Journée SCF ALSACE

13 mars 2025 — Faculté des Sciences et Techniques de Mulhouse

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PROGRAM

08:30 **Get together**

09:00 – 09:15 Opening Vincent Bizet and Arnaud Spangenberg

Session 1 – *Chair: Vincent Bizet*

09:15 – 09:45 **Morgan Cormier** (Prix Jean Normant 2024)

"Development of New Photocatalytic Systems for Organic Synthesis : From Heterogeneous Catalysis to Near Infrared Chemistry"

09:45 – 10:00 **Ariana Villarroel Marquez**

"Photochemical bricks and understanding towards 3D-Conductive Photopolymers"

10:00 – 10:15 **Eliott Jung**

"Synthesis of bioinspired complex polycyclic motifs supported by DFT mechanistic Studies"

10:15 – 11:00 **Coffee break + Poster session**

Session 2 - *Chair: Karine Mougin*

11:00 – 11:30 **Liva Dzene** (Distinguished SCF junior member 2023)

"Synthesis of novel materials inspired by clay mineral structures"

11:30 – 11:45 **Loïc Groslambert**

"Chalcogen Bonds and Telluronium salts: An Emerging Tool for Catalysis"

11:45 – 12:00 **Paul Covin**

"Controlling surface chemistry to influence plasma polymers morphology"

12:00 – 14:00 **Lunch + visit of the Mat-Light 4.0 plateforms**

Session 3 - *Chair: David Leboeuf*

14:00 – 14:30 **Michael Parmentier** (Prix Yves Chauvin 2024)

"From medchem route to multi kg manufacturing– a process development story"

14:30 – 14:45 **David-Jérôme Pham**

“Chiral [2 + 3] Covalent Organic Cages Based on 2,2’-BINOL Units”

14:45 – 15:00 **Laurine Tual**

“Sulfur ylide-mediated ring expansion to access highly functionalized 1,4-thiazepines“

15:00 – 15:15 **Maxime Steinmetz**

“Encapsulated Cationic Ruthenium and Rhodium Catalysts: Controlling The Catalytic Outcome By Confinement”

15:15 – 15:30 **Dorian Schutz**

“Regio- and stereoselective azidation of activated *N*-allenamides: an entry to α, β, γ and δ-amido-azides”

15:30 – 16:15 **Coffee break + Poster session**

Session 4 - *Chair: Stefan Chassaing*

16:15 – 16:30 **David Matchavariani**

“Regio- and stereoselective halogenation reactions of SF_5-alkynes”

16:30 – 16:45 **Ademola Adeniji**

“The Role of Porous Carbon Properties for High Performance Sodium-ion capacitors”

16:45 – 17:15 **Valentyn POZHYDAIEV** (PhD Prize SCF-Alsace 2024)

"Difunctionalization of Electron-Poor Alkenes: Pushing Limits of Impossible with HFIP"

17:15 – 17:30 Poster/OC Prizes and closing remarks

SPEAKERS

Morgan CORMIER began his training in organic synthesis at the University of Lorraine. He then obtained a PhD in organic chemistry from the University of Rouen in the COBRA laboratory, under the supervision of Drs. Michaël DE PAOLIS and Jacques MADDALUNO. During his thesis, he was interested in the synthesis of of a natural product, tridachiapyrone B, and undertook methodological studies in polar organometallic chemistry. He then joined the group of Prof. Ilan MAREK at the Technion Institute of Technology (Haifa, Israel) for a first postdoctoral internship before a second experience at the ISM in Bordeaux in the group of Prof. Eric FOUQUET and Dr. Philippe HERMANGE. In 2018, Morgan was recruited as a Lecturer at the University of Haute-Alsace (UHA), where he teach at the Ecole Nationale Supérieure de Chimie de Mulhouse (ENSCMu) and carried out his research at the Laboratoire d'Innovation Moléculaire et Application (LIMA). He joined the Radical Chemistry Heterocycles and Interfaces (CRHI) team led by Professor Jean-Philippe GODDARD and defended his Habilitation à Diriger des Recherche (HDR) in 2024 at the UHA. His research interests are centered around the development of new photocatalytic systems applied to organic synthesis including homogeneous, heterogeneous, near-infrared photocatalysis and photoclick. In 2024, he was the laureate of the Jean NORMANT prize from the Organic Chemistry Division (DCO) of the SCF.

Michael PARMENTIER obtained his master's degree in chemistry from the University of NANCY. In 2004, he began his doctoral studies at the University of MONTREAL (CANADA) in the laboratory of Prof. Hélène LEBEL where he completed the total synthesis of an interleukin inhibitor and developed metal-catalyzed aziridination reactions using nitrenes. In 2009, he returned to Europe and joined the group of Prof. Andreas PFALTZ at the University of BASEL as a postdoctoral researcher working on C-H activation reactions applied to hydrogen isotope exchange reactions in close collaboration with Hoffman-La-Roche laboratories. Since 2012, he is a process chemist at NOVARTIS (BALE) in chemical and analytical development. Over the years, he has contributed to the development of several pharmaceutical compounds at the multi-kilogram scale. In addition to his scientific activities, Michael has managed exchanges with the academic world for many years, including the establishment of academic collaborations and the development of internship programs. Since 2018, he is member of the directory board of the School of Chemistry, Polymers and Materials (ECPM) in STRASBOURG and an active member of the Bureau of the Division of Industrial Chemistry (DCI) and of the SCF-ALSACE. He co-organizes the French Industrial Chemical Symposium (FICS) which highlights research and development in industrial chemistry. Michael recently became a Novartis Leading Scientist and won the Yves CHAUVIN Prize, which is awarded to an industrial chemist by the Division of Organic Chemistry (DCO).

Liva DZENE is a lecturer at ENSCMu since 2017. Her career path was built around the desire to discover the world and the thirst to know what lies beyond the horizon. This motivated her to pursue international studies and take an interest in the field of research. She began her studies in Latvia in chemical engineering at the Technical University of Riga. Then, she obtained an Erasmus Mundus excellence scholarship to continue her studies in the “International Master in Advanced Clay Science” program between three countries: at the University of Poitiers in France, at the University of Aveiro in Portugal and the University of Ottawa in Canada. Passionate about research, she defended a thesis at the Institute of Chemistry of Environments and Materials in Poitiers on the reactivity of the surface of clay minerals. Today, her research at the Institute of Materials Sciences in Mulhouse focuses on the synthesis of lamellar materials inspired by the structures of natural clay minerals. These are nanosheets that are found everywhere: in the deepest cracks of the ocean, in soils and on the surface of Mars, in various formulations such as creams and paints, and in composite materials with cement and polymers. In 2023, she was named a Junior Distinguished Fellow of the SCF.

Valentyn POZHYDAIEV is originally from Kyiv, Ukraine, he obtained his BSc and MSc degrees in chemistry at the Université de Strasbourg. After 1-semester internship at BASF in Ludwigshafen, he started his PhD studies under the supervision of Pr. Joseph Moran and Dr. David Lebœuf. His research focused on the development of methodologies using hexafluoroisopropanol as a solvent to unlock the reactivity of highly electronically deactivated substrates. His work was rewarded with the SCF-Alsace PhD prize 2024. He is currently working as a postdoctoral associate with Prof. J. M. Lehn in Strasbourg.

Oral communications

OC1

Journée SCF Alsace 2025 – March 13th 2025 – Mulhouse

Photochemical bricks and understanding towards 3D-Conductive Photopolymers

Ariana Villarroel Marquez[1], Christian Ley[1], Céline Croutxé-Barghorn[1], Xavier Allonas[1]

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Organic electroactive materials have emerged and grown as a fascinating research and technological area. Representative examples of their application replacing on some fields their classical inorganic analogues are on expansion, i.e. on flexible functional materials for Organic photovoltaics (OPVs), Organic light-emitting diodes (OLEDs) or bioelectronics.[1]

To go further on applications development, *i.e.* to target customizable and complex architectures and materials generation, deeper physico-chemical understanding, characterization and control of polymerization processes of these materials is required. In this context, the potential of additive manufacturing is undeniably to produce in a reduced time and in a more ecological manner conductive organic and/or hybrid materials.[2]

From a fundamental point of view, knowledge on new strategies of photoinitiating systems are required to be explored and characterized by photochemical and real-time spectroscopy techniques. In addition, Confocal Raman Microscopy (CRM) will be presented for its power to characterize the intrinsic chemical properties of organic materials. Highly solved spatio-temporal description of chemical composition on the surface and more importantly along the depth of the material, will allow to correlate the formation and history of the analyzed coating films and materials.

In brief, a complementary "bricks" toolbox constituted of fundamental chemical, photochemical, electrochemical and spectroscopic techniques (*i.e.* RT-FTIR, CRM) will shed light on fundamental-experimental investigation of active semi-conducting materials. New pathways on their additive manufacturing will bring advances on a more complex and stricter environmental and industrial regulations global context.

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[1] a) Groenendaal, L. B.; Jonas, F.; Freitag, D.; Pielartzik, H., Reynolds, J. R. Poly(3,4-ethylenedioxythiophene) and its derivatives: past, present and future. Adv. Mater., 12(7), 2000, 481- 494. b) Swager, T. M. 50th anniversary perspective: Conducting/semiconducting conjugated polymers. A personal perspective on the past and the future. Macromolecules. 50(13), 2017, 4867-4886. [2] a) Loterie, D., Delrot, P., Moser, C. High-resolution tomographic volumetric additive manufacturing. Nat. Comm., 11(852), 2020; b) Bao, Y., Paunović, N.; Leroux, J. Challenges and opportunities in 3D printing of biodegradable medical devices by emerging photopolymerization techniques. Adv. Funct. Mater., 32(15), 2022, 2109864.

OC2

Synthesis of bioinspired complex polycyclic motifs supported by DFT mechanistic studies

Eliott JUNG,[1,2] *Valérie BÉNÉTEAU*,[1] *Patrick PALE*,[1] *Stefan CHASSAING*,[1*] *and Christophe GOURLAOUEN*[2*]

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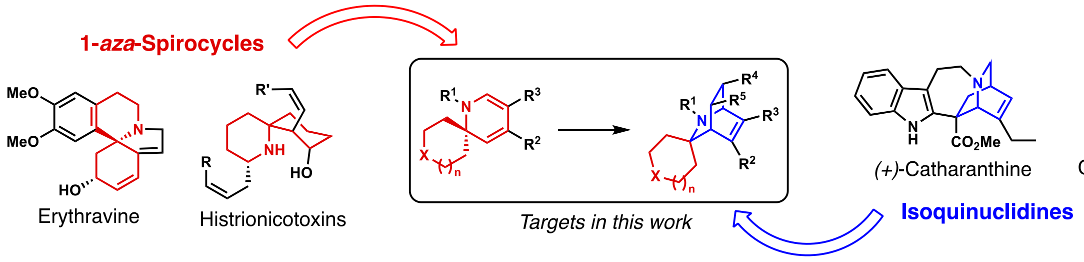
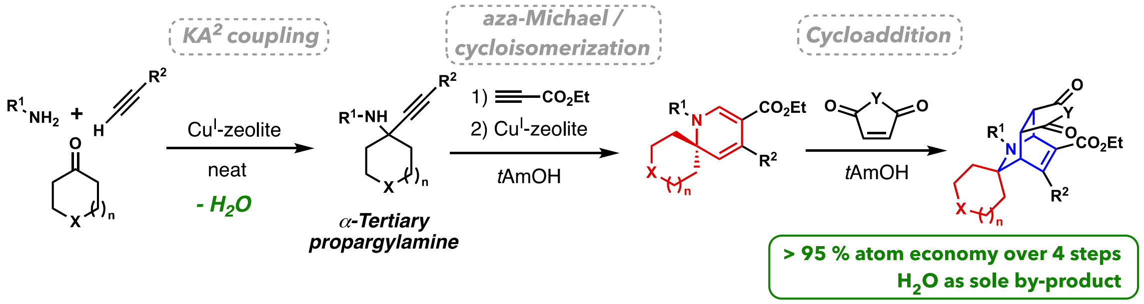
Constructing 3D *aza*-polycyclic architectures remains a big challenge in organic synthesis. In particular, much synthetic efforts have been devoted to 1-azaspirocyclic and isoquinuclidine ring systems, due to their presence in many natural products of biological relevance (**Scheme 1**).[1,2] Our goal is to go further in 3D structural complexity by accessing to unprecedented architectures merging these two *aza*-cyclic systems of high relevance.



Scheme 1

Herein, we wish to report our synthetic approach towards this complex azaspiro/isoquinuclidine hybrid skeleton from simple starting materials (**Scheme 2**). Our approach starts with a 3-step sequence, including 2 steps under Cu^I-zeolite catalysis (*i.e.,* KA^2 coupling and enyne cycloisomerization reactions)[3], that first furnishes 1-azaspirocyclic systems featuring a 1,2-dihydropyridine motif. The potential of the resulting 1,2-dihydropyridine motif as diene is finally exploited to construct the additional isoquinuclidine ring system *via* a formal cycloaddition process.[4] DFT calculations are conducted in parallel to rationalize the reaction mechanism and energetic pathway of the cycloaddition process. Noteworthy is that this methodology is highly atom and step economical, with water as sole by-product during the whole 4-step sequence.



Scheme 2

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OC3

Chalcogen Bonds and Telluronium salts: An Emerging Tool for Catalysis

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Interactions based on σ-hole on halogen or chalcogen atoms have recently emerged. They have been recognized as non-covalent interaction (NCI) and rationalized using the concept of σ-hole.[1] Covalently bonded chalcogens exhibit an area with a positive electrostatic potential along the σ* orbitals allowing them to interact with a Lewis Base. Compared to halogen, chalcogen atoms like tellurium are able to promote multiple σ-holes, favouring σ-hole interactions (Figure 1A). Tellurium derivatives proved to be very effective as catalysts due to their strongest Lewis acidity compared to Selenium and Sulphur, but their use in catalysis is still scarce.

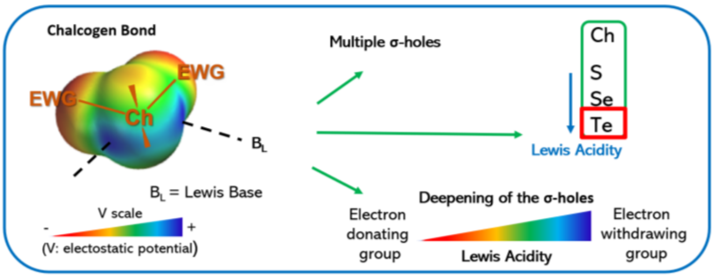

Figure 1A: Generalities concerning chalcogen bond and σ-holes

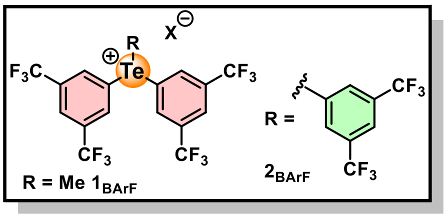

Figure 1B: Examples of Telluroniums salts

Nevertheless, applications based on ChBs have developed rapidly in recent years and significant progress has been made in the field of crystal engineering[2] and catalysis.[3] However, their involvement in stereoselective processes remains relatively unexplored.[4] Furthermore, the study of these interactions has been very limited in solution due to their weakness of interaction, and in particular, due to competitive interactions such as solvation. Thus, a better understanding of these interactions in solution would be of crucial interest, particularly for developing effective organocatalysts.[5] Telluronium salts developed in our laboratory (Figure 1B) have shown very interesting catalytic properties and exhibit strong affinities for various Lewis base systems, allowing their study in solution and deepening the understanding of chalcogen bond formation.[6,7] A series of telluronium salts was synthesized and evaluated in various reactions[8] (Friedel-Crafts reaction, bromolactonization of ω-unsaturated carboxylic acids, and Aza-Diels-Alder reactions such as Povarov-type reaction[9]).

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Journée SCF Alsace 2025 – March 13th 2025 – Mulhouse

Controlling surface chemistry to influence plasma polymers morphology

Paul Covin[1], Aissam Airoudj[1], Cédric Noël[2], Florence Bally-Le Gall[1], Thierry Belmonte[2], Vincent Roucoules[1], Jamerson C. de Oliveira[1]*
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Plasma polymerisation is a dry process that uses plasma, an ionised gas composed of charged particles such as electrons, ions and free radicals. The plasma can be generated from an organic molecule (precursor) in the vapour phase exposed to an external energy source, in this case an electromagnetic field. The reactive species generated in the plasma then react following different mechanisms to finally form a coating on a surface known as a plasma polymer. In the literature, several studies have shown that the resulting coating can be nanostructured. However, the origin of this nanostructuration has not yet been clearly identified. Experimentally, it has been shown that several experimental parameters can have an impact on the morphology of the coating obtained. These parameters include plasma deposition conditions (power, duty cycle, frequency)[1] or the surface chemistry of the substrate[2]. By varying these parameters, it is possible to obtain coatings ranging from thin films to nanostructures on the surface.

In this work, the idea is to focus on the effect of surface chemistry on the morphology of the plasma polymer obtained. Indeed, a complete understanding of the contribution of surface chemistry could make it possible to progress towards the origin of nanostructuration. In order to study that, we selected as strategy the preparation of varied surface chemistries through the fabrication of reactive self-assembled monolayers (SAMs). It is well known that SAMs can chemically modify surfaces without significant topographical changes. In addition, if they are reactive, they can be coupled with simple methods for chemical modification, such as thiol-ene click chemistry, known for its straightforwardness and simplicity[3]. Thus, a combination of SAMs and thiol-ene click chemistry was employed in the current work. Vinyl-terminated self-assembled monolayers were generated and subsequently post-functionalised using thiol-ene click chemistry via a maskless lithography system. The different surface chemistries were then subjected to citronellal plasma polymer deposition. Finally, the coatings were characterised to establish a link between surface chemistry and plasma polymer morphology.

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OC5

Journée SCF Alsace 2025 – March 13th 2025 – Mulhouse

Chiral [2 + 3] Covalent Organic Cages Based on 2,2′-BINOL Units

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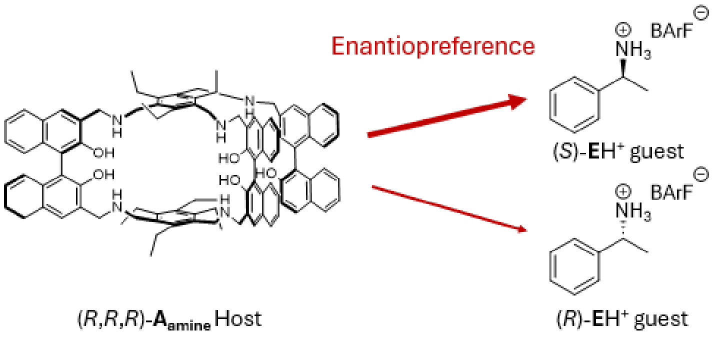
Chiral covalent organic cage is an emerging class of architecture with various applications such as gas separation, chiral separation, and catalysis.[1] Combining dynamic covalent chemistry and chiral building blocks, self-assembly of chiral cages can be achieved.[2] In this contribution, a [2+3] enantiopure covalent organic cage ($\mathbf{A}_{\text{imine}}$) was synthesized through the condensation between a 3,3′-diformyl 2,2′-BINOL unit with a triamino spacer in near quantitative yields.[3] Then, the reduction of the imine bonds of cage $\mathbf{A}_{\text{imine}}$ into irreversible amine bonds was performed to increase cage stability. Binding studies of cage $\mathbf{A}_{\text{amine}}$ with enantiopure phenylethylammonium cations (EH$^+$) were preformed using UV-vis spectroscopy and DOSY NMR and a higher binding constant between (*R*)-EH$^+$ and (*R*,*R*,*R*)-$\mathbf{A}_{\text{amine}}$ compared to (*S*)-EH$^+$ was obtained. This enantiopreference is in agreement with results obtained through molecular dynamics simulation.



Scheme showing an enantiopreference for the binding of (*R*,*R*,*R*)-$\mathbf{A}_{\text{amine}}$ with (*S*)-EH

1. Montà-González, G.; Sancenón, F.; Martínez-Máñez, R.; Martí-Centelles, V. Purely Covalent Molecular Cages zand Containers for Guest Encapsulation. *Chem. Rev.* **2022**, *122*, 13636–13708

2. Ono, K.; Iwasawa, N. Dynamic Behavior of Covalent Organic Cages. *Chem. Eur. J.* **2018**, *24*, 17856–17868

3. Mohan, M.; Pham, D-J.; Fluck, A.; Chapuis, S.; Chaumont, A.; Kauffmann, B.; Barloy, L.; Mobian, P. *Chem. Eur. J.* **2024**, *23*, e202400458

OC6

Sulfur ylide-mediated ring expansion to access highly functionalized 1,4-thiazepines

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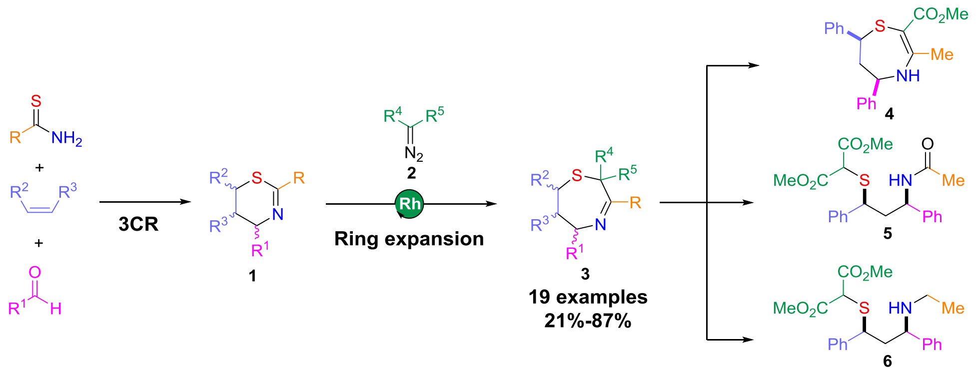
The pharmaceutical industry is currently faced with the need for molecular diversity and structural originality to discover new drug candidates. Heterocycles play a key role in the structure of bioactive molecules.[1] Among them, mixed sulfur and nitrogen (N,S)-heterocycles, especially 5- and 6-membered rings, have demonstrated their interest in medicinal chemistry and pharmaceutical industry.[2] Medium-sized rings are however under-represented due to the difficulty of synthesis. In this context, the development of new synthetic routes is crucial to access complex and original (N,S)-heterocyclic structures efficiently and in a minimum of steps.

Here we report a ring expansion of 6-membered (N,S)-rings leading to new diversified 7-membered (N,S)-heterocycles. Starting from 1,3-dihydrothiazine precursors **1** obtained via a three-component reaction developed by our group,[3] the ring expansion proceeds via their reaction with a metallocarbene to yield 1,4-thiazepines **3**. The metallocarbene is generated in situ by decomposition of the diazo compound 2 in the presence of a rhodium(II) complex. After optimisation, the scope of the reaction was investigated by varying both the 1,3-dihydrothiazine **1** and the diazo partner **2**. Finally, the reactivity of the 1,4-thiazepines was explored and allowed to obtain new (N,S)-heterocycle **4**, amidothioether **5** and aminothioether **6**.



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OC7

Encapsulated Cationic Ruthenium and Rhodium Catalysts: Controlling The Catalytic Outcome By Confinement

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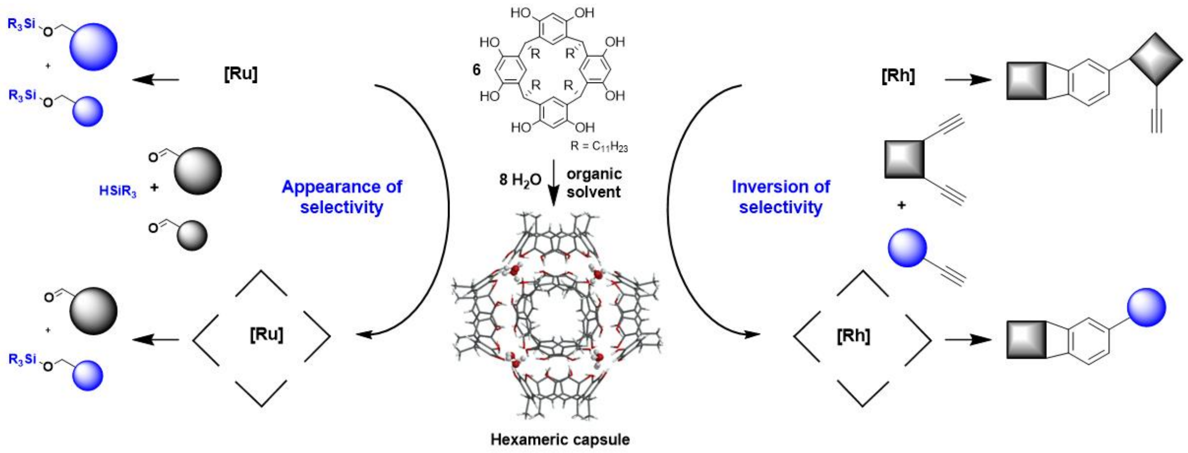
Catalysis with molecular containers is an emerging field due to its similarity with enzymes.[1] Two ways of making large assemblies exist: *i*) the formation of covalent cages or metallo-capsules but their synthesis require several steps, like in the case of the pallado-trimeric-resorcinarene, previously reported;[2] *ii*) supramolecular assemblies, which are easily achievable like the self-assembled capsule based on 2,8,14,20-tetra-undecyl-resorcin[4]arene discovered by Atwood.[3] By using this hexameric host, two new complexes of ruthenium and rhodium were encapsulated. The formation of inclusion complexes was deduced from UV/Vis and NMR (^{1}H, ^{31}P and DOSY) spectroscopies in the same way as in our previous example based on a neutral ruthenium catalyst.[4] The embedded ruthenium complex was evaluated in the competitive hydrosilylation of mixtures of aldehydes. With the encapsulated catalyst, the smaller aldehyde is converted faster than more sterically hindrance aldehydes. On the other hand, the rhodium complex was used to modify the catalytic outcome of the [2+2+2] cycloaddition. With the unencapsulated catalyst, we mainly observe the formation of the homocycloaddition product, while in the presence of the supramolecular assembly the heterocycloaddition product is favored. These two examples clearly show the benefic role played by the self-assembling capsule, which is able to select a reagent from a mixture of substrates or to modify the nature of the formed products.



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OC8

Regio- and stereoselective azidation of activated *N*-allenamides: an entry to α, β, γ and δ-amido-azides

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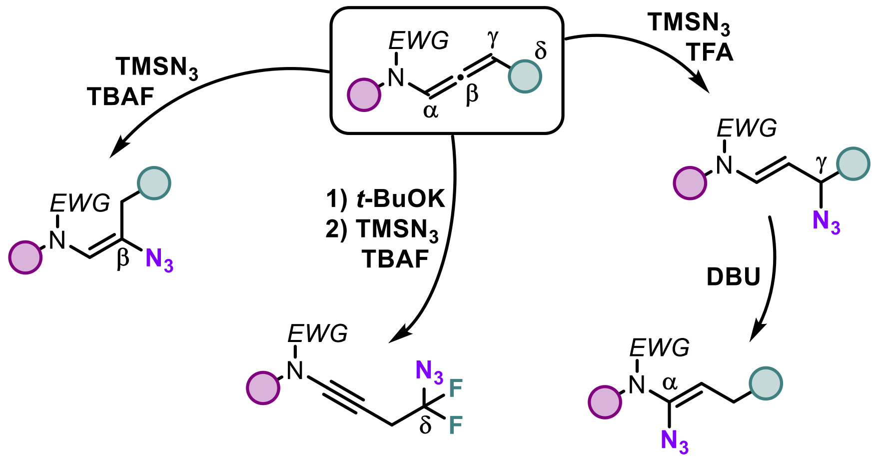
Organic azides are versatile synthetic intermediates. Among them, the unique features of vinyl-azides have turned these compounds into critical building blocks for the construction of *N*-heterocycles. The remarkable properties of the azide group connected to an alkene moiety allow this functional group to act as an electrophile, an enamine-type nucleophile or a radical acceptor.[1] The multifaced reactivity of these highly versatile synthons have generated a great inspiring variety of intermediates such as iminodiazonium ions, nitrilium ions, iminyl radicals and metal enaminyl radicals upon heating-, metal-or light-induced processes.[2] Following our interest in the preparation of nitrogen-containing building blocks, we envisioned that *N*-allenamides would be ideal candidates to generate vinyl azides.

A totally controlled regiodivergent azidation of activated *N*-allenamides is presented. Using $TMSN_3$/TBAF, b-azidation of *N*-allenamides occurred exclusively, yielding vinyl azides. Conversely, employing a TFA/$TMSN_3$ mixture resulted solely in the formation of g-azides. A subsequent azide shift of the latter with DBU produced a-amido vinyl azides. Additionally, d-difluorinated azides featuring an ynamide were selectively synthesized from ene-ynamides.[3]



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OC9

Journée SCF Alsace 2025 – March 13th 2025 – Mulhouse

Regio- and stereoselective halogenation reactions of SF_5-alkynes

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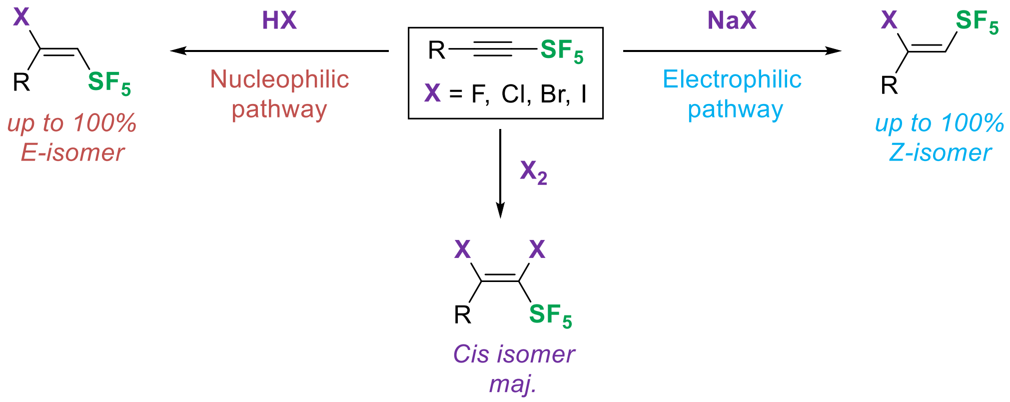
SF_5-Containing haloalkenes are usually obtained by the addition of SF_5X gas (X = Cl, Br) onto the corresponding terminal alkynes but the E-stereoselectivity is usually observed under radical condition,[1] or a mixture of E/Z isomers under thermal conditions.[2] Recently, our group proved that SF5-alkynes are highly reactive toward the addition of N-, O-, and S-nucleophiles yielding in all cases a single regio- and stereoisomer.[3] We then wondered if the SF_5-alkynes could react both as electrophiles or nucleophiles depending on the reaction conditions, so we selected the hydrohalogenation as benchmark reactions. Herein is presented efficient strategies to perform hydrohalogenation with all the halogens (I, Br, Cl and F) and methods to access both the E and the Z-SF_5-haloalkenes following two different mechanisms, with relative configuration of all the stereoisomers confirmed by X-ray diffractions. Dihalogenation reactions with I_2, ICl and Br_2 are also discussed. Moreover, preliminary DFT calculations are presented to confirm the reaction mechanisms and to explain the high regio- and stereoselectivity.[4]



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OC10

The Role of Porous Carbon Properties for High Performance Sodium-ion capacitors

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The potential of sodium ion capacitors exhibiting high energy and power density has seen their adoption on the rise. They typically consist of negative electrode made of hard carbon (where Na ion insertion takes place) and a positive electrode composed of activated carbon (involving adsorption/desorption of the negative electrolytic ions),[1] Figure 1a. However, activated carbons are often limited by their low discharge specific capacity (< 100 mAh/g) in comparison with the hard carbon anode with a discharge capacity > 300 mAh/g.[2] Thus, this has necessitated the synthesis of new porous materials and the investigation of how the properties of these materials affect their electrochemical performance. In this work, we described the development of porous carbon using soft-salt templating method where nitrogen and oxygen functionalities are incorporated into the carbonaceous structure. This helps in achieving textural modification consisting of large specific surface area (up to 2650 m^2/g), graphitic domains, and a tuned pore size that satisfies electrolytic ion size requirement of 0.8 nm. The developed porous carbon achieved a capacity of 189 mAh/g in $NaPF_6$ electrolyte. Linear trends (Figure 1b) showed that the improved specific capacity is as result of the well-developed textural properties such as the high specific surface area which enhance the electric double layer capacitance. The SIC full-cell configuration, which comprises a hard carbon anode and the optimal positive electrode material, achieves a high energy density and power output with an excellent cycle life.

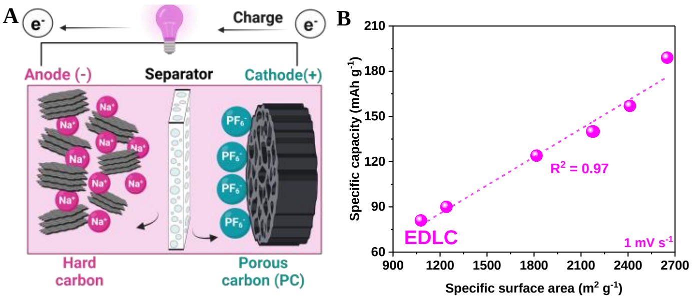

Figure 1: (a) Graphical representation of sodium ion capacitor full cell. (b) Plot of the specific capacity versus the specific surface area highlighting the electric double layer capacitive (EDLC) mechanism.

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Posters

Synthesis and study at the micro / nano scale of Poly(Diiododiacetylenes): on the road to carbyne?

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After the discovery of fullerenes, carbon-nanotubes and graphene, one carbon allotrope described as "illusive"[1] has still not been studied properly: the carbyne.

This allotrope is defined as an infinitely long polyyne molecule (–[C≡C–]n)[2]. It is a major subject of interest with not well known physical properties: Young's modulus, nature of conductivity, charge mobility, possibility of a Seebeck effect etc. Also, its stability remains the major barrier to its large-scale production[3], and the definitive evidence of its solid form synthesis has yet to be obtained.

Taking in account that carbyne has been being try to synthesize from other allotrope (CNT or graphene)[4], by liquid laser ablation (LAL)[5] and by chemical assembling[6] we want to propose and develop new alternative method of obtaining carbyne from polydiidodiacetylene or PIDA – a long 1D conjugated polymer, where carbon chain substituted with only single-atom - iodine.

In this work using host-guest topochemical polymerization strategy following N. S. Goroff *et al.*[7] and L. Luo *et al.*[8] we developed and optimized the procedure of obtaining Host-PIDA co-crystal in gram-scale. We show using FTIR, Raman spectroscopy, as well as XRD, EDX, and NMR, that it is possible to remove the host molecules and isolate a stable PIDA polymer. We will show our first tentative of producing a PIDA-based Organic Field Effect Transistor (OFET) and first results of electrical measuring.

Next step – transformation of PIDA to carbyne, can be made by de-iodination of the PIDA via several methods: chemically - reaction with bases, physically – thermal, light irradiation or atom by atom using the STM technique.

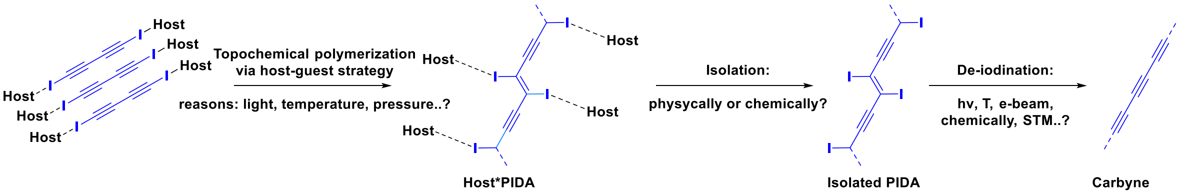

Figure. *Short schema of research project: carbyne synthesis from conjugated polymer*

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P2

Journée SCF Alsace 2025 – March 13th 2025 – Mulhouse

Near-Infrared Photooxidation of Dihydrotetrazine for Applications in Bioconjugate Chemistry

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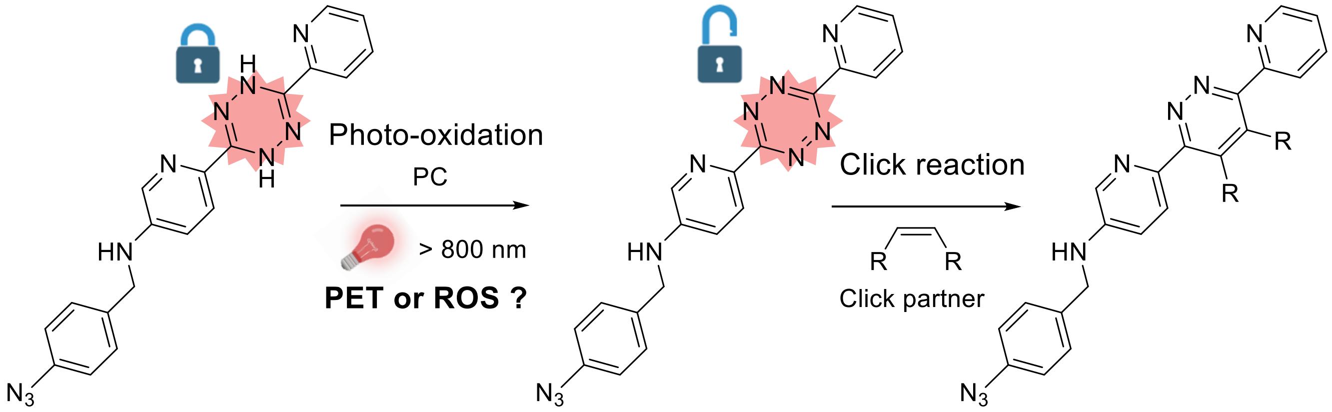
Synthetic chemists aspire to control each parameter involved in organic transformations, such as efficiency, selectivity (chemo-, regio-, enantio-selectivity), and kinetics. The next level of control needed for applications is the reaction's temporal and spatial trigger. This is particularly required for biological/pharmaceutical applications such as drug delivery or medical diagnostics.[1] Governing the reaction through a simple switcher is appealing, and the photo-click concept is a wonderful tool for achieving this goal. In this case, the click reaction, which has many advantages (kinetic, selectivity…), is triggered by light. Until now, the photoclick concept has been developed from UV to visible light.[2] However, near-infrared light presents many advantages, such as light penetration, biocompatibility and low energy.[3]

Based on our previous works on NIR-photocatalysis driven by cyanines and squaraines[4,5], we tackle the challenge of NIR-Photoclick. Herein, the NIR-photooxidation of dihydrotetrazine to deliver the clickable tetrazine is presented. This study includes photocatalyst design, optimization, and mechanistic discussion. The last point is crucial to reach the best photocontrol. Does the reaction proceed through a photoinduced electron transfer, reactive species of O_2 or both?



Scheme 1: Near-Infrared Light triggered click reaction

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SYNTHESIS AND STUDIES OF OLEOGELS AS SUBSTITUTES FOR STRUCTURAL FATS

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Trans-unsaturated fatty acids (TFA) in the diet represent a major public health problem because they increase the frequency of cardiovascular diseases. TFAs are present in many solid fats of animal origin or in margarines, resulting from the hydrogenation of vegetable oils. However, these solid fats are necessary to texture the lipid phases of food. In this context, many studies are being carried out to replace solid fats in foods. One of the most promising ways is to solidify cis-unsaturated oils (liquid at room temperature) by organogelators. These small molecules gel solvents at low concentrations, typically a few percent by weight [1] self-assembling into a solid 3D network in oil. Organogelators capable of gelling edible oils are called oleogelators. Examples of oil gelators are easily found in the literature, but for food applications, they must be without adverse effects when taken orally. In the present work we have synthesized *N*-acyl-amino acids because this compounds are endogenous i.e. naturally present in the body. We have studied the thermodynamic properties of the gels formed with it by micro differential calorimetry (µ-DSC), and their mechanical properties as a function of temperature. From these measurements, we mapped out the c-T phase diagram. The structures have been investigated by cryo-SEM, WAXS, and FTIR, and were correlated with thermal and mechanical behaviour.
These gels are also under investigation to understand the impact of gelation on pancreatic digestion.

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P4

Journée SCF Alsace 2025 – March 13th 2025 – Mulhouse

Development of new methods for the synthesis of nitrogen-containing heterocycles catalyzed by gold(I)-polyoxometalates complexes

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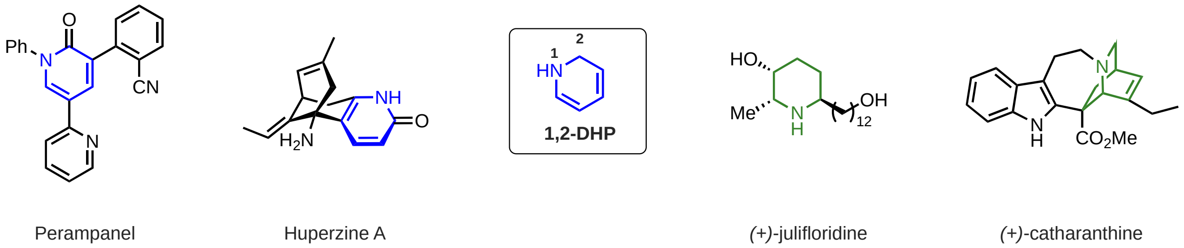
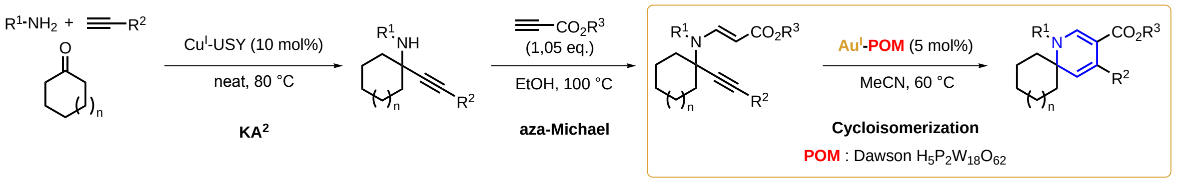
Nitrogen-containing heterocycles have always attracted considerable interest in organic synthesis and medicinal chemistry due to their wide range of biological activities. Currently, approximately 60 % of drugs are based on nitrogen-containing heterocycles, highlighting their importance in the design of new drugs.[1] Among these structures, 1,2-dihydropyridines, although rare, exhibit interesting biological activities, notably on the nervous system.[2] These molecules also serve as key intermediates in synthesizing piperidines and isoquinuclidines, scaffolds found in natural alkaloids.[3] (**Scheme 1**).



Scheme 1

Therefore, accessing the 1,2-dihydropyridine framework has been the subject of significant research. Among the various approaches reported, the cycloisomerization of aza-1,5-enynes has emerged as an attractive tool due to its excellent atom economy. In our laboratory, we developed a route to highly functionalized spiro-1,2-dihydropyridines using heterogeneous copper(I)-doped zeolite catalysis (Cu^{I}-USY Ultra-Stable Y).[4] To address the limitations of the zeolite-catalyzed version, this project proposes using gold(I)-based heterogeneous catalysts supported on polyoxometalates (POMs).[5] In addition to being generally inexpensive, easy to prepare, and straightforward to recover/recycle, our supported catalysts have proven highly efficient for various significant organic transformations, allowing access to key molecular "building blocks" for the chemical and pharmaceutical industries under "green" conditions.



Scheme 2

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Ultrafast sunlight-induced polymerization: Unveiling 2-phenylnaphtho[2,3-d]thiazole-4,9-dione as a unique scaffold for high-speed and precision 3D printing

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Abstract:

In my study, A series of 15 novel dyes based on the 2-phenylnaphtho[2,3-*d*]thiazole-4,9-dione scaffold and 1 compound based on the 2,3-diphenyl-1,2,3,4-tetrahydrobenzo[*g*]quinoxaline-5,10-dione scaffold are synthesized and studied as photoinitiators. These compounds are used in two- and three-component high-performance photoinitiating systems for the free radical polymerization of trimethylolpropane triacrylate (TMPTA) and polyethylene glycol diacrylate (PEGDA) under natural sunlight conditions. Remarkably, the conversion of TMPTA can reach ~60% within a mere 20 seconds, while PEGDA attains a 96% conversion within 90 seconds. To delve into the intricate chemical mechanisms governing free radical polymerization, an array of analytical techniques is employed. Specifically, UV-visible absorption and fluorescence emission spectra, steady-state photolysis experiments, stability experiments, fluorescence quenching experiments and electron spin resonance spin trapping (ESR-ST) experiments, collectively contribute to a comprehensive understanding of the photochemical mechanisms. Of particular interest is the revelation that, owing to the superior initiation ability of the various dyes, high-resolution 3D patterns can be successfully manufactured by direct laser write (DLW) technology and 3D printing. This underscores the efficient initiation of free radical polymerization processes by the newly developed dyes under both artificial and natural light sources, presenting an avenue for energy-saving and environmentally friendly polymerization conditions.

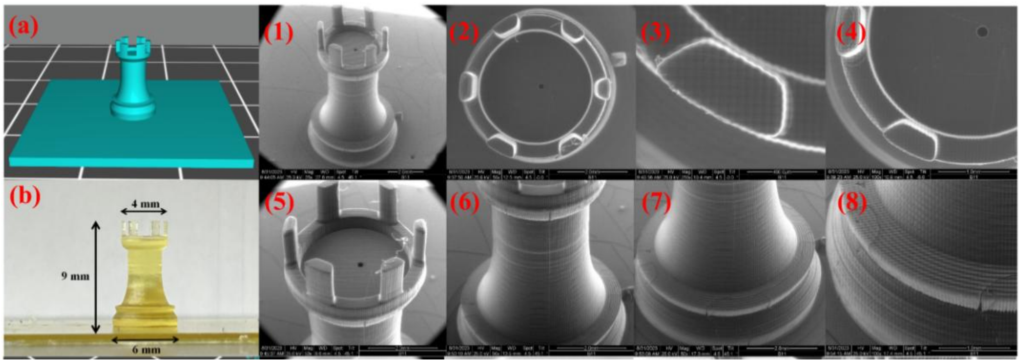

Figure 1. Digital and SEM photos of 3D printed objects.

P6

Novel High-Performance Glyoxylate Derivative-based Photoinitiators for Free Radical Photopolymerization and 3D Printing with Visible LED

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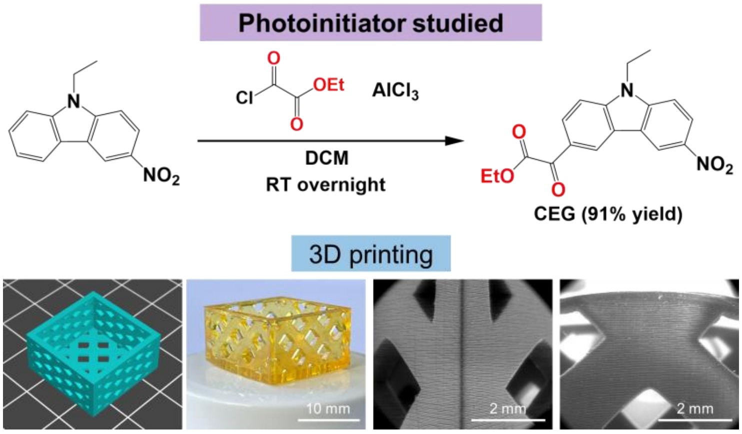
Investigations concerning the glyoxylate moiety as a photocleavable functional group for visible light photoinitiator, particularly in the initiation of free radical photopolymerization, remains limited. This study introduces innovative carbazole-based ethyl glyoxylate derivative (CEG), synthesized and found to exhibit excellent photoinitiation abilities as monocomponent photoinitiating systems. [1] Notably, the structure demonstrates robust absorption in the near-UV/visible range, surpassing the commercial photoinitiator. Moreover, the newly developed glyoxylate derivative showed higher acrylate function conversions compared to a benchmark photoinitiator (MBF) in free radical photopolymerization. Elucidation of the photoinitiation mechanism of CEG was achieved through comprehensive analysis involving the decarboxylation reaction and electron spin resonance spin trapping. Furthermore, their practical utility was confirmed during 3D printing processes, enabling the successful fabrication of 3D printed object. This study introduces pioneering concepts and effective strategies in molecular design of novel photoinitiators, showcasing their potential for highly advantageous applications in 3D printing.



Scheme. Chemical structure, synthetic route, and 3D printing application of the ethyl glyoxylate derivative (CEG).

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Quantification of functional groups and active sites of activated carbons by TPD-MS and their role in the performance of aqueous supercapacitors

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Activated carbons have been widely used in aqueous supercapacitors thanks to their high specific surface area. Their surface groups and active surface area (ASA), which are carbon edge planes and defects, are quantified by means of thermodesorption coupled with mass spectrometry (TPD-MS). New correlations with capacitance have been established in acidic, neutral and basic electrolytes. ASA analysis has been developed for graphitic materials (Laine et al.[1]) but leads to material burn-off and ASA overestimation, when applied to activated carbons. The measurement of burn-off gases shows that oxygen chemisorption temperature should be lowered to 150°C for activated carbons (Figure 1, left). The quantification of oxygenated surface groups, by means of the deconvolution of TPD-MS desorption rate profiles, highlights for the first time, a linear improvement in capacitance with increasing carboxylic acid and phenol-ether groups. On the contrary, carbonyl-quinones are detrimental to capacitance. A new approach consisting in the deconvolution of the ASA profiles is proposed and highlights the correlations between the ASA groups, like carbonyls-quinones, and an enhanced capacitance (Figure 1, right). The energy storage mechanism is mainly governed by capacitive phenomena but pseudo-capacitive reactions, due to the oxygenated surface groups and active sites, also contribute to the capacitance depending on the electrolyte.

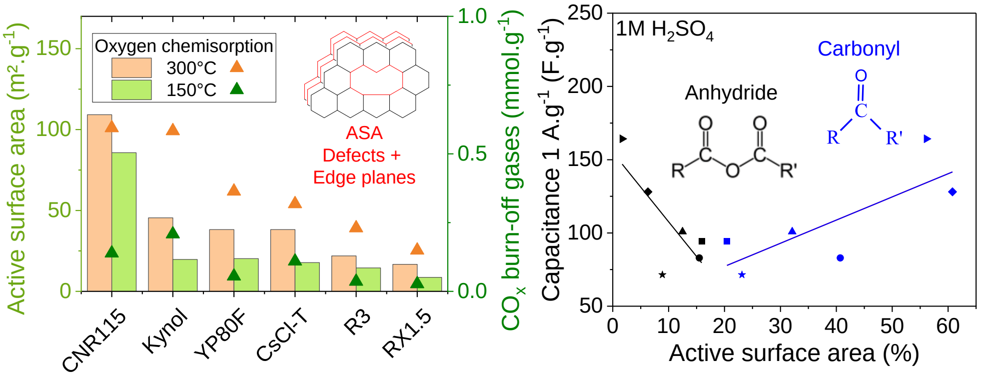

Figure 1: Active surface area and burn-off gases for ASA oxygen chemisorption at 300°C and 150°C (left) and correlations between capacitance and ASA anhydride and carbonyl groups (right)[2]

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P8

Study of the adsorption properties of radon and xenon in zeolites, a Grand Canonical Monte Carlo simulation study.

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The detection of rare events, such as dark matter and/or neutrino-less double beta decay, in the field of subatomic physics, employs ultra-sensitive detectors, usually based on a target of liquefied noble gases, such as xenon. Nevertheless, radon, a radioactive noble gas present within the target in trace amounts constitutes the main source of background and therefore needs to be removed. Microporous materials, such as zeolites or MOFs, has shown an interesting potential in separation of noble gases binary mixtures [1]. However, separating radon from xenon appears as particularly challenging, due to their similar atomic dimensions, in addition to their extremely limited reactivity.

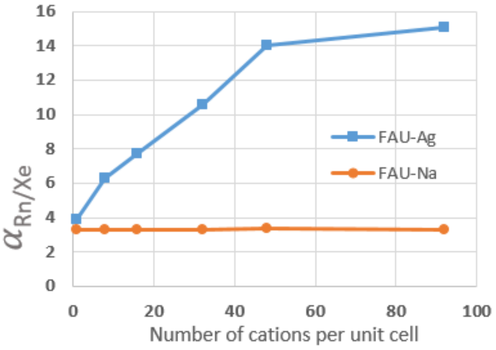
For that purpose, we have applied the Grand Canonical Monte Carlo (GCMC) technique to simulate radon and xenon adsorption properties, such as room temperature adsorption isotherms, the Henry constants and the adsorption heat evolution with loading, in order to optimize parameters of zeolites to selectively adsorb radon. This systematic study explored the influence of the Si/Al ratio, the chemical nature of the extra-framework cations, as well as their crystallographic positions. Moreover, to investigate the effect of the framework topology, three zeolites with differing largest pore openings were considered: FAU (12MR), FER (10MR), and LTA (8MR).

The observations revealed that although the Rn/Xe adsorption properties are influenced by the zeolite topology, the primary factors driving adsorption selectivity are the chemical nature of the cations, their concentration and accessibility. Consequently, as illustrated in Table 1, the adsorption properties of LTA zeolite are consistently superior to those of FAU structure. Nevertheless, as shown in Figure 1, increasing the amount of Ag^+ in accessible crystallographic sites, significantly enhances the adsorption properties, compared to Na^+ cations.

Table 1: Rn/Xe adsorption selectivity of FAU-(Na^+/Ag^+) and LTA-(Na^+/Ag^+) with Si/Al ratio = 1.

Si /Al =1	**FAU**		**LTA**	
	Ag^+	**Na^+**	**Ag^+**	**Na^+**
$\alpha_{Rn/Xe}$	14,8	3,2	22,2	4,3

Figure 1: Evolution of Rn/Xe adsorption selectivity in Ag-FAU and Na-FAU as a function of the number of cations per unit cell.



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Synthesis and Photophysical properties of substituted dibenzoylmethane derivatives for organic electronic applications

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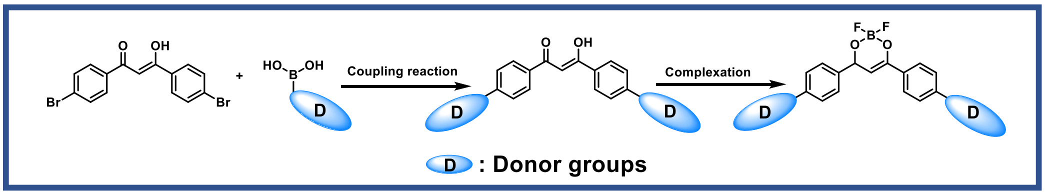
Organic Light Emitting Diodes (OLEDs) are widely used in organic electronics due to their advantage over traditional liquid crystal displays, in particular the high-quality of displays going from rigid to flexible types. However, there are a number of critical issues that need to be addressed before the use of OLEDs can be expanded, the most important of which are performance and cost. Recent OLED material development has therefore focused on the design, synthesis, and application of highly efficient, low-cost and long-lived materials. Nowadays, iridium complexes (2nd generation OLEDs based on metal complexes) are the commercially available dyes that are used in these displays. To circumvent those rare and expensive metals, Thermally Activated Delayed Fluorescence (TADF) is being increasingly studied (as it is the 3rd generation of OLED technology) and has emerged as a highly promising technology for enhancing the efficiency of OLED (Organic Light-Emitting Diode) devices by using 100 % internal quantum efficiency (IQE). Following the group's preliminary work showing that the curcuminoid boron difluoride complexes can be used as near infrared TADF emitters, we plan to develop new boron difluoride emitters that emit in the visible part of the spectrum.



Here, we report on the synthesis of substituted dibenzoylmethane boron difluoride derivatives that are appended with electrodonor groups. The synthesis and the photophysical properties will be described and the pre-requirement for TADF application of those dyes will be discussed.

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Journée SCF Alsace 2025 – March 13th 2025 – Mulhouse

Engineering the Nature of the Excited States in Curcuminoid Borondifluoride Derivatives Through Molecular Design: Polymethine *vs.* Charge-Transfer State

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Harvesting triplet excited states is crucial to obtain an efficient Organic Light-Emitting Diodes (OLEDs).[1] Hence, Thermally Activated Delayed Fluorescence (TADF) has gained much interest as a replacement for conventional phosphorescence using expensive and rare noble metals.[2] It is admitted TADF occurs through a small energy difference between the first singlet and triplet excited states (ΔE_{ST}). Researchers have mostly been focused on reducing this gap, mainly through intramolecular charge transfer (CT) and twisting the donor and acceptor (*i.e.* a disconnection between the HOMO and LUMO).[2] However, it has been shown that Spin-Orbit Coupling (SOC) also plays a role in reverse intersystem crossing.[3] Nevertheless, curcuminoid borondifluoride derivatives ($CurcBF_2$) exhibit TADF properties even if the structure is planar, inducing a rather large ΔE_{ST}[4]. Theoretical calculations coupled with experimental measurements have shown that TADF results from a high SOC between the electronic configurations of singlet and triplet excited states[4] or from the formation of an intermolecular CT state yielding a system with a small ΔE_{ST}[5]. Therefore, $CurcBF_2$ TADF mechanism represents a different way to efficiently harvest triplet excited states. Within $CurcBF_2$ derivatives, it has been shown that the nature of the excited state can be tuned between CT excited state and π-π^* polymethine.[6] In consequence, $CurcBF_2$ design can be achieved to select the nature of its lowest excited state. While CT emitters have been shown to be TADF, to date, these properties haven't been explored yet in $CurcBF_2$ polymethine. This work is devoted to the development of new $CurcBF_2$ and the rationalization of the structure-TADF properties relationship.

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Enhancing Surface Area of HNO_3-Activated Digestate-Derived Biochar for Methylene Blue Adsorption: RSM-CCD Optimization and Mechanistic Study

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Abstract

This study highlights the potential of anaerobically treated sewage sludge, a by-product of anaerobic digestion (AD) produced in large quantities by wastewater treatment plants (WWTPs), which is further thermally activated to yield biochar. This biochar serves as a template for nitric acid modification, enabling efficient pollutant remediation. Herein, we investigated the removal efficiency of methylene blue (MB) using modified biochars under different acid nitric concentrations. The results demonstrated that BC-HN9 exhibited the best MB sorption performance and was therefore selected for further analyses, including characterization, the evaluation of adsorption parameter effects, and investigations of kinetic and isotherm models. It was determined that both chemical and physical interactions contribute to MB sorption, with the maximum adsorption capacity, obtained using the Langmuir isotherm model at 25°C, being 176.05 $mg{\cdot}g^{-1}$. Additionally, thermodynamic investigations confirmed that the process is endothermic and occurs spontaneously. The mechanism underlying the adsorption of MB dye was analyzed using a suite of advanced techniques, including assessments of pH impact, point of zero charge (pHPZC), FTIR spectroscopy, BET surface area analysis, and XPS. This method demonstrates a scalable approach to producing activated biochars, providing both an effective pathway for fabricating high-value carbon materials and a practical means of mitigating environmental pollution associated with biomass waste.

Key-words: Digestate, Biochar activation, Surface functionalization, Optimization, Mechanisms.

Journée SCF Alsace 2025 – March 13th 2025 – Mulhouse

Enhanced Solar-Driven Photocatalytic Decomposition of Ciprofloxacin antibiotic Using Innovative g-C_3N_4/BiOCl/Ag_2MoO_4 Nanocomposites

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Abstract

This study investigates a g-C_3N_4/BiOCl/Ag_2MoO_4 nanocomposite for photocatalytic degradation of Ciprofloxacin. The synthesized composite and its individual components were characterized using XRD, FTIR, SEM, TEM, and EDX, confirming the formation of highly crystalline nanoparticles. The ternary nanocomposite achieved a 90% reduction in Ciprofloxacin within 100 minutes, driven by solar-powered redox reactions. Its enhanced performance is due to the synergistic effect in the heterojunction, improving charge carrier separation and it is supported by UV-vis, DRS and active species capture, which propose a detailed photocatalytic mechanism. The nanocomposite also demonstrates sustained photocatalytic efficacy and recyclability over four cycles. This research presents a sustainable and cost-effective solution for water pollutant degradation with potential for environmental remediation.

Key-words: Nanocomposite, Photocatalytic degradation, Heterojunction, Solar-powered redox reactions, Mechanisms.

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Sunlight-driven of photocatalytic reduction for Cr(VI) and photocatalytic degradation of Orange G dye using Ag_3PO_4/g-C_3N_4/CuO nanocomposite

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Abstract

This study presents the design and the characterization of a novel ternary photocatalyst, Ag_3PO_4/g-C_3N_4/CuO, synthesized via a co-precipitation process. Structural and optical analyses (XRD, FTIR, XPS, SEM, TEM, BET, UV-Vis DRS) were carried out and confirmed its unique properties. This composite was found to exhibit remarkable efficiency in the degradation of Orange G dye and the reduction of Cr(VI) under solar light, with EDTA acting as an electron donor. Moreover, compared to its individual components (Ag_3PO_4, g-C_3N_4, and CuO), it demonstrates the occurrence of a synergistic effect, leading to an enhanced photocatalytic activity. The influence of various parameters (photocatalyst dosage, initial Cr(VI) concentration, EDTA amount, and pH) was investigated. Furthermore, the designed Ag_3PO_4/g-C_3N_4/CuO nanocomposite was found to maintain good stability over four cycles. The trapping experiments reveal that electrons (e^-) and superoxide radicals ($\bullet O_2^-$) play the key role in the Cr(VI) reduction. In overall, the improved solar-driven photocatalytic performance of Ag_3PO_4/g-C_3N_4/CuO nanocomposite was attributed to a better electron-hole pair separation and to the formation of a double Z-scheme heterojunction, highlighting its potential for wastewater treatment.

Key-words: Ternary photocatalyst, Photocatalytic degradation, Z-scheme Heterojunction, Solar-powered redox reactions, Mechanisms.

On the road to germanene

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Among the systems that have most intrigued scientists in recent years, monoelemental honeycomb lattices single layers, called xenes, occupies an important place. Their predicted electronic properties hold out the promise of fantastic breakthroughs. Arrived later than graphene, their best-known representative, the germanene, a Ge-based cousin, is still being studied.

As it is difficult, not to say impossible, to obtained a germanene layer in a freestanding phase, severable experimental research groups tried to first grow it on different substrates prior to peeling[1]. Our works on two of them, namely Al(111)[2] [3] and Ag(111)[4], let appear that a wide range of investigation techniques is required to completely grasp the complexity of those systems. The various structures obtained on those surfaces, and their chemical composition, could only be fully described thanks to the additional contribution of DFT (Density Functionnal Theory). In this poster, we focus on this contribution.

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Journée SCF Alsace 2025 – March 13th 2025 – Mulhouse

Photochemical S-N bond cleavage of *N*-(8-quinolinyl)sulfoximines; generation of nitrenes for the synthesis of 7,8-diaminoquinolines and derivatives

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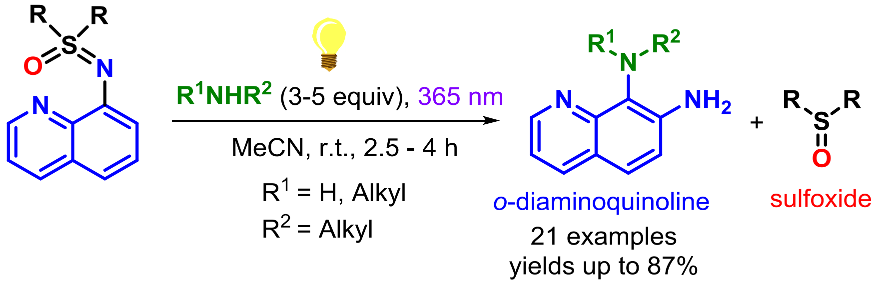
Sulfoximines have emerged as important scaffolds in many fields of organic and pharmaceutical chemistry. Their stability and the possibility to form hydrogen bonding, make them suitable target molecules in drug discovery[1]. Their easy access in a wide structural variety and the presence of a stereogenic center at the sulfur atom, made sulfoximines promising chiral ligands in metal catalyzed reactions[2]. Recent investigations of the photochemical degradation of *N*-phenyl dibenzothiophene sulfoximines showed the formation of reactive nitrene species[3].

Herein, we report the synthesis of novel *N*-(8-quinolinyl)sulfoximines and their use as efficient and safe sources of nitrenes for organic synthesis. Placed under photochemical conditions, these sulfoximines lead to the formation of nitrene species able to react *in situ* with nucleophilic secondary or primary amines. The transformation occurs with the concomitant release of a sulfoxide and leads to various 7,8-diaminoquinoline derivatives in moderate to high yields. The obtained products belong to the interesting class of 8-aminoquinolines, compounds that are used in the therapy of latent malaria[4].



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UNVEILING THE POTENTIAL OF PHOTOBASE IN PHOTOSYNTHESIS OF GOLD NANOPARTICLES IN ORGANIC SOLVENT

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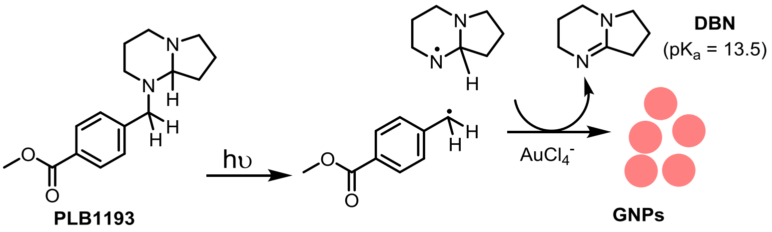
Gold nanoparticles (GNPs) have attracted considerable interest in nanoscience and nanotechnology due to their unique electronic, chemical, and optical properties, particularly their plasmonic behavior[1]. In this study, we introduce a novel and scalable photochemical method for synthesizing small-sized AuNPs in alcoholic solvents, utilizing a photolatent base (photobase) as a reducing agent for the first time. Our approach employs an oil-soluble amidine-based photobase (PLB1193), which, upon UV irradiation, undergoes Norrish type I cleavage, generating primary radicals and releasing a strong base [2,3]. These reactive species play a crucial role in reducing gold ions to their atomic state, facilitating nanoparticle formation and growth.

We systematically investigated the influence of different solvents, stabilizers, and irradiation parameters under batch conditions and successfully adapted this method to a commercially available photochemical reactor. Furthermore, we demonstrated the efficacy of PLB1193 as a reducing agent for synthesizing AuNPs in acrylate resins, highlighting its potential for nanocomposite applications. This work paves the way for the use of photobases and photoacids in the controlled synthesis of gold and other noble metal nanocomposites, offering new perspectives for future developments in this field.



Schemes: Photochemical cleavage of the amidine derivative PLB-1193 to release of DBN and simultaneous preparation of GNPs

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Journée SCF Alsace 2025 – March 13th 2025 – Mulhouse

Title: Photoallergic contact dermatitis: a novel EPR approach to assess xenobiotic-mediated radicals in sun exposed skin

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Photoallergic contact dermatitis (PACD) is a common disease caused by the activation of the immune system after repeated contact of the skin with xenobiotics that are activated under sunlight exposure. The first key step leading to skin photo-sensitization and further clinical expression of PACD is the binding of the chemical activated by irradiation to a skin protein, forming an antigenic complex that triggers the immune system [1]. There is no treatment for PACD other than symptomatic. This is why risk assessment of chemicals present in consumer goods continues to be essential to prevent PACD. In this context, understanding the chemical mechanism(s) of action of skin photo-sensitizers is necessary.

Ketoprofen (KP) is a non-steroidal anti-inflammatory drug that can be delivered as a tablet or cream for topical use. It is also one of the most common photo-allergens, with numerous clinical cases reported [2]. KP presents a benzophenone (BP) unit with a side chain attached. Moreover, KP can be at the origin of PACD to other common molecules containing BP units, such as octocrylene and oxybenzone, both used as UV-filters in sun tanning creams. Understanding how KP reacts in the skin may give insights to understand those cross-reactivities.

BP derivatives as KP are thought to become photo-reactive by formation of radical intermediates able to react with skin proteins through radical mechanisms (1+1 electron transfer) [3] although this has never been proved in the skin. To deepen our knowledge and thus help risk assessment procedures, electron paramagnetic resonance studies are carried out to investigate, from the test tube to further use of reconstructed human epidermis 3D models, if radicals are formed from these compounds in the skin [4].

However, the generated radicals are often too short-lived (nanoseconds to milliseconds), making their direct detection with a simple EPR experiment unfeasible. To overcome this limitation, indirect approaches are suitable: (i) EPR spin-trapping (ST), which allows the identification of the nature of the radical species, and (ii) EPR spin-scavenging (SC), which provides kinetic insights.

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Journée SCF Alsace 2025 – March 13th 2025 – Mulhouse

3D printing of Carbon Architecture using bio-based resins

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Carbon-based materials are increasingly gaining attention for various applications, particularly in energy storage, due to their low cost, excellent electrical conductivity, and high specific surface area. However, most of the carbons produced are in powder form, which complicates their shaping and requires the use of binders that can alter their performance. This challenge can be overcome by combining additive manufacturing and heat treatment. [1] This project focuses on the development of photosensitive resins, composed of photosensitive polymers and bio-based resins that can be shaped by Digital Light Processing (DLP) or by volumetric printing, enabling the rapid shaping of complex and varied structures (Figure 1). Volumetric printing is a relatively new technique in which a dose of light is received by a volume of photoresist, enabling the rapid formation of layer less objects on the order of a centimetre. [2] Numerous factors such as structure, composition, and porosity play a crucial role in determining the performance of printed objects.[3] Particular attention is being paid to controlling porosity (micro-, meso-, or macro-porosity) using physicochemical activation methods or the development of multi-phase inks to enhance performance, with the aim of exploiting these structures in energy storage devices (batteries, supercapacitors) or for water remediation.

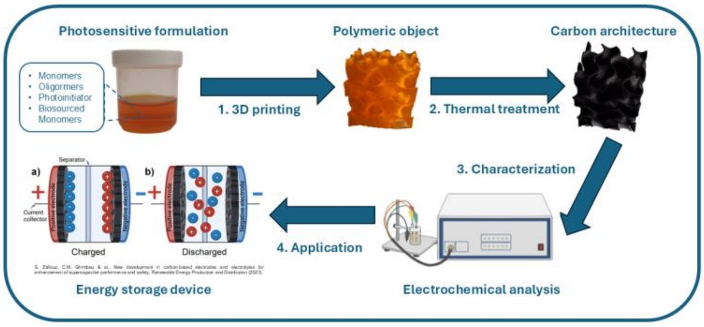

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Figure 1 Global outline of the subject

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Straightforward Access to Pentafluorosulfanylated Phenols and Aminophenols via [4+2] Diels-Alder Cycloaddition Reaction

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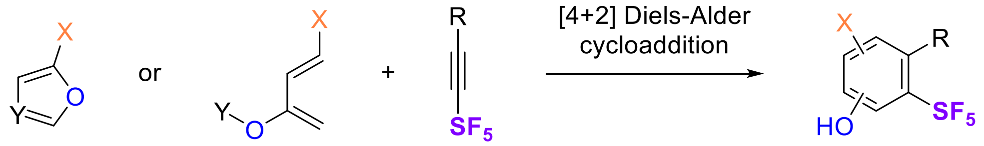
Nowadays, increased efforts are deployed to broaden the access to pentafluorosulfanyl (SF_5) compounds. [1] SF_5-aromatics are usually prepared by oxidative fluorination of thiols or sulfur derivatives under very harsh reaction conditions which are poorly compatible with most of functional groups. Therefore, linear multi-step syntheses are then required to install subsequently functional groups. In contrast, SF_5-alkynes are easily accessible building blocks that demonstrate wide applicability for the synthesis of functionalized SF_5-products.[2] Herein, we capitalize on the polarization of SF_5-alkynes to develop a convergent and highly regioselective synthesis of SF_5-phenols and SF_5-aminophenols, performed in a single step of Diels-Alder cycloaddition. A counter-intuitive regioselectivity is observed, which is rationalized by experimental and computational experiments. Further post-functionalizations are also proposed, making this strategy very appealing to access multi-functionalized SF_5-compounds.[3]



- Access to highly functionalized SF_5-aromatics

- Convergent synthesis
- Neutral conditions
- Several post-functionalizations

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Azobenzene Isomerism and Kinetic Asymmetry in Chemical Reaction Network

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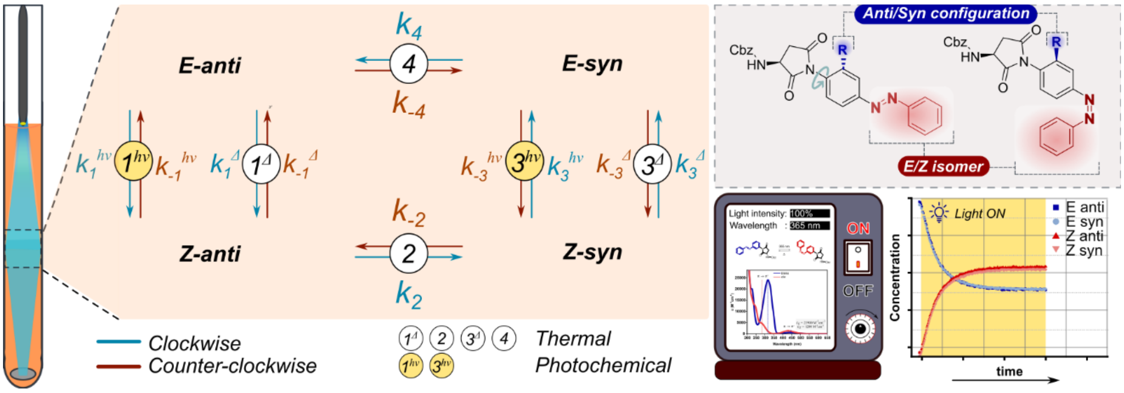
As a highly tunable, controllable, clean, and renewable energy source, light presents significant potential to power molecular motors.[1,2,3] However, the efficient operation of light-driven molecular motors remains a considerable challenge, requiring the precise integration of thermal and photoinduced reactions to achieve controlled motion. This work presents a family of axially chiral molecular rotors incorporating an azobenzene photoswitch, designed to couple photoinduced and thermal processes within a chemical reaction network. The photoisomerization of azobenzene induces kinetic asymmetry, biasing thermal interconversion between anti and syn conformations of trans and cis rotors. Using in-situ light irradiation NMR, the temporal evolution of the four species within the reaction network was tracked, providing insights into the dynamic behavior of rotor interconversion. Furthermore, kinetic asymmetry enables directional light-driven ratcheting[4,5] evolution of the chemical reaction network. This new family of molecules contributes to the development and understanding of minimal chemical reaction networks operated away from equilibrium.



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Journée SCF Alsace 2025 – March 13th 2025 – Mulhouse

Synthetic lipopeptides to fight against multiresistant fungal infections

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As invasive fungal infections (IFI) are increasingly common in the nosocomial setting (>1.6 million patients die annually of IFI[1]), the WHO published in 2022 a fungal priority pathogen list, counting as a first step to prioritize fungal pathogens and promote a research that until then was somehow left behind.

Echinocandins (ECs), as part of the more recent antifungals, are cyclic lipopeptides (LPs) which non-competitively inhibit the β-(1,3)-D-glucan synthase (GS)[2] (found exclusively in fungi), leading to the loss of the fungal cell wall integrity[3]. Their specificity gives them the advantage of being well-tolerated, but despite their evident potential only 4 ECs are currently on the market and some examples of resistant strains have already been identified[4].

The aim of the project Fungipep is to identify new drug candidates inhibiting the GS with the objective of skirting emerging resistance encountered with currently available ECs. Another important aspect of this project is to elucidate the inhibition mechanisms used by these original lipopeptides as the recognition site of ECs on the FKS1 catalytic unit of GS has never been totally confirmed.

To reach these high goals, a first part of the project was focused on the development of a SPPS methodology (sometimes associated to click-like bioconjugate chemistry), to access unprecedented EC analogues. For now, around 40 original LPs were generated and all of them were tested on various strains of fungi, making it possible to quickly evaluate their bioactivity and adjust their structure accordingly.

The synthetic routes developed during this project were also exploited to synthesize innovative molecular tools like LPs carrying a fluorophore. These will later be used in fluorescence microscopy to try to confirm the binding site of ECs by FRET experiments (in association with a GS fusion protein that we have designed and are currently bioproducing).

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Journée SCF Alsace 2025 – March 13th 2025 – Mulhouse

Hybrid talc-like materials for light-driven applications: Synthesis for dye encapsulation and use as specific reagent for 3D Printing

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The sol-gel process enables the formation of clay-mimicking compounds having unique properties [1]. This one-step method is performed at room temperature and involves the use of an organotrialkoxysilane (OTAS) ($RSi(OR')_{3,}$ where R stands for an organic moiety with different functionalities and R' for a methyl or ethyl group)) as silicon sources, an aqueous or organic-solvent based solution of magnesium salt, and in some cases, an aqueous solution of sodium hydroxide [2]. By this way, the organic moieties are covalently bonded to the silicon of the tetrahedral sheets, pointing in the interlayer space and present at the surface. Since many OTAS are on the market, tailor made Hybrid Talc-like Materials (HTM) can be prepared.

The objective of this study is to compare HTM made from one or a mixture of OTAS (methacryloxypropyltrimethoxysilane (MAPTMS), 3-aminopropyltrithoxysilane (APTES), phenyltriethoxysilane (PTES)), their abilities to encapsulate dyes and participate in a Digital Light Processing (DLP) radical polymerization through methacrylate functions [3].Different key parameters governing the formation of HTM were studied among which are the type of magnesium and silicon sources and the reaction time. Absolute ethanol was chosen as a solvent and the Si to Mg molar ratio in the mixture was equal to 4/3 as needed in an HTM. In each case, the pH was adjusted to 9 by addition of and aqueous solution of sodium hydroxide before being left under stirring for different durations. The solids were then recovered by centrifugation and dried at 60°C. The samples collected after drying presented different textures from viscous to grindable solids. X-Ray diffraction patterns displayed all four peaks. The first one between (4.9 and 7.9) °2θ and the others around 22; 35.5; 59 °2θ, correspond to (0 0 1), (0 2 0, 1 1 0), (1 3 0, 2 2 0) and (0 6 0) reflections, respectively, characteristic of an HTM [4]. Based on the (0 0 1) reflection, the calculated basal distances corresponding to the sum of the layer and interlayer thickness vary from 11.2 to 18.5Å depending on the silicon sources. The position of the (0 6 0) reflection agrees with the formation of a trioctahedral layer with divalent cations in the octahedral sheet as expected for a talc structure. Chemical analysis by XRF as well as IRTF and ^{29}Si solid state NMR are underway to gather more information about the structure of the different samples. HTM containing dyes will be prepared and deeply characterized to determine their photochemical properties. The last step will be to introduce HTM in a polymer matrix to prepare 3D samples.

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IDENTIFICATION AND CHARACTERIZATION OF CARBON QUANTUM DOTS IN PM1 EMITTED IN SMOKE FROM DOMESTIC WOOD COMBUSTION

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Objective: For the first time in 2006, Carbon Quantum Dots (CQDs) were observed and since, they have become an attractive material due to their properties. In fact, their biocompatibility, water solubility and non-toxicity make them interesting in several applications as medical ones. In parallel, Green nanotechnology has been developing and Green synthesis of CQDs soon started to appear involving for example, fruit juices or even waste such as diesel soot. Herein, we decided to investigate CQDs in soot from biomass combustion and, by using Raman spectroscopy methods developed for the characterization of Graphite/graphene and their defects, we had developed a methodology able to characterize any CQDs using Raman and X-ray Photoelectron Spectroscopy (XPS), Energy Dispersive X-ray Spectroscopy (EDX), scanning and transmission electron microscopy (SEM and TEM).

Method: Combustion tests were carried out on a log-burning insert. Beach woodlogs of 33 cm length were used with a moisture content of 12%. Samples were made using an Electrical Low-Pressure Impactor containing 13 impaction stages corresponding to aerodynamic diameters ranging from 29 nm to 9.9 µm. Silicium wafers were scotched on each stage to collet those soots. Multiple sample sets were created, varying in length of collection and time of start of sampling.

Results: Raman Spectroscopy on the smallest particles exhibits clear D and G bands characteristics of nano-crystalline graphitic structures. Furthermore, using Ferrari and Robertson theoretical model, we estimated the percentage of sp^3 bonding in our particles which were between 14 and 17%. We show also that the slope of the Raman signal in the region of the G and D bands, which reveals a possible photoluminescence contribution, proves to be a relevant observable for revealing the presence of CQdots. This is corroborated by XPS measurements where C1s core level peaks exhibited a clear Doniach Sunjic shape which is characteristic of sp2 bonds. sp^3 (defected graphitic species) and carbon-oxygen bonding also spotted with the presence of potassium (revealed by two core level peaks K2p1/2 and K2p3/2) on some samples were also discussed. SEM images showed aggregates of spherical objects and TEM images pointed the spherical core shell structures of these particles. Such structures commonly named nano-onions, are the CQDs that we were looking for.

Conclusion/opening: We efficiently proved that CQDs are present in wood combustion soot Further photophysical analysis will be done to correlate the fine interpretation of Raman spectra with the optical properties.

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Journée SCF Alsace 2025 – March 13th 2025 – Mulhouse

Volumetric 3D Printing: Principles, Processes, and Challenges

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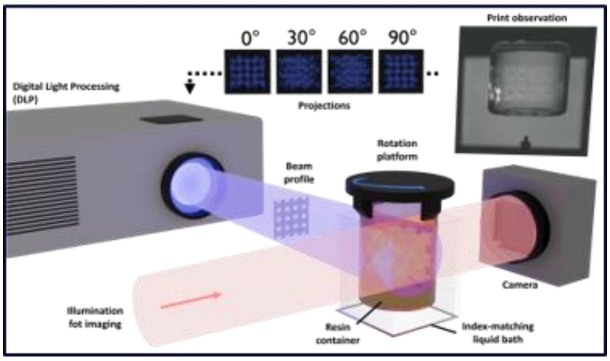

Figure 1: Working of a volumetric printer

3D printing changed the manufacturing processes by enabling the creation of complex, customized objects directly from digital models. Traditionally, 3D printing has relied on additive processes, where materials are deposited or cured one thin layer at a time. Unlike conventional methods, volumetric printing creates entire objects simultaneously, using carefully calibrated light patterns to solidify the desired shape in seconds (*Figure 1*). In particular, tomographic volumetric additive manufacturing (VAM) has attracted many attentions due to its potential to allow ultra-fast fabrication of advanced and functional constructs.[1] This technique opens doors to faster production speeds, higher resolution, and new applications in fields ranging from bioprinting to industrial manufacturing.

Our work aims to provide an in-depth explanation of how volumetric printing operates, with a particular focus on the process of projection creation, projection modification, development, and potential challenges[2]. We will explore how the volumetric printer generates projection patterns, how these projections are dynamically modified to optimize printing accuracy, reduce artifacts, and account for variations in material properties. We will address common pitfalls, such as light scattering, over-curing, and resolution limitations, and propose potential solutions to overcome these challenges.

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SYNTHESIS OF SELF-ASSEMBLING VIOLOGENS

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Structurally controlled self-assembly of redox active building blocks comprising aromatic cores remains a challenge.[1,2] Among redox active π-conjugated aromatic cores, viologens, with their low-energy LUMO and unique redox activity, are an interesting class of compounds and may provide the opportunity of studying electronic conduction in fibrils if adequately functionalized.[3] Many examples of H-bond directed self-assembly of fibrils using amide-functionalized low-weight molecular gelators have been reported in the literature.[4] The building blocks designed in this work are represented in Figure 1 and incorporate three different interaction sites: electrostatic interactions (from the viologen core), hydrogen bonding (via four amide groups), and van der Waals interactions (using long alkyl chains). This communication will present the synthesis and characterization of the viologen derivatives by various methods, including solid state NMR.

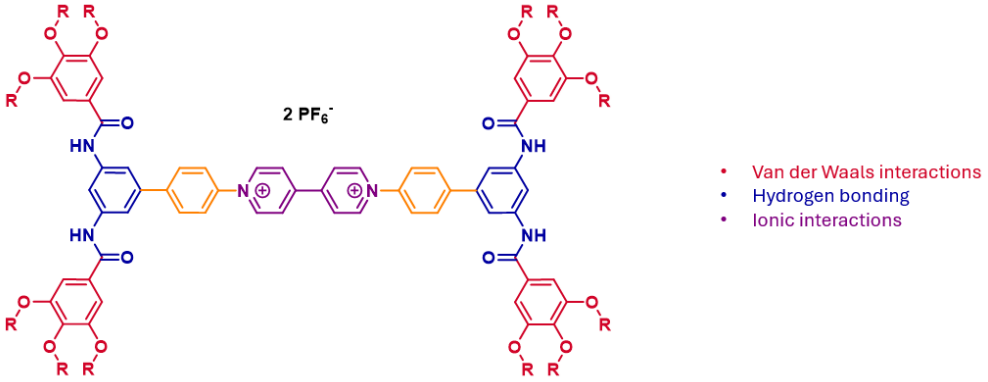

Figure 1 Representation of the target molecules with the three different interactions sites.

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Journée SCF Alsace 2025 – March 13th 2025 – Mulhouse

4D Printing and Stimuli-responsive Liquid Crystals

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In recent decades, 3D printing has undergone remarkable advancements both in technology and materials. However, a significant limitation of most 3D printable materials is their static nature, unable to respond or adapt to changes in their environment. This restricts their applicability in smart technologies requiring dynamic behavior. To address this challenge, the concept of "4D printing" has emerged, where time is integrated as a fourth dimension into 3D geometries, enabling new functionalities such as responsiveness and adaptivity to external stimuli. Among various fabrication methods at the microscopic scale, two-photon polymerization (TPP) has emerged as a well-established technique for creating intricate micro-objects with stimuli-responsive surface properties and high resolution[1].

In this work, we develop microstructures capable of dynamic movement by leveraging specific processes and materials. Our focus is on custom programming these structures at the micrometer scale. Liquid crystals (LCs)[2], known for their optical properties and responsiveness to external stimuli, serve as the ideal material[3]. We fabricate objects with precisely controlled orientation, enabling both thermal and photo actuation. To realize this, we introduce a novel method and tailored LC resins compatible with 3D microfabrication via TPP. This technique solidifies the nematic phase orientation during fabrication, ensuring precise three-dimensional control of LC molecular alignment (see Figure 1).

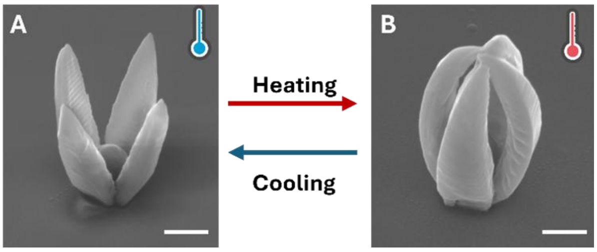

Figure 1. SEM images of 3D printed programmable LC clamp structure in A) open form at room temperature and in B) closed form at 200 °C upon heating. Scale bar: 30 µm.

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Journée SCF Alsace 2025 – March 13th 2025 – Mulhouse

Synthesis of a Membrane Induced by Light and Electrospinning for Filtration

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Introduction and objectives:

Liquid filtration relies on the use of high-performance membranes whose porous structure must be controlled to meet the requirements of a wide range of applications (water purification, drug delivery through dressings, or macromolecule filtration...) Among membrane manufacturing processes, electrospinning stands out for its ability to produce non-woven nanofibers, generally between 100 nm and 1000 nm in diameter, with high porosity.[1] The aim of the project is therefore to develop a high-performance membrane using an innovative, environmentally-friendly approach, by combining electrospinning and photopolymerization, in order to crosslink urethane acrylate oligomers *in situ* using a photoinitiator[2]. The residence time of the solution from the needle to the collector is inferior to one second with jet velocity from around 0.5 m/s. Photo-electrospinning will enable faster polymerization, control over fiber chemical properties and porosity, and the reduction or elimination of the use of toxic solvents.[3]

Method & Results:

The methodology adopted invoves the formulation and characterization of photopolymerizable solutions, focusing on the selection of commercially available urethane acrylate oligomers and the optimization of their kinetics and rheological properties. Polymerization efficiency is monitored by using real time Fourier transform infrared spectroscopy RT-FTIR, to track acrylate conversion over time, while the gel point and the evolution of viscoelastic properties under irradiation are assessed by photorheology measurement. These analyses ensure a suitable behavior of the formulation for fiber formation. Electrospinning is then used to generate nanofibrous fibers while ensuring their photo-crosslinking under UV irradiation.

Initial RT-FTIR results, under irradiation of 20 mW/cm², show an acrylate conversion rate of 70 to 100% within 120 seconds, depending on the oligomer used. This conversion rate is driven by the photopolymerization process, where light irradiation triggers the oligomers polymerization. Photorheological studies reveal a gel point ranging from 0.6 to 3 seconds, ensuring very rapid solidification of the formulations. Futur work will focus on integrating these formulations into electrospinning, as well as refining the conditions to precisely control fiber diameter and membrane porosity. Additionally, in-depth characterization of morphological properties, mechanical performance and filtration efficiency will be conducted.

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Journée SCF Alsace 2025 – March 13th 2025 – Mulhouse

Role of Cerium in the performance of a CuO/SBA15 adsorbent for SOx removal in the presence of water vapour

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In the fight against air pollution caused by human activities, Flue Gas Desulfurization (FGD) processes have been an effective means of reducing the harmful effects, on health and ecosystems, of SO_2 for many years. Nevertheless, these technologies suffer from high cost, energy and water consumption and produce large amount of unusable by-products. One solution to eliminate SOx from industrial flue gas stream, is the adsorption on a regenerable porous material. In this context, we have developed an adsorbent composed of a CuO-based active phase supported on an organized mesoporous SBA-15 silica. This CuO active phase has the ability (i) to catalyse the oxidation of SO_2 to SO_3 and then react with this latter to form copper sulfate $CuSO_4$; (ii), to be regenerable under a reducing atmosphere and to release SO_2 for its valorization into sulfur products. The effectiveness of this CuO/SBA-15 adsorbent in SOx trapping has been demonstrated in multicycle (desulfurization/regeneration cycles) and multigas (presence of SO_2, CO/CO_2, NO/NO_2), at a relative high temperature (450°C) [1]. However, it has been found that the FGD performance of the CuO/SBA-15 decreases significantly in the presence of water vapor[2]. One of the reasons of this deactivation is the migration and coalescence of the CuO active phase. To minimize this phenomenon, the addition of cerium oxide (CeO_2), allows to improve and stabilize the dispersion of CuO phase on the siliceous support[3]. The incorporation of cerium has revealed an important increase of the performance of the CuO-based adsorbent, performance stable along cycling experiments, due to a synergetic effect between Cu and Ce species, which promotes the oxidation of SO_2 to SO_3.

For a possible application at industrial level of this new technology, it is now necessary to replace the SBA-15 silica support which is more expensive, by commercial porous silicas. It is the aim of this work: the synthesis of copper/cerium based adsorbents using commercial K60 as silica support and the study of their performance in SOx trapping. The characterization of the materials before and after DeSOx experiments by XRD, N_2 physisorption, TEM and XPS, will permit to well understand the mechanisms of SOx trapping and the role of the support, and to optimize this adsorbent in terms of synthesis and DeSOx/regeneration operational conditions.

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Additive Manufacturing of Transparent Fused Silica Glass

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3D printing is experiencing exponential growth and is gaining ground in many sectors, thanks in particular to the emergence of new materials, including glass 3D printing. This material stands out for its exceptional chemical, thermal and mechanical stability, making it suitable for high-precision applications such as optics and biomedical applications.[1] Since its introduction in 2017, 3D printing of glass has seen major advances, facilitated by the rise of innovative technologies such as two-photon printing and volumetric 3D printing.[1-3] These advances open up new prospects for innovative applications, such as micro-optical components and microfluidic systems.

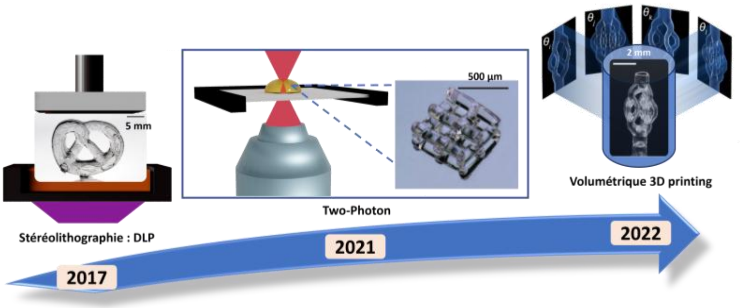

Figure 1 : 3D glass printing developments.

However, these technologies still have certain limitations, particularly in terms of resolution and printing speed. Recent research has also focused on controlling glass porosity, with a view to extending its applications to fields such as catalysis and liquid/gas separation.

In this context, the challenge of our research lies in the development and characterization of photosensitive resins specifically adapted to these printing technologies, as well as in the design of an approach combining these two techniques in order to overcome the limitations associated with the use of a single method. Formulations will be optimized to improve printing speed, resolution and porosity control, based on in-depth analysis of photo-physical properties (FTIR, photorheology, etc.). This will be followed by detailed characterization of the printed structures to assess their mechanical properties and the porosity of the resulting glass.

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Macrocyclic ligands giving access to robust photosensitizers based on copper complexes

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A recent study conducted by our two teams has shown that macrocyclic ligands containing a coordinating unit of the diphosphine or diimine type can be used to stabilize $[Cu(NN)(PP)]^+$ complexes in solution and enhance their luminescent properties.[1] We now aim at developing even more efficient and robust copper complexes. To achieve this, cyclodextrin (CD)-based macrocyclic diphosphines will be combined with functionalized diimines (bpy, phen, etc.) with electron-donating and electron-withdrawing group, which should prevent any ligand exchange reactions regardless of the metal's oxidation state. Such a molecular architecture has the potential to further increase the stability of the targeted complexes and enhance their photophysical properties. The design of highly robust photosensitizers based on these principles should ultimately open up new perspectives in photocatalysis, as it will avoid the use of complexes based on environmentally harmful and expensive second- and third-row transition metals.[2]

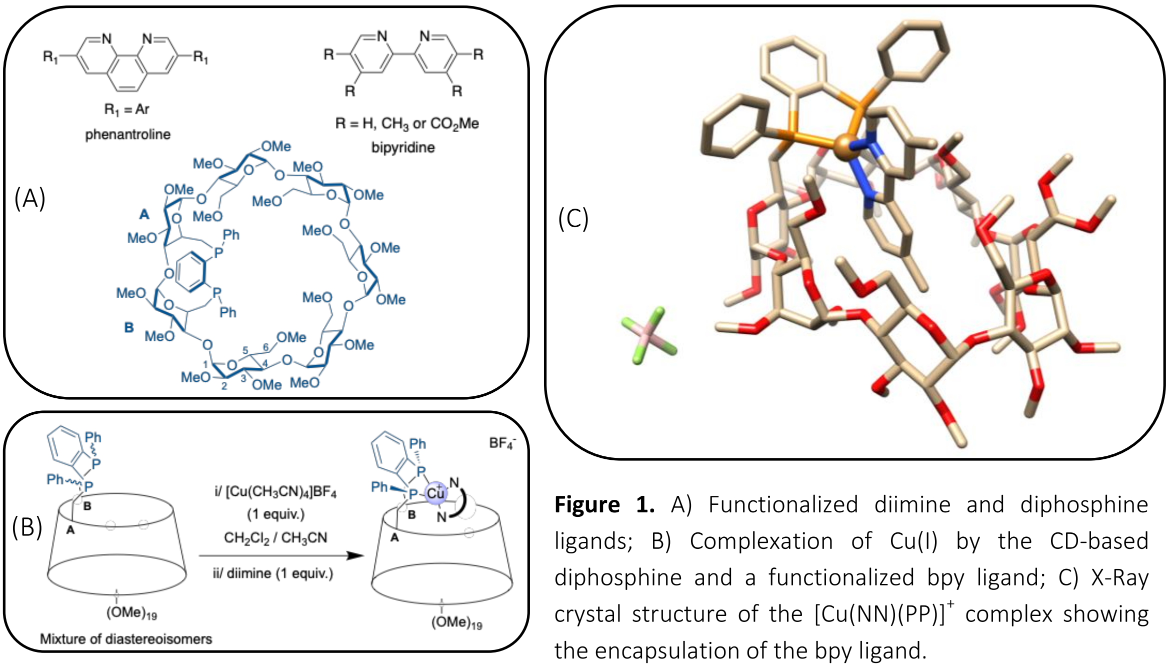

Figure 1. A) Functionalized diimine and diphosphine ligands; B) Complexation of Cu(I) by the CD-based diphosphine and a functionalized bpy ligand; C) X-Ray crystal structure of the $[Cu(NN)(PP)]^+$ complex showing the encapsulation of the bpy ligand.

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Intermediates in the formation of supramolecular grids

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Metallo-supramolecular architectures consisting of ligands and metal ions disposed like in a grid[1] are investigated with increasing interest. Numerous examples of those consisting of four ligands and four metal ions and called [2x2]-grids are known. Less abundant are the studies dealing with the intermediates which may appear in the formation of such grids.

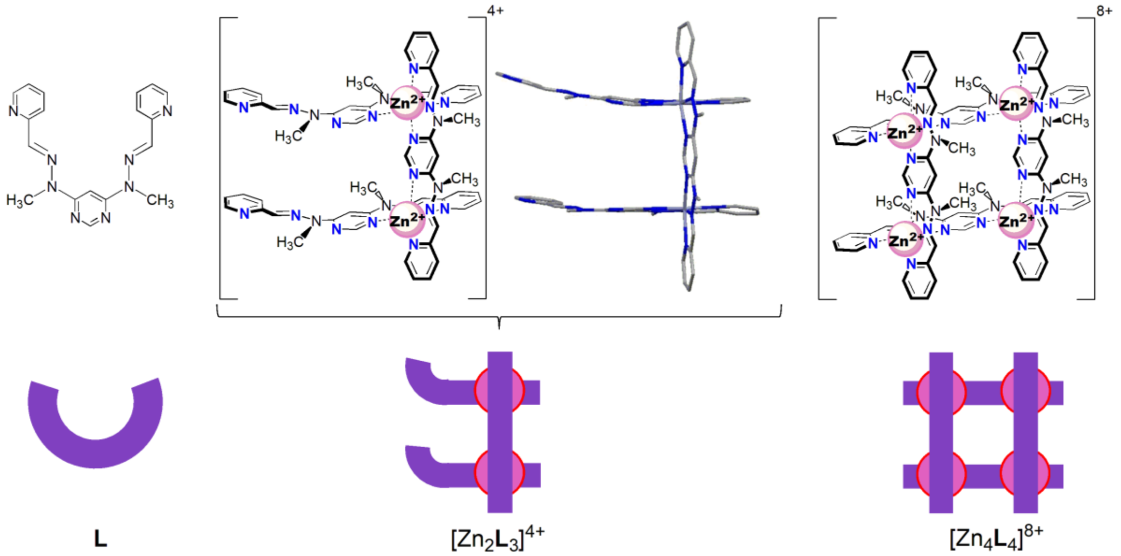

Figure 1. Structural formulae and stylized representations of compounds **L**, $[Zn_2\mathbf{L}_3]^{4+}$ and $[Zn_4\mathbf{L}_4]^{8+}$. A simplified representation of the X-ray structure of complex $[Zn_2\mathbf{L}_3]^{4+}$ is shown; anions are not shown.

Reaction of ligand **L** with one equivalent of Zn(II) triflate produces the grid-like complex $[Zn_4\mathbf{L}_4]^{8+}$ (Figure 1). Observation through ^1H 1D and DOSY NMR at Zn^{2+}:**L** molar ratios between 0.5 and 1, suggested the presence of some unknown compounds together with the known complexes $[Zn\mathbf{L}_2]^{2+}$ and $[Zn_4\mathbf{L}_4]^{8+}$. Attempts to obtain single crystals were successful after addition of KPF_6 or $NaSbF_6$ and revealed the new architecture $[Zn_2\mathbf{L}_3]^{4+}$, that contains one fully coordinated ligand and two partly coordinated ones, and can be seen as an intermediate in the formation of the grid-like complex.

We have also shown that the composition of such reaction mixtures can be reversibly modulated upon addition of controlled amounts of a stronger ligand which encapsulates the metal ions. The modulation through pH-changes is being investigated.

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Elaboration of photoinitiator for volumetric 3D printing

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Following the emergence of volumetric 3D printing, the composition of photosensitive resins must be rethought especially with regard to optical properties (concentration of initiators,...) and physico-chemical properties (viscosity,...). In particular, we wish to use controlled radical photopolymerization (CRP) particularly Reversible Deactivation Radical Polymerization reactions whose advantages in the context of a 3D printing by DLP have only recently been highlighted (self-repairing properties, more homogeneous mechanical properties, bulk and reconfigurable surface properties...).[1] Transposing CRP to volumetric 3D printing is therefore a major challenge in the field of photopolymerization 3D printing and would allow for the first time, to combine the advantages of volumetric 3D printing (speed of printing) with those of CRP.

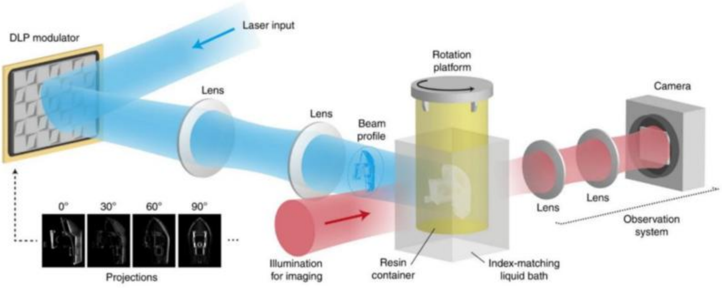

Figure 1: Concept diagram of tomographic 3D printing[2]

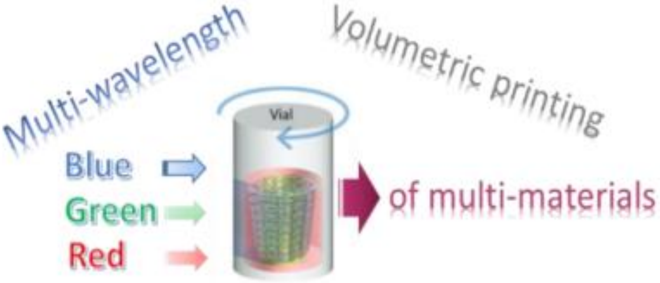

Figure 2: Printing of multi-materials via multi-wavelength printing

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Photoresponsive bi-functional monomers: synthesis & photolysis

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ABSTRACT:

Two-photon stereolithography (TPS)based on photopolymerization has emerged as one of the most efficient techniques in realization of three-dimensional (3D) microstructures. The interest in TPS can be explained by its characteristics as direct microfabrication without masking and achieving high resolution near to 100 nm.[1] The introduced of the concept of stimulated emission depletion (STED)[2] by Stefan W. Hell has led to an important advance in optical microscopy and found many applications in biology.[3] The idea of this concept resides on using a second laser beam in a way to confine the excitation laser to a smaller volume by deactivating a portion of the excited molecules. Wegner's group had translated this concept to optical lithography, except that most of the existing photoinitiators are not suitable for this process.[4] In this context, and to circumvent this issue, we suggest using the concept of self-immolative polymers (SIP)[5] as an alternative strategy.

With this respect, we describe herein firstly, the synthesis of a new series of self-immolative monomers (SIMs) bearing two different functions. An acrylate as cross-linking group and an o-nitrobenzyl as a photoclivable group. Secondly, the photolysis of these SIMs followed by UV absorption and ^{1}H NMR.

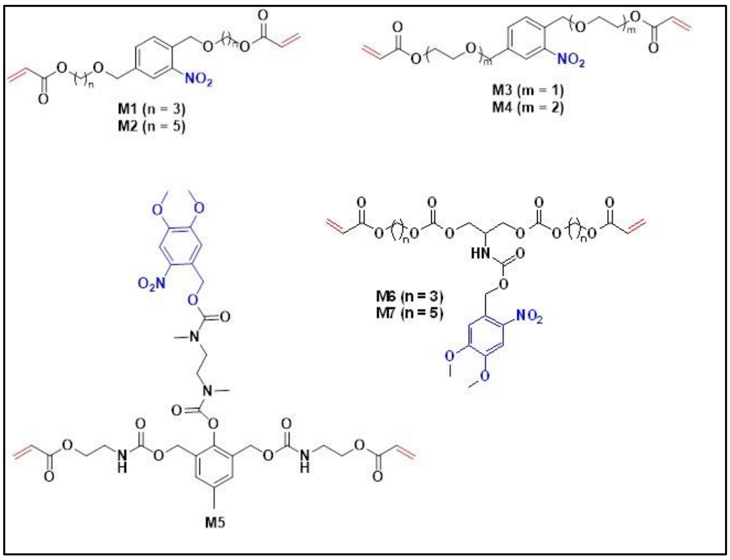

Figure 1 : Structures of synthesized monomers.

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Journée SCF Alsace 2025 – March 13th 2025 – Mulhouse

Adsorption of Oxygenated Polycyclic Aromatic Compounds (O-PAC) onto zeolites for the depollution of groundwater

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Polycyclic Aromatic Hydrocarbons (PAHs) are mainly detected in soils and groundwater near industrialized sites as the result of incomplete combustion of organic matter such as petroleum, gas or coal[1]. In addition to be nocuous for the environment, these compounds are known for their highly carcinogenic, mutagenic and teratogenic potential. Sixteen of them are classified as priority pollutants by the US Environmental Protection Agency since 1976. A lot of studies report methods of remediation, especially by chemical processes. However, other molecules can be produced during these treatments as by-products; it's notably the case of Oxygenated Polycyclic Aromatic Compounds (O-PACs)[2]. The later are not subject to regulations governing polluted sites and soils but preliminary investigations show a larger potential of pollution because of their high polarity, solubility and environmental transfer. A solution of this problem can be the use of physical treatments such as adsorption. This method, especially using carbon materials, has been examined and has been proven to be efficient in numerous studies[3]. Zeolite, another material that is competitive in terms of costs and efficiency and also more eco-friendly thanks to its regenerability, has been identified.

This study focuses on one PAH (Fluorene (FLU)), two O-PACs (Fluorenone (FLUone) and Dibenzofuran (DBFUR)) and three zeolites (MFI, FAU and *BEA framework types). 100 mL of aqueous spiked solution (1 mg/L) were stirred with 10 mg of zeolite powder for different contact times ranging from 15 min. to 24 h. After centrifugation, the supernatant was analyzed by HPLC to determine the concentration of pollutants remaining in the solution.

First results of this study show high potential of zeolites for the remediation of PAHs and O-PACs from groundwater. For example, after 1 h, MFI-zeolite adsorbed 90% of DBFUR. FAU-zeolite adsorbed the three molecules with rates above 70%. The *BEA-zeolite adsorbs 70% of FLU and 80% of FLUone. Textural properties of the adsorbent, such as its pore size and its specific surface area, are key parameters. Moreover, the Si/Al ratio plays an important role as it influences the hydrophobic character of the zeolite and therefore its affinity with the pollutant. Other characteristics and interactions have to be considered to explain precisely these adsorption phenomena.

Next steps will be to apply this method with other initial conditions, to determine the mechanism of adsorption and to study the performance of zeolite after regeneration step.

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Journée SCF Alsace 2025 – March 13th 2025 – Mulhouse

Development of a new palladium-catalyzed decarboxylative coupling using arylsulfonium salts for aryl-aryl bond formations.

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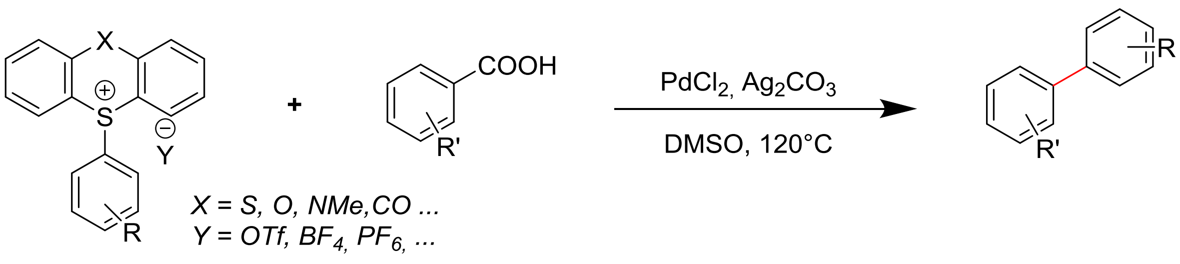
The formation of new carbon-carbon bonds is a subject of constant development in organic chemistry. Reactions allowing formation of such bonds represent often crucial steps in the synthesis of natural products or various organic molecules presenting interesting applications, like active ingredients for pharmaceuticals, monomer patterns for polymerizations or many other fields as agrochemicals, or even materials.

Arylsulfonium salts suscite currently huge interest in organic chemistry using either palladium (Pd) catalysts or a light source especially for various carbon-carbon or carbon-heteroatom bond formations. During this thesis, we are interested in studying the potential of these various arylsulfonium salts for the specific creation of aryl-aryl bonds using pallado-catalysis. Among the numerous synthetic strategies that can be envisaged to achieve the formation of this aryl-aryl bond, we envisaged a decarboxylative coupling between arylsulfonium salts and arene carboxylic acids (***Scheme 1***). Decarboxylative coupling was previously studied in the group, using either iodoaryl group[1] or iodonium salts[2], but using arylsulfonium salts for this type of reaction is original and has never been reported in the literature to date. To this end, a complete methodology was carried out in order to determine the best reaction conditions and the synthetic potential of this new reaction, by describing several examples of coupling and changing the type of substitution of the aryl motif in order to see their influence on the reaction.

Afterwards, since some arylsulfonium salts absorb near UV light, it will be interesting to study the potential of these salts for aryl-aryl bond formations under mild near UV light irradiation. This property has recently been used for photopolymerizations, but very little studied in organic synthesis.



Scheme 1: Decarboxylative coupling reaction studied in this thesis

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Development of photocurable hybrid adhesives

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Cyanoacrylates are a family of molecules with very high adhesive qualities, better known to the general public by their commercial name "Super Glue". Applied in a thin layer, they react almost instantaneously with ambient humidity on contact with the substrates to be bonded. The main mechanism followed by the curing reaction of cyanoacrylates is an anionic polymerization. The adhesions obtained, although very strong, have a number of major shortcomings: poor mechanical performance[1] (too brittle) and a certain chemical instability[2], among others.

One way to overcome these deficiencies is to add a second type of molecule to the formula. By mixing two components, we obtain hybrid adhesives that perform better, bond more varied substrates and resist impact better. In addition, they only begin to harden when exposed to a light source[3]. This enables the user to reposition the parts to be bonded, clean up any drips, then fix the bond in a matter of seconds (when a low-intensity LED is switched on).

The second type of monomer used in the formula are acrylates. Acrylates polymerize mainly by a radical mechanism, and it's the interaction between anionic and radical polymerization that we are trying to understand. To date, there is no literature describing how these two mechanisms come together in the same reaction. To this end, hybrids will be analyzed using methods that enable the curing of the various components to be tracked independently. This information, coupled with multiple chromatographic, spectroscopic and microscopic techniques, will enable us to determine the reaction mechanism followed.

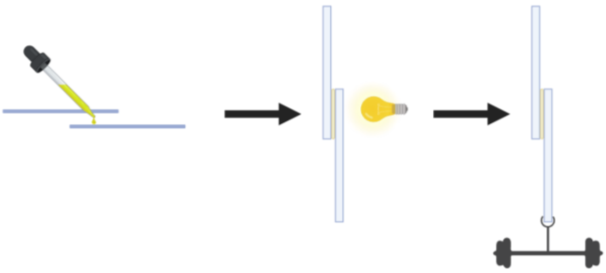

Figure 1. Schematic representation of the bonding process

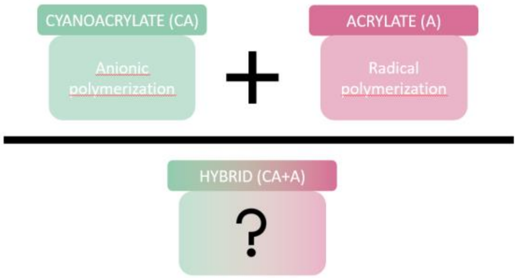

Figure 2. Interaction of the polymerization mechanisms

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Study of a New Cascade Reaction from Bifunctional *exo*-Glycals

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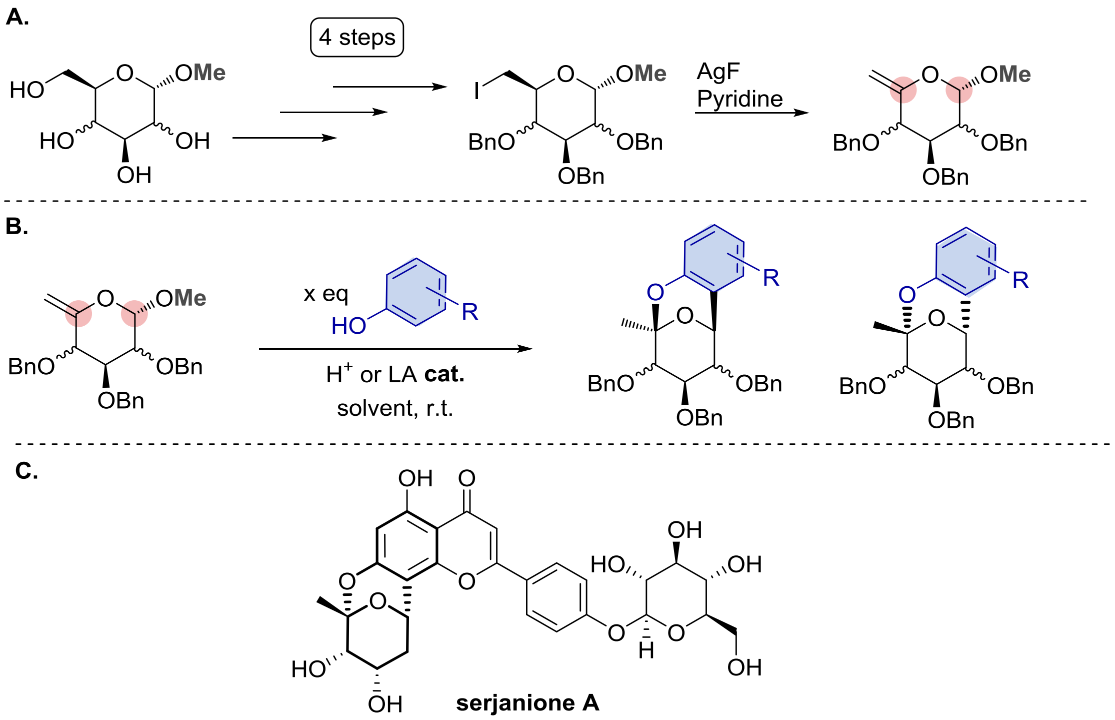
Cascade reactions are a particularly interesting approach for generating complex molecules rapidly and efficiently in a single synthetic step. Based on the recent discovery of a new bis-glycopyranoside rearrangement in our group,[1] we envisioned to use bifunctional *exo*-glycals, which possess two reactive "anomeric" centers located on either side of the endocyclic oxygen to develop a novel cascade reaction enabling the construction of (pseudo) natural carbohydrate-containing polycyclic skeletons. Diversely protected bifunctionalized *exo*-glycals derived from D-glucose, D-mannose and D-galactose has been synthesized according to a well-known 5-step reaction sequence (Scheme 1A).[2] The *exo*-glycals synthesized were engaged in a carbocation cascade reaction proceeding through a Friedel-Crafts-type reaction in the presence of phenolic partners and a carefully chosen catalyst (Brønsted/Lewis acids). A multi-parameter study has been carried out to lead to the target molecules as efficiently as possible (Scheme 1B). Ultimately, we hope to extend this novel cascade reaction to the synthesis of natural molecules of therapeutic interest, such as serjanione A (Scheme 1C).[3]



Scheme 1.

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Design of new luminescent hybrid materials based on layered oxides

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The design of hybrid materials to achieve new functionalities constitutes a highly researched area.[1] These materials have proved to be very relevant, combining the strengths of the two worlds, organic and inorganic, while compensating the drawbacks. Especially in the field of luminescent materials, organic compounds generally exhibit good luminescence quantum yields, and their structure can be easily and finely modulated to allow adjustment of optical properties (excitation and emission wavelengths, or lifetimes of excited states). However, they are often relatively unstable, either chemically or thermally, and are prone to photo-bleaching.

In this respect, the combination of luminescent organic molecules with inorganic structures is particularly interesting, as it combines the advantages of organic systems (structural versatility, property tuning) with those of inorganic compounds (thermal stability, structural rigidity).[2] It may also bring improved properties to the hybrid material thus formed, such as better control of luminescence lifetime.

Here, I will present the first results of chromophore insertion into the Aurivillius $Bi_2SrTa_2O_9$ phase *via* its protonated $H_2Bi_{0.1}Sr_{0.85}Ta_2O_7$ (HBST) form, as well as the photophysical properties of the hybrid compounds obtained. The chosen chromophores are derived from 1,8-naphthalimide and (2)/(4)-bromo-1,8-naphthalimide, which possess Thermally Activated Delayed Fluorescence (TADF) properties,[3] functionalised by different anchoring groups. The insertion of such large organic molecules into the HBST phase proceeds *via* a pre-functionalisation step to increase the interlamellar distance using long amines or alcohols spacers[4].

I will describe the structural characterisation of the obtained hybrid compounds. Then I will discuss their photophysical properties, notably the emission wavelength and quantum yield and the various parameters that could tune their photophysical properties (insertion rate, co-insertion, nature of the chromophore). Such approach has been described in the case of Layered Double Hydroxide-based hybrids,[5,6] but to the best of our knowledge has not been attempted for layered oxides.

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Autoinductive effects in the zinc-catalyzed alkylation of benzaldehyde mediated by simple chiral *β*-amino alcohol ligands

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The design of chiral catalysts presents a fundamental challenge due to the intrinsic complexity of catalytic systems, which often limits the effectiveness of approaches solely based on mechanistic and structural principles. Consequently, the development of asymmetric reactions commonly begins with an empirical exploration of well-known privileged chiral structures, assuming that the active catalytic species exists as a monomer. However, since Kagan's 1986 identification of catalyst aggregation and "Non-Linear Effects" (NLEs),[1] it has been shown that chiral structure alone is not always predictive of the system's overall behavior, adding further intricacies to the mechanistic interpretation of asymmetric catalysis.[2,3]

In our study, we investigated in detail the mechanism of the enantioselective diethylzinc addition of benzaldehyde in the presence of the first chiral β-amino alcohol ligands that had been used for this reaction, published in 1984 by Oguni and co-workers.[4] Our work was achieved through a combination of non-linear effect studies and other related studies such as the variation of the catalyst loading. It has been demonstrated that these catalytic systems are in fact considerably more complex than was previously assumed. In particular, the self-induction phenomena in the reaction demonstrate that the reaction generates higher enantiomeric excesses with a lower catalyst loading and overall, these enantioselective reactions are part of Systems Chemistry.[5]

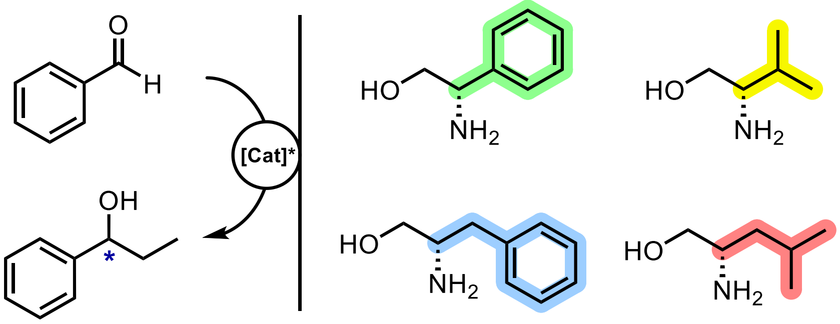

Figure 1. General scheme of the catalytic reaction and molecular structure of the chiral ligands used

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