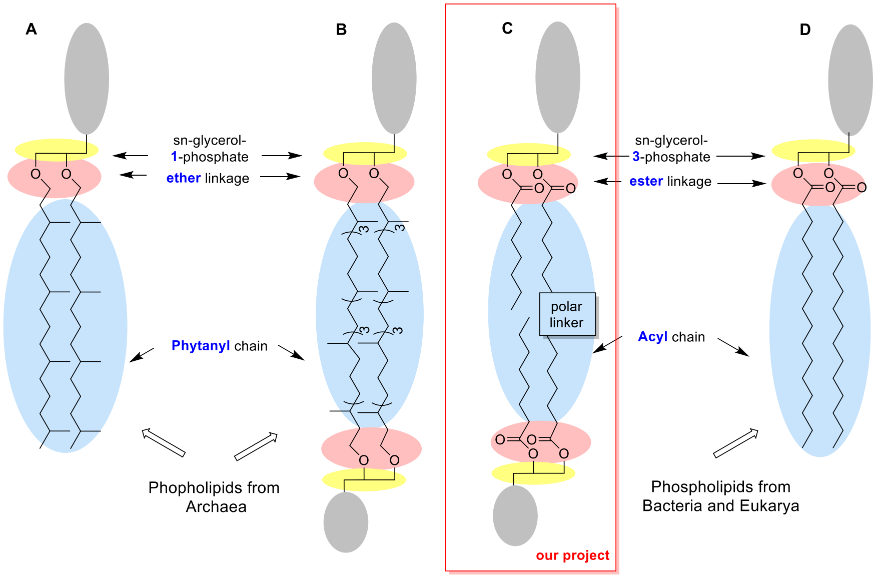

Figure: Representation of phospholipids from Archaea (A) and from Bacteria and Eukarya (D). The arrows indicate the main differences. The proposed lipid structure stabilizing the membrane of polyextremophilic archaeon *Thermococcus barophilus* [3](B). The newly designed class of bola-lipids from our group (C).

Several polar linkers were tested in the structure of our designed amphiphiles. They were able to deliver bolasomes (liposomes from bola lipids), either alone or in mixture with other natural phospholipids (with a ratio of 1:9) such as dipalmitoyl phosphatidylcholine (DPPC) and 1,2-dimyristoyl-sn-glycero-3-phosphocholine (DMPC). We investigated the stability of vesicles, using dynamic light scattering (DLS), by monitoring over a period of time the PDI and vesicle's size.

Bola amphiphiles proved to be unstable when used alone during the formulation step, however, they did show an improvement in the stability profile of liposomes obtained in mixture with natural phospholipids. The stability testing process will be detailed, along with the main results obtained with the different composition of the vesicles.

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Journées Grand Sud-Ouest de la Société Chimique de France
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Gold carbyne complexes: Myth or Reality?

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Chemists long neglected gold because it was considered as a noble and therefore chemically inert metal. The interest for gold rose in the late 90s and gold catalysis is currently undergoing significant development. First, gold chemistry was limited to its Lewis acid properties, but the design of chelating (P,P) and hemilabile (P,N) ligands allowed the investigation of new reactivities such as oxidative addition, migratory insertion…[1] or even opened the way to new unusual bonding situations such as in gold carbene complexes (P,P)AuC=R$^+$.[2]

In this work we further study this chemistry by investigating the possibility of creating gold carbynes complexes $L_nAuC{\equiv}R$. We were inspired by previously synthesized and characterized gold carbene complexes thanks to enhanced backdonation from gold.

In collaboration with the team of D. Bourissou, we carried out calculations to help the design of new plausible gold carbyne complexes. Recently, carbyne like gold and copper complexes have been synthesized but the metal-carbon bond has no triple bond character (Figure 1a).[3] Using Density Functional Theory (DFT) and Natural Bond Analysis (NBO), we studied the influence of the "ancillary" ligands on the metal center and of the substituents on the carbon on the geometrical parameters and the electronic structure of L_nAuCR complexes. The point is to identify some target gold complexes presenting some degree of gold-carbon triple bond. In our study, three different types of bonding situation have been highlighted (Figure 1b): new gold complexes with carbyne like character, metalla-carbenes and metal vinylidenes.

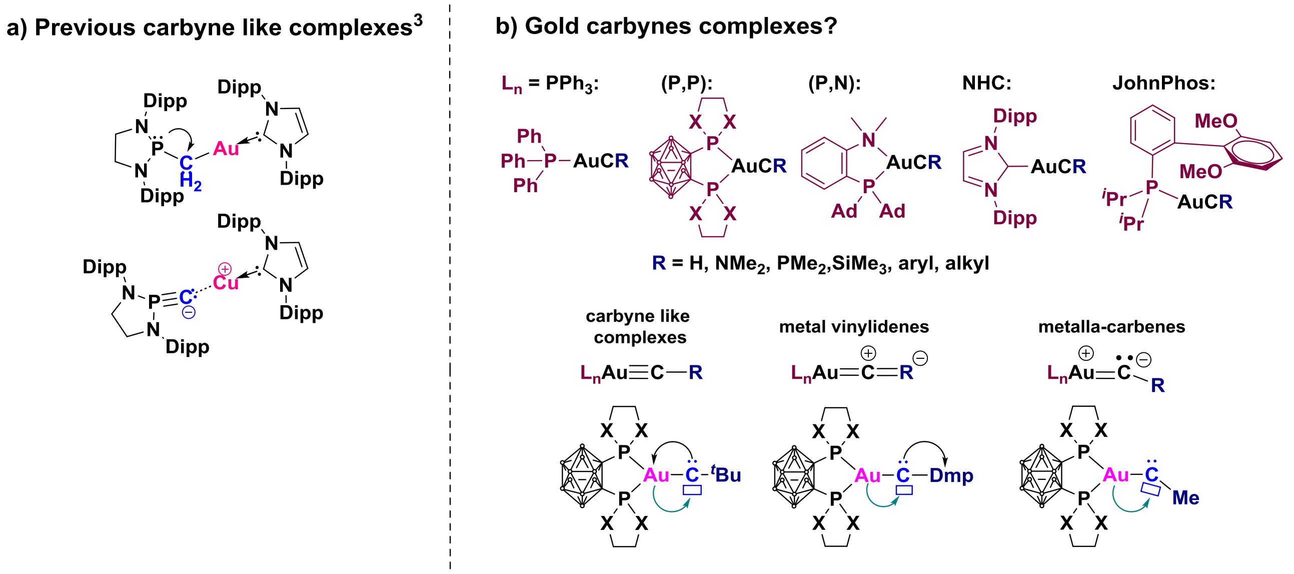

Figure 1: a) Isolated gold carbenes complexes using a (P,P) chelating ligand. Back-donation Au→carbene shown in MO and NLMO. b) Gold carbynes like complexes studied with the different structures identified.

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Probing chirality on surfaces: Aromatic oligoamide foldamers monolayers on gold for nonlinear chiroptical characterization

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The detection of chirality on surfaces and interfaces is crucial for various applications, such as determining protein activity or rationalizing the role of chiral surfaces as templates for asymmetric synthesis.[1] However, the development of organic compounds that can yield chirality at the surface level, while being detected by surface-sensitive techniques remains a significant challenge.

Aromatic oligoamide foldamers based on quinoline units are known to fold into helical scaffolds due to hydrogen bonding, aromatic stacking, and electrostatic repulsions. By inserting a camphanyl chiral inducer at the N-terminus, the handedness of the helices can be controlled. Additionally, each quinoline monomer can be functionalized either with a solubilizing chain, an electron-donor/withdrawing group, or an anchoring function that allows for chemical grafting on substrates, making these compounds highly versatile and adequate to achieve chiral discrimination on surfaces.[2] Moreover, they have proven to possess high hyperpolarizability, especially when functionalized with electron-donor/withdrawing groups, indicating important non-linear optical (NLO) activity, particularly through second-harmonic generation (SHG).[3] This even-order NLO phenomenon is known to be related to chirality.

In this work, a family of thiolated quinoline octamers functionalized with different electron-donor groups was synthesized and chemically grafted onto gold substrates. The film thicknesses were determined to be consistently below 2 nm for all the compounds, confirming the formation of uniform monolayers, with a stable and well-organized arrangement across the gold substrate. Reflectivity-SHG studies enabled the chiral discrimination at the surface level, providing valuable insights into the behavior of these compounds in the context of surface chirality.

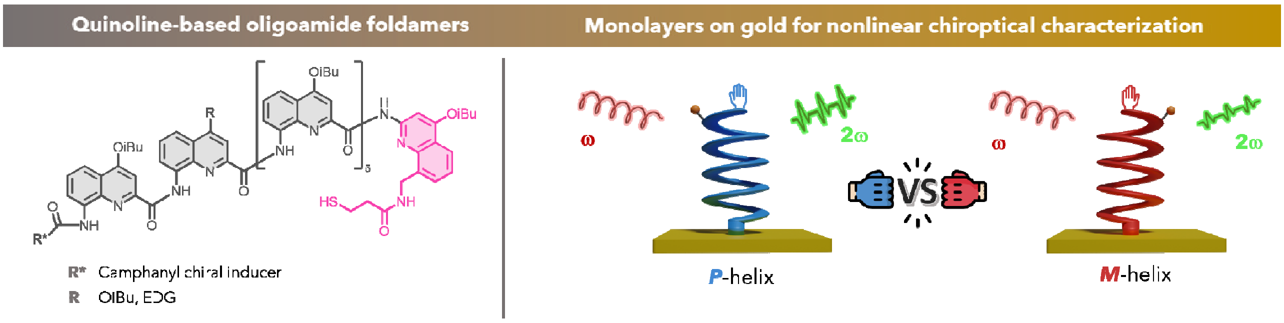

Figure 1 : Chemical structure of chiral quinoline octamers functionalized with an electron-donor group (EDG) and their deposition onto a gold substrate for nonlinear chiroptical characterization.

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Journées Grand Sud-Ouest de la Société Chimique de France
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Mesure de la tension de surface de particules atmosphériques à l'aide de la microscopie à force atomique

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Les aérosols atmosphériques sont bien connus pour leur impact sur la qualité de l'air et le changement climatique. En absorbant et en évaporant l'eau en phase gaz, les aérosols peuvent agir comme des noyaux de condensation (CCN) et induire la formation de nuages, ce qui influe sur le bilan radiatif de la Terre.[1] La teneur en eau liquide des aérosols, qui varie en fonction de l'humidité relative (HR), régit les transitions de phase, le partage liquide-gaz, l'absorption des gaz à l'état de traces, les réactions en phase aqueuse et les propriétés microphysiques des particules. Les propriétés de surface des particules atmosphériques, telles que la tension superficielle, peuvent affecter leur réactivité et en particulier modifier les interactions entre la particule et la vapeur d'eau et donc affecter leur potentiel d'activation des gouttelettes de nuages. Les processus de vieillissement des aérosols se produisant à l'interface gaz/particules modifient également leurs propriétés de surface via des mécanismes complexes encore incomplètement décrits. Les recherches actuelles se focalisent sur les propriétés des aérosols organiques secondaires, particules formées *in situ* dans l'atmosphère et pour lesquelles les mécanismes de formation et vieillissement sont mal connus.

Des développements récents, utilisant des approches de particules individuelles, permettent d'étudier les processus de vieillissement chimique et l'évolution des propriétés microphysiques à l'échelle de la particule.[2] Dans ce contexte, nous avons étudié l'évolution de la tension de surface de gouttelettes uniques à l'aide de la microscopie à force atomique (AFM) dans des conditions d'humidité contrôlées. Les tensions de surfaces de particules composées de mélanges de MBTCA (acide 3-méthylbutane-1,2,3 tricarboxylique), un traceur de la formation d'aérosol organique secondaire (AOS) et de composés inorganiques d'intérêt atmosphérique ont été déterminées en fonction de leur composition et de l'humidité relatives. Les résultats expérimentaux ont été comparés aux modèles thermodynamiques basées sur la théorie de Köhler.[3]

Remerciements

Les auteurs souhaitent remercier l'Université de Bordeaux, l'Agence française pour la transition écologique (ADEME), le programme LEFE-CHAT du CNRS-INSU, l'ANR SOAPHY ANR-21-CE29-0031la Région Nouvelle Aquitaine LEVIAERO (convention n° AAPR2022-2021-17126210), pour leur soutien financier.

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Journées Grand Sud-Ouest de la Société Chimique de France
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Molecular stacks and organic solar cells: Synthesis of sulphur and nitrogen analogues of pyrenes and their study as low-bandgap materials

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Silicon is currently a key material in the field of electronics. For instance, integrated circuits present on the chips of various equipment that surround us include them. However, over the past two decades, semi-conducting organic compounds have come to compete with silicon and other inorganic materials in various domains such as display modules via the AMOLED technology. In commercial solar cells, silicon is also widely used but leads to certain drawbacks from which organic materials could easily overcome such as the difficulty of their implementation and their high density[1]. In the field of solar cells, prospective studies[2] showed that polymers with low band gaps (LBG) are required to obtain better photovoltaic yields.[3]

With the aim of preparing new LBI polymers, this work describes the synthesis of an original monomer, a sulfur and nitrogeous analogue from pyrene, in seven steps from 3-bromothiophene. UV-visible absorption and steady-state emission spectroscopy studies reveal that this molecular structure have lower gap (0.65 eV) compare to pyrene. Moreover, single X-ray diffraction confirms the planar and aromatic structure of this original monomer, and the molecular organization shows a 1-D slipped-stack arrangement with short interplanar distance that should favor charge carrier transport. Finally, the alternation of bond lengths is very low, which is a guarantee of effective delocalization between the two positions concerned by future polymerizations.

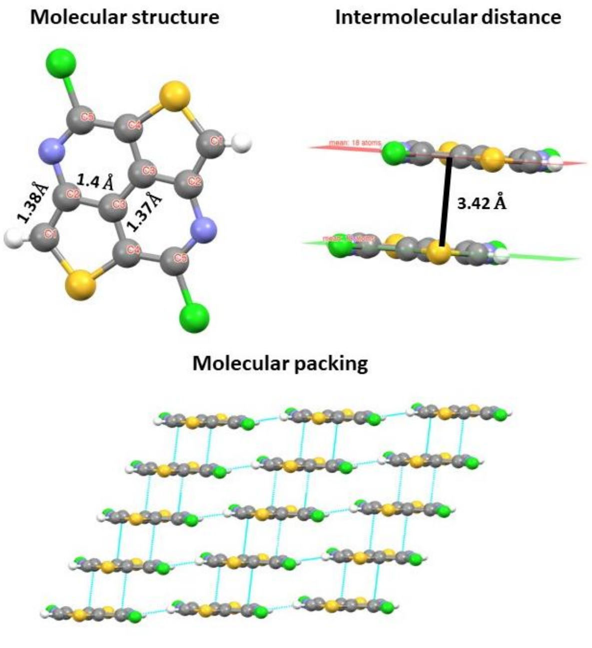

Figure 1: X-ray crystal structure and molecular packing of the new pyrene analogue

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Journées Grand Sud-Ouest de la Société Chimique de France
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New LED-activated RF-based nanomaterials for applications in anticancer photodynamic therapy

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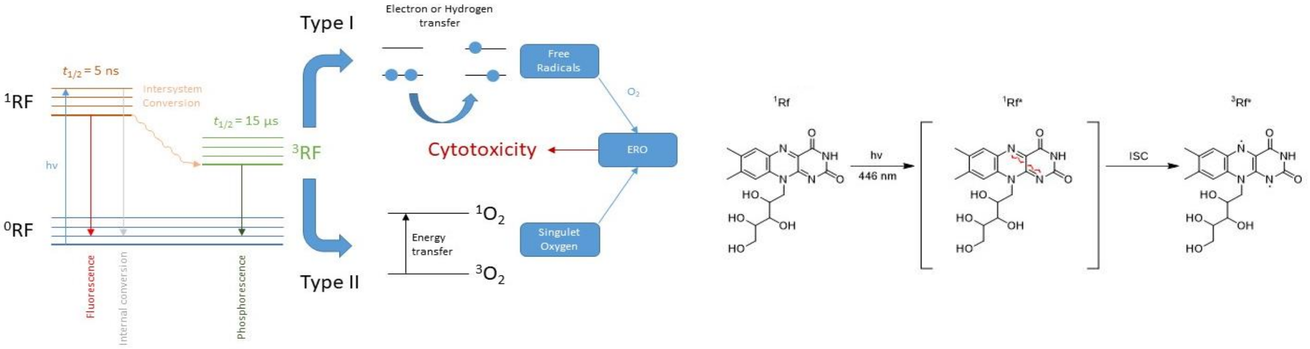
Riboflavin (RF, vitamin B2) and its metabolically active derivatives (FMN – flavin mononucleotide and FAD – flavin adenine dinucleotide) are natural compounds involved in a plethora of fundamental physiological events. The ribityl chain within riboflavin contributes to its solubility and forms strong hydrogen bonds with various biological targets. Meanwhile, the isoalloxazine core induces redox, fluorescence, and photosensitizing properties. For example, when exposed to blue light (λ = 455 nm), RF transitions to a singlet state, efficiently undergoing intersystem crossing to a highly stable triplet state (t1/2 = 15 µs). This excited state can promote type I and type II photosensitive reactions exploitable in tumor and microorganisms destruction, or in tissue engineering. (Scheme)

Thanks to these properties, our group is actively involved in the development of (RF)-based nano-devices for anticancer therapy. Previously, we successfully engineered self-assemblies of RF-conjugated phospholipids, resulting in a compact lamellar morphology[1], or a vesicular morphology by adding a bulky group on the isoalloxazine core.[2]

Recently, we focused on developing halogenated flavin-enriched and targeted nano-vesicles with enhanced photosensitivity for anticancer photodynamic therapy (PDT). In this context, we have achieved photosensitizing and biological assays (in vitro radical production, cell viability and cell irradiation)[3] of a home made chemical library of halogenated flavin derivatives. The results demonstrate an enhancement in the photosensitivity of these molecules, leading to an improvement in post-irradiation toxicity.

Based on the most photosensitive halogenated flavins, the synthesis of different series of amphiphiles is underway. To ensure the vesicular organisation required for photodynamic therapy, molecular dynamics studies (using all-atom simulations in water or biphasic systems and coarse-grained simulations) are also conducted to investigate the self-assembling properties of these molecules and select the best candidate for biomedical applications.



Scheme : Jablonski diagram and PDT application

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Journées Grand Sud-Ouest de la Société Chimique de France
1-2 Février 2024, Bordeaux

Propriétés hygroscopiques d'aérosols organiques d'intérêt atmosphérique - Etude à l'échelle de la particule unique

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Les aérosols atmosphériques font l'objet d'une grande attention ces 20 dernières années en raison de leur impact sur le changement climatique et la santé humaine. Les aérosols organiques secondaires (AOS), générés dans l'atmosphère suite à l'oxydation in situ de composés organiques volatils (COV), peuvent représenter jusqu'à environ la moitié de la masse totale des aérosols submicroniques dans l'air[1] au niveau global. Les COV peuvent avoir différentes sources biogéniques ou anthropiques. Les COV biogéniques (e.g., les monoterpènes tels que l'α- et le β-pinène) sont principalement émis par la végétation et peuvent conduire à la formation d'AOS biogéniques (AOSB). À ce jour, les observations sur le terrain et les expériences en laboratoire mettent en évidence la complexité des processus physico-chimiques impliqués lors de la formation et du vieillissement atmosphérique des AOSB. Selon leurs propriétés de surface, les aérosols peuvent interagir dans l'atmosphère avec l'eau atmosphérique omniprésente, agissant alors comme noyau de condensation de nuage. Ce processus représente aujourd'hui l'une des sources d'incertitudes les plus étudiées du bilan radiatif de la Terre[2]. Par ailleurs, la teneur en eau des aérosols impacte grandement leur réactivité. La capacité des particules à absorber ou désorber de la vapeur d'eau – l'hygroscopicité – est décrite par les équations de Maxwell de transfert de masse[3].

Dans ce travail, nous avons évalué les propriétés d'hygroscopicité d'aérosols riches en composés organiques. Les transitions solide-liquide (déliquescence) ou liquide-solide (efflorescence) engendrées par l'absorption ou la désorption de vapeur d'eau sur les surfaces de particules modèles d'AOS ont été étudiées à l'échelle de la particule unique grâce à un dispositif de lévitation acoustique couplé à un microspectromètre Raman. Ainsi la taille et de la composition des particules peuvent être simultanément déterminées en fonction du temps d'exposition et du taux l'humidité relative dans des conditions in situ. Dans un premier temps, les expérimentations menées sur l'acide maléïque et les sels NaCl et $(NH_4)_2SO_4$ dont les propriétés d'hygroscopicité sont largement décrites dans la littérature, ont permis de valider notre démarche expérimentale. Ces données ont été comparées aux modèles thermodynamiques (E-AIM). Dans un second temps, nous avons appliqué cette méthodologie à l'étude des propriétés d'hygroscopicité de l'acide 3-méthyl-1,2,3-butanetricarboxylique (MBTCA), considéré comme un marqueur pertinent de la formation et du vieillissement des AOSB monoterpéniques. Les propriétés d'hygroscopicité de particules individuelles contenant des solutions de MBTCA en mélange avec NaCl ou $(NH_4)_2SO_4$ ont été déterminées. Il a notamment été montré que les particules composées d'un mélange de molécules organiques et inorganiques se comportent différemment des particules composées d'un seul composant.

Remerciements :
Les auteurs remercient l'ANR pour le financement du projet SOAPHY (ANR-21-CE29-0031) et la Région Nouvelle Aquitaine pour son soutien au projet LEVIAERO (convention n° AAPR2022-2021-17126210).

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1-2 Février 2024, Bordeaux

Tunable rheological behavior of ionomer dispersions via formulation

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Ionomers are commonly used in the formulation of inks [ionomer/solvent/catalyst] for Catalyst Layer (CL) fabrication of Proton Exchange Membrane Fuel Cells (PEMFCs)[1]. PEMFCs have been paving the way for clean mobility for the past few decades. As a zero-emission electricity source, this technology has a promising energy supply potential. Despite the overall electrode fabrication process being quite simple[2] and numerous innovations on PEMFC components having emerged, there is to this day no state-of-the-art rationalization of formulating inks and fabricating CLs. This gray area comes from a lack of understanding on the links between properties, structures and performance within the CL fabrication process.

This work is part of an exploratory thesis project on the formulation and rheology of catalyst inks, centered on ionomer interactions with the solvent and catalyst. We present here the establishment of three dispersions formulation protocols, namely *Fresh*, *Heated* and *Guimauve*, and their respective impact on the rheological behavior of ionomer dispersions. N-propanol / water solvent mixtures are used, and the ionomer concentration is fixed at 4wt%[3]. Rheological behavior is analyzed through shear rate sweep experiments, where shear rate is stepped down logarithmically from $100s^{-1}$ to $0.1s^{-1}$. A 40mm sanded cone and plate geometry is used with a fixed gap of 0,7mm.

As for the impact of the N-propanol / water solvent ratio on dispersion viscosity, it is identified as linear on the *Fresh* samples, with an exponential increase on *Heated* samples, and negligible on *Guimauve* samples. Rheological behaviors exhibited by *Fresh* samples are exclusively Newtonian. A Herschel-Bulkley type shear-thinning behavior is identified for the highest-alcohol *Heated* sample, while a Bingham type shear thinning yield stress behavior is seen on the lowest-alcohol *Guimauve* sample. Overall, the rheology of the samples is found to be strongly dependent on the formulation protocol. Ionomer conformation is next to be assessed by small-angle scattering experiments.

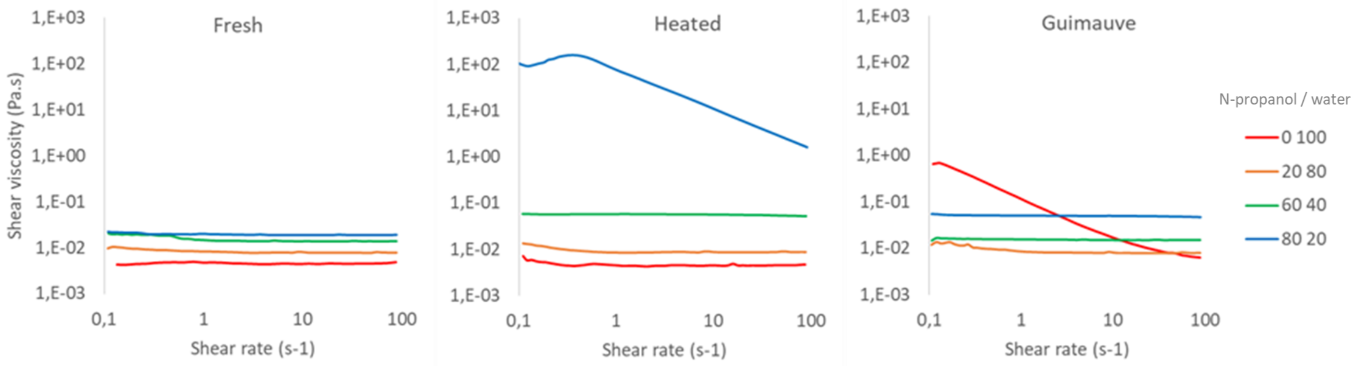

Figure 1 : Effect of formulation on ionomer dispersion rheoological behavior

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Theoretical characterization of the spectroscopic properties of microsolvated aromatic compounds

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As a product of biomass and coal combustion, aromatic compounds are emitted into the atmosphere as precursors of Van der Waals complexes with solvents such as water and ammonia. The chemical and photochemical transformations that these complexes undergo under atmospheric conditions lead to the formation of secondary organic aerosols (SOAs). The role of these aerosols in the thermal equilibrium of the atmosphere is not completely understood, but it is known that is fundamental. The mechanisms of SOAs formation are an active area of research and within this the determination of spectroscopic properties of the precursors, as well as a characterization of the precursor-solvent interactions. A first step in understanding the effects of solvation on the stability and optical properties of these systems is to employ a simple theoretical model of microsolvation. In this work CREST[1] is used to explore the conformational space of m-cresol, o-cresol and 1,2,4-benzenetriol in the gas phase, as well as forming microsolvated complexes with water and ammonia. The electronic and vibrational structures are theoretically determined by UV and IR spectra using the (TD)DFT/B3LYP/aug-cc-pvz method, taking into account the population of each conformation according to a Boltzmann distribution. The modifications observed in terms of spectroscopic properties are discussed on the basis of the specific interactions with the “solvent” molecules.

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Revisiter le couplage sp-sp^3 des chlorures tertiaires et des alcynes silylés

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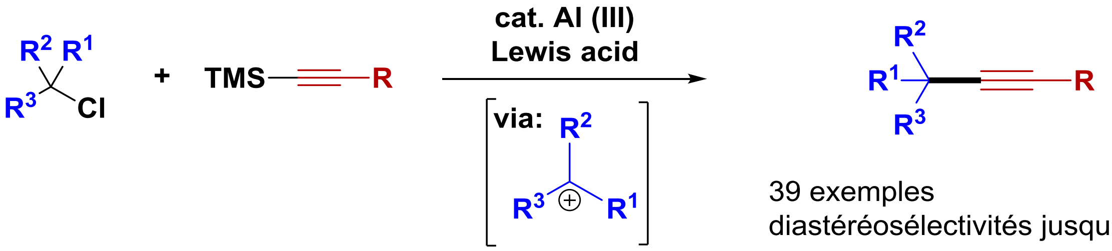
La réaction de couplage sp-sp^3 a suscité un intérêt important ces dernières années avec l'émergence de réactions de couplage radicalaire. Malgré des progrès majeurs, les réactions radicalaires souffrent d'un manque de praticité en raison de l'utilisation de photo-catalyseurs coûteux et de la préparation en plusieurs étapes des substrats correspondants. Par conséquent, nous avons porté notre attention sur le couplage cationique sp-sp^3, qui utilise des halogénures tertiaires facilement accessibles et de nombreux alcynes silylés disponibles dans le commerce. Dans cette communication, nous démontrons que le couplage cationique possède une portée beaucoup plus large et une meilleure tolérance aux groupes fonctionnels que ce qui avait été publié précédemment, et peut même, dans certains cas, donner lieu à des réactions hautement diastéréosélectives.



39 exemples
diastéréosélectivités jusqu'à >98:2

Towards the total syntheses of *O-labeled oxylipins

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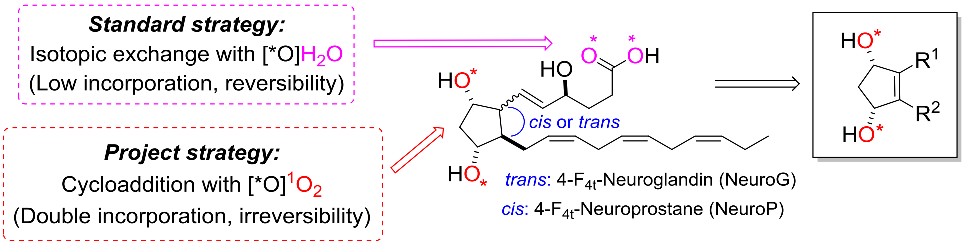

*Scheme : Strategies for the syntheses of *O-labelled oxylipins*

Oxylipins are oxidized metabolites of polyunsaturated fatty acids (PUFAs) with various biological applications. For example, 4-F4t-neuroprostane is a racemic non-enzymatic metabolite that was proven to play a key role in the stabilization of ryanodine receptors implicated in arrhythmias and diaphragm disorders.[1] However, whereas its deuterated analogue has been synthesized as analytic standard, there is no *O-labeled analogue described, despite the great benefits offered by such compounds. For example, while the ^{17}O isotope, with a 5/2 spin, is directly suitable for NMR studies or may be detected *in vitro*/*in vivo* by NMR/MRI techniques, $^{18}O/^{17}O$ can be used for their isotopic differences within the natural non-labelled NeuroP in mass spectrometry studies to monitor its *in vivo* metabolism.[2] The standard strategy for *O-labelling, i.e. isotopic exchange on the carboxylic group, could be envisioned, but it has typically low incorporation, it is reversible and the labeling can be lost during metabolization (β oxidations). Moreover, it does not correspond to the O atoms introduced by dioxygen oxidation in the biosynthetic pathways. On the contrary, using a method recently developed in the laboratory,[3] we will investigate a new strategy that will be devoid of all these problems by enabling the dual labeling of the cyclopentenediol core by cycloaddition of $^1O_2$ with cyclopentadienyls and *in situ* reduction.

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Journées Grand Sud-Ouest de la Société Chimique de France
1-2 Février 2024, Bordeaux

Soft NHC-organocatalysed Stetter reaction in aqueous coacervate droplets

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Advances in modern synthetic chemistry must comply with the need for a lower environmental impact[1], which has led in recent years to the development of a softer chemistry drawing inspiration from Nature. The formation of C-C bonds, which often requires the use of metals and organic solvents, is a central issue in organic chemistry. We recently reported the creation of C-C bonds in water via the Stetter reaction[2]; a bio-inspired organocatalyzed reaction using N-heterocyclic carbenes (NHCs), structural thiamin cofactor mimics. Due to their low water solubility, organic substrates form water-separated organic droplets and this hydrophobic environment promotes the Stetter reaction despite the NHC sensitivity to hydrolysis. The aim of this work is to study the Stetter reaction in polymer-rich aqueous microdroplets called "coacervates" and demonstrate the potential of these mildly hydrophobic environments to promote organic catalysis. Coacervates form spontaneously in water without the need of organic solvents[3] and can be recycled. This project will thus explore the potential of coacervate microenvironments for soft chemistry. We will present here our very preliminary results. We have first designed new azolium-derived organocatalysts to study the influence of catalyst structure on the reactivity, kinetics and selectivity of the Stetter model reaction in presence of coacervates or within coacervates of various internal polarity.

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Journées Grand Sud-Ouest de la Société Chimique de France
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Design of new elastin-like polypeptides for enzymatic modifications

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Elastin-like polypeptides (ELPs) are genetically-engineered protein-like polymers composed of (Val-Pro-Gly-Xaa-Gly) pentapeptide sequence repeats (Xaa being a natural or non-natural amino acid residue other than Pro).[1] They are widely explored for various biological and biomedical applications regarding their exquisite control in terms of molecular structure (sequence and length) and their lower-critical phase solution (LCST) behavior, a dual advantage for their purification from protein lysates and self-assembly properties. Devoid of bioactive properties, different strategies are used to provide ELPs with bioactive groups. Over the past ten years, our group has explored chemoselective chemical post-modifications at methionine residues (Xaa=Met) to functionalize ELPs with different pendant groups (e.g., lipid chains, bioactive peptides, saccharides).[2] We now want to develop a new method to modify ELPs using enzymatically-catalyzed reactions on tyrosine residues.[3] Orthoquinone moieties obtained by specific oxidation of the phenol side chain of Tyr by tyrosinases are indeed prone to nucleophilic attack by different types of nucleophiles (e.g., constrained cyclooctynes, anilines, thiols, N-terminal proline).

Herein, we will focus on the design and synthesis of tyrosine containing polypeptides, either at the ELP chain end or grafted along the polypeptide backbone. The chemical and physical-chemical characterizations of the different bioconjugates using different techniques will be detailed as well as the first attempts of their enzymatic modifications.

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Journées Grand Sud-Ouest de la Société Chimique de France
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Ex situ generation of $^{18}O_2$ and $^{17}O_2$ from endoperoxides for *O-labelling and mechanistic studies of oxidations by dioxygen

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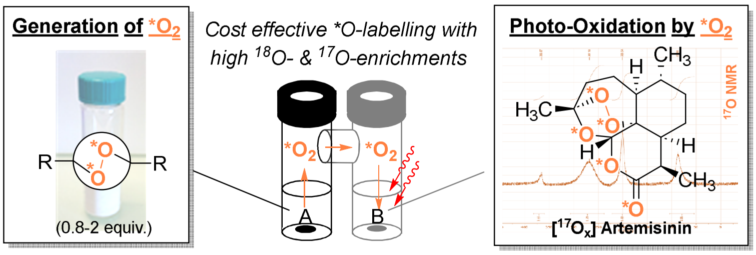
Among the various elements, oxygen plays a key role in many functional groups, and its isotopic labelling often proves determinant for mechanistic insights. Indeed, [^{18}O] can be easily differentiated by mass analysis from the predominant [^{16}O] and recent advances in NMR instrumentation allows efficient detection of the chemical shift of [^{17}O] (-30 to +1000 ppm). It is however necessary to use isotopically enriched compounds because of the low natural abundance of [^{18}O] and [^{17}O] (0.204% and 0.037%, respectively). Synthetic methodologies for the incorporation of labelled oxygen (*O) have been extensively studied.[1] They generally rely on the use of one of the cheapest isotope precursors: [*O]H_2O, but often require harsh conditions limiting their use to simple synthons, and/or involve reversible isotopic exchange yielding lessened isotopic enrichments. Some examples using gaseous *O-labelled dioxygen were reported, whose *O-atom molar cost is comparable to [*O]H_2O. However, the need to employ large excesses of this gas and the difficulty to manipulate it precisely greatly increase the overall cost of these procedures, which made them under-used. To solve these major drawbacks, we developed solid and stable precursors that can release quasi-stoichiometric amounts of [$^{18}O_2$] and [$^{17}O_2$]. After activation in a two-chamber glassware,[2] these compounds generated quasi-stoichiometric amounts of [*O_2]dioxygen that can be photosensitized to oxidise various substrates. This method provided in a single step ^{18}O- and ^{17}O-labelled endoperoxides, quinones and phenols, in moderate to good yields and very high isotopic enrichments (up to 83%). As exemplified by the syntheses of [$^{18}O_x$]artemisinin and [$^{17}O_x$]artemisinin, this strategy is particularly suitable for affordable investigation of the chemical mechanisms involved in dioxygen oxidations using mass spectrometry and ^{17}O NMR.[3]



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Unraveling the chemical mechanism of MND formation in red wine during bottle aging : Identification of a new glucosylated hydroxyketone pro-precursor

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During bottle aging, the development of wine aroma through low and gradual oxygen exposure is often positive in red wines, but can be unfavorable in many cases, resulting in a rapid loss of fresh, fruity flavors. Prematurely aged wines are marked by intense prune and fig aromatic nuances that dominate the desirable bouquet achieved through aging (Pons *et al*., 2013). This aromatic defect, in part, is caused by the presence of 3-methyl-2,4-nonanedione (MND). MND content was shown to be lower in nonoxidized red wines and higher in oxidized red wines, which systematically exceeds the odor detection threshold (62 ng/L). Concentrations up to 340 ng/L were evidenced in the most oxidized red wines as well as MND content up scaling was observed whatever the oxidation level. Very recently, we identified two new hydroxyketones (2-hydroxy-3-methylnonan-4-one) associated with MND distribution in aged red wines. We demonstrated that in red wine, their oxidation can produce MND (Peterson *et al*., 2020). To date, the origin of these precursors were not studied. During preliminary experiments, the presence in wine of a glycosylated form of this hydroxyketone was suggested by hydrolysis experiments. Based on the literature, we hypothesized the presence of a corresponding glucosylated precursor and developed a strategy for its organic multi-step synthesis. First, the MND hydroxylated precursor of MND was synthesized by aldolization (Crévisy *et al*., 2001). Then, we optimized strategies for the *O*-glycosidation step. For this, the tetrabenzylated glucose was activated by imidation reaction. Several deprotection methods for the glucoside moiety were then experimented. Finally, the use of palladium on carbon for the hydrogenolytic debenzylation lead to the target compound. A multi-step purification process (LC, HPLC) was carried out to reach sufficient purity. Glycosylated standard was characterized by Nuclear Magnetic Resonance (NMR) and by High Resolution Mass Spectrometry (HRMS) and then used to develop an LC-MS/MS for its identification in grapes and wines. The first analytical results lead to look deeper into the search for glucosylated compounds in various oenological samples (grapes, musts, red wines), affected or not by the nuances of "dried fruits".

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Trifluoromethylated N,O- and N,S-acetals: new reversible functions for vitrimer application

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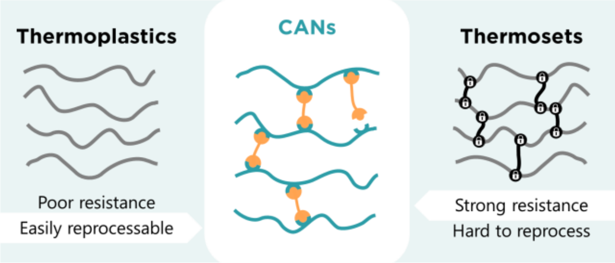
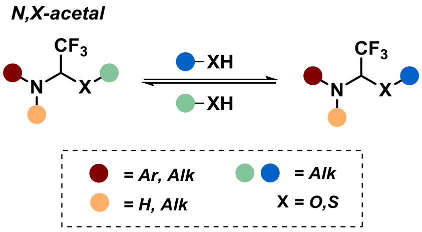
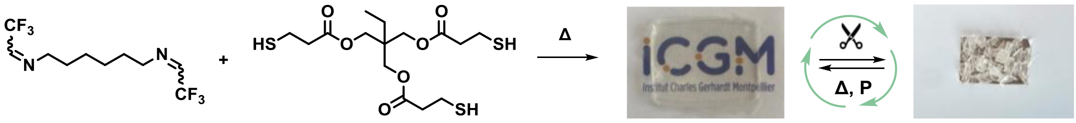
Vitrimers (or CANs), introduced by L. Leibler in 2011, are a new class of polymers combining the reshaping and recyclability properties of thermoplastics with the mechanical and chemical properties inherent to thermosets.[1] Vitrimers have a 3D crosslinked structure similar to thermosets, but feature exchangeable/reversible crosslinking bonds. The incorporation of fluorinated groups is a means to activate functional groups in order to promote exchange reactions without the need of a catalyst[2,3], but also to access new functional groups which are usually too unstable, such as N,O-acetals and N,S-acetals. These fluorinated acetals can undergo respectively alcohol and thiol exchanges. This work presents the synthesis of trifluoromethylated monomers and their incorporation into new N,O-acetals and N,S-acetals vitrimers.







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Journées Grand Sud-Ouest de la Société Chimique de France
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Design and synthesis of aza-helicene derivatives for the study of chiroptical properties in solutions, towards optoelectronic applications

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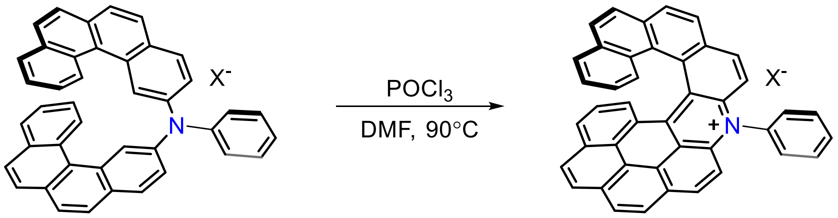
Circularly polarized luminescence (CPL) from chiral luminophores is an ideal approach for the direct generation of circularly polarized light. CPL-active chiral luminophores have widespread application prospects in 3D displays, optical sensors, and optical information storage or encryption. Among these, helicenes are undoubtedly the most extensively harnessed mainly because of their appealing helical shape combined with inherent electronic delocalization, resulting in unique spectral and optical features.

Molecular engineering provides a platform to further refine the photophysical properties of these helicenes. The modulation of helicene opto-electronic properties can be envisaged either via the introduction of one or more heteroatoms in the π-conjugated structure, resulting in heterohelicenes such as phosphahelicenes, azahelicenes, borahelicenes and silicahelicenes with strongly modified chiroptical response compared to carbohelicenes; or by enhancing their specific chiroptical properties through the design of multiple helicenes or π-extended systems, thereby promoting large π-electron delocalization and affording unique optoelectronic properties.

In the context of the first method, a convenient and modular synthesis route towards π-extended aza-helicenium encompassing ten aromatic fused rings, starting from simple triarylamine derivatives was developed.[1] The extended aza-helicenium showed multi-band electronic circular dichroism and remarkable long-wavelength CPL emission, with high absorption and luminescence dissymmetry factors, both in organic and aqueous media. In regard to the second method, through molecular engineering we are developing various aza-helicenes with extended π-conjugation as well as additional nitrogen atoms in the helical structure so as to modulate the chiroptical properties.



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Journées Grand Sud-Ouest de la Société Chimique de France
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Bio-inspired dendritic aromatic polyesters from bio-sourced phenolic acids and monosaccharides

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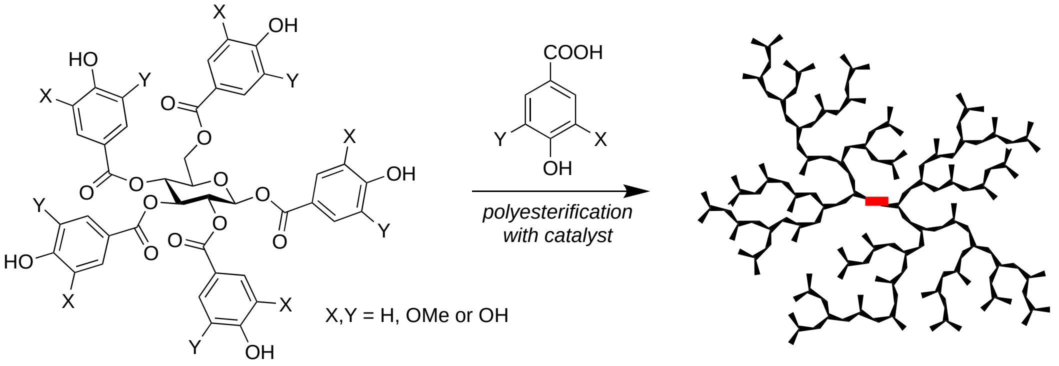
The theoretical concept of hyperbranched polymers was proposed in the 1940s by Flory, who employed statistical methods to explore the molecular size distribution of three-dimensional polymers during gelation.[1] Various types of hyperbranched polyesters (HBPEs), including aliphatic, aliphatic-aromatic and aromatic variants, have been extensively studied, developed and even commercialized for various applications over the past four decades.[2] However, to the best of our knowledge, there is currently no reported research on bio-based aromatic HBPEs. This project will introduce novel bio-based aromatic HBPEs to the field, which not only have a bio-sourced nature, but are also bio-inspired by the polyester structure of polyphenolic plant gallotannins. We are currently focusing on the polycondensation of phenolic acid ABn-type monomers originating from lignin and vegetable tannins. These phenolic acids are readily available multifunctional precursors that contain one carboxylic acid group (A) and up to three alcohol moieties (B). The core of the targeted aromatic polyesters is composed of a glucopyranose to which phenolic acids such as vanillic, protocatechuic and gallic acids are esterified according to in-house methodologies.[3] The polymerization process will be performed in bulk using an organocatalyst with the aim of controlling the degree of branching.[4] The selection of the appropriate phenolic acid monomers will enable us to adjust the density of branching and, consequently, the properties of the resulting materials, such as their rheological behavior.



Star-polymers (X,Y = H or OMe)
to hyperbranched polymers (X and/or Y = OH)

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Journées Grand Sud-Ouest de la Société Chimique de France
1-2 Février 2024, Bordeaux

Toward the preparation of photocathodes based on new organic photosensitizers and nanosized $CuMO_2$ delafossite particles.

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In the ongoing transition towards sustainable energy sources, dye-sensitized photoelectrochemical cells (DSPEC)[1] (***Fig.1***) represent a promising technology for the development of renewable energies. DSPECs facilitate the production of green hydrogen through the solar-driven splitting of water molecules. These intricate systems are constructed using photoactive electrodes comprising mesoporous semiconductors, onto which photosensitizers and water-splitting catalysts are immobilized. Specifically, the photocathodes in DSPECs traditionally incorporate nickel oxide as p-type semiconductor. However, inherent limitations such as low transparency and hole conductivity have prompted the exploration of alternative materials. Among these alternatives, some members of the delafossite family ($CuMO_2$, where M stand for a trivalent cation) exhibit promising features, including improved transparency and conductivity.

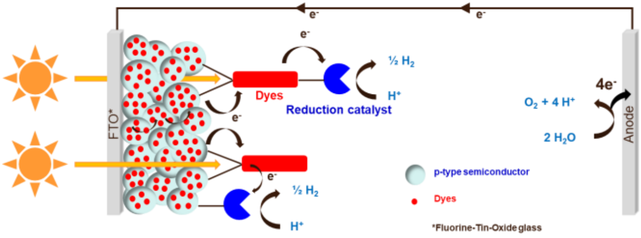

Fig. 1: Schematic representation of a DSPEC for water splitting based on a photocathode.

This presentation will provide a comprehensive overview of the advancements in my PhD project, focusing on three main areas: synthesis of organic photosensitizers, preparation of $CuMO_2$ particles and their formulation as inks for coating onto fluorine-doped tin oxide glass (FTO) substrates. To achieve this, new dyes endowed with phosphonic acid anchors derived from **P1** (***Fig.2a***), a well-described sensitizer for p-type dye-sensitized solar cells[2] were synthesised and characterized. Still within the framework of enhancing DSPEC, a solvothermal reaction technique was performed, utilizing microwave irradiation at low temperatures to obtain sub-micron-sized $CuGaO_2$ particles (***Fig.2b***). Inks where formulated from those particles using ethyl cellulose and then coated onto FTO glass to yield nanocrystalline porous $CuGaO_2$ films.

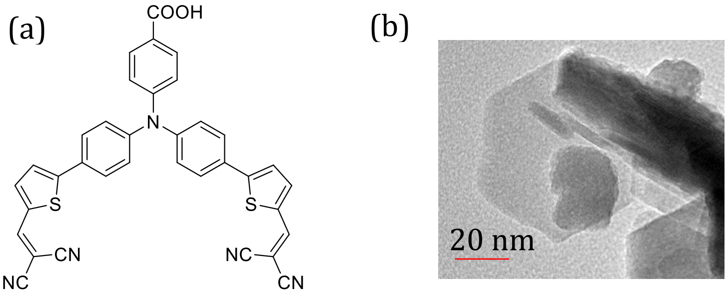

Fig. 2: Chemical structure of **P1** (a) and MET images of $CuGaO_2$ particles (b)

After highlighted the key steps on both organic photosensitizers and inorganic semiconductors synthesis, preliminary tests of dyes grafting on $CuGaO_2$ films will be discussed.

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[1] Licheng, S. et.al. *Energy Environ. Sci.* **2015**, 8, 760
[2] Pastore, M. et. al. *Appl. Energy Mater.* **2021**, 4 (6), 6180

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GAFFEx

GAthering of Fundamentally Failed Experiments

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With more than 5 millions scientific publications last year, publishing volumes are concerned by an exponential inflation (+5%/year) pushed by a strong international and financing competition. Despite this increased number of available studies, worldwide researchers are still producing non successful data not reaching their audience and making scientist powerless to answer the crisis of reproducibility[1]. Designated as “negative”, “null”, “inconclusive”, “sub-optimal” because they do not allow any hypothesis or a result to be confirmed, those results are still seen as fruitful for researchers and their community. Trying to explain why publishers are struggling publishing them, few studies identified several bottlenecks to be opened for those results to be share thus answering some of open science, reproducibility, scientific integrity and sobriety challenges[2]. In this context the platform GAFFEx.org is being developed to meet those challenges and facilitating negative results valuation by answering scientist issues in this specific field. Based on an adapted editorial model, GAFFEx.org is thus willing to offer a straightforward, robust, transparent system of submission and peer review including i) a submission form linked to an automated edition to save researcher time, ii) an open peer review system to allow a fast and robust evaluation without adding any charge to scientist peer review duties, iii) a focus around single experiments to avoid scientist to reveal any confidential or competitive activities and iv) an attribution of DOIs and registration through ORCIDs to ensure proper assignation, citation and record. Ultimately the platform is being developed by volunteers gathered under the banner of a non-profit organization, supported by several universities (UGA, UCBL) and research services (Datacc) to ensure that proposed features are fitting researchers needs and stave off any data monetization.

“Fails matter”

1) Baker, M. 1,500 scientists lift the lid on reproducibility. *Nature* **533**, 452–454 (2016). https://doi.org/10.1038/533452a
2) Herbet, M., Leonard, J., Santangelo, M., & Albaret, L. (2022). Dissimulate or disseminate? a survey on the fate of negative results. Learned Publishing, 35(1), 16-29. https://doi.org/10.1002/leap.1438

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