Journées Nord-Ouest Européennes des Jeunes Chercheurs (JNOEJC)

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Journées du Groupe Français des Polymères Grand-Ouest (GFP)

Université Rouen Normandie
6 – 7 juin 2024

https://jnoejc2024.sciencesconf.org/

Sommaire

Plan du site

L’évènement se déroule sur le campus de Mont-Saint-Aignan de l’université de Rouen Normandie dans le bâtiment CURIB n°25 au 25 rue Lucien Tesnière, 76130 Mont-Saint-Aignan.

Les repas seront servis à partir de 12h au restaurant universitaire CROUS, le Paronama, 5-10 minutes à pied du bâtiment CURIB. Il sera possible de prendre une entrée, un plat et un dessert. Le café sera servi en fin de repas au même endroit.

Le diner de Gala se déroulera au restaurant All Sport Café au 10 Quai Ferdinand de Lesseps, 76000 Rouen. Le All sport café est accessible en voiture et en teor 1 arrêt Luciline en direction de CHU Charles Nicolle ROUEN.

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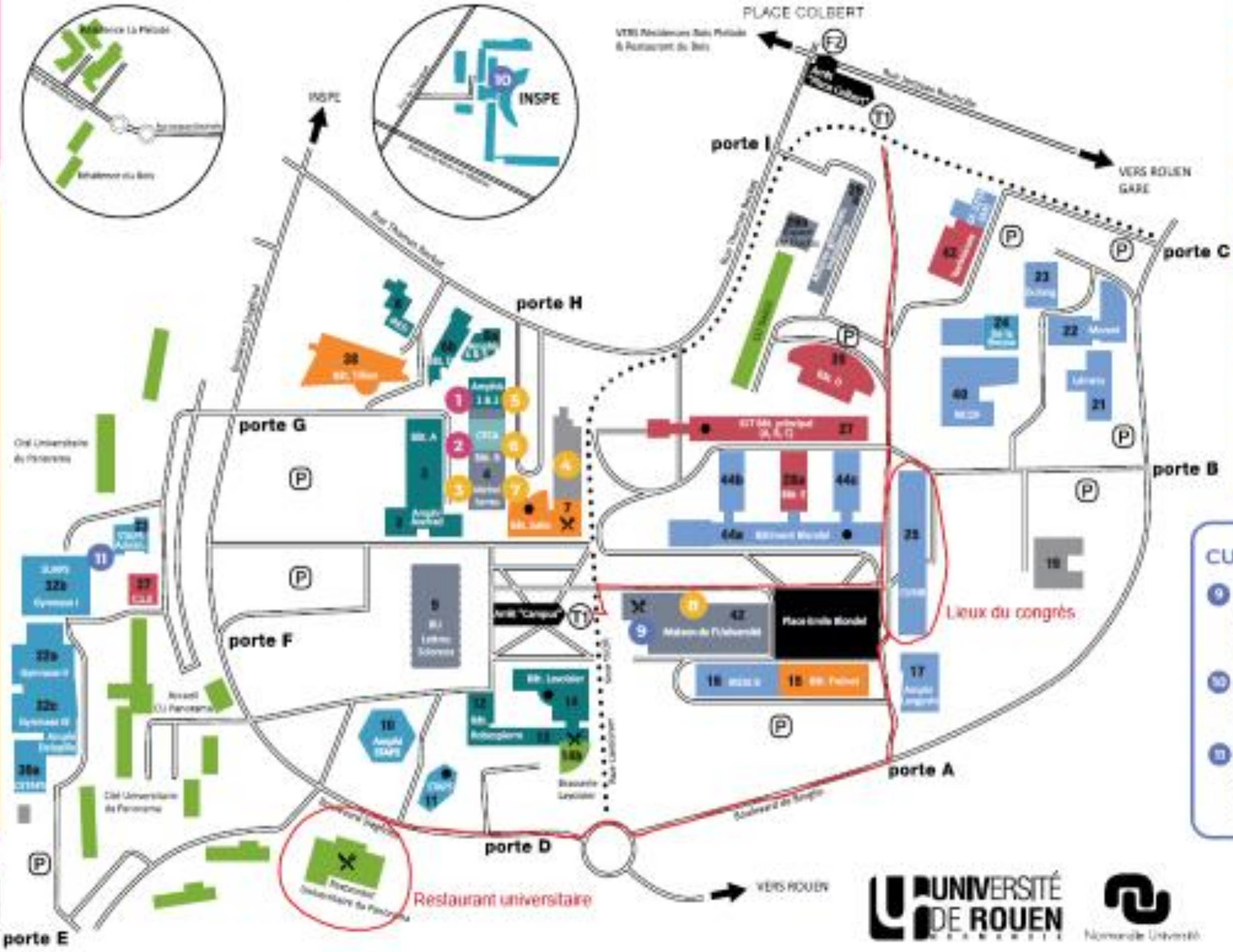
* Tous ces services sont regroupés au coeur du campus, dans l'Espace Michel Serres dédié à l'accompagnement des étudiants.

CAMPUS DE MONT-SAINT-AIGNAN



CULTURE ET SPORT

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Programme

Programme JNOEJC - GFP Grand-Ouest 2024

Jeudi 6 juin 2024		
9h00	Acceuil des participants bâtiment 25 CURIB, Campus Mont-Saint-Aignan)	
9h45	Mots d'accueil	
10h00	Laure Biniek	
11h00	Floriane Richard (CO1)	Vincent Oreve (CO5)
11h15	Bayan Almasri (CO2)	Warren Lhuillier (CO6)
11h30	Souraya Alameddine (CO3)	Marine Verger (CO7)
11h45	Rachida Benmammar (CO4)	Chrystal Lopes (CO8)
12h00	Repas	
13h30	Jutta Rieger	
	Session 1	**Session 2**
14h30	Tharin Sensan (CO9)	Qurat-Ui-Ain Riaz (CO13)
14h45	Bao Ding (CO10)	Gabriel Cormier (CO14)
15h00	Mathieu Henin (CO11)	Bator Khol (CO15)
15h15	Roukaya Achour (CO12)	Thi Mo Nguyen (CO16)
15h30	Session Poster	
16h30	Mahamat Tahir Mustafa (CO17)	Muyronova Veronika (CO22)
16h45	Giulia Gemelli (CO18)	Hadjer Asmaa Zerini (CO23)
17h00	Jana Harb (CO19)	Ava Bousselat (CO24)
17h15	Ludvina Chailly (CO20)	Abdulrahman Alamer (CO25)
17h30	Isabelle Fabrizi (CO21)	Mariia Savchuk (CO26)
20h30	Diner de Gala	

Vendredi 7 juin		
8h30	Ilaria Fratoddi	
9h30	**Session 1**	**Session 2**
	Patricia Ynes Batista (CO27)	Arthur LeCoz (CO31)
9h45	Adeline Delaporte (CO28)	Guillaume Demily (CO32)
10h00	Bochra Seaali (CO29)	Nicolas David (CO33)
10h15	Zoghlami Wala (CO30)	Sawssen Nasri (CO34)
10h30	Session Poster	
11h30	Prix de thèse ORIL/SCF Normandie	
12h00	Repas	
13h30	Louis Fensterbank	
	Session 1	**Session 2**
14h30	Louis Delegue (CO35)	Laurenzo Palio (CO38)
14h45	Pierre Otuszewski (CO36)	Ophélie Montiege (CO39)
15h00	Azad Kichibayov (CO37)	Jad Baltaji (CO40)
16h00	Remise des Prix	
16h30	Clôture du congrès	

* Conférences plénières en amphi CURIB

* Session 1 en salle 66

* Session 2 en amphi CURIB

Les pause café ainsi que les sessions
poster se feront dans le hall du bâtiment CURIB

Conférences Plénières

Tailoring the structure of porous conducting polymers to convert heat into electricity

Quentin Weinbach[1], Naoures Hmili[1], Emma Gottis, Alain Carvalho[1], Marc Schmutz[1], Doru Constantin[1], Jérôme Combet[1], Nicolas Stein[2], Laure Biniek[1*]

1. Université de Strasbourg, CNRS, Institut Charles Sadron UPR22, F-67000 Strasbourg, France
2. Université de Lorraine, CNRS, IJL, F-57000 Metz, France
Email*: laure.biniek@ics-cnrs.unistra.fr

Abstract: PEDOT:PSS is the conducting polymer of choice for sustainable and flexible thermoelectric applications at ambient conditions. The non-hazardous substance can be processed from water dispersion showed a thermoelectric conversion efficiency, zT, of 0.45 at room temperature in thin films.[1] Complementary to this strategy, we focus our attention on developing lightweight and a few mm size PEDOT:PSS materials that present superior control over thermal conductivity, by implementing porosity. We describe here the different strategies (based on gelation and controlled drying) to produce varied porous structure. We use a combination of electron microscopy, spectroscopy and XR- scattering techniques to reveal their structure at different scale. We evaluate the thermoelectric properties and discuss the structure-properties relationships. In particular, the channel-like macroporous structure yields record low thermal conductivity due to the control of the low solid and gas heat conductions.[2] Finally, the measurement of the output TE performance through the one leg set-up demonstrates for the first time the potential of the porous materials to generate power (few µW) out from a small temperature difference (36 °C).[3]

References:

[1] O. Bunova et al. Nature Materials, 2011, 10, 429–433. [2] Q. Weinbach et al., J. Mater. Chem. C, 2021, 9, 10173. [3] Q. Weinbach et al, Front. Electron. Mater. 2022, 2:875856.

Stimuli-responsive polymers and assemblies by RAFT polymerization

Jutta Rieger[1]

[1] Institut Parisien de Chimie Moléculaire, Sorbonne Université, 4, place Jussieu, 75005 Paris

jutta.rieger@sorbonne-universite.fr

Abstract: Stimuli-responsive polymers find application in various domains, for instance as sensors or in the biomedical field.[1] Among them, thermo-responsive polymers can exhibit either a Lower Critical Solution Temperature (LCST) or an Upper Critical Solution Temperature (UCST), depending on whether the phase separation occurs by increasing (LCST) or by decreasing (UCST) the solution temperature. Currently, the number of UCST polymers that exhibit such property in water - in the temperature range of interest - remains limited. The development of rational design strategies to devise thermo-responsive polymers or thermo-responsive polymer assemblies appears therefore of importance.

In this presentation, I will discuss several thermo-responsive systems in water that we have been developing over the last years [2,3], and demonstrate that the temperature-dependent solution properties of polymers are greatly dependent on their (macro)molecular structure and supramolecular assembly.

References

[1] Q. Zhang, Y. Zhang, Y. Wan, W. Carvalho, L. Hu, M. J. Serpe, *Progr. Polym. Sci.* **2021,** *116*, 101386

[2] a) N. Audureau, F. Coumes, J.-M. Guigner, T. Phuong Thu Nguyen, C. Ménager, F. Stoffelbach, J. Rieger, "Thermoresponsive properties of poly(acrylamide-*co*-acrylonitrile)-based diblock copolymers synthesized (by PISA) in water." *Polym. Chem.* **2020**, *11*, 5998. b) N. Audureau, C. Veith, F. Coumes, T. P. T. Nguyen, J. Rieger, F. Stoffelbach, "RAFT-polymerized *N*-cyanomethylacrylamide-based (co)polymers exhibiting tunable UCST behavior in water." *Macromol. Rapid Commun.* **2021**, 42, 2100556; c) N. Audureau, F. Coumes, C. Veith, C. Guibert, J.-M. Guigner, F. Stoffelbach, J. Rieger, "Synthesis and characterization of temperature-responsive *N*-cyanomethylacrylamide-containing diblock copolymer assemblies in water." *Polymers* **2021**, *13*, 4424; c) N. Audureau, F. Coumes, J.-M. Guigner, C. Guibert, F. Stoffelbach, J. Rieger, "Dual thermo- and pH-responsive *N*-cyanomethylacrylamide-based nano-objects prepared by RAFT-mediated aqueous PISA" *Macromolecules* **2022**, *55*(24), 10993.

[3] a) C. Debrie, N. Coudert, J. Abdul, S. Harrisson, O. Colombani, J. Rieger, "Controlling the composition profile of acrylic acid copolymers by tuning the pH of polymerization in aqueous dispersed media" *Macromolecules* **2023**, 56, 21, 8497. b) C. Debrie, N. Coudert, J.-M. Guigner, F. Coumes, C. Guibert, S. Harrisson, F. Stoffelbach, O. Colombani, J. Rieger, "Effect of pH on the incorporation of acrylic acid units in the core of polymer nanoparticles prepared by PISA and on their morphology." *Polym. Chem.* **2024**, ASAP.

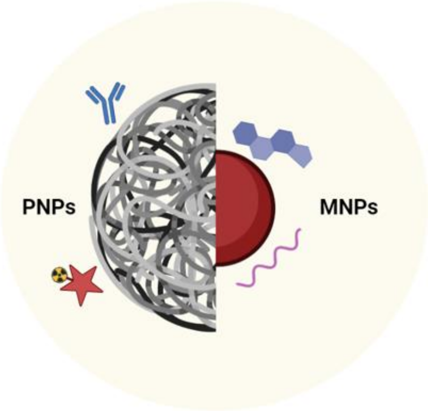
Hydrophilic nanomaterials: functionalized metal nanoparticles and acrylate-based nanopolymers as multimodal agents in nanomedicine

Ilaria Fratoddi

Department of Chemistry, Sapienza University of Rome, P.le Aldo Moro 5, 00185 Rome, Italy

Abstract: Hydrophilic nanostructures are being extensively studied in nanomedicine and biotechnology, to design and develop diagnostic, monitoring, and therapeutic devices [1,3]. In these fields, the role of surface chemistry is of primary importance, and up to now, a wide range of advanced nanomaterials have been used as nanoplatforms. Different shapes, sizes, core, and surface compositions have been explored, either based on soft polymeric nanoparticles (PNPs) or metallic core nanoparticles (MNPs) [4,5]. Herein, hydrophilic acrylate-based nanopolymers and metal nanoparticles are studied as promising nanocarriers for drug delivery, imaging and radiotherapeutic agents.

The synthesis and characterization of acrylates-based co-polymeric nanoparticles obtained *via* surfactant-free radical emulsion polymerization reaction using radical initiators in mild conditions are presented. Methyl methacrylate (MMA), acrylic acid (AA), and *N,N*-dimethylacrylamide (DMAA) monomers were used to synthesize hydrophilic PNPs also in the presence of organic dyes and as a functionalizing layer for MNPs. Hydrophilic metal nanoparticles were also obtained, starting from gold and silver precursors by a wet chemistry approach. Surface functionality was controlled by a proper selection of stabilizing thiols bearing charged functionalities, *i.e.*, sulfonate or amine end-groups. PNPs and MNPs formation, colloidal stability, and surface chemistry were assessed by spectroscopic, structural and morphology techniques. Different bioactive molecules, in particular hydrophobic drugs, organic dyes, and radio-imaging agents were loaded on the PNPs and MNPs and tested in different cellular environments to assess their cytocompatibility and synergic drug efficacy effect.



References

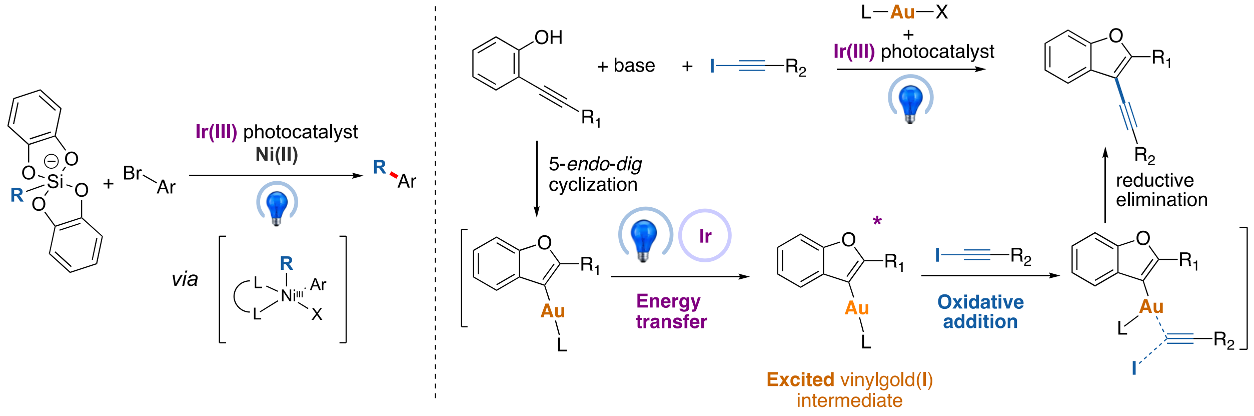
[1] S. Cerra et al., *Mater. Sci. Eng. C* **2020**, *117*, 111337.
[2] T.A. Salamone et al., *J. Colloid Interface Sci.***2023**, 649, 264.
[3] S. Cerra et al., *Coll. Surf. B*, **2021**, *203*, 111727.
[4] S. Lorenzoni et al., *Coll. Surf. B*, **2022**, *219*, 112828.
[5] I. Venditti et al., *Part. Part. Syst. Charact*. **2022**, 2100282.

Organometallic Catalysis under Visible Light

Louis Fensterbank[1,2]

[1] Institut Parisien de Chimie Moléculaire, Sorbonne Université, 4, place Jussieu, 75005 Paris
[2] Collège de France, 11 place Marcelin Berthelot, 75005 Paris
louis.fensterbank@college-de-france.fr

Abstract: Over the last decade, we have been involved in the implementation of organometallic catalysis to the development of sustainable radical chemistry. We have introduced bis-catecholato silicates as versatile sources of alkyl radicals upon photocatalysis.[1] Using Ir(III) or organic photocatalysts, alkyl radicals can be engaged in intermolecular reactions. This process can be merged with Ni-catalyzed C_{sp2}-C_{sp3} cross-coupling reactions. In parallel, and following our interest in gold catalysis, our recent efforts in photoredox/gold dual catalysis will also be presented.[2] We have notably evidenced the first examples of photosensitized oxidation additive to a gold(I) complex leading to C_{sp2}-C_{sp} cross-couplings.[3,4]



References

1. (a) Corcé, V.; Chamoreau, L. M.; Derat, E.; Goddard, J.-P.; Ollivier, C.; Fensterbank, L. *Angew. Chem. Int. Ed.* **2015**, *54*, 11414-11418. (b) Cartier, A.; Levernier, E.; Corcé, V.; Fukuyama, T.; Dhimane, A.-L.; Ollivier, C.; Ryu, I.; Fensterbank, L. *Angew. Chem. Int. Ed.* **2019**, *58*, 1789-1793.
2. Xia, Z.; Khaled, O.; Mouriès-Mansuy, V.; Ollivier, C.; Fensterbank, L. *J. Org. Chem.* **2016**, *81*, 7182-7190.
3. Xia, Z *et al. Nat. Chem.* **2019**, *11*, 797-805.
4. Zhao, F. *et al.* Coupling. *Nat. Commun.* **2022**, 13:2295.

Communications Orales

CO-01

Green Chemistry Innovation: Novel Bio-Based Emollients for Environmentally Friendly Cosmetics

Floriane Rischard,[1,2] Amandine Flourat,[2] Ecaterina Gore,[1] Géraldine Savary[1]

[1] *Université Le Havre Normandie, Normandie Univ, URCOM UR 3221, F-76600 Le Havre, France*
[2] *URD Agro-Biotechnologies Industrielles (ABI), CEBB, AgroParisTech, 51110 Pomacle, France*

floriane.rischard@doct.univ-lehavre.fr, https://urcom.univ-lehavre.fr/

Keywords: Clean-label formulations, Multifunctionality, Bio-based emollients, Sensory Analysis

Abstract: The extensive ingredient lists and potential environmental and health impacts of cosmetic formulations have raised concerns.[1] Ferulic acid, obtained from agricultural by-products,[2] has been found to possess antimicrobial, UV-filtering and antioxidant properties.[3] This led to the development of a chemo-enzymatic method to convert ferulic acid into a cosmetic-grade emollient. The novelty of this project lies on the development of 12 novel bio-based emollients, using green chemistry principles, and assessing their protective and emollients characteristics.

These new emollients exhibited properties similar to that of commercial benchmarks,[4] enabling the formulation of stable oil-in-water emulsions without controversial ingredients. Our research demonstrates the significant potential of these ingredients in formulating cosmetics that are both environmentally and consumer-friendly. They offer innovative and competitive functional characteristics compared to traditional benchmarks.

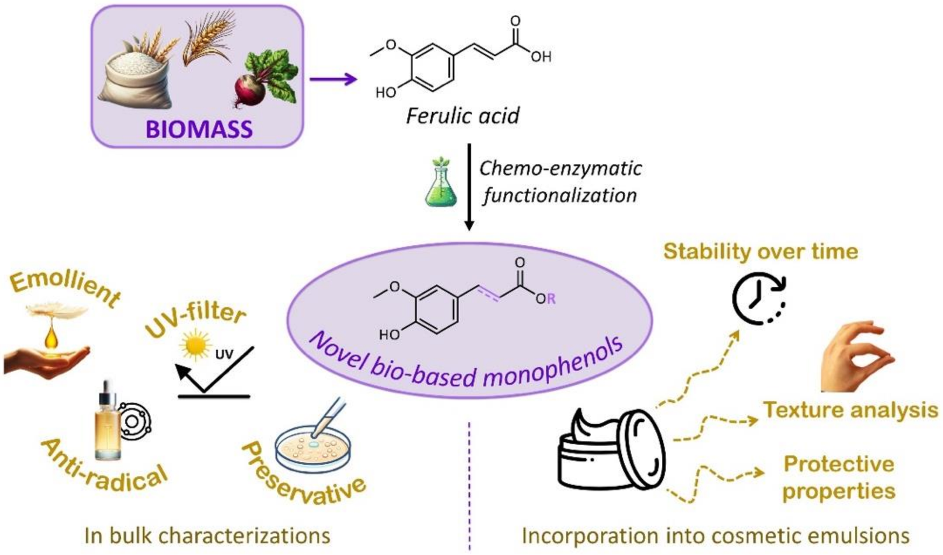


Figure 1 Graphical abstract of the presented work project

References:

1. Wang, J. *et al. Int. J. Environ. Res. Public Health.* **2016**, *13* (8), 782.
2. Buranov, A. U. *et al. Food Chem.* **2009**, *115* (4), 1542-1548.
3. Rioux, B. *et al. Green Chem. Lett. Rev.* **2022**, *15* (1), 116-127.
4. Rischard, F. *et al. ACS Sustainable Chem. Eng.* **2023**, *11* (48), 16955-16964.

CO-02

Deciphering the Secrets of PET Polyesters

Bayan Almasri[1,2*], Youssef Bakkour[2], Christian Rolando[1]

[1]Minitaturisation pour la Synthèse l'Analyse et la Protéomique (MSAP, UAR 3290 CNRS), Université de Lille, Villeneuve d'Ascq, France
[2]Chemistry department, Laboratory of Applied Chemistry (LAC), Lebanese University, Tripoli, Lebanon

*Presenting author: bayan.almasri1234@gmail.com & https://msap-lab.fr/

Keywords: PET; depolymerization; mass spectrometry; ageing; environment.

Abstract: Polyethylene terephthalates (PET) are one of the most abundant polymers in our daily life as they are the main polymers in polyesters textiles, food containers and bottles. Formed of terephthalic acid and ethylene glycol, these polyesters constitute a pollution source either as macro-PET or after degradation into micro- and nano-PET. Many analytical studies had been performed on PET but their identification on molecular level are not satisfying as they are not allowing the study of their structural modifications after ageing [1]. So, it's crucial to study the degradation mechanisms of these samples after exposure to the environment (irradiation, micro-organisms, salinity…) and to quantify them. Our methodology combining soft chemical depolymerization and ultra-high resolution mass spectrometry is a promising solution and proved its success on environmental PET. A solubilization in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) was performed prior to a transamidation using *N,N'*-dimethyl-1,3-propanediamine (DMAPA) at room temperature or 57 °C. After extraction with ultrapure water and ethyl acetate, the products were analyzed by MALDI FTICR MS and LC ESI Orbitrap MS. Many PET containers and bottles from different countries, brands and contents were analyzed in addition to marine samples. For each, a specific signature was determined. Dimers, oligomers, crosslinked, oxidized products and additives were successfully identified.

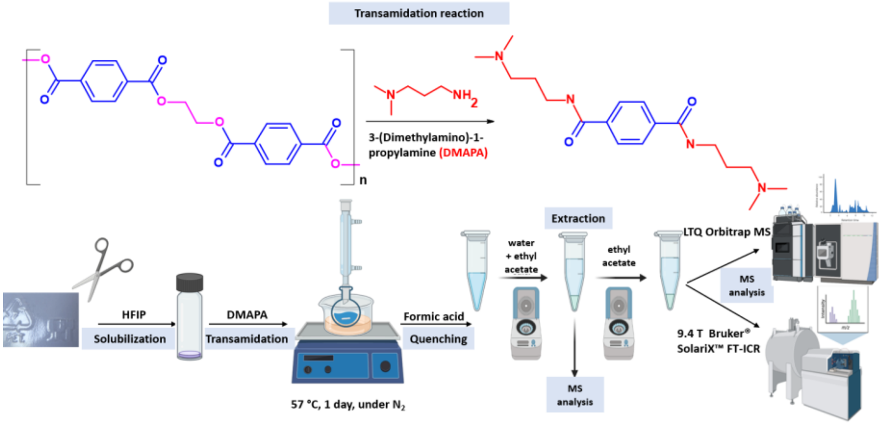


Figure 1 Methodology of depolymerization and analysis of PET samples.

Reference:
1. Ivleva, N.P., *Chemical reviews*, **2021**, 121(19):11886- 11936.

CO-03

Development of thermosensitive, reversible and recyclable flocculant

Souraya .ALAMEDDINE[1], Daniela .Vuluga [1], Wim .Thielemans,[2] Gaëlle .Morandi [1]

[1] INSA Rouen Normandie – Université de Rouen Normandie – UMR6270 PBS (Polymères, Biopolymères, Surfaces) – Rouen – France
[2] KU Leuven- Campus Kulak Kortrijk (Sustainable Materials Lab) -Kortrijk-Belgium

souraya.alameddine@insa-rouen.fr ; https//www.pbs.cnrs.fr

Keywords: Microalgae, Flocculant, Thermosensitive polymers, Cellulose nanocrystals (CNCs)

Abstract: Microalgae are a promising source of biosourced materials (biofuels, pigments, vitamins, etc.). However, the production of microalgae on a large scale remains limited by the enormous cost of the harvesting phase which constitutes 20 to 30% of the total cost, due to the small size of the microalgae (3 – 30 µm), and the low concentration in the culture medium (0.5 – 5 g/L) which makes all conventional harvesting techniques long and energy-intensive [1]. In order to solve this problem, the use of a flocculating agent in the harvest seems an interesting solution [2]. Microalgae have negatively charged proteins on their membrane walls which give them significant colloidal stability. Flocculants are chemical compounds, positively charged, which interact with microalgae to form aggregates which can then be separated by sedimentation or flotation. However, the flocculants used generally remain trapped in the biomass and contaminate it, which limits their use [3].

This thesis subject therefore aims to develop a new family of flocculants based on cellulose nanocrystals modified by cationic centers (to induce flocculation) and by thermosensitive polymer chains (to selectively mask and unmask the cationic charges to harvest and/or recycle the flocculant). This approach will constitute the first example of the use of thermosensitive polymers in the field of harvesting microalgae.

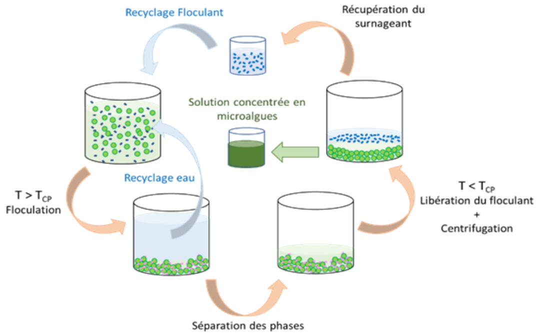


Figure 1 Representation of the complete microalgae culture cycle, flocculation, concentration of the solution in microalgae and release/recycling of flocculant.

References:

1. U, Suparmaniam; M.K, Lam.; Y. Uemura, ;J.W, Lim; K.T, Lee;S.H, Shuit, .Sustain. Energy Rev. 2019, 115, 109361.
2. D, Vandamme; I, Foubert; K, Muylaert, . Trends Biotechnol. 2013, 31, 233–239.
3. N, Uduman; Y, Qi; M, Danquah; G, Forde; A, Hoadley. J. Renew. Sustain. Energy 2010, 2.

CO-04

E-Beam irradiation to recycle polymers from e-waste containing Brominated flame retardants

Rachida Khadidja Benmammar [1], Zohra Bouberka [2], Philippe Supiot [1], Corinne Foissac [1] and Ulrich Maschke [1]

1. Unité Matériaux et Transformations (UMET), UMR 8207, CNRS, INRAE, Université de Lille, 59000 Lille, France
2. Laboratoire Physico-chimique des Matériaux, Catalyse et Environnement (LPMCE), Université des Sciences et de la Technologie « Mohammed Boudiaf » d'Oran (USTO-MB), 31000 Oran, Algerie
rachida.benmammar@univ-lille.fr

Keywords: Recycling; Polymers; Brominated flame retardants; Electron beam irradiation.

Abstract: New policies promoting the circular economy of Waste Electrical and Electronic Equipment (WEEE) aim to foster recycling innovations [1,2]. Current plastic waste incineration practices generate significant pollution and health impacts, as well as substantial economic and energy losses over time [3,4]. Polybrominated diphenyl ethers (PBDEs) are a group of halogenated biphenyls containing bromine atoms that have been used extensively as Brominated Flame Retardants (BFRs) in a variety of end products, including plastics, construction, textiles, electronics, and furniture materials [5,6].

In recent years, electron beam (EB) processing has become a promising tool in both basic and applied sciences. The plastics, automotive, electrical wire, and cable industries are increasingly using EB processing to improve articles quality by enhancing the long-term thermal and mechanical properties of materials [7]. The EB process is recognized as a more environmentally friendly, faster, and more cost-effective alternative to the solvent-based technologies. EB has not yet been used in industry for the decontamination of brominated polymers. However, it has been shown to be remarkably effective in removing toxic molecules. The parameters of a laboratory EB plant have been optimized to decontaminate Acrylo-butadiene-styrene (ABS) and Polycarbonate (PC) containing 10% in weight of PBDE, polymers commonly found in WEEE. The results showed a degradation rate of 87% for the ABS-PBDE system and 91% for the PC-DBDE system, both after exposure to an irradiation dose of 1800 kGy as shown in Figure 1.

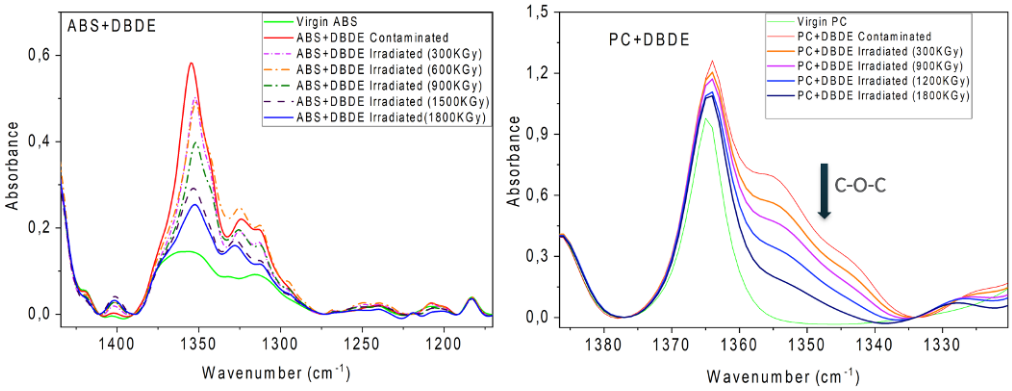


Figure 1. FTIR spectra of ABS-PBDE and PC-PBDE as a function of time irradiation: evolution of the C-O-C ether band vibration of PBDE between 1250 and 1390 cm^{-1}

CO-05

Selective Pd-catalysed C(sp^{3})–H functionalization of 2-aminocyclobutane-1-carboxylique acids (ACBCs)

Vincent Oreve,[1] Iman Traboulsi,[1] David J. Aitken,[2] Yvan Ramondenc,[1] Thomas Boddaert,[2]
Cédric Schneider[1]
[1]COBRA laboratory, UMR-6014, IRCOF, 76821 Mont-Saint-Aignan, France
[2]Université Paris-Saclay, ICMMO, 91400, Orsay
vincent.oreve1@univ-rouen.fr

Keywords: β-amino acid; C-H activation; C(sp^{3})–H; α/β peptide; foldamer

Abstract: In the area of foldamer science, *cis*- and *trans*-cyclobutane β-amino acid derivatives (ACBCs)[1] are building blocks particularly attractive as monomer units for the preparation of peptidomimetic architectures due to their resistance to proteolysis and displaying structural mimicry.[2,3] Although there is an increasing demand for their synthetic access, the development of efficient, selective, and step and atom economical approach to functionalize the *cis*- and *trans*-ACBC at the peripheral sites remains a challenge.[4] In addition, selective Pd-catalyzed auxiliary-directed C(sp^{2}) / C(sp^{3})–H functionalization to derivatize amino acids (AAs) side-chains has emerged as an efficient and straightforward route to further extend the range of non-proteinogenic AAs available as means to increase the structural diversity of the peptides.[5] Surprisingly, β-AAs have received very scant attention and, as far as we know, **no example has been reported for the Pd-catalysed C(sp^{3})–H functionalization of cyclobutane β-AAs**.[6] Herein, during this talk, I will present you our recent research and development on the regio- and stereoselective Pd-catalyzed *syn* vicinal direct C(sp^{3})–H functionalization of *cis*- and *trans*-ACBCs. A large scope of substituted cyclobutane β-amino acid derivatives (arylated, alkynylated, alkenylated and alkylated) at the peripheral C_4 position as well as the late stage C(sp^{3})–H functionalization of hybrid peptides containing ACBCs will be thus presented.

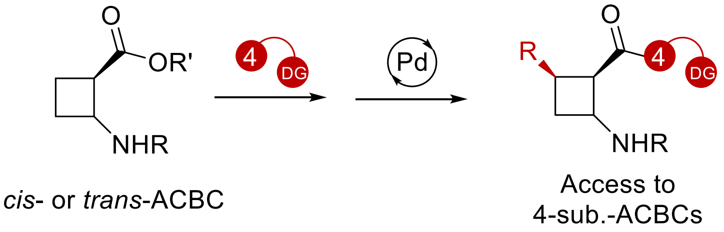


Figure 1 Pd-catalyzed direct C(sp^{3})–H functionalization of *cis*- and *trans*-ACBCs using directing groups

References:
[1](a) V. Declerck, D. J. Aitken *Amino Acids* **2011**, *41*, 587-598. (b) M. Martin-Vila, C. Minguillon, R. M. Ortuno, *Tetrahedron:Asymmetry* **1998**, *9*, 4291-4294. [2] (a) F. Fülöp, T. A. Martinek, G. K. Toth *Chem. Soc. Rev*. **2006**, *35*, 323-334. (b) P. G. Vasudev, S. Chatterjee, N. Shamala, P. Balaram *Chem. Rev*. **2011**, *111*, 657-687. (c) C. Cabrele, T. A. Martinek, O. Reiser, L. Berlicki *J. Med. Chem*. **2014**, *57*, 9718-9739. [3] C. M. Grison, J. A. Miles, S. Robin, A. J. Wilson, D. J. Aitken *Angew. Chem. Int. Ed*. **2016**, 55, 11096-11100. [4] (a) Z. Chang, F. Boyaud, R. Guillot, T. Boddaert, D. J. Aitken *J. Org. Chem.* **2018**, *83*, 527-534. (b) Z. Chang, R. Guillot, T. Boddaert, D. J. Aitken *J. Org. Chem*. **2019**, *84*, 10518-10525. [5] (a) B. V. S. Reddy, L. R. Reddy, E. Corey *J. Org. Lett*. **2006**, *8*, 3391-3394. (b) D. L. Tran, O. Daugulis *Angew. Chem. Int. Ed*. **2012**, *51*, 5279-5281. (c) A. F. Noisier, M. A. Brimble *Chem. Rev*. **2014**, *114*, 8775-8806. [6] (a) D. Antermite, D. P. Affron, J. A. Bull *Org. Lett*. **2018**, *20*, 3948-3952. (b) S. Chowhurry, R. Vaishnav, N. Panwar, W. Haq *J. Org. Chem*. **2019**, *84*, 2512-2522. (c) Z. Wang, Y. Fu, H. Liu, J. Wang *J. Org. Chem.* **2020***, 85, 7683-7693.*

CO-06

Highly Regioselective Metal-Free Arylation of Planar Chiral Sulfur-Based [2.2]Paracyclophanes

Warren Lhuillier,[1] Vincent Tognetti,[2] Annie-Claude Gaumont[1] and Stéphane Perrio[1]

[1] Normandie Univ, ENSICAEN, UNICAEN, CNRS, LCMT, 14000 Caen, France
[2] COBRA laboratory, Normandie Univ, UNIROUEN, INSA Rouen, CNRS, 76000 Rouen, France

warren.lhuillier@unicaen.fr

Keywords: [2.2]Paracyclophane; Sulfoxide; Sulfonium; Phenol; Pummerer; Arylation

Abstract: [2.2]paracyclophane ([2.2]PCP) is an original 3D carbon architecture consisting in two benzene rings opposite to each other and covalently linked at the *para* positions by CH_2–CH_2 groups.[1] [2.2]PCP derivatives are characterized by a high rigidity, strong π-π interactions and planar chirality (a single substituent is enough to have enantiomers). In the last few years, [2.2]PCP chemistry has progressed tremendously, in terms of functionalization and applications (bio- and materials science). However, examples of sulfur-containing building blocks remain scarce.

We wish to present in this communication an innovative and metal-free approach to functionalize, in a highly regioselective manner, planar chiral sulfur-based [2.2]paracyclophanes **(Figure 1)**.[2] The methodology we developed is based on the use of readily available [2.2]PCP sulfoxides[3] and phenols as starting materials. Under the conditions of an interrupted Pummerer reaction, an aryloxy sulfonium salt is generated and further isomerizes to form a [2.2]PCP–aryl bond. The optimization of the operating conditions, the study of the scope and limitations of the process will be highlighted. A mechanistic proposal, supported by theoretical calculations using DFT, will be also presented.[4]

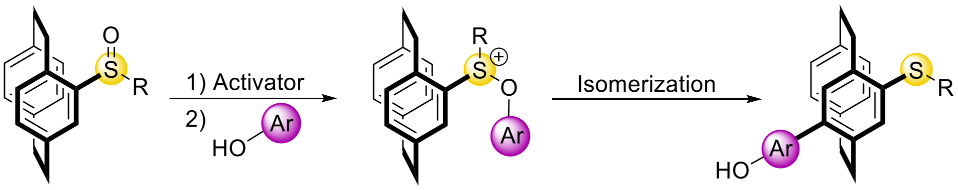


Figure 1 Reaction investigated from sulfinyl substituted [2.2]PCP in this study

References:

1.(a) Hassan, Z.; Spuling, E.; Knoll, D. M.; S. Bräse, *Angew. Chem. Int Ed.* **2020**, *59*, 2156–2170. (b) Weiland, K. J.; Gallego, A.; M. Mayor, *Eur. J. Org. Chem.* **2019**, 3073–3085.

2. For literature precedents, see for example: (a) Enders, M.; Friedmann, C. J.; Plessow, P. N.; Bihlmeier, A.; Nieger, M.; Klopper, W.; Bräse, S. *Chem. Commun.* **2015**, *51*, 4793–4795. (b) Rowlands, G.; Seacome, R. J. *Org. Biomol. Chem*. **2005,** *3*, 3873–3876**.**

3. Lohier, J.-F.; Foucoin, F.; Jaffrès, P.-A.; Garcia, J. I.; Sopková–de Oliveira Santos, J.; Perrio, S.; Metzner, P. *Org. Lett.* **2008**, *10*, 1271–1274.

4.(a) Yanagi,T.; Yorimistu, H. *Chem. Eur. J.* **2021**, *27*, 13450–13456. (b) Bisht, R.; Popescu, M. V.; He, Z.; Ibrahim, A. M.; Crisenza, G. E. M.; Paton, R. S.; Procter, D. J. *Angew. Chem. Int. Ed.* **2023**, e202302418.

CO-07

Photocurrent response and mobility of charge carriers in $La_2Ti_2O_7$

Marine Verger[1], Redouane Douali[2], Freddy Krasinski[2], Jean-François Blach[1] and Sébastien Saitzek[1]

[1]*Univ. Artois, CNRS, Centrale Lille, Univ. Lille, UMR 8181, Unité de Catalyse et Chimie du Solide (UCCS), F-62300 Lens, France*
[2]*ULCO, Unité de Dynamique et Structure des Matériaux Moléculaires (UDSMM) EA 4476, F-62100 Calais, France*
…
marine_verger@ens.univ-artois.fr and http://www.uccs.univ-artois.fr/accueil.htm

Keywords: Photocurrent; Mobility; Wide-bandgap semiconductors; Photoactive materials

Abstract: $La_2Ti_2O_7$ with a layered-perovskite structure has ferro/piezo-electric properties with a high Curie (~1500°C) temperature allowing use in extreme environments [1]. Furthermore, this oxide has a remarkable photocatalytic property under UV irradiation [2] and is part of the wide bandgap semiconductor family. For these photocatalytic applications, the study of electronic properties under light excitation is necessary to understand the mechanisms involved in photodegradation or for improving efficiency. However, there are very few articles on charge carrier mobility and the electronic properties of lanthanum dititanate [3]. The aim of this study is to explore these properties. Firstly, after synthesizing $La_2Ti_2O_7$ by glycine-assisted sol-gel method. The transient photocurrents will be studied as a function of wavelength, light power density and applied voltage (Figure 1). Secondly, thin films synthesized by the laser ablation method will be developed in order to study the mobility of charge carriers using the time-of-flight technique.

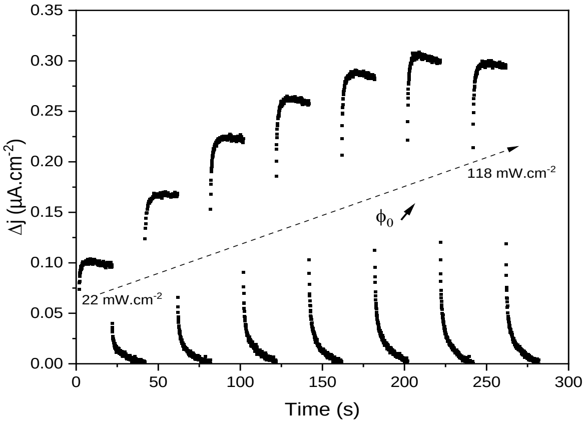


Figure 1 Transient on/off photocurrent response of $La_2Ti_2O_7$ for various light power density (ϕ_0) (λ=450 nm, V_{bias}=1V).

References:

1. S. Nanamatsu, M. Kimura, K. Doi, S. Matsushita, N. Yamada, Ferroelectrics, **1974**, 8 (1), 511-513.
2. S. Leroy, J-F. Blach, M. Huvé, B. Léger, N. Kania, J-F. Henninot, A. Ponchel, S. Saitzek, J. Photoch. Photobio. A, **2020**, 401 (1), 112767.
3. S. Leroy, R. Douali, C. Legrand, F. Krasinski, F. Blanchard, P. Roussel, S. Saitzek, J-F. Blach, *ACS Appl. Electron. Mater.* ***2021****, 3 (7), 3167–3176*

CO-08

Combining enantio-purification with mechanochemistry.

Chrystal LOPES,[1] Clément Brandel,[1] Valérie Dupray,[1] Oleksii Shemchuk,[2] Tom Leyssens,[2]
Yohann Cartigny[1]

[1]Univ Rouen Normandie, Normandie Univ, SMS, UR 3233, France
[2]Institute of Condensed Matter and Nanosciences, Université Catholique de Louvain, Belgium
chrystal.lopes1@univ-rouen.fr

Keywords: Mechanochemistry, Deracemization, Green Chemistry, Enantiomeric Separation, Crystallization

Abstract: In the pharmaceutical field, more than 50% of the commercialized organic molecules are chiral.[1] The corresponding enantiomers can have different biological and chemical properties in contact of a living organism due to their respective chirality. As the counter enantiomer can exhibit a potential toxicity, an enantiopure drug is preferred and required the use of a separation process.

Many methods to access an enantiopure molecule have been developed. Among them, chiral HPLC or asymmetric organic synthesis are available, but crystallization processes are generally preferred due to their low cost. Among enantio-purification methods, the deracemization process combines enantioconversion (via a racemization thanks to the use of a racemizing agent) and crystals dissolution/crystallization.[2] Despite its capacity to reach high enantiomeric excess (theoretically 100%), this process has some drawbacks : (i) the take-off time of the classical deracemization processes in solution reaches hours and even days and (ii) the racemization reaction (in solution) requires solvent that can be toxic and has to be treated.

During the last decades, interest in mechanochemistry has significantly increased. Mechanochemical reactions are described as reactions induced by a mechanical impact by using no (or a minimum amount of) solvent. The present project has for objective to tackle deracemization issues by associating this process to mechanochemistry (Figure 1a). The model compound used for this proof of concept is the *1-(4-chlorophenyl)-4,4-dimethyl-2-(1,2,4-triazol-1-yl)pentan-3-one*, (Cl-TAK, Fig. 1b). Results of this study demonstrate that this combination give access to enantiopure solid with a take-off time of the process that is significantly reduced comparing to a classical deracemization.[3]

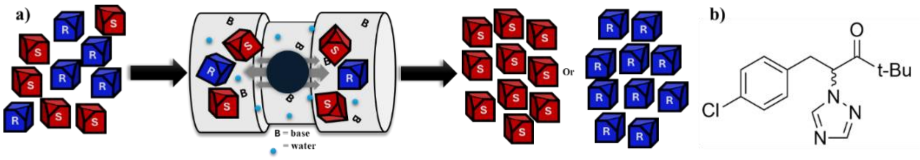


Figure 1 : a) Schematic representation of mechanochemical reaction b) Cl-TAK, model compound.

References:

(1) Nguyen, L. A.; He, H.; Pham-Huy, C. Chiral Drugs: An Overview. *Int. J. Biomed. Sci. IJBS* **2006**, *2* (2), 85–100. (2) Sögütoglu, L.-C.; E. Steendam, R. R.; Meekes, H.; Vlieg, E.; T. Rutjes, F. P. J. Viedma Ripening: A Reliable Crystallisation Method to Reach Single Chirality. *Chem. Soc. Rev.* **2015**, *44* (19), 6723–6732. https://doi.org/10.1039/C5CS00196J. (3) Lopes, C.; Cartigny, Y.; Brandel, C.; Dupray, V.; Body, C.; Shemchuk, O.; Leyssens, T. A Greener Pathway to Enantiopurity: Mechanochemical Deracemization through Abrasive Grinding. *Chem. – Eur. J.* **2023**, *29* (35), e202300585. https://doi.org/10.1002/chem.202300585.

CO-09

RAFT Polymerization of Bio-based Myrcene: Investigating Radical Activation and Processes

Tharin Sensan[1], Sagrario Pascual[1], Laurent Fontaine[1], Sandie Piogé[1]

[1]*Méthodologies et Synthèses de Polymères (MSP), Institut des Molécules et Matériaux du Mans (IMMM),*
UMR CNRS 6283, Le Mans Université, Avenue Olivier Messiaen 72085, Le Mans, France
tharin.sensan.etu@univ-lemans.fr

Keywords: Bio-based polymer, Polymyrcene, Radical Polymerization

Abstract: Bio-based polymers, particularly those derived from terpenes like myrcene, are gaining attention from both research and industry in recent decades, presenting a renewable alternative to petroleum resources. Myrcene shows promise in enhancing specific material properties, notably in elastomers.[1] While polymyrcene synthesis has been achieved through various methods (anionic, cationic, and coordination polymerization) involving toxic solvents and catalysts, radical polymerization stands out for its simpler and more controlled process, potentially applicable in an aqueous medium. However, challenges persist, such as low monomer conversion in bulk polymerization[2] and gel formation in emulsion processes.[3]

This study aims to explore the impact of different radical activation methods and processes on the reversible addition-fragmentation chain transfer (RAFT) polymerization of myrcene in order to enhance myrcene conversion and achieve polymyrcenes with controlled molecular weights and microstructure. Two main approaches are examined : RAFT polymerization in bulk and in an emulsion system. Various radical activation methods were employed to assess their influence on the macromolecular characteristics and microstructure of polymyrcene. In bulk polymerization, photo-irradiation, thermal activation, and sono-activation have been used. A significantly higher monomer conversion was observed using thermal activation compared to the other activation methods. Size exclusion chromatography (SEC) confirmed the formation of well-defined polymyrcenes ($1.1 < Đ < 1.5$) through all radical activations. However, only photo-irradiation activation yielded well-defined polymyrcene microstructure (>90% of 1,4-addition). Emulsion-based RAFT polymerization of myrcene was also studied using thermal, redox, and photo-irradiation activation. In general, monomer conversion was higher in emulsion than in the bulk process; however, with photo-irradiation activation, monomer conversion rates were similar between the two processes. Nonetheless, gel formation was only observed in emulsion when using thermal or redox activation.

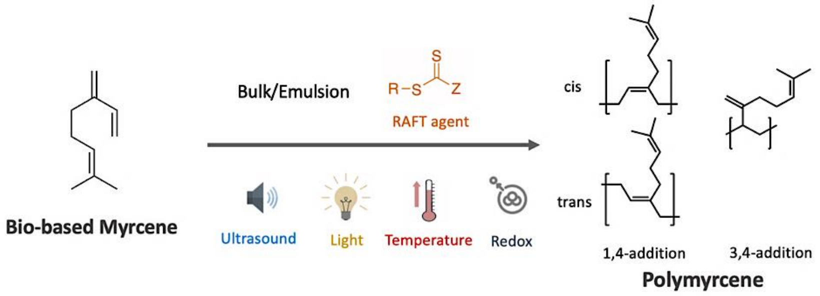


Figure 1 Synthesis of polymyrcene *via* RAFT polymerization: exploring different radical activation methods in bulk and emulsion systems.

References:
(1) Sahu, P.; Bhowmick, A. K.; Kali, G. *Processes* **2020**, *8* (5), 553. (2) Hilschmann, J.; Kali, G. *Eur. Polym. J.* **2015**, *73*, 363–373. (3) Pablo-Morales, Á.; Treviño, María Esther; Saldívar-Guerra, E. *Macromol. React. Eng.* **2022**, *16* (3), 2200007.

CO-10

Elaboration of Biobased Nonisocyanate Polyurea Materials with Shape-Memory Properties

Bao Ding[1], Nadège Follain [2], Nasreddine Kébir[1]

[1]INSA Rouen Normandie, CNRS, Normandie Univ, PBS UMR6270, Rouen F-76000, France

[2] Univ Rouen Normandie, CNRS, Normandie Univ, PBS UMR6270, Rouen F-76000, France
* bao.ding@insa-rouen.fr

Keywords: biobased materials; polyurea; NIPUrea; shape memory; thermosetting material.

Abstract: In this research, we explored the development of biobased thermosetting polymers using a novel transurethane polycondensation approach, aimed at addressing the environmental impact of traditional materials derived from non-renewable resources [1]. By incorporating DADS as a source of dynamic disulfide bonds, we introduce the possibility of topological rearrangement in the polymer's cross-linked network structure. This study compares the new materials to control materials using MDA to varying degrees, as well as to a version without DADS or MDA. Our results reveal that materials containing a 2:1 ratio of MDA and DADS, relative to NIPUrea, can retain a shape memory effect at room temperature. Importantly, the material containing DADS in the same ratio exhibits exceptional topological reconfiguration capabilities at high temperature, as well as robust shape memory properties of a permanent second shape, even after repeated cycling. This suggests that the incorporation of disulfide bonds considerably improves the adaptability and resilience of these polymers. In addition, the study confirms that these modifications do not adversely affect essential material properties such as thermal stability and mechanical strength, offering a sustainable alternative to conventional thermoset polymers [2].

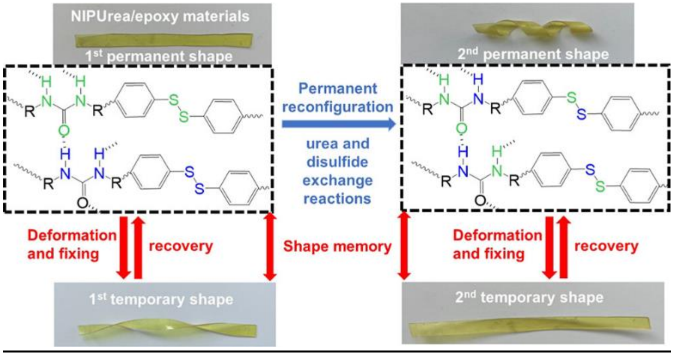


Figure 1. Schematic diagram of dynamic network exchange and shape-memory properties [2].

References:

[1] a) Lendlein, A., Gould, O.E.C. Reprogrammable recovery and actuation behaviour of shape-memory polymers. Nat Rev Mater.2019,4, 116–133. b) Xia, Y. He, F. Zhang, Y. Liu.Y, Leng. J, A Review of Shape Memory Polymers and Composites: Mechanisms, Materials, and Applications. Adv. Mater. 2021, 33, 2000713.

[2] Ding B., Follain N., Kébir N. Elaboration of Biobased Nonisocyanate Polyurea Materials with Shape-Memory Properties. *ACS Appl. Polym. Mater.* 2023, 5, 12, 10416–10425.

CO-11

Synthesis of PET Nanoparticles and Study of their Degradation

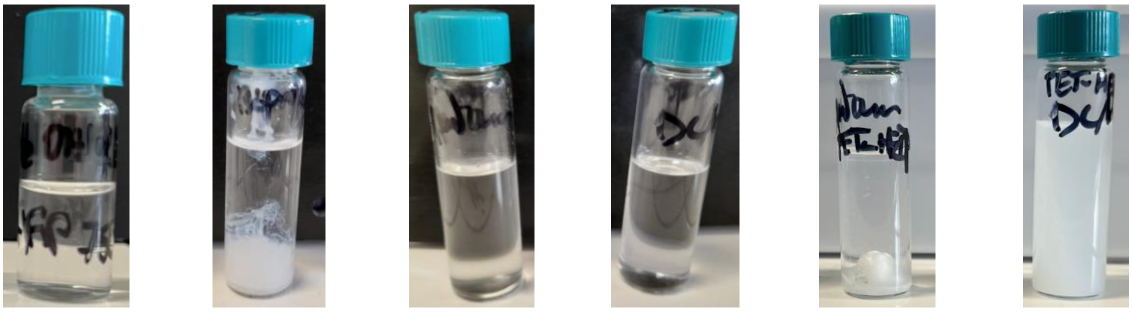
Mathieu HENN[1,*], Bayan ALMASRI[1], Christian ROLANDO[1]
[1]Minitaturisation pour la Synthèse l'Analyse et la Protéomique (MSAP, UAR 3290 CNRS), Université de Lille, Villeneuve d'Ascq, France
*Presenting author: mathieu.henn.etu@univ-lille.fr & https://msap-lab.fr/

Keywords: Polyethylene terephthalate; nanoparticles; UV & thermal degradation; mass spectrometry.

Abstract: Polyethylene terephthalates (PET) are pervasive plastics in our environment. Unfortunately, only small amount (20%) of the 3.5 million of tons of PET produced in Europe each year is recycled (https://www.pet-europe.org/). Upon environmental degradation they generate micro- & nano-plastics which ubiquitously present in oceans and rivers, but also especially for the smaller nanoplastics in air. So, there is a strong need to produce PET nanoparticles for studying their toxicity *in vitro* and *in vivo*.

Three methods have been described for producing PET nanoplastics. The first one consists in grinding the PET pellets creating even at low temperature free radicals which may further with air oxygen. The two other methods start by the dissolution of PET pellets in a fluorinated solvent followed by reprecipitation. Both methods are followed by a tedious purification of nanoparticles. We reproduced both experiments and we obtained a few percent yield as much of the precipitate was bulk PET.

So, we develop an original strategy adapted to produce nanoparticles in a microfluidic system. Firstly, we explored the solubility of the HFIP, PET solution. We noticed that the solution instantaneously afforded cotton like flakes in isopropanol and was soluble in pentane and dichloromethane. By adding ethyl acetate, we obtained a bulk PET precipitate in pentane. We were delighted to obtain almost stable nanoparticles in dichloromethane. These conditions are suitable for microfluidic experiments we are currently investigating [1]. These nanoparticles have been exposed to UV at 395 nm. We will present their degradation products studied by mild depolymerization and mass spectrometry and we will compare them to the degradations of environmental PET collected on North Sea beaches.



(a) 5 mg of PET in 1 mL HFIP

(b) Solution (a) in 5 mL isopropanol

(c) Solution (a) in 5 mL pentane

(d) Solution (a) in 5 mL CH_2Cl_2

(e) Solution (c) with 1 mL AcOEt

(f) Solution (d) with 1 mL AcOEt

Figure 1 PET nanoparticles creation.

Reference:

1. Ftouni, J., Penhoat, M., Addad, A., Payen, E., Rolando, C., & Girardon, J. S. *Nanoscale*, **2012**, 4(15), 4450-4454.

CO-12

Stimuli-responsive hydrogels based on near-infrared light-sensitive self-immolative polymers for controlled drug release

Roukaya ACHOUR, kedafi BLEKHIR, Patrice WOISEL
Univ. Lille, CNRS, INRAE, Centrale Lille, UMR 8207-UMET-Unité Matériaux et Transformations, F-59000 Lille, France
Roukaya.achour1@centralelille.fr https://umet.univ-lille.fr/detailscomplets.php?id=859&lang=fr

Keywords: stimuli-responsive polymers, self-immolative polymers, hydrogels, controlled release, UV-NIR.

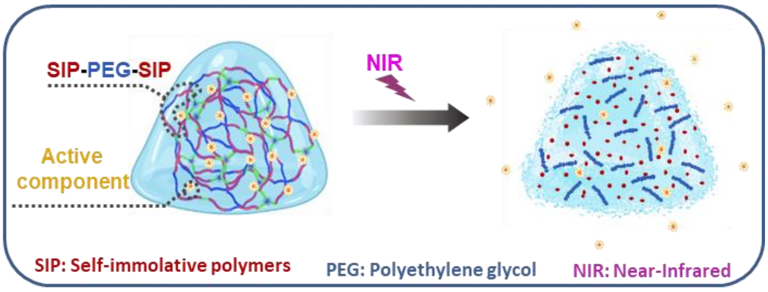


Figure: Schematic representation of the synthesized hydrogel and its controlled depolymerization under light stimuli

Abstract: Stimuli-responsive polymers (SRPs) have the particularity to alter their physicochemical properties in response to external stimuli. Depending on their chemical structure, they can react to stimuli like temperature, pH, or light, making them valuable in biomedical applications, particularly for controlled drug delivery. Various SRP-based systems have been developed, including three-dimensional matrices, fibers, nanoparticles, hydrogels etc. Among these systems, hydrogels are particularly interesting in the biomedical field due to their biocompatibility and mechanical properties. However, these systems face challenges such as uncontrolled degradation kinetics in physiological environments, stimulus intensity depending on fluctuations in this environment, passive drug release (before stimulus application), limited penetration depth of external stimuli (such as light), prolonged latency time, and inertia. This project focuses on developing hydrogels using a new category of polymers, self-immolative polymers (SIPs), which undergo rapid depolymerization upon stimulation. In this work, the developed SIPs are sensitive to near-infrared (NIR) and ultraviolet (UV) light.

An original monomer structure was synthesized as part of this work, and its polymerizability was demonstrated and optimized (with conversions up to 93%). This monomer allowed the synthesis of various self-immolative macromolecular architectures, including linear homopolymers, di- and tri-block copolymers, as well as star-shaped amphiphilic structures. It was also demonstrated that the molecular weights of these macromolecular architectures are controllable. The depolymerization of all these macromolecular architectures in response to light was studied using various methods, showing rapid responses compared to the literature (on the order of minutes). The behavior of the developed hydrogel was also studied, demonstrating its ability to release its contents in a short time (5 minutes) under light exposure.

CO-13

Isolation of Sub-Pollen Particles (SPPs) by different methods of filtration

Qurat-Ul-Ain Riaz[1], Najiha Azarkan[1], Nicolas Visez[1] and Marie Choël[1]

[1]Univ. Lille, CNRS, UMR, 8516, LASIRE - Laboratoire de Spectroscopie pour les Interactions, la Réactivité et l'Environnement, F-59000, Lille, France

quratulain.riaz.etu@univ-lille.fr

Keywords: Pollen; subpollen particles (SPPs); cytoplasmic granules; allergy; asthma

Abstract: Since the industrial revolution, there has been an increase in pollen allergy among young adults, with 39% now affected.[1] While the whole pollen grain is retained in the upper airways, its fragmentation can result in the release of numerous sub-pollen particles (SPPs) which are capable of penetrating deep into the bronchi and triggering allergic asthma. These particles were isolated from the cytoplasm of pollen grains in the laboratory after rehydration of 0.05 g of pollen in 2 mL of milliQ water and filtration using three different methods. The first method (A) uses vacuum filtration through a paper filter with 11 µm of retention value while the other method (B) uses a 5-µm hydrophilic cellulose acetate syringe filter. A third method (C) consists of Eppendorf tube with filtration this time a smaller quantity of pollen is added into the filtration tube 0.01g in 0.4 mL of milliQ water. A total of 300 SPPs were observed individually under a light microscope for each pollen type in order to obtain the size of the SPPs and compare it with literature values.[2]

Table SPP sizes (mean diameter ± std dev. in µm) reported in the literature and obtained experimentally.

Type of pollen	Cecchi *et al.* (2021)	Method A	Method B	Method C
Ambroisia artemisiifolia	2.1 ± 1.2	3.520 ± 0.67	2.632 ± 0.511	2.424 ± 0.622
Phleum pratense	3.8 ± 1.1	3.761 ± 0.79	3.359 ± 0.653	3.893 ± 0.750
Betula pendula	3.5 ± 1.1	3.139 ± 0.641	3.251 ± 0.608	3.260 ± 0.473
Olea sp	3.6 ± 1.7	3.494 ± 0.699	2.929 ± 0.634	3.377 ± 0.318
Cupressus sp	2.9 ± 0.9	2.642 ± 0.419	2.547 ± 0.424	2.606 ± 0.337
Parietaria officinalis	1.9 ± 1.1	2.536 ± 0.649	2.648 ± 0.585	2.978 ± 0.473
Lollium perenne	NA	2.479 ± 0.393	3.003 ± 0.632	2.795 ± 0.264

The comparison of SPP sizes between experimental results and literature values for distinct pollen species reveals variations that could be due to changes in experimental circumstances, sample preparation, or measurement methods. Despite the differences in SPP sizes, it's worth noting that Method A offers distinct advantages in terms of cost-effectiveness and environmental sustainability.

References:

(1) Platts-Mills, T. A. E. The Allergy Epidemics: 1870-2010. *J. Allergy Clin. Immunol.* **2015**, *136* (1), 3–13.

(2) Cecchi, L.; Scala, E.; Caronni, S.; Citterio, S.; Asero, R. Allergenicity at Component Level of Sub-pollen Particles from Different Sources Obtained by Osmolar Shock: A Molecular Approach to Thunderstorm-related Asthma Outbreaks. *Clin. Exp. Allergy* **2021**, *51* (2), 253–261.

CO-14

Masked thiocarbonyl strategy for the synthesis of thietane scaffolds

Gabriel Cormier,[1] Maria I. Lapuh,[1] David J. Aitken, [1] Clémence Allain,[2] Thomas Boddaert[1]

[1]Université Paris-Saclay, CNRS, ICMMO, 91405 Orsay, France
[2]Université Paris-Saclay, ENS Paris-Saclay, CNRS, PPSM, Gif-sur-Yvette 91190, France
gabriel.cormier@universite-paris-saclay.fr

Keywords: Photochemistry; thietane; thia-Paternò–Büchi reaction; domino sequence; thiocarbonyl

Abstract: Photochemical reactions constitute powerful tools for the creation of chemical diversity from simple starting materials.[1] They provide access to specific and complex molecular structures, that are difficult to prepare otherwise.[2] These transformations induced by light absorption are attractive in the context of sustainable development and they can address this challenge more efficiently when they are incorporated in domino reactions.[3,4,5] Combined with thermal reactions or even better with other photochemical transformations, this strategy is economical in terms of time, energy, waste and can avoid the isolation of unstable intermediates.

Due to their poor stability, thiocarbonyl compounds have been underexploited chromophores, especially in the so-called « Thia-Paternò–Büchi reaction », a [2+2]-photocycloaddition between excited thione derivatives and alkene partners, to prepare thietanes. Divided into two axes, this presentation will describe a straightforward access to a large collection of sulfur-containing four-membered heterocycles through an innovative two-step domino photochemical reaction including a Norrish II fragmentation of phenacyl[6] or pyrenacyl sulfides,[7] which generates thiocarbonyl intermediates in-situ, and a thia-Paternò–Büchi reaction with both electron-poor and -rich olefins.

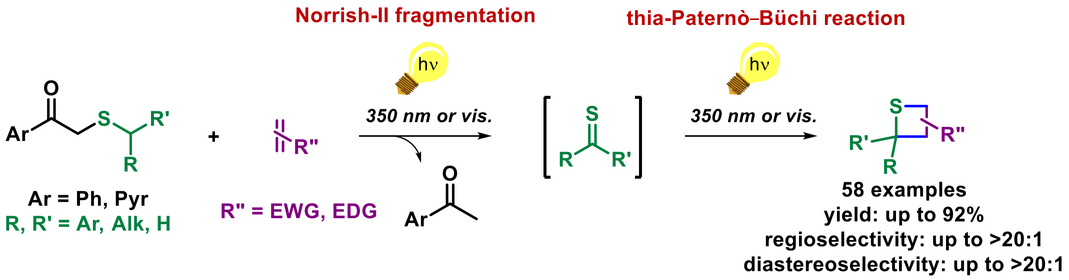


Figure 1: Photochemical domino reaction for the synthesis of thietane scaffolds

References:
1. Bach, T.; Hehne, J. P. *Angew. Chem, Int. Ed.* **2011**, 46, 1000-1045.
2. Beeler, A. B. *Chem. Rev.* **2016**, 17, 9629-9630.
3. Schaumann, E. *Topics in Current Chemistry, Springer.* **2007**, 1-34.
4 Buendia, J.; Chang, Z.; Eijsberg, H.; Guillot, R.; Xie, J.; Frongia, A.; Secci, F.; Robin, S.; Boddaert, T.; Aitken, D. J. *Angew. Chem, Int. Ed.* **2018**, 57, 6592-6596.
5 Kassir, A. F.; Guillot, R.; Scherrmann, M.-C.; Boddaert, T.; Aitken, D. J. *Org. Lett.* **2020**, 22, 8522-8527.
6 Lapuh, M. I.; Cormier, G.; Chergui, S.; Aitken, D. J.; Boddaert, T. *Org. Lett*. **2022**, 24, 8375-8380.
7 Cormier, G.; Allain, C.; Boddaer, T. *submitted article.*

CO-15

ZnO nanopillars and liquid crystals for hybrid solar cells : A new frontier in photovoltaics

KHOL Bator[1], MATHIEU Christian[1], SAITZEK Sébastien[1], BLACH Jean-François[1]

[1] Unité de catalyse et chimie du solide (UCCS), UMR 8181 CNRS Université d'Artois, Faculté des sciences Jean Perrin, 62300 Lens, France

bator.khol@univ-artois.fr

Keywords: Hybrid solar cells**;** Liquid crystals**;** Nano-pillars**;** P/N Heterojunctions; Electrodeposition

Abstract: With the ever-increasing global population and the resulting energy demand, it is crucial to develop renewable energy sources to replace fossil energies. In this context, our research focuses on designing a simple and cost-effective alternative to current silicon-based solar cells, which also have relatively polluting chemistry [1]. This work aims to develop solar cells by exploiting P/N heterojunctions based on semiconducting liquid crystals materials ([1] benzothieno[3,2-b][1] benzothiophene: (Ph-BTBT-10)) and zinc oxide (ZnO) nano-pillars [2,3]. In this work, we present the synthesis of ZnO nanopillars with a nanometric controlled diameter by electrodeposition on different substrates (glass with transparent conducting oxides and Platinum layer deposited on Silicon substrate), followed by the impregnation of Ph-BTBT-10 liquid crystal molecules on the ZnO nano-pillars. The electrodeposition method offers an optimal architecture (figure 1.a) to maximize the surface of interaction between ZnO nano-pillars and the Ph-BTBT-10 molecules [4]. The structure of these nanowires is characterized by X-ray diffraction (figure 1.b) and scanning electron microscopy. These analyses demonstrate the specific growth of nano-pillars with a strong anisotropy which can described by the c-axis perpendicular to the substrate. In addition, the electrical behavior of these samples was analyzed by a photo-electrochemical setup equipped with different light diodes, Mott-Schottky curves). And finally, the current-voltage characteristic of our solar cell was measured under the light provided from a solar simulator (figure 1.c).

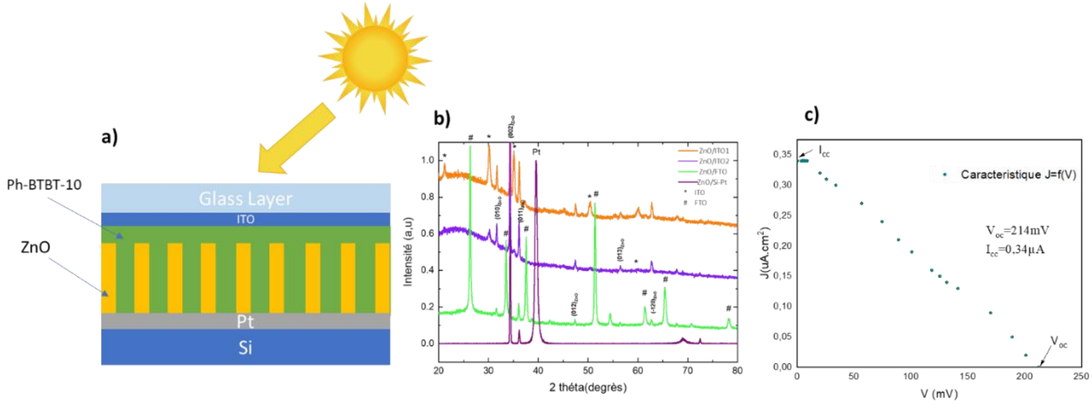


Figure 1 a) Concept of the hybrid solar cell b) X-Ray diffractograms obtained on ZnO nano-pillars grown on various substrates c) Characteristic J=f(V) of the solar cell

[1] S. Sanchez, "Fabrication of Nanostructured Solar Cells Based on ZnO Nanowires", PhD thesis, Université de Grenoble, 2012. [2] H. Iino, T. Usui, and J.-I. Hanna, "Liquid crystals for organic thin-film transistors", Nature communications, vol. 6, p. 6828, Apr. 2015, DOI: 10.1038/ncomms7828. [3] M. Dhennin, "Films minces organiques auto-organisés et dopés en nanoparticules pour des applications photovoltaïques", Master, UCCS, Faculté Jean Perrin Lens, 2022. [4] E. Niemec, "Durability of a Nanostructured Zinc Oxide Coating Developed by Soft Chemistry for Antibacterial and Self-cleaning Surfaces", PhD thesis, Université polytechnique Hauts-de-France et l'INSA Hauts-de-France, 2021.

CO-16

Halo Pentafluorosulfanylation of Alkynes

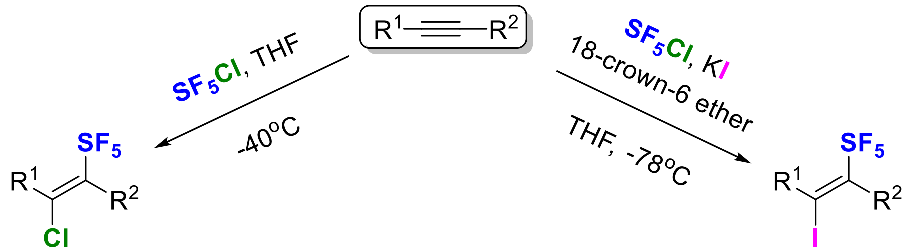
Thi Mo Nguyen[1], Nicolas Blanchard[2], Vincent Bizet*[2], Dominique Cahard*[1]

1) CNRS, UMR 6014 COBRA, Normandie Université, 76821 Mont Saint Aignan, France
2) CNRS, LIMA, UMR 7042, Université de Haute-Alsace, Université de Strasbourg, 68000 Mulhouse
thi-mo.nguyen@univ-rouen.fr

Keywords: Pentafluorosulfanylation; radical addition; alkynes

Abstract: The pentafluoro-λ^6-sulfanyl group is an intriguing and emerging functional group inorganic chemistry due to its high potential in a wide range of applications.[1] While the oxidative fluorination of organic thiols and disulfides was developed to access Ar-SF_5 compounds,[2] the chemistry of pentafluorosulfanyl aliphatic compounds is still underdeveloped because of the limited number of pentafluorosulfanylation reagents (essentially SF_5Cl and SF_6).[3] During the JNOEJC 2024, we will report on a robust protocol enabling the SF_5Cl addition to alkynes, providing a variety of *(E)*-chloro-pentafluorosulfanyl alkenes by using a solution of SF_5Cl in THF in absence of any additive.[4a] Besides, we will also demonstrate the direct synthesis of unprecedented *(E)*-iodo-pentafluorosulfanyl alkenes by means of a combination of SF_5Cl and KI as iodine source, as we would expect from manipulating the unknown SF_5I reagent.[4b]

Figure 1 Halo pentafluorosulfanylation of alkynes



References:

[1] (a) Colby, D. A. *Chem. Med. Chem.* **2017**, 12, 18, 1481-1490; (b) Jacquemin, D.; Colman, Z. *RSC. Adv*. **2017**, 7, 25566-25574; (c) Chan, J. M. W. *J. Mater. Chem. C.* **2019**, 7, 12822.

[2] (a) Umemoto, T. **2010**, Process for preparation of arylsulfur pentafluorides from arylsulfur halotetrafluorides and a fluoride source under hydrous conditions, WO2010014665A1; (b) Umemoto, T.; Garrick, L. M.; Saito, N. *Beilstein J. Org. Chem*. **2012**, 8, 461–471; (c) Pitts, C. R.; Bornemann, D.; Liebing, P.; Santschi, N.; Togni, A. *Angew. Chem. Int. Ed*. **2019**, 58, 1950–1954.

[3] Popek, L.; Nguyen, T. M.; Blanchard, N.; Cahard, D.; Bizet, V. *Tetrahedron*, **2022**, *117-118*, 132814.

[4] (a) Nguyen, T. M.; Popek, L.; Matcharaviani, D.; Blanchard, N.; Bizet, V.; Cahard, D. *Org. Lett.,* **2024**, 26, 1, 365–369; (b) Nguyen, T. M.; Legault, C. Y.; Blanchard, N.; Bizet, V.; Cahard, D. *Chem. Eur. J.,* **2023***,* 29, e202302914.

La chimie verte s'invite chez les membranes

Mahamat Tahir Moustapha, Virginie Dulong, Louise Hespel et Corinne Chappey
Univ Rouen Normandie, INSA Rouen Normandie, CNRS, PBS UMR 6270, F-76000 Rouen, France
Mahamat_tahir.moustapha.etu@univ-lemans.fr ; virginie.dulong@univ-rouen.fr ; louise.hespel@univ-rouen.fr ;

corinne.chappey@univ-rouen.fr

Mots clés: membranes poreuses, PLA, éthyle lactate, chimie verte

Abstract : Les membranes polymères sont utilisées dans de nombreuses applications, dans différents domaines à savoir la séparation de gaz, le traitement de l'eau, la libération de médicaments ou l'emballage. Cependant, même si les membranes sont très utiles dans la préservation et la sauvegarde de l'environnement, souvent leur élaboration ne respecte pas les principes de la chimie verte. Les solvants utilisés pour leur élaboration sont très souvent des solvants organiques pouvant être cancérogènes, mutagènes et toxiques pour la reproduction (CMR) et les polymères utilisés sont d'origine pétrosourcée et non biodégradables ce qui nuit à l'environnement(1).

L'objectif principal de ce projet de recherche de Master 2 est d'élaborer des membranes poreuses vertes c'est à dire de remplacer les solvants CMR par des solvants verts tels que le lactate d'éthyle, d'utiliser un polymère biosourcé et biodégradable pour élaborer la matrice et un agent porogène à base de polymère naturel (l'alginate modifié ou non par la Jeffamine®). Le poly(acide lactique) (PLA) a été choisi comme matrice car il est issu de la biomasse, biocompatible et biodégradable en compostage industriel(2). Ces choix obéissent ainsi aux cinquième, septième et dixième principes de la chimie verte.

Après détermination des conditions optimales expérimentales (tests de solubilisation, concentration massique en PLA, température de solubilisation…), nous avons élaboré des membranes par la méthode d'inversion de phase induite par l'eau : les solutions de polymères avec ou sans agent porogène sont coulées sur une plaque en verre puis plongées dans un bain de non-solvant (ici l'eau) à une température et un temps donné.

Nous avons modifié l'alginate de sodium par la Jeffamine® M-2005(3) afin d'obtenir un dérivé présentant des propriétés thermosensibles dans le but d'obtenir un agent porogène capable de contrôler la taille des pores des membranes en fonction de la température du bain de non-solvant.

Les membranes ont été caractérisées par microscopie optique, par DSC (Calorimétrie différentielle à balayage) et par ATG (Analyse Thermogravimétrique) afin de déterminer la structure symétrique ou asymétrique des membranes, la taille des pores et les propriétés thermiques des membranes.

References

(1) Galiano, F.; Ghanim, A. H.; Rashid, K. T.; Marino, T.; Simone, S.; Alsalhy, Q. F.; Figoli, A. Preparation and Characterization of Green Polylactic Acid (PLA) Membranes for Organic/Organic Separation by Pervaporation. *Clean Technol. Environ. Policy* **2019**, *21* (1), 109–120.

(2) Chinyerenwa, A. C.; Wang, H.; Zhang, Q.; Zhuang, Y.; Munna, K. H.; Ying, C.; Yang, H.; Xu, W. Structure and Thermal Properties of Porous Polylactic Acid Membranes Prepared via Phase Inversion Induced by Hot Water Droplets. *Polymer* **2018**, *141*, 62–69. https://doi.org/10.1016/j.polymer.2018.03.011.

(3) Karakasyan, C.; Lack, S.; Brunel, F.; Maingault, P.; Hourdet, D. Synthesis and Rheological Properties of Responsive Thickeners Based on Polysaccharide Architectures. *Biomacromolecules* **2008**, *9* (9), 2419–2429.

CO-18

Identification of Artists' Oil Paint Film Precursors & Structure

Giulia Gemmeli[1,*], Bayan Almasri[1], Christian Rolando[1]

[1]Minitaturisation pour la Synthèse l'Analyse et la Protéomique (MSAP, UAR 3290 CNRS), Université de Lille, Villeneuve d'Ascq, France

*Presenting author: giulia.gemelli.etu@univ-lille.fr & https://msap-lab.fr/

Keywords: Oil paintings' film; unsaturated fatty acids; inorganic pigments.

Abstract: Oil paints are among the most widespread painting media of all time. They are constituted of both pigments and binder. The binder is composed of siccative oil, the most common being linseed, poppy and walnut oil. Linseed oil triacylglycerols (TAGs) mainly contain linolenic acid, C18 fatty acid with 3 double bonds (C18:3) whereas poppy oil TAGs mainly contain linoleic acid, C18 fatty acid with 2 double bonds (C18:2). In presence of oxygen and light, these oils polymerize forming a 3-dimensional insoluble network and it is precisely the quantity and the presence of unsaturations composing the fatty acid chains that are crucial in their siccativation process [1]. So chemically they belong to the unsaturated polyesters family. An original method was developed. It is based on mild transamidation cleavage of glycerol esters untangling the 3D work and affords modified and crosslinked fatty acids together with oil degradation products. We chose *N,N*-dimethylpropane-1,3-diamine bearing a tertiary amine for increased ESI sensitivity. We started the study from paint mock-ups prepared using oil paint tubes by the most well-known paint manufacturers and aged from one week to a couple of years. The protocol was then optimized on samples of tenths of micrograms for coping with the very tiny quantities from precious artworks in museums or forensic investigations. Then, µg-scale samples containing different pigments taken from a reference set of historical canvases ranging from the beginning of the 19th to the early 20th century were then analyzed with the same protocol and processed through statistical methods for exploring the effects of metals on the polymerization process and on the formation of oil degradation products.

Unsaturated triacylglycerol. Blue: Linolenic, green: Linoleic, red: Oleic acids.

Figure 1 Analysis by MALDI FTICR MS of a 10 µg sampling on a historical canvas dated 1884.

Reference:

1. Bonaduce, I., Duce, C., Lluveras-Tenorio, A., Lee, J., Ormsby, B., Burnstock, A., & Van Den Berg, K. J. *Acc. Chem. Res.*, **2019**, 52(12), 3397-3406.

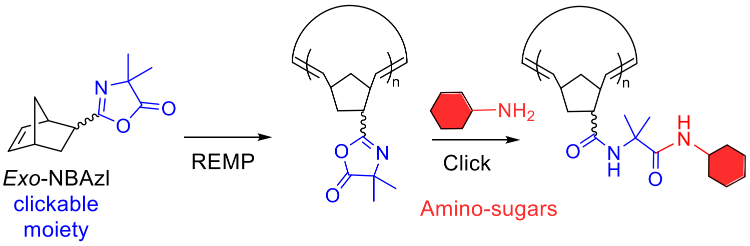
Cyclic clickable polymers by ring-expansion metathesis polymerization for multivalency

Jana Harb, Clément Gonnot, Fabien Boeda, Laurent Fontaine and Véronique Montembault
Institut des Molécules et Matériaux du Mans (IMMM), UMR 6283 CNRS
Le Mans Université, Avenue Olivier Messiaen, 72085 Le Mans Cedex 9, France
Jana.Harb@univ-lemans.fr

Keywords: Cyclic polymer; Ring-expansion metathesis polymerization (REMP); Cyclic ruthenium catalyst; Norbornenyl azlactone; Post-polymerization modification (PPM).

Abstract: Cyclic polymers have recently attracted growing interest in fields such as materials science and biomedicine.[1] Unlike linear polymers, cyclic polymers have a closed loop structure with no chain ends, giving them distinct physical and biological properties despite similar chemical structure and average molecular weight. The ring-closure and ring-expansion methods have become two of the most popular and effective approaches to prepare these fascinating macromolecules. The ring-closure method involves linking the ends of linear polymer chains, while the ring-expansion approach relies in the consecutive insertion of cyclic monomers into the growing chain. The ring expansion approach is superior to the ring-closure approach, due to its ability to generate high molecular weight cyclic polymers without contamination by linear polymers while avoiding the excessively diluted reaction conditions required by the ring-closure. Ring-expansion metathesis polymerization (REMP) represents one of the latest advancements in the ring-expansion approach. Utilizing a cyclic ruthenium-based catalyst, REMP enables the synthesis of high molecular weight cyclic polymers.[2]

In this study, we explore the ring-expansion metathesis polymerization (REMP) of norbornenyl azlactone (NBAzl) using a cyclic ruthenium-based catalyst (CB6) to synthesize a clickable azlactone-functionalized cyclic platform P(NBAzl). The CB6 initiator was synthesized using a procedure adapted from the literature.[3] To confirm the cyclic structure of the obtained polymers, linear P(NBAzl) polymers with comparable average molecular weights and dispersities were synthesized.[4] These polymers are promising for a variety of applications, as they can be post-modified with active molecules thanks to the azlactone clickable moiety. As an example, cyclic P(NBAzl) polymers were post-modified with functionalized amino-sugars derived from mannose and glucose to produce cyclic glycopolymers of varying lengths and their inhibitory effect was evaluated against a full range of lectins.



Scheme 1. Synthesis of a cyclic poly(norbornenyl azlactone) platform by REMP and PPM with functionalized amino-sugars

References:

(1) Wang, T.-W.; Golder, M. R. *Polym. Chem.* **2021**, *12* (7), 958–969.
(2) Chen, C.; Weil, T. *Nanoscale Horiz.* **2022**, *7* (10), 1121–1135.
(3) Wang, T.-W.; Huang, P.-R.; Chow, J. L.; Kaminsky, W.; Golder, M. R. *J. Am. Chem. Soc.* **2021**, *143* (19), 7314–7319.
(4) Gonnot, C.; Scalabrini, M.; Roubinet, B.; Ziane, C.; Boeda, F.; Deniaud, D.; Landemarre, L.; Gouin, S. G.; Fontaine, L.; Montembault, V. *Biomacromolecules* **2023**, *24* (8), 3689–3699.

CO-20

New process for the production of UV polyurethane foams

CHAILLY Ludvina[1], LECAMP Laurence[1], KEBIR Nasreddine[1]
[1] *INSA Rouen Normandie - University of Rouen Normandie - UMR6270 PBS, Rouen, France*
ludvina.chailly@insa-rouen.fr

Keywords: Polyurethane foams, non-isocyanate polyurethane, transurethanization.

Abstract: The polyurethane foams market is expected to increase by 7.5% over the next few years.[1] They are widely used in a variety of industries, such as construction, automotive thanks to their low density, good heat and sound insulation, but also interesting mechanical properties.[2]

Manufacturers produce these foams mainly at room temperature, via an exothermic polyaddition reaction between an isocyanate, a polyol and water. This process generates and releases CO_2 gas, creating gas cells in the polymer and leading to foam expansion.[3]

However, in view of the toxicity of isocyanate monomers and stricter regulations on their use, two alternative ways of synthesizing isocyanate-free polyurethane foams have emerged. The most common involves a polyaddition reaction between polyamines with poly(cyclic carbonate)s leading to poly(hydroxyurethane)s. Another possible alternative is the use of the polycondensation by transurethanization route, which has the advantage of giving conventional polyurethane structures. In addition, with this technique, telechelic NIPU oligomers can easily be prepared as precursor of NIPU materials with fast crosslinking kinetics at room temperature.[3]

This presentation will focus on a new process for obtaining isocyanate-free polyurethane foam, using the transurethanization process.

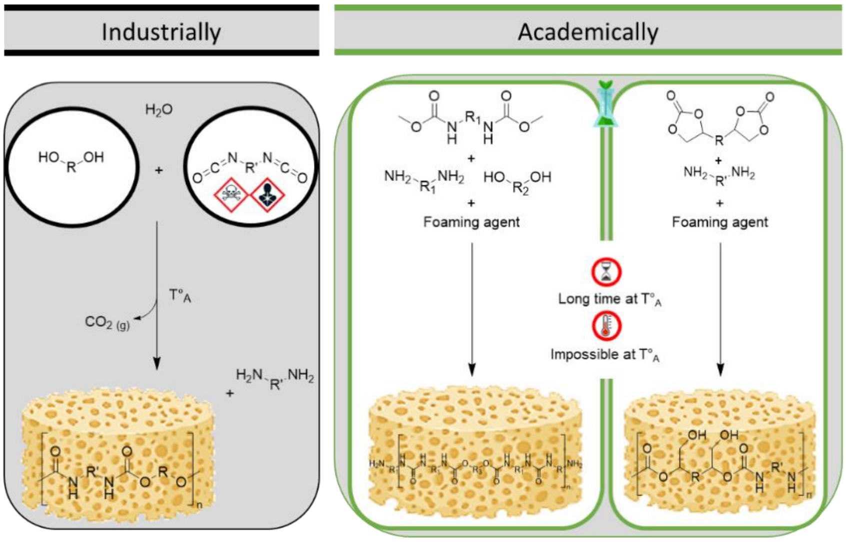


Figure 1. Main pathways of polyurethane foam.

References:
(1) Polyurethane Foam Market Size To Reach $73.57Bn By 2030. https://www.grandviewresearch.com/press-release/global-polyurethane-foam-market (accessed 2024-04-18). (2) Jin, F.-L.; Zhao, M.; Park, M.; Park, S.-J. Recent Trends of Foaming in Polymer Processing: A Review. Polymers 2019, 11 (6), 953. (3) Valette, V.; Kébir, N.; Tiavarison, F. B.; Burel, F.; Lecamp, L. Preparation of Flexible Biobased Non-Isocyanate Polyurethane (NIPU) Foams Using the Transurethanization Approach. React. Funct. Polym. 2022, 181, 105416.

CO-21

Amylopectin chain length distribution (CLD) by Fluorescence-assisted Capillary Electrophoresis (FACE) down to single starch granules

Isabelle Fabrizi[1,*], Christian Rolando[1], Nicolas Szydlowski[2], Fabrice Bray[1]

[1]Minitaturisation pour la Synthèse l'Analyse et la Protéomique (MSAP, UAR 3290 CNRS), Université de Lille, Villeneuve d'Ascq, France
[2]Unité de Glycobiologie Structurale et Fonctionnelle (UGSF, UMR 8576 CNRS), Université de Lille, Villeneuve D'Ascq, France
*Presenting author: Isabelle.fabrizi.etu@univ-lille.fr, https://msap-lab.fr/

Keywords: Starch, Single granule, Capillary Electrophoresis

Abstract: Starch is a main storage form of carbon for plants and is composed of glucose residues linked together by α-1,4 O-glycosidic linkages and branched through α-1,6 bounds [1]. The two polymers composing starch as amylose and amylopectin form water insoluble granules ranging from 1 to up to 100 µm in diameter depending of their botanical origin. Furthermore, a wide range of granule morphologies also exists regarding their origins (plant species, organs, tissues, cells) [2, 3]. In the present work, we developed a miniaturized method for determining amylopectin chain length distribution (CLD) by fluorescence-assisted capillary electrophoresis (FACE). The method relies on single granule entrapped with fused silica capillaries followed by starch gelatinization and debranching. Sample desalting on Hypersep^{TM} Hypercarb^{TM} tips following APTS-labelling and the use of nanovials allowed for the fluorescence analysis of undiluted samples.

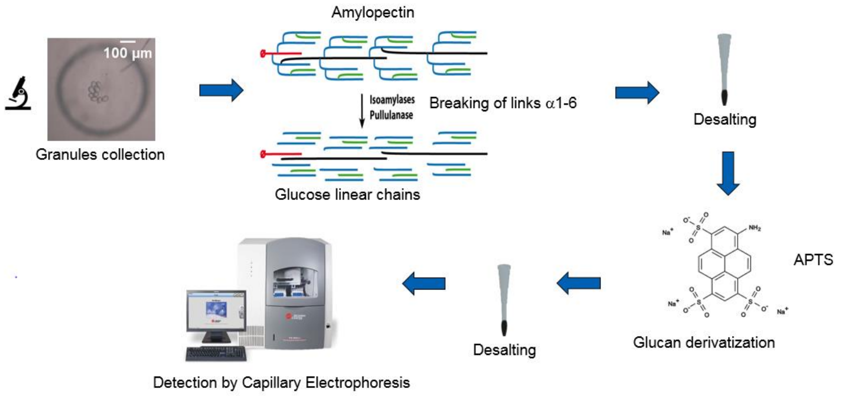


Figure 1 Methods for granules collection and glucans derivatization by APTS followed by Capillary Electrophoresis detection.

References:

1. Buleon A, Colonna P, Planchot V, Ball S. Starch granules: structure and biosynthesis. *Int. J. Biol. Macromol.* 1998;23(2), 85-112.

2. Verbeke J, Penverne C, D'Hulst C, Rolando C, Szydlowski N. *Carbohydr. Polym.,* **2016**, 152, 784-91.

3. Helle S, Bray F, Putaux J-L, Verbeke J, Flament S, Rolando C, et al. Intra-Sample Heterogeneity of Potato Starch Reveals Fluctuation of Starch-Binding Proteins According to Granule Morphology. *Plants*, **2019**, 8(9), 324.

CO-22

Stereoselective Preparation of CF_3-Containing Cyclopropanes and Nucleophilic Halogenation at Non-Classical Carbocation

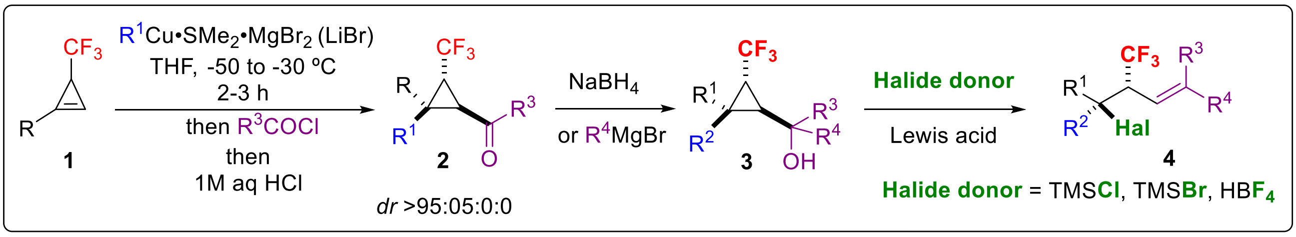
Veronika Myronova,[1] Dominique Cahard,[1] Ilan Marek[2]

[1] *UMR 6014 CNRS COBRA, Normandie Université, 76821 Mont Saint Aignan, France*
[2] *Mallat Family Laboratory of Organic Chemistry, Schulich Faculty of Chemistry and the Resnick Sustainability Center for Catalysis Technion - Israel Institute of Technology, Haifa 3200009, Israel*

veronika.myronova@univ-rouen.fr
https://www.lab-cobra.fr/cobra/

Keywords: Fluorine; Non-Classical Carbocation; Cyclopropanes; Halogenation; Stereoselectivity.

Abstract: The construction of molecules featuring adjacent stereocenters that include fluorinated motifs, is a challenging task in organic chemistry. To address this issue, we carried out copper-mediated carbometalations of CF_3-containing cyclopropenes **1** to afford highly substituted cyclopropanes **2** with excellent regio- and diastereoselectivity.[1] The carbometalation proceeds with anti diastereofacial preference towards the CF_3 group. The relative configuration was assigned by ^1H NMR and by single crystal X-ray diffraction.



We further demonstrated that CF_3-cyclopropyl carbinol derivatives **3** undergo regio- and diastereoselective nucleophilic substitution at the quaternary carbon center to provide acyclic products **4** as a single diastereomer.[2] The tertiary alkyl chlorides, bromides, and fluorides feature two adjacent stereocenters decorated with halogens and the trifluoromethyl motif. They are diastereomerically pure and can be obtained in just four catalytic steps from commercially available alkynes.

References:
1. Myronova, V.; Cahard, D.; Marek, I. Stereoselective Preparation of CF_3-Containing Cyclopropanes. *Org. Lett*. **2022**, *24*, 9076-9080.
2. Myronova, V.; Cahard, D.; Marek, I. Stereoselective Nucleophilic Halogenation at CF_3-Substituted Non-Classical Carbocation. *Org. Lett*. **2024**, *in press*.

CO-23

Elaboration of microstructured films based on metallic or semiconductor nanoparticles for light energy conversion.

ZERINI Hadjer Asmaa, MATHIEU Christian, HENNINOT Jean-François

Laboratory UCCS, Faculty des Sciences Jean Perrin, University Artois, Lens France

zerinihadjer@gmail.com

Keywords : gold nanoparticles, gelatin, Luminescent films, light energy conversion, fluorescence, ultrasound.

Abstract : The subject presented concerns the development of composite films based on gold nanoparticles (NPs) or quantum dots intended for energy conversion in the context of the development of new photovoltaic cells [1]. In this work, different concentrations of gold nanoparticles [2] were integrated into a gelatin matrix intended to stabilize them after structuring by ultrasound. These colloidal films are synthesized by the "doctor blade coating" method then characterized by different methods such as scanning electron microscopy to identify the morphology of the films and see the dispersion of these NPs in the gelatin. Another technique developed to characterize the Dispersion of NPs is based on the use of a fluorescence spectrometer in goniometric mode. An organic dye (eosine) is integrated into the gelatin films in addition to the gold nanoparticles. We use an optical fiber to locally excite the luminescence of this dye in the film and another to detect it. Knowing that nanometric gold amplifies the absorption of incident radiation by plasmon effect and consequently the fluorescence signal of the dye present near the gold, we are thus able to map the uniform distribution of the gold nanoparticles in the plane of the film. Secondly, we structured the gold NPs in a gelatin matrix using standing ultrasound waves, in collaboration with the IEMN laboratory (Valenciennes) [3]. This time, the spectrometric analysis makes it possible to confirm the structuring of the NPs into fine micrometer-sized cords within the gel. In the future, NPs will be replaced by quantum dots (ZnS/CdSe), which are of great interest for future photovoltaic cells [4].

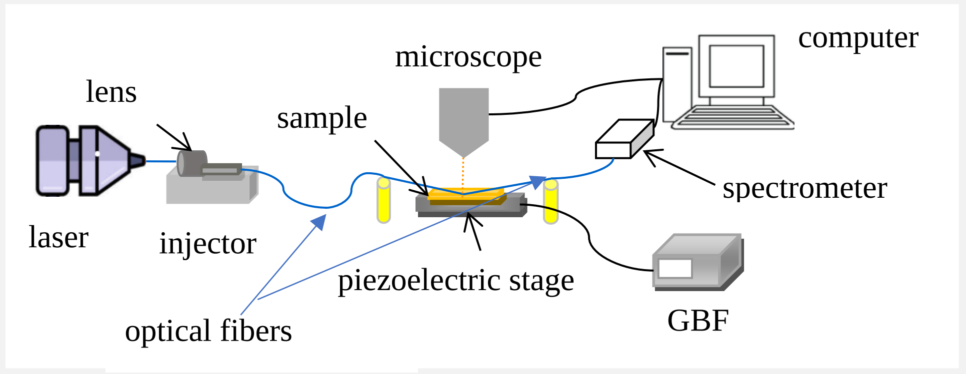


Figure 1 Schematic view of the measurement of fluorescence in goniometric mode.

References :

1. Na Zhou *et al*, Plasmon-enhanced light harvesting enhanced photocatalysis, photodynamic therapy and photovoltaics, RSC Adv., **2015**, 5, 29076. **2.** Jingfang Zhou *et al*, Functionalized gold nanoparticles: Synthesis, structure and colloid stability, Journal of Colloid and Interface Science 331 **2009** 251–262. **3.** Haim Sazan et al,Directed assembly of nanoparticles into continuous microstructures by standing surface acoustic waves, Journal of Colloid and Interface Science 536 **2019** 701–709. **4.** Sopit Phetsang *et al,* Investigation of a gold quantum dot plasmonic gold nanoparticle system for improvement of organic solar cells, Nanoscale Adv. **2019**, 1, 792.

CO-24

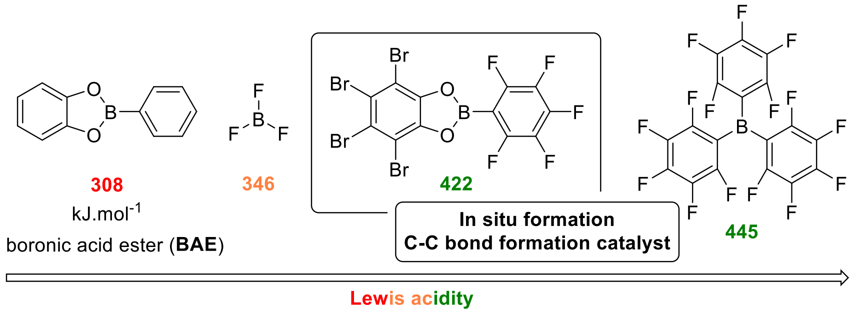
Revisiting the Lewis Acidity and Reactivity of Boronic Acid Esters.

Ava Bousselat, [1] Pr. Jacques Rouden [1] and Dr. Jérôme Blanchet [1]*

[1]Calvados, Laboratoire de chimie moléculaire et thioorganique (LCMT), Caen, France
ava.bousselat@ensicaen.fr ; https://www.lcmt.ensicaen.fr/

Keywords: Lewis acidity; Catalyse; Organic Chemistry; Boronic acid ester.

Abstract: Lewis acids, essential elements in the realm of organic chemistry, exhibit a spectrum of applications spanning pharmaceuticals, agrochemicals, and materials science. Particularly within the domain of main-group chemistry, Lewis acids present alternatives to transition metals, thereby driving this exploration into halogenated boronic acid esters (BAEs). Despite the well-known role of BAEs as fundamental building blocks, their catalytic capabilities have remained underexamined. Through an investigation into their Lewis acidity, our results uncovered strengths comparable to recognized boron trifluoride and tris(pentafluorophenyl)borane. Additionally, we delved into the catalytic efficacy of BAEs in the Hosomi-Sakurai allylation of aldehydes, revealing superior performance when compared to boron trifluoride. This research lays the groundwork for further advancements in this fields.[1]



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[1] Bousselat, A.; Rouden, J.; Blanchet, J.; *J. Org. Chem.* **2024**, Soumise.

CO-25

The Impact of titanium dioxide and copper additives on bentonite for degradation of organic contaminant

Abdulrahman Al-Ameri ,[12] Zohra Bouberka, [12] Touaa, Nesrine Dalila, [12] Kahina Bentaleb, [12] Zohra Taibi , [12] Ulrich MASCHKE[2]

[1]Laboratoire Physico-Chimie des Matériaux-Catalyse et Environnement (LPCMCE), Université des Sciences et de la Technologie d'Oran Mohamed Boudiaf (USTOMB), BP 1505, El M'naouer, Oran 31000, Algeria.
[2]Department, Institution, Unité Matériaux et Transformations (UMET), UMR 8207, Univ. Lille, CNRS, INRAE, Centrale Lille, F-59000 Lille, France.
ulrich.maschke@univ-lille.fr

Keywords: Photocatalysis; sol-gel method; Nanoparticles;

Abstract: This work presents the preparation and characterization of Ti-Cu-bentonite, where the supported Ti-Cu nanoparticles were generated using a sol-gel method (Figure 1), and subsequently, mixed with a suspension of Bentonite for eliminate and degrade the contaminates organics, A powder X-ray (fluorescence, diffractogram) of (Bentonite, TB (Tio2-Bentonite), TCB (Tio2-Cu-Bentonite)) revealed the quantity and dispersion of TiO2 particles from the anatase and rutile phases, as well as Ti-Cu on the surface of the Bentonite, and Zeta potential measurements show that the interactions between Orange G and the different materials are complex and are strongly influenced by pH and that the addition of and Cu to the composites seems to modulate the effect of pH on the charge of surface, which have a significant impact on the adsorption capacity of the dye, And on the other hand, a weight loss (10%) was observed over the temperature range between 70 and 600 °C where the TGA results clearly indicate that the sample is thermally stable up to 800 °C. No weight loss was observed after 600 °C for TC and TCB and after 700 °C for Bentonite, due to the high thermal stability of the composites. The tests show the capacity of the prepared TCB to eliminate organic pollutants and degrade them. At pH = 3, it was able to adsorb the highest possible amount of Orange-G and showed a high ability to degrade pollutants using a UV-visible lighting source. "LC8" (Figure 2) up to 100%, It has also been shown that it purifies organic pollutants present on its surface, which means that it renews itself and can be reused directly more than once.

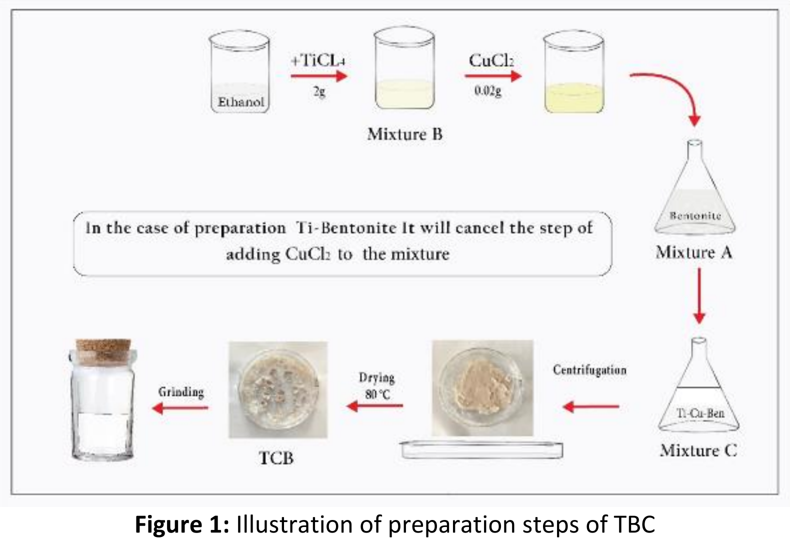


Figure 1: Illustration of preparation steps of TBC

CO-26

Synthesis of Pyrano[2,3-c]pyrroles from vKAMAs

Mariia Savchuk,[1] Giang Vo-Thanh,[2] Sylvain Oudeyer,[1] Hélène Beucher[1] and Jean-François Brière[1]

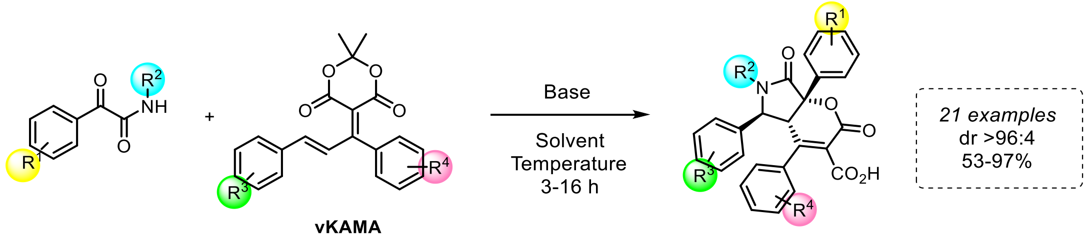
[1]INSA Rouen Normandie, Univ Rouen Normandie, CNRS, Normandie Univ, COBRA UMR 6014, INC3M FR 3038, F-76000 Rouen, France.
[2]Institut de Chimie Moléculaire et des Matériaux d'Orsay. CNRS UMR 8182, Université Paris Saclay, 91405 Orsay Cedex, France.

mariia.savchuk@univ-rouen.fr; https://www.lab-cobra.fr/equipes/heterocycles/

Keywords: Organic synthesis; Alkylidene Meldrum's acids (AMAs); Catalysis; Aza-Michael addition; Domino process; Vinylogy; Diastereoselectivity; Stereoselectivity; Cyclization

Abstract: Pyrrolidine is one of the most common heterocycle in organic synthesis and pharmaceuticals (more than 37 medicaments known).[1] Bicyclic pyrrolidines such as pyrano[2,3-c] pyrrole derivatives are valuable molecules, because of their conformational restriction may be useful for better bio-target interections (Scheme below).[2] On the other hand, vinylogous ketone-derived alkylidene Meldrum's acids (vKAMA) proved to be versatile platform molecules involved in the various 1,6-conjugate additions involving C-C bond formation, and were recently applied in the thio-Michael addition reaction by our group to obtain thiochromanes.[3] Thus, we decided to challenge the aza-Vinylogue-Michael-Aldol-Cyclocondensation (aza-VMAC) reaction with α-ketamides as readily available substrates to lead to an unprecedented C-N bond formation with this type of substrate.

To our delight, the vKAMAs showed an excellent performance in the aza-VMAC reaction affording a new entry to pyrano[2,3-c]pyrrole derivatives, encompassing the relative control of three contiguous stereocenters in an excellent diastereoselectivity and good to excellent yields (21 examples, 53-97% isolated yields, >96:4 dr).[4]



Domino aza-VMAC reaction with vKAMAs

References:

1. Taylor, R.D.; MacCoss, M.; Lawson, D.J. *J. Med. Chem.* **2014**, 5845–5859.
2. Savych, A.; Mykhalchuk, V.; Melnychuk, P.; Isakov, A.; Savchuk, T.; Timoshenko, V.; Siry, S.; Pavlenko, S.; Kovalenko, D.; Hryshchuk, O.; Reznik, V.; Chalyk, B.; Yarmolchuk, V.; Rusanov, E.; Mykhailiuk, P. *J. Org. Chem.* **2021**, 13289–13309.
3. Milbeo, P.; Lebrêne, A.; Savchuk, M.; Vo-Thanh, G.; Oudeyer, S.; Beucher, H.; Brière, J.-F. *Chem. Eur. J.* **2023**, 29, e202301311.
4. Savchuk, M.; Vo-Thanh, G.; Oudeyer, S.; Beucher, H.; Brière, J.-F. *Org. Biomol. Chem.* **2024**, 2948-2952.

CO-27

CO_2 - Selective Membranes Blends and Copolymers

Patricia Ynes BATISTA PEGUERO[1], Fabrice BUREL[1], Laurent LEBRUN[2]

[1] *Polymers Biopolymers Surfaces Laboratory (PBS-UMR 6270), INSA de Rouen, Saint-Étienne-du-Rouvray, France*
[2] *Polymers Biopolymers Surfaces Laboratory (PBS-UMR 6270), University of Rouen, Mont-Saint-Agnan, France*

patricia.batista@insa-rouen.fr

Keywords: CO_2, membrane, reformable.

Abstract: Today's global energy demand and industrialization require large quantities of fossil fuels, resulting in huge CO_2 emissions into the atmosphere from power plants[1]. Currently, anthropogenic CO_2 is considered to be the main cause, and there is a strong demand for CO_2 capture technologies[2] to reduce its concentration in the atmosphere.

The synthesis of polymers from renewable resources is also driven by the need to reduce our dependence on petroleum-derived products and to develop sustainable materials technologies. Among renewable resources, hydroxybenzaldehyde, is an aromatic molecule that can be found in nature and can also be produced on a large scale from waste. It can be used as an aroma, but can also be involved in the development of reformable materials.

In this context, the COSMOS project aims to develop new reversible thermosets materials containing polyamines and hydroxybenzaldehyde derivatives, characterize them and evaluate their membrane properties in terms of permeability and selectivity to gases (N_2, CO_2).

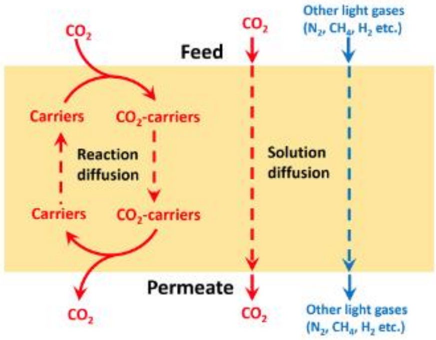


Figure 1 Gas permeation through selective CO_2 transport membranes[3].

References:

(1) Vinoba, M.; Bhagiyalakshmi, M.; Alqaheem, Y.; Alomair, A. A.; Pérez, A.; Rana, M. S. Recent Progress of Fillers in Mixed Matrix Membranes for CO_2 Separation: A Review. Separation and Purification Technology. Elsevier B.V. 2017, pp 431–450. https://doi.org/10.1016/j.seppur.2017.07.051.

(2) Kárászová, M.; Zach, B.; Petrusová, Z.; Červenka, V.; Bobák, M.; Šyc, M.; Izák, P. Post-Combustion Carbon Capture by Membrane Separation, Review. Separation and Purification Technology. Elsevier B.V. May 1, 2020. https://doi.org/10.1016/j.seppur.2019.116448.

(3) Xie, K.; Fu, Q.; Qiao, G. G.; Webley, P. A. Recent Progress on Fabrication Methods of Polymeric Thin Film Gas Separation Membranes for CO_2 Capture. Journal of Membrane Science. Elsevier B.V. February 15, 2019, pp 38–60. https://doi.org/10.1016/j.memsci.2018.10.049.

CO-28

Non-animal encapsulation of α-tocopherol by complex coacervation: interactions with cosmetic systems

Adeline Delaporte[1], Michel Grisel, Ecaterina Gore

[1]*Université Le Havre Normandie, URCOM UR 3221, F-76600 Le Havre, France*
adeline.delaporte@doct.univ-lehavre.com ; https://urcom.univ-lehavre.fr/

Keywords: Complex coacervation; Tocopherol; Bio-based polymers, skin-care formulation; fungal chitosan; gum arabic

Abstract: Natural topical delivery systems (creams, emulsions, gels) often contain biologically active molecules such as antioxidants. α-tocopherol is a hydrophobic vitamin (Vitamin E) extensively used as an anti-age and antioxidant agent in cosmetic formulations. However, its use is often limited due to its low stability[1]. Complex coacervation, a method involving the self-assembly of oppositely charged polymers through electrostatic interactions, holds promise for encapsulating α-tocopherol. This technique enables high loading capacities and high encapsulation efficiencies; making it an excellent approach to enhance the oxidative stability and controlled release of biologically active ingredients [2]. The present work introduces a cross-sectional study to explore 1) the encapsulation of α-tocopherol using fungal chitosan (FC), a cationic polysaccharide derived from fungal sources, combined with gum arabic (GA) by complex coacervation and 2) the interactions of these new delivery systems containing encapsulated Vit. E with oil-in-water emulsions and their impact on macroscopic properties such as texture.

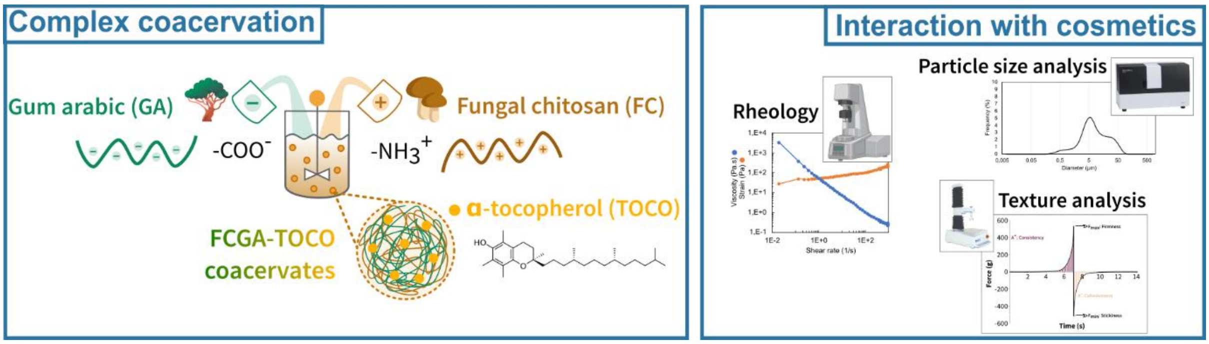


Figure 1 Schematic representation of the methods of complex coacervation and the characterizations of their interactions with cosmetics.

References:

(1) Silva, S.; Ferreira, M.; Oliveira, A. S.; Magalhães, C.; Sousa, M. E.; Pinto, M.; Sousa Lobo, J. M.; Almeida, I. F. Evolution of the Use of Antioxidants in Anti-Ageing Cosmetics: Antioxidants in Anti-Ageing Cosmetics. *Int J Cosmet Sci* **2019**, *41* (4), 378–386. https://doi.org/10.1111/ics.12551.

(2) Timilsena, Y. P.; Akanbi, T. O.; Khalid, N.; Adhikari, B.; Barrow, C. J. Complex Coacervation: Principles, Mechanisms and Applications in Microencapsulation. *Int. J. Biol. Macromol.* **2019**, *121*, 1276–1286. https://doi.org/10.1016/j.ijbiomac.2018.10.144.

CO-29

Elaboration of nanostructured surfaces by deposition of polymeric Janus Nanorods

Bochra SEAALI,[1] Marylène VAYER,[2] Christophe SINTUREL.[3]

Interfaces, Confinement, Materials and Nanostructures (ICMN, UMR 7374 CNRS- Université d'Orléans)
[1]bochra.seaali@cnrs-orleans.fr, [2]marylene.vayer@cnrs-orleans.fr, [3]christophe.sinturel@univ-orleans.fr.

Keywords: Polymer thin film, nanostructured surfaces, polymer self-assembly, Janus nanorods

Abstract: nowadays, producing well-ordered periodic nanoscale patterned surfaces at the sub-10 nm level with low density of defects and sharp interfaces still remains a great challenge. In this context, polymeric Janus nanorods (JNRs) which are asymmetrical nanoparticles that exhibits two faces of different chemistries, are considered as a promising candidate to achieve this purpose, but their potential remains very little explored.
Recently, our academic partners* have developed a robust and versatile strategy to self-assemble end-functionalized polymers into JNRs that are several hundreds of nanometers long(up to µm-range) with an average diameter ca. 10 nm[1]. By the deposition of such developed anisotropic objects on a solid substrate using different deposition techniques (i.e., Drop-casting, Spin-coating, Dip-coating), we have indeed proved that these JNRs has the ability to self-organize and form a highly anisotropic patterns on the substrate with a periodic distance of 12 nm (using AFM measurements in Peak-Force Quantitative Nanomechanical Mapping mode, see Figure.1). However, forming a 2D aligned surfaces relevant to advanced lithography applications requires a high level of control over the deposition as well as the orientation of these nanocylinders. For this reason, Langmuir-Blodgett deposition technique wasalso employed to guide their self-assembly into highly oriented nanopatterned monolayer.
The results concerning the deposition of JNRs on silicon substrate using several techniques including Langmuir-Blodgett deposition as a function of the deposition parameters and the experimental conditions that govern their orientation processes will be presented.

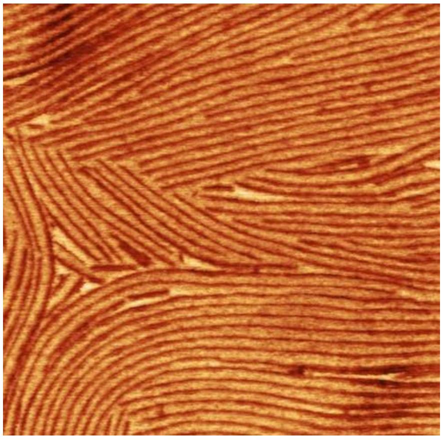


Figure 1 Adhesion AFM image of JNRs with poly(dimethylacrylamide) (PDMAc, DPn = 83) on one side and Poly(N-acrylolmorphine) (PNAM, DPn = 48) on the other side. Measurement carried out on a droplet of a JNRs colloidal suspension after evaporation.

References:
1. Han, S.; Pensec, S.; Yilmaz, D.; Lorthioir, C.; Jestin, J.; Guigner, J.-M.; Niepceron, F.; Rieger, J.; Stoffelbach, F.; Nicol, E.; Colombani, O.; Bouteiller. Nature Commun. 2020, 11, 4760.

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* This PhD project is a part of the ANR-JASUR research project. Collaboration between IPCM (Sorbonne University) for macromolecular synthesis of JNRs, IMMM (Le Mans University) for the supramolecular self-assembly in solution, and ICMN (Orleans University) for surface deposition as thin films and physical characterizations of the patterns.

CO-30

Decontamination of plastic waste by supercritical fluids and UV-visible light

Wala Zoghlami[1,2], Isaline Lhoste,[2] Klaudia Wilk,[2] Karine Seaudeau-Pirouley,[2] Philippe Supiot[1], Ulrich Maschke[1]

Unité Matériaux et Transformations (UMET), Université de Lille, Cité scientifique, 59655 Villeneuve d'Ascq, France

Innovation Fluides Supercritiques (IFS), 26000 Valence, France

wala.zoghlami.etu@univ-lille.fr ulrich.maschke@univ-lille.fr

Keywords: Decontamination; Polymers; recycling; Supercritical fluids; UV-VISIBLE irradiation; WEEE.

Abstract: This project concerns the management of plastic waste, with a specific focus on polymers containing brominated flame retardants (BFRs). The recycling of plastic waste from electrical and electronic equipment containing BFRs presents a number of challenges, the most significant of which is the recent introduction of regulations pertaining to the environmental toxicity and bioaccumulation of these substances.

The objective of this project is to develop a sustainable process for the decontamination of these plastics, thereby enabling their reintegration and reuse in the recycling process. The proposed process combines two methods that have proven highly effective for decontaminating plastics on a laboratory or even pilot scale: supercritical fluid treatment using supercritical carbon dioxide (sc-CO2) and UV-irradiation. The supercritical carbon dioxide (sc-CO_2) solvent is non-toxic and exhibits intermediate properties between liquids and gases, conferring it high diffusivity and solubility (Figure 1) [1]. The irradiation experiments were conducted at room temperature using a light source under vacuum conditions in a vacuum seal developed at UMET. The study will involve the application of the aforementioned techniques to the model systems, with subsequent characterization of the resulting effects through comparison of the properties of the initial and treated samples. A variety of analytical techniques will be employed to assess the polymer's evolution and the presence of contaminants in parallel.

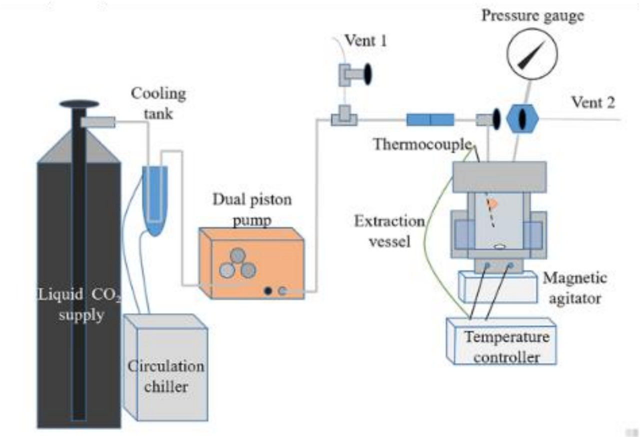


Figure 1: Schematic illustration of the experimental Sc CO_2 extraction system [1].

Reference:

1. Xia, D., et al. "On-line spectroscopic study of brominated flame retardant extraction in supercritical CO2." Chemosphere, vol. 263, 2021, 128282. ISSN 0045-6535. https://doi.org/10.1016/j.chemosphere.2020.128282

CO-31

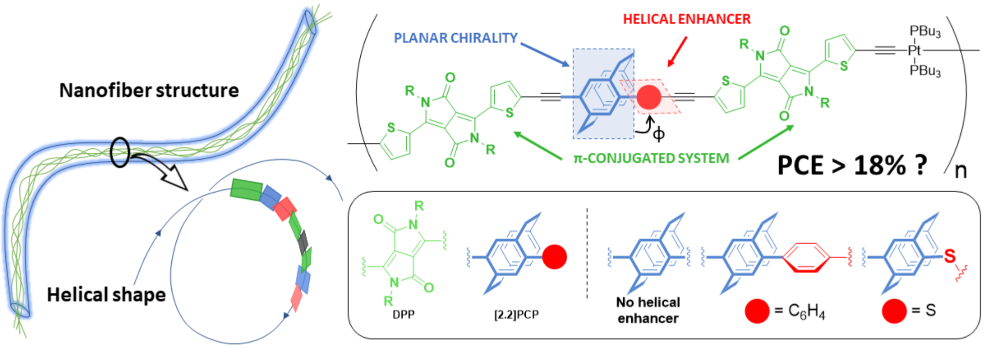
[2.2]Paracyclophane-based Stereoregular [Pt] Conjugated Oligomers for Solar Cells Applications

Arthur LE COZ,[1] Pierre D. HARVEY,[2] Ganesh D. SHARMA,[3] Cyprien LEMOUCHI,[1] Stéphane PERRIO[1]

[1] Normandie Univ, ENSICAEN, UNICAEN, CNRS, LCMT, 14000 Caen, France
[2]Département de Chimie, Université de Sherbrooke, 2550 Boulevard de l'Université, Sherbrooke, Quebec, Canada
[3]Department of Physics, The LNM Institute of Information Technology, Jamdoli, Jaipur, Rajasthan 302031, India
arthur.le-coz@ensicaen.fr

Keywords: [2.2]paracyclophane; [Pt]-oligomers; planar chirality; helicity; solar cells

Abstract: Organic solar cells offer a number of advantages light weight and a good flexibility. However, their power conversion efficiencies (PCE) are still well below those of silicon-based cells (PCE 25-26%).[1] Platinum oligomers are suitable donors, mixed with an acceptor, a PCE off 15% have been achieved, close to international record of 19.2% reached with conjugated polymers.[2] Their performance can be improved (objective, PCE > 18%) by preparing fiber-shaped stereoregular [Pt]-oligomers to promote charge transport and nanosegregation of the active layer. By now, none fiber have been obtained with [Pt]-oligomers, the aim of our work is to promote their formation with the insertion of a planar chiral [2.2]paracyclophane ([2.2]PCP) platform[3] in diketopyrrolopyrrole (DPP) containing conjugated ligand. The use of enantiomerically pure [2.2]PCP should produce the first stereoregular [Pt]-oligomers, while the insertion of a helical enhancer should increase the dihedral angle (ϕ) and promote helicoidal structure for the preparation of the fibers. Initial results, including the synthesis aspects and first target characterizations, will be presented in this communication.



References:

1. Yoshikawa, K.; Kawasaki, H.; Yoshida, W.; Irie, T.; Konishi, K.; Nakano, K.; Uto, T.; Adachi, D.; Kanematsu, M.; Uzu, H.; Yamamoto, K. *Nature Energy* **2017**, *2*, 17032.
2. Qassab, M.; Lohier, J.-F.; Marineau-Plante, G.; Wayzani, A. A.; Herbinet, R.; Durandetti, M.; Hardouin, J.; Karsenti, P.-L.; Pluart, L. L.; Harvey, P. D.; Lemouchi, C.; Sharma, G. D. *ACS Appl. Energy Mater.* **2023**, *6*, 12452–12467.
3. Lohier, J.-F.; Foucoin, F.; Jaffrès, P.-A.; Garcia, J. I.; Sopková–de Oliveira Santos, J.; Perrio, S.; Metzner, P. *Org. Lett.* **2008**, *10*, 1271–1274.

CO-32

Pulsed laser deposition of $Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O_3$ thin films on polycrystalline Al_2O_3 substrates for energy harvesting

Guillaume Demily[1], Donovan Ledru[1], Moustapha Azankoud[1], Renaud Valois[1], Mégane Lheureux[1], Antonio Da Costa[1], Anthony Ferri[1], Denis Remiens[2], Freddy Ponchel[2], Rachel Desfeux[1] and Marie-Hélène Chambrier[1]

[1]Univ. Artois, CNRS, Univ. Lille, UMR 8181 - UCCS – Unité de Catalyse et Chimie du Solide, F-62300, France
[2]Univ. Polytechnique Hauts-de-France (UPHF), CNRS, UMR 8520, Institut d'Electronique, de Microélectronique et de Nanotechnologie (IEMN), Site de Valenciennes, F-59300, Valenciennes, France

guillaume_demily@ens.univ-artois.fr, mhelene.chambrier@univ-artois.fr, http://www.uccs.univ-artois.fr/accueil.htm

Keywords: Thin film; $Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O_3$; Pulsed laser deposition; X-Ray Diffraction; Piezoelectric properties; Energy harvesting

Abstract: Piezoelectric ceramics and films are essential components in many sectors including medical, automotive, civil, and military industries. These functional materials are used in sensors, transducers, generators and other applications. One of the most commonly used piezoelectric compounds is $PbZr_{1-x}Ti_xO_3$ (PZT). In recent years, the focus has shifted towards eco-responsible, lead-free materials[1] due to environmental concerns and regulations governing electrical and electronic equipment[2,3]. A notable example is $Ba_{1-x}Ca_xTi_{1-y}Zr_yO_3$ (BCTZ), an oxide with promising piezoelectric properties. In this work, BCTZ targets were synthesized by solid-solid route involving carbonate and oxide precursors, then deposited on $SrTiO_3$ single-crystal substrates by pulsed laser deposition (PLD). Using this kind of substrate, the deposition parameters were optimized to obtain high-quality heteroepitaxial films. Next, BCTZ thin films were grown onto Al_2O_3 polycrystalline substrates (with or without a metallic $LaNiO_3$ bottom electrode) to measure the material's piezoelectric performances. Recently, a BCTZ film was deposited onto a Al_2O_3 beam equipped with interdigitated Pt electrodes for energy harvesting studies. In this presentation, structural and electrical results obtained through various complementary techniques such as X-ray diffraction, scanning electron microscopy and piezoelectric force microscopy will be addressed and discussed.

This work, supported by the Hauts-de-France Region (France), is part of a project titled "Optimization of Piezoelectric Properties in eco-responsible functional oxides for ENergy harvesting (OPPEN)".

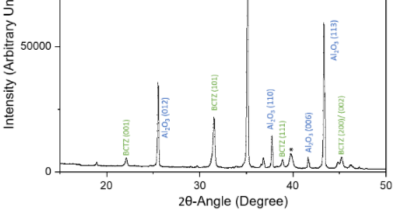


Figure 1 X-Ray Diffraction pattern of a BCTZ thin film grown on an alumina beam. Both film and substrate peaks are found; a peak due to the use of silver paint during PLD is also noted.

References:

1. W. Liu and X. Ren, Phys. Rev. Lett. 103, 257602 (2009). https://journals.aps.org/prl/abstract/10.1103/PhysRevLett.103.257602

2. Restriction of Hazardous Substances in Electrical and Electronic Equipment (RoHS). https://environment.ec.europa.eu/topics/waste-and-recycling/rohs-directive_en (accessed May 02, 2024)

3. Waste from Electrical and Electronic Equipment (WEEE). https://environment.ec.europa.eu/topics/waste-and-recycling/waste-electrical-and-electronic-equipment-weee_en (accessed May 02, 2024)

CO-33

Synthesis of α-chloroarylacetic acid *via* electrochemical carboxylation of α,α-dichloroarylmethane derivatives

Corentin Maret,[1] Nicolas David,[1] David Pierrot,[1] Eric Léonel,[2] Vincent Levacher,[1] Jean-François Brière,[1] Sylvain Oudeyer[1]
[1]COBRA laboratory, Normandie Univ, UNIROUEN, INSA Rouen, CNRS, 76000 Rouen, France
[2]Electrosynthèse, Catalyse et Chimie Organique Université Paris-Est Créteil, CNRS, ICMPE, UMR 7182 2 rue Henri Dunant, 94320 Thiais, France
sylvain.oudeyer@univ-rouen.fr

Keywords: Electrochemistry; carboxylation; electrocarboxylation

Abstract: α-chlorophenylacetic acids **1** are versatile synthetic intermediates involved in the synthesis of several drugs.[2] Therefore, several methods were reported to synthesize α-chlorophenylacetic acids including chemical (mainly oxidation of α-chloroaryl acetaldehydes[3] or chlorination of α-hydroxyarylacetic acid[4]) or electrochemical approaches but none of them proved to be general. As far as electrochemical approaches are concerned, the electrocarboxylation reaction of α-chloroaryl derivatives have been extensively studied.[5] On the other hand, electrocarboxylation of α,α-dichloro species remains elusive.[6] To the best of our knowledge, only one example has been described (R^1 = H, Ar = Ph) with low yield and selectivity (Cl *vs* H).

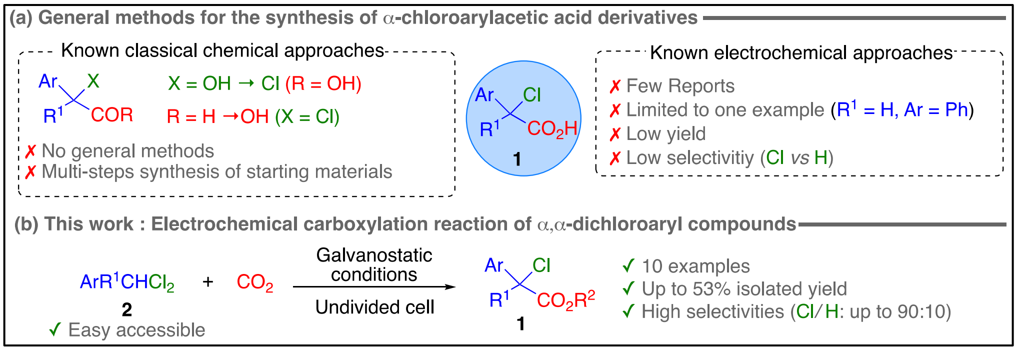


Figure 2 General approach and our approach towards chloroaryl compounds

We would like to report herein our contribution to the electrocarboxylation reaction of α,α-dichloroarylmethane **2** derivatives in order to provide an efficient and selective synthesis of chloroarylacetic acid derivatives **1** (Scheme b).[7]

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[2] For examples, see: (a) Frank, R.; Bahrenberg, G.; Christoph, T.; Schiene, K.; DeVry, J.; Damann, N.; Frormann, S.; Lesch, B.; Lee, J.; Kim, Y.-S. and Kim, M.-S. (2010) PCT International Application WO2010/127856. (a) Murakami, K.; Ohashi, M.; Matsunaga, A.; Yamamoto, I.;Nohira, H. *Chirality* **1993**, *5*, 41–48.

[3] For an example, see: Paraskevas, S. M.;Paraskevas, M. S. *Catal. Commun.* **2004**, *5*, 687–690.

[4] For an example, see: Carnell, A. J.; Kirk, R.; Smith, M.; McKenna, S.; Lian, L. Y.;Gibson, R. *ChemMedChem* **2013**, *8*, 1643–1647.

[5] For examples, see: Murtaza, A.; Qamar, M. A.; Saleem, K.; Hardwick, T.; Zia Ul, H.; Shirinfar, B.;Ahmed, N. *Chem Rec* **2022**, *22*, e202100296 and references therein.

[6] (a) Silvestri, G.; Gambino, S.; Filardo, G.; Greco, G.;Gulotta, A. *Tetrahedron Lett.* **1984**, *25*, 4307–4308. (b) Silvestri, G.; Gambino, S.; Filardo, G.; Tiitta, M.; Sjöström, M.; Wold, S.; Berglind, R.;Karlsson, B. *Acta Chem. Scand.* **1991**, *45*, 987–992.

[7] C. Maret, N. David, D. Pierrot, E. Léonel, V. Levacher, J.-F. Brière, S. Oudeyer, *Molecules* **2023**, *28*, 6704

CO-34

Terminal Alkyne Carboxylation via Mechanocatalysis under Reactive CO_2 Atmosphere

Sawssen Nasri, Anne Ponchel, and Stéphane Menuel

Univ. Artois, CNRS, Centrale Lille, Univ. Lille, UMR 8181, Unité de Catalyse et Chimie du Solide (UCCS)
rue Jean Souvraz, SP 18, 62300 Lens, France

sawssen.nasri@univ-artois.fr

Keywords: mechanochemistry, catalysis, carboxylation

Abstract: In the context of reducing the energy and environmental impact of organic chemistry processes, mechanochemistry emerges as a promising alternative[1]. Mechanochemistry involves the use of mechanical energy to activate a chemical reaction. Energy is supplied by moving beads (vibratory mills or planetary mills). Furthermore, mechanochemistry enables solvent-free reactions with significant reductions in reaction times[2].

The carboxylation of unsaturated compounds via mechano-catalysis under a reactive CO_2 atmosphere holds significant promise for the valorization of synthons and the synthesis of high-value carbonyl compounds[3]. Additionally, the direct carboxylation of aromatic compounds aligns with the approach of CO_2 valorization by utilizing it as a carbon source through the development of eco-friendly technologies. (Figure 1)

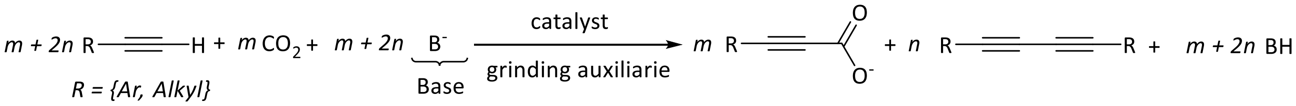


Figure 1 *carboxylation and carbon-carbon coupling are competing reactions in this study*

We will present the results obtained using phenylacetylene as a model substrate. We will demonstrate the significance of grinding auxiliaries on the obtained results. We will discuss the mechanical influence of grinding auxiliaries, particularly auxiliaries on the catalyst reactivity as well as the selectivity of the obtained products. Additionally, we will present the impact of grinding on the abrasion phenomena of reactors and beads.

References:

1. S. L. James, C. J. Adams, C. Bolm, D. Braga, P. Collier, T. Friščić, F. Grepioni, K. D. M. Harris, G. Hyett, W. Jones, A. Krebs, J. Mack, L. Maini, A. G. Orpen, I. P. Parkin, W. C. Shearouse, J. W. Steed, D. C. Waddell, *Chem. Soc. Rev.* **2012**, *41*, 413–447. DOI: 10.1039/C1CS15171A.
2. S. Menuel, B. Doumert, S. Saitzek, A. Ponchel, L. Delevoye, E. Monflier, F. Hapiot, *J. Org. Chem.* **2015**, *80*, 6259–6266. DOI: 10.1021/acs.joc.5b00697.
3. I I. C. Tommasi, *Catalysts* **2019**, *9*, DOI 10.3390/catal9010037. DOI: 10.3390/catal9010037

CO-35

Combine stable isotopes, carbon-14 dating and paleoproteomics in a single sample preparation protocol

Louis Delegue[1,*], Delphine Decruyenaere[2], Christian Rolando[1], Fabrice Bray[1]

[1]*Minitaturisation pour la Synthèse l'Analyse et la Protéomique (MSAP, UAR 3290 CNRS), Université de Lille, Villeneuve d'Ascq, France*
[2]*UMR 7209 AASPE, Archéozoologie et Archéobotanique - Sociétés, Pratiques et Environnements, 75005, Paris, France*
*Presenting author: louis.delegue.etu@univ-lille.fr & https://msap-lab.fr/

Keywords: Paleoproteomics, archaeology, High resolution mass spectrometry

Abstract: A wealth of information is contained in archaeological teeth and bones. It is possible to obtain information on the age of samples with carbon-14 dating or amino acid racemization, animal diet with stable isotope analysis and taxon and proteome identification with paleoproteomics. Currently, there is no single preparation method for all these techniques. Unfortunately, it is not always possible to take several samples from bones or teeth, due to their rarity. In this study, we demonstrate for the first time that it is possible to combine these different analyses using a single bone collagen extraction protocol. Based on a collagen extraction method used for isotopic analysis developed at MNHN, paleoproteomic and amino acid racemization analyses were integrated. Paleoproteomic analysis enabled taxa to be identified from supernatants from the demineralization and decontamination stages of the samples, using ZooMS analysis on the MALDI FTICR. Amino acid racemization was performed on freeze-dried collagen after acid hydrolysis and derivatization with Marfey's reagent. Analysis was performed using nanoLC-MSMS orbitrap.

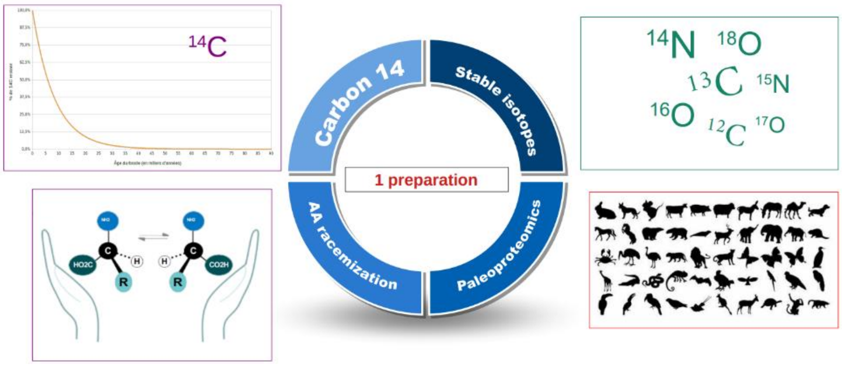


Figure 1 Diagram of the study, proposing the combination of 4 different analyses based on an archaeological sample preparation. The 4 methods are carbon-14 dating, stable isotopes, paleoproteomics and amino acid racemization.

References:

1. Cersoy, S., Zirah, S., Marie, A., & Zazzo, A. Toward a versatile protocol for radiocarbon and proteomics analysis of ancient collagen. *J. Archaeol. Sci.*, **2019**, 101, 1-10.

2. Bray, F., Fabrizi, I., Flament, S., Locht, J. L., Antoine, P., Auguste, P., & Rolando, C. Robust High-Throughput Proteomics Identification and Deamidation Quantitation of Extinct Species up to Pleistocene with Ultrahigh-Resolution MALDI-FTICR Mass Spectrometry. *Anal. Chem.*, **2023**, 95(19), 7422-7432.

Exploring extraction methods for a complete metabolomic and proteomic analysis of potato tubers using high resolution mass spectrometry

Pierre Otuszewski[1,2,*], Nicolas Szydlowski[2], Fabrice Bray[1]

[1]*Minitaturisation pour la Synthèse l'Analyse et la Protéomique (MSAP, UAR 3290 CNRS), Université de Lille, Villeneuve d'Ascq, France*
[2]*Unité de Glycobiologie Structurale et Fonctionnelle (UGSF, UMR 8576 CNRS), Université de Lille, Villeneuve D'Ascq, France*
*Presenting author: pierre.otuszewski.etu@univ-lille.fr, https://msap-lab.fr/, https://ugsf.univ-lille.fr/

Keywords: Extraction methods, Proteomic, Metabolomic, FT-ICR, Orbitrap, Mass spectrometry

Abstract: Metabolomics allows identification of a wide range of metabolites. Exploring the diversity of these molecules requires a methodological workflow that can comprehensively extract, detect, and identify them. Proteome analysis is often needed for a complete understanding of a biological system. This study explores three extraction methods capable of providing the best extraction of metabolites and proteins in a plant system. Each of these techniques was tested on lyophilized potato tuber powder, with the aim of understanding the behaviour of several potato cultivars when exposed to cold storage. Due to sample complexity, direct injection on FTICR mass spectrometers and LC-MS/MS were used for metabolomics and proteomics analyses, respectively. Three extraction methods were used for this study: MTBE extraction, chloroform extraction and methanol extraction. Two milligrams of potato tuber powder were used for each extraction method. eFASP[1] protocol was used to prepare peptides from complete proteins before proteomic analyses.

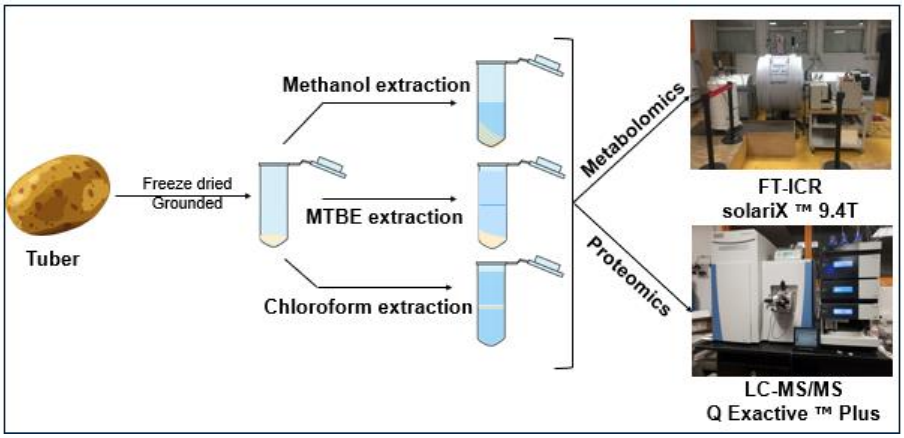


Figure 1: **Pipeline for a simultaneous proteomic and metabolomic analyses.** The freeze-drying process took place in a freeze-dryer. Grounding was done manually using a mortar and a pestle.

References:

1 Erde, J.; Loo, R. R. O.; Loo, J. A. Enhanced FASP (eFASP) to Increase Proteome Coverage and Sample Recovery for Quantitative Proteomic Experiments. *J. Proteome Res.* **2014**, *13* (4), 1885–1895.

CO-37

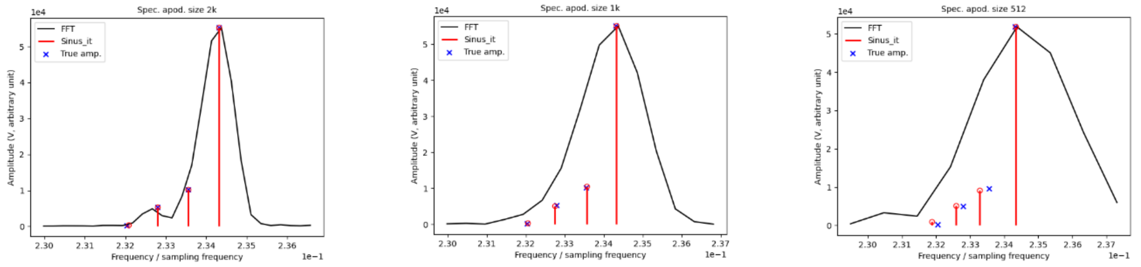
Super-Resolution for Fourier Transform Spectroscopies by Differential Evolution (DE) Algorithm

Azad Kicibayov[1,2*], Marc Haegelin[1], Pierre Collet[3], Ulviyya Abdulkarimova[2], Christian Rolando[1]

[1]*UAR CNRS 3290 MSAP, University of Lille, 59650 Villeneuve d'Ascq, France*
[2]*Data Science & Artificial intelligence, French-Azerbaijani University, Baku, Azerbaijan*
[3]*Instituto Tecnológico para la Innovación en Salud y Bienestar, Universidad Andrés Bello, Valparaiso, Chile*
*Presenting author: a.kichibayov@ufaz.az & https://msap-lab.fr/

Keywords: Fourier Transform (FT) spectroscopies; super-resolution; differential evolution algorithm.

Abstract: The raw signal from any Fourier Transform (FT) spectroscopy is constituted by sum of damped sine in the time domain called transient. From this transient a spectrum in the frequency domain is obtained by a Discrete Fourier Transform (DFT). The frequency domain spectrum is then transformed in the desired scale for example ppm in NMR or *m/z* in mass spectrometry. DFT has a major limitation: The peak width in the spectrum is proportional to the transient duration in the time domain. Obtaining peaks in the spectrum sharper than those obtained by DFT is called super-resolution. Our algorithm, sinus_it, was applied on simulated as well as experimental signals acquired on a Bruker SolariX 9.4 Tesla FTICR mass spectrometer. Sinus_it searches a sum of sine that fits the transient using a differential evolution algorithm which belongs to the broader class of evolutionary algorithm. In an evolutionary algorithm, like in Nature, a population of solutions is evolved toward better solutions by mutation and mixing solutions. Sinus_it determines for each sine the intensity, frequency and damping factor. Preliminary results which showed that Sinus_it running time is proportional to data points in the transient and sines to be searched. In all cases a super-resolution near the theoretical limit of 4 was obtained. In other words, we can use only the first quarter of the transient where the signal is more intense affording more accurate isotopic ratios. Genetic evolutionary algorithms are by nature stochastic, which mean that the results of a run depend on the random numbers drawn. By running Sinus_it about thirty times or more we will show that the standard deviation on sine parameters is low and inversely proportional to the signal to noise ratio. The high accuracy of Sinus_it is proved by the perfect linear dependence of the phases with the starting point in the gradient.



Transient size 2k points
Transient size 1k points
Transient size 512 points

Figure 1 Glutathione full isotope pattern, coarse isotopic distribution, black FFT, red sinus_it, blue cross true values

Reference:

1. Principle of genetic evolutionary algorithm, in Tsutsui, S., & Collet, P. (Eds.). *Heidelberg: Springer*,**2013**, (Vol. 453).

Telomerization of butadiene catalyzed by Pd-NHC complexes

Lorenzo Palio,[1,2] Isabelle Suisse,[1] Clément Dumont,[1] Steven P. Nolan[2] and Mathieu Sauthier[1]

[1] *Unité de Catalyse et de Chimie du Solide, Université de Lille, Villeneuve d'Ascq, France*
[2] *Department of Chemistry, University of Gent, Gent, Belgium*

uccs.univ-lille.fr/index.php/en/catalysis-and-molecular-chemistry
www.chemistry.ugent.be

Keywords: Palladium; Telomerization; Green chemistry; Catalysis; Butadiene; Carbene.

Abstract: The telomerization reaction of butadiene with alcohols catalyzed by Palladium complexes represents an environmentally friendly and 100% atom economic way to obtain octadienyl ethers[1,2]. We recently investigated the reaction employing aliphatic and investigated the activity of a series of Palladium N-heterocyclic carbenes (Pd-NHC) as catalysts[3]. This time we focused the work on the use of aromatic alcohols, since there has been very little research on this particular reaction[1]. The project aims to study the behavior of different Pd catalysts in the telomerization of a series of phenols, focusing particularly on the guaiacol due to its role as model substrate for the lignin[4,5]. Further experiments on the telomerization of butadiene with lignin will be performed in the last part of this project.

Figure 1 Pd-catalyzed telomerization of butadiene with guaiacol.

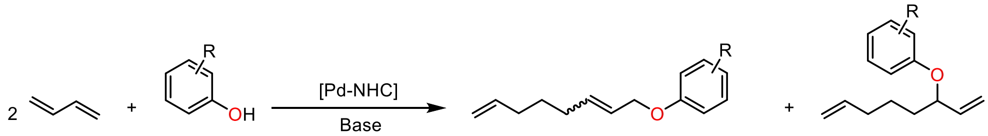
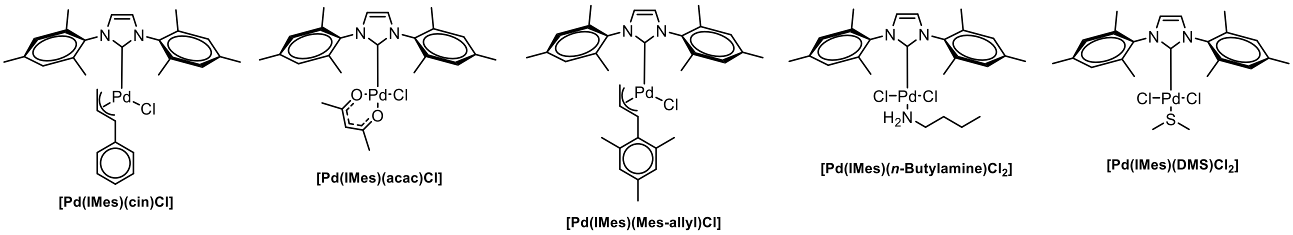


Figure 2 Pd-NHC architectures.



References:

1. Behr, A.; Becker, M.; Beckmann, T.; Johnen, L.; Leschinski, J.; Reyer, S. Telomerization: Advances and Applications of a Versatile Reaction. *Angew. Chem. Int. Ed.* **2009**, *48* (20), 3598–3614.
2. Faßbach, T. A.; Vorholt, A. J. The Telomerization of 1,3 Dienes – A Reaction Grows Up. *ChemCatChem* **2019**, *11*, 1153–1166.
3. Palio, L.; Dumont, C.; Suisse, I.; Sauthier, M.; Nolan, S. P. Telomerization of Butadiene with Ethanol Mediated by Palladium N-Heterocyclic Carbene Catalysts. *J. Catal.* **2024**, *429*, 115216.
4. Dumont, C.; Gauvin, R. M.; Belva, F.; Sauthier, M. Palladium-Catalyzed Functionalization of Kraft Lignin: Ether Linkages through the Telomerization Reaction. *ChemSusChem* **2018**, *11* (10), 1649–1655.
5. Hausoul, P. J. C.; Tefera, S. D.; Blekxtoon, J.; Bruijnincx, P. C. A.; Klein Gebbink, R. J. M.; Weckhuysen, B. M. Pd/TOMPP-Catalysed Telomerisation of 1,3-Butadiene with Lignin-Type Phenols and Thermal Claisen Rearrangement of Linear Telomers. *Catal Sci Technol* **2013**, *3* (5), 1215–1223.

CO-39

Electrochemical carbo-alkoxy-functionalization of 1,3-dienes

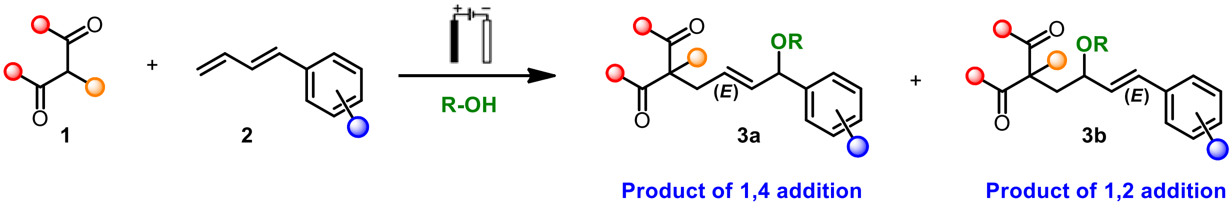
Ophélie Montiège,[1] Marion Siccardi,[1] Hélène Beucher,[1] Jean-François Brière,[1] Cédric Schneider[1]

[1]*INSA Rouen Normandie, Univ Rouen Normandie, CNRS, Normandie Univ, COBRA UMR 6014, INC3M FR 3038, F-76000 Rouen, France.*
Ophelie.Montiege@insa-rouen.fr, https://www.lab-cobra.fr/equipes/heterocycles

Keywords: Carbo-alkoxy-functionalization; 1,3-dienes; 1,3-dicarbonyls; radical-polar crossover reaction; metal-free; electrochemistry, MCR.

Abstract: From an economic and environmental perspective, the development of efficient reaction for the synthesis of structurally complex architectures through the difunctionalization of 1,3-dienes has attracted increasing interest of the industrial and academic communities.[1] Whereas the development of a radical cascade process has emerged as a powerful tool for the difunctionalization of 1,3-dienes, this strategy under electrochemical conditions and metal free remains limited to only few examples[2] and represents a major challenge in synthetic organic chemistry.

In this context (Scheme below), we report here a novel, metal-free, oxidant-free and electro-mediated methodology for the regio- and stereoselective carbo-alkoxy-functionalization of 1,3-dienes, which provides an eco-efficient multicomponent reaction (MCR) towards various valuable (*E*)-polyfunctionalized alkene products. More than 25 compounds have been synthesized with a regioselectivity for the 1,4 adduct reaching up to 95:5. The method exhibits a great tolerance towards functional groups, when starting with substituted-1,3-dicarbonyls **1** and dienes **2** substrates.



27 examples synthesized
Ratio (1,4 addition : 1,2 addition) up to 95:5

Electrochemical carbo-alkoxy-functionalization of 1,3-dienes.

References:
1. a) Wu Zhengxing, Z. W. *Chin. J. Org. Chem.* **2017**, *37*, 2250. b) Xiong, Y.; Sun, Y.; Zhang, G. *Tetrahedron Lett.* **2018**, *59*, 347. c) Herrmann, N.; Vogelsang, D.; Behr, A.; Seidensticker, T. *ChemCatChem* **2018**, *10*, 5342. d) Wu, X.; Gong, L.-Z. *Synthesis* **2019**, *51*, 122. e) Huang, H.-M.; Garduño-Castro, M. H.; Morrill, C.; Procter, D. J. *Chem. Soc. Rev.* **2019**, *48*, 4626. f) Li, G.; Huo, X.; Jiang, X.; Zhang, W. *Chem. Soc. Rev.* **2020**, *49*, 2060.
2. a) Zhang, H.; Guo, L.; Yang, C.; Xia, W. *Synthesis* **2023**, *55*, 3033. b) Sheta, A. M.; Mashaly, M. A.; Said, S. B.; Elmorsy, S. S.; Malkov, A. V.; Buckley, B. R. *Chem. Sci.* **2020**, *11*, 9109. c) Ren, S.-Y.; Zhou, Q.; Zhou, H.-Y.; Wang, L.-W.; Mulina, O. M.; Paveliev, S. A.; Tang, H.-T.; Terent'ev, A. O.; Pan, Y.-M.; Meng, X.-J. *J. Org. Chem.* **2023**, *88*, 5760.

Atmospheric fate of Myrtenal: study at the single particle scale

Jad Baltaji, Myriam Moreau, Yeny Tobon,

Univ. Lille, CNRS, UMR 8516-LASIRE– Laboratoire de Spectroscopie pour Les Interactions, La Réactivité et L'Environnement, F-59000, Lille, France.[2]Lasire, University Lille, Lille, France
…
jad.baltaji.etu@univ-lille.fr

Keywords: myrtenal; atmospheric aerosols, single particles, atmospheric chemistry.

Abstract: Terpenes are abundantly emitted from vegetation into the troposphere. They react readily with atmospheric species, such as H_2O, ozone, OH, and NO_3 radicals, and with light, resulting in several first-generation terpene oxidation products (FGTOP).[1] These products, having a brief existence in the atmosphere, swiftly undergo oxidation reactions, generating secondary oxidation products.[2] In this context, we present the research conducted on Myrtenal, a FGTOPgenerated mainly from the oxidation of α-pinene[1]. The gas phase reaction of some atmospheric species with myrtenal has been addressed in the literature[1,2]. However, studies on the chemical behavior of myrtenal in the condensed phase are lacking in the literature. This study intends to understand the behavior of single droplets containing myrtenal when particles are exposed to various environmental circumstances. To observe their behavior, we employed an innovative setup combining an acoustic levitation system with a Raman microspectrometer that includes a high-speed video camera (figure 1). This allowed us to monitor the changes in particle composition and morphology over time as the reactions progressed. Research on myrtenal revealed significant differences in reactivity between individual particles and bulk conditions. Additionally, we investigated the hygroscopic properties of the particles before and after reactions. Interestingly, the products formed from myrtenal oxidation did not alter the particles' hygroscopicity.

References:
Mutzel, A., Rodigast, M., Iinuma, Y., Böge, O., Herrmann, H., *Atm. Env.* **2016.** 130, 136-144.
Fakih, M., Roth, E., Tomas, A., Chakir, A., *Int. J. Chem. Kin*. **2023**. *55,* 751-759

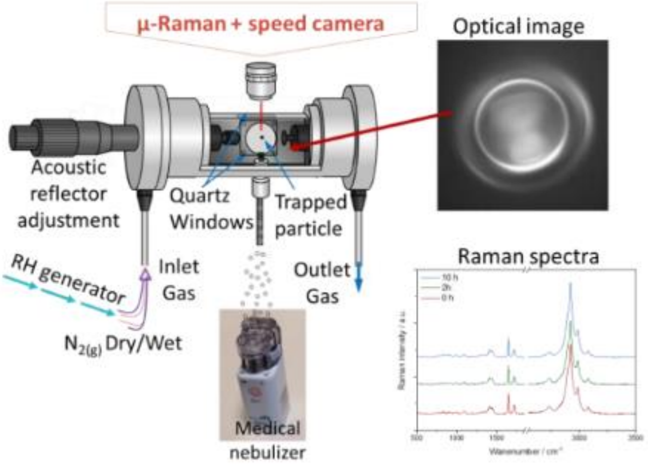


Figure 1 Schematic illustration of the environmental acoustic levitation cell coupled to

Posters

P-01

Using light and neutron scattering to characterize self-assembled Janus Nanocylinders in Organic solvents

Rihab Zguir [1], M.Ji [2], D.Siefker[2], F.Niepceron [1], C.Sinturel [3], M.Vayer[3] , B.Seaali[3], S.Pensec [2], J.Rieger [2],R. Schweins [4], L.Bouteiller [2], E.Nicol [1], O.Colombani [1]

[1]Le Mans Université, IMMM–UMR CNRS 6283, Le Mans, [2] Sorbonne Université, CNRS, Institut Parisien de Chimie Moléculaire, Equipe Chimie des Polymères, Paris, [3]Interfaces, Confinement, Matériaux et Nanostructures (ICMN), CNRS-Université d'Orléans, Orléans [4] Institut Max von Laue - Paul Langevin, DS / LSS, Grenoble.

Rihab.Zguir.Etu@univ-lemans.fr

Keywords: Supramolecular self-assembly, Janus nanorods, scattering techniques

Abstract: To support the ever-growing microelectronics industry, the techniques for miniaturizing chips have been carried out by a method called nanolithography[1]. In this context, our aim in the *JASUR* ANR project is to produce large scale, sub-10 nm, nanopatterned surfaces with a low density of defects and sharp interfaces by depositing and aligning Janus nanorods (JNRs). JNRs are one-dimensional nanoparticles that exhibit two sides with different compositions and functionalities (Janus character) [2,3]. My work in this context is to prepare the JNR by self-assembly through cooperative hydrogen bonding in organic solvent (Figure 1) and control their dimensions by playing with the chemical structure of the building blocks, the formulation and the process conditions.

The design of JNRs is very difficult to achieve because of their nanometric dimensions, anisotropy and non-symmetry. Prior to our work, only two examples existed in the literature to prepare such structures[4,5] by supramolecular self-assembly, both relying on the incompatibility between polymer arms to induce the Janus character. Recently, we showed that using complementary and non-symmetric tris-urea stickers allowed forcing the Janus character independently of the incompatibility between the polymer arms[1] (Figure 1). The self-assembly was mainly studied in aqueous medium.

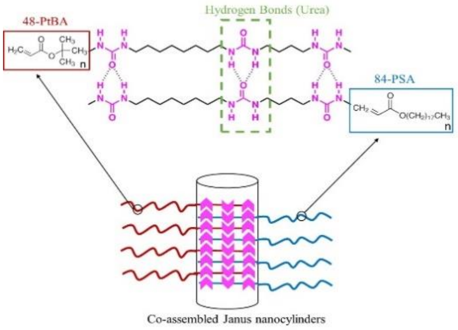


Figure 3. Concept of supramolecular Janus nanorods formation

For the purpose of the *JASUR* project, being able to prepare JNR in organic solvents in order to control the extent of self-assembly and therefore the characteristics of the particles is sought for. Here, we present preliminary results showing that static and dynamic light scattering, as well as small angle neutron scattering can be used to probe the dimensions and local structure of the particles formed by self-assembly in organic solvents, with some limits and advantages of the techniques. It was moreover shown that upon direct dispersion of chloroform, the system hardly associated leading to very small particles. In cyclohexane, long nanocylinders are obtained, with fewer defects with a co-solvent approach than with a direct-dispersion route.

References: **1**. Sharma, E. et *al. Nanomaterials*.**2022.***12*,2754. **2**. Han, S. et al, *Nature Commun*. **2020**. *11*, 4760. **3**. Choisnet, T et al, *ACS Nano*.**2021**.*15*, 2569-2577.**4**. Walther, A et *al. Am. Chem. Soc*. **2009**. *131*, 4720–4728. **5**. Danial, M.et *al. Nat. Commun*.**2013**. *4*, 2780.

P-02

Upcycling tire waste into phosphorus-containing telechelic oligomers by cross-metathesis

Alexis Perrot, Annie-Claude Gaumont and Isabelle Dez*

Laboratoire de Chimie Moléculaire et Thio-organique, Normandie Université, UNICAEN, ENSICAEN, CNRS, Caen, France
alexis.perrot@ensicaen.fr, https://www.lcmt.ensicaen.fr/

Keywords: polymer upcycling; rubber waste; metathesis; depolymerisation; phosphorus

Abstract: One billion tires reach their end-of-life every year worldwide, and the resulting waste is either "down-cycled" for low-value applications or simply discarded into the environment. However, almost half of the mass of a tire consists in polydienes that can be repurposed with a suitable chemical recycling strategy. In particular, the Ru-catalysed cross-metathesis depolymerization reaction is a promising route for upcycling rubber waste because of its robustness, high tolerance for various functional groups, and, importantly, the simultaneous end-functionalisation of the resulting oligomers.[1–3] Here, we present the synthesis of telechelic polymers obtained *via* metathetic depolymerisation of polyisoprene in the presence of phosphorus-containing chain-transfer agents.[4] Under mild reaction conditions, phosphonated polymers with M_n from 3 to 9 kg mol^{-1} and relatively low dispersities are prepared in moderate to high yields. This upcycled raw material can, in turn, be used for higher value-added applications where phosphorus-rich materials are desired. Moreover, the oligomers can be used as a starting platform for new materials by leveraging the wide scope of phosphorus chemistry.

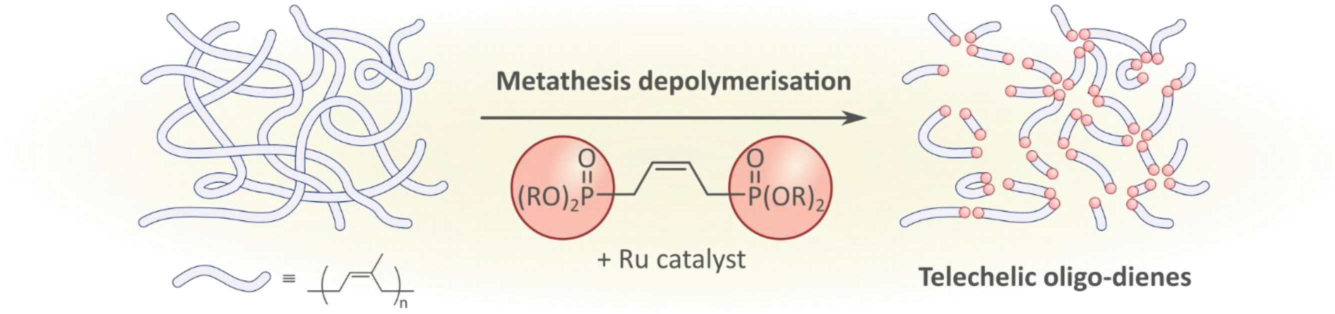


Figure 1. Ru-catalysed metathetic depolymerization of polyisoprene into telechelic phosphonated oligomers.

References:

1. Zümreoğlu-Karan, B.; Bozkurt, Ç.; Imamoğlu, Y. *Polym. J.* **1992**, *24* (1), 25–29.
2. Solanky, S. S.; Campistron, I.; Laguerre, A.; Pilard, J.-F. *Macromol. Chem. Phys.* **2005**, *206* (10), 1057–1063.
3. Michel, X.; Fouquay, S.; Michaud, G.; Simon, F.; Brusson, J.-M.; Carpentier, J.-F.; Guillaume, S. M. *Eur. Polym. J.* **2017**, *96*, 403–413.
4. Jambou, C.; Pilard, J.-F.; Gaumont, A.-C.; Dez, I. *Eur. Polym. J.* **2023**, *185*, 111805.

Synthesis of telechelic oligomers by flow chemistry

Djemel-Dine Bazille,[1,2] Julien Legros[2], Fabrice Burel[1], Daniela Vuluga[1]

[1] *INSA Rouen Normandie, CNRS UMR 6270, PBS, 685 Avenue de l'Université, 76800 Saint-Étienne-du-Rouvray, France*
[2] *Univ Rouen Normandie, CNRS, INSA Rouen, COBRA, 76821 Mont-Saint-Aignan, France*

djemel-dine.bazille@insa-rouen.fr

Keywords: Organolithium, anionic polymerization, flow chemistry, polymyrcene, end-functionalization

Abstract: Flow technology is a process that is gaining importance in organic chemistry: it exhibits many advantages over classical batch conditions for reactions that require very precise time control, very safe conditions, or that are difficult to scale-up.[1] In the frame of the research performed at the MM team of PBS laboratory, microflow reactors are used to access bio-based polymers with precise functionalization (Figure 1).[2]

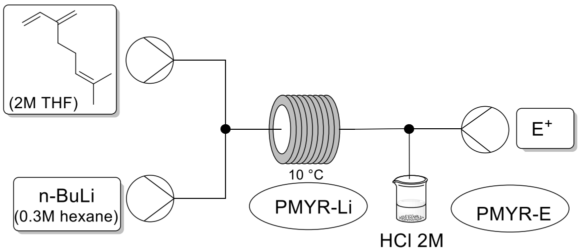


Figure 1 stainless steel flow assembling for polymyrcene synthesis

Here, we now report that telechelic polymyrcenes can be synthesized through anionic polymerization in flow. Due to the specific features of flow reactors, varying parameters (flow rate, reactor length,…) the *Mn* of the telechelic polymer can be easily tuned and various functional groups can be introduced, notably by using gas-liquid conditions.

References:
1. Plutschack, M.B.; Pieber, B.; Gilmore, K.; Seeberger, P.H.; *Chem. Rev.*, **2017**, 117, 11796-77893.
2. Pérez, K.; Leveneur, S.; Burel, F.; Legros, J.; Vuluga, D.; *React. Chem. Eng.,* **2023**, 8, 432-441.

P-04

Deciphering the Secrets of PET Polyesters

Bayan Almasri[1,2*], Youssef Bakkour[2], Christian Rolando[1]

[1]Minitaturisation pour la Synthèse l'Analyse et la Protéomique (MSAP, UAR 3290 CNRS), Université de Lille, Villeneuve d'Ascq, France
[2]Chemistry department, Laboratory of Applied Chemistry (LAC), Lebanese University, Tripoli, Lebanon
*Presenting author: bayan.almasri1234@gmail.com & https://msap-lab.fr/

Keywords: PET; depolymerization; mass spectrometry; ageing; environment.

Abstract: Polyethylene terephthalates (PET) are one of the most abundant polymers in our daily life as they are the main polymers in polyesters textiles, food containers and bottles. Formed of terephthalic acid and ethylene glycol, these polyesters constitute a pollution source either as macro-PET or after degradation into micro- and nano-PET. Many analytical studies had been performed on PET but their identification on molecular level are not satisfying as they are not allowing the study of their structural modifications after ageing [1]. So, it's crucial to study the degradation mechanisms of these samples after exposure to the environment (irradiation, micro-organisms, salinity…) and to quantify them. Our methodology combining soft chemical depolymerization and ultra-high resolution mass spectrometry is a promising solution and proved its success on environmental PET. A solubilization in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) was performed prior to a transamidation using *N,N'*-dimethyl-1,3-propanediamine (DMAPA) at room temperature or 57 °C. After extraction with ultrapure water and ethyl acetate, the products were analyzed by MALDI FTICR MS and LC ESI Orbitrap MS. Many PET containers and bottles from different countries, brands and contents were analyzed in addition to marine samples. For each, a specific signature was determined. Dimers, oligomers, crosslinked, oxidized products and additives were successfully identified.

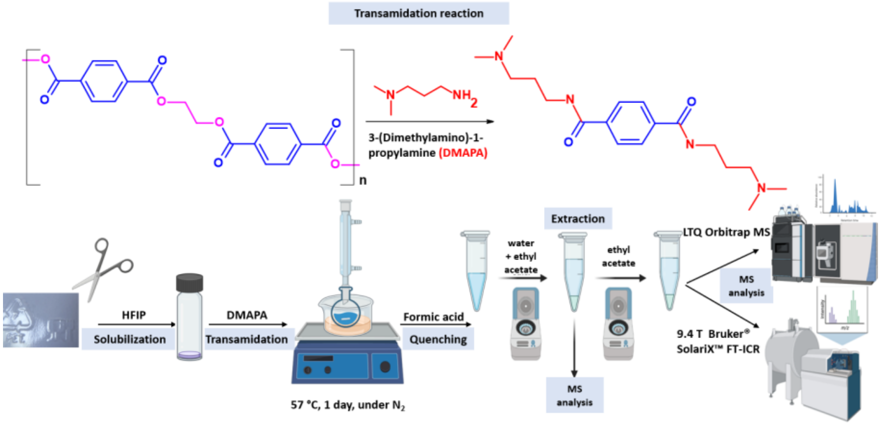


Figure 1 Methodology of depolymerization and analysis of PET samples.

Reference:
1. Ivleva, N.P., *Chemical reviews*, **2021**, 121(19):11886- 11936.

Modification of vegetable oil for treatment and trapping of organophosphates based pesticides

Bruna Brocardo Ferreira,[1] Daniela Vuluga-Legros[1], Elisa Souza Orth[2]

Affiliation 1 :[1]Polymers, Biopolymers and Surfaces - PBS, INSA, Rouen, France
Affiliation 2 :[2]Grupo de Catálise e Cinética - GCC, UFPR, Curitiba, Brazil
bbrocardoferreira@insa-rouen.fr

Keywords: Pesticides; organophosphates; vegetable oil; treatment; trapping.

Abstract: Organophosphates (OPs) have been known for their use in the agriculture industry for almost 100 years, since the synthesis of Parathion in the 30s.[1] Because of their high toxicity, since the second world war, these compounds also play an important role in the composition of chemical warefare.[2] Given the growing consumption of organophosphates (OPs) based pesticides, leading to water contamination and, at the same time, ascending stocks of banned OPs, new ways of treatment and trapping of OPs have been gaining attention in the scientific community.[3] In this work, we present new products based on different ways of functionalization of a affordable vegetable oil for recovering and hydrolyzing OPs.[1,4] (**Figure 1**).

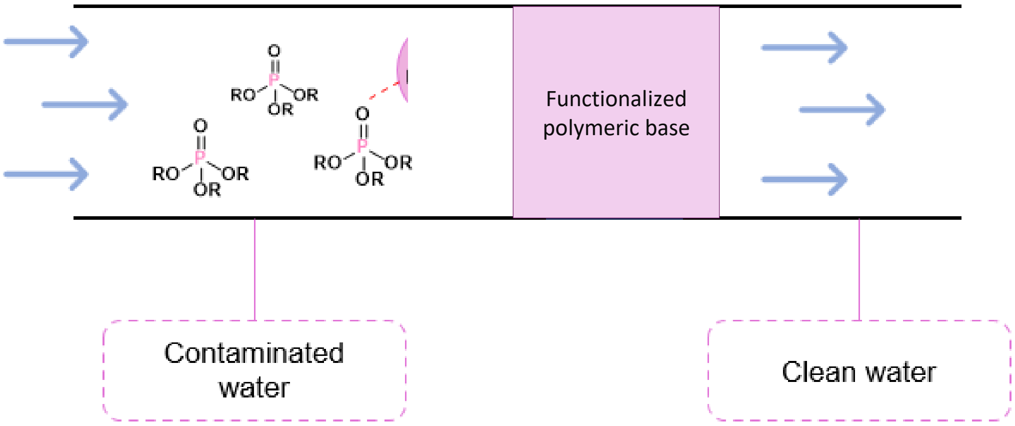


Figure 1 Treatment of water contaminated with OPs.

References:
1. SILVA, V. B. et al. Chem. Rec. **2021**, 21 (10), 2638–2665.
2. RAJAN, D. K. et al. Environ. Res. 2024, 244 (117947), 1-16
3. AI, S.; CHEN, X.; ZHOU, Y. Environ. Pollut. **2024**, 343 (123218), 1-13
4. GEELHAND DE MERXEM, L.; VULUGA, D.; LECAMP, L. Polym**. 2021**, 217 (123454), 1-9.

P-06

High oxidation degree of cellulose as a binder for silicon-based anodes for lithium-ion batteries.

Mohamed ELMOUHINNI,[1,3] Jean-Pierre Bonnet,[1] Dominique cailleu,[2] Véronique Bonnet[3]

[1]Laboratoire de Réactivité´ et Chimie des Solides (CNRS UMR 7314), Université de Picardie Jules Verne, 15 rue Baudelocque, 80039 Amiens, France
[2]Plateforme-analytique, Institut de Chimie de Picardie FR CNRS 3085, Université de Picardie Jules Verne, 33 rue Saint Leu, 80039 Amiens, France
[3]Laboratoire de Glycochimie, des Antimicrobiens et des Agroressources, (CNRS UMR 7378), Université de Picardie Jules Verne, 10 rue Baudelocque, 80039 Amiens Cedex, France.
mohamed.elmouhinni@u-picardie.fr

Keywords: Oxidized cellulose; Binder; Polysaccharide; silicon; Lithium-ion batteries

Abstract:

Oxidized cellulose is being investigated as a possible binder for silicon anodes in lithium-ion batteries, to address concerns such as low cycle life and quick capacity reduction caused by silicon volume expansion[1,2]. Carboxyl groups in oxidized cellulose produce strong hydrogen bonds with silicon particles and copper current collectors, indicating potential for electrode stability during charge cycles. High-energy ball milling is used to investigate various anode compositions in terms of compositional uniformity. Cellulose is oxidized by TEMPO treatment after NaOH/Urea chemical alteration, shifting from cellulose I to II and perhaps improving compatibility with silicon. To investigate variations in oxidized cellulose from various sources (Microcrystalline cellulose, and alpha cellulose), characterization methods such as XRD, FTIR, SEM, and Solid state NMR are used, in addition to laser granulometry, XRD, and SEM for silicon particle examination. However, electrochemical testing of the oxidized cellulose in coin cells has yet to be performed. These discoveries, subject to electrochemical confirmation, represent a step forward in silicon-based lithium-ion battery technology.

References:

1. Goodenough, J. B.; Kim, Y. Challenges for Rechargeable Li Batteries. Chem. Mater. 2010, 22 (3), 587–603. https://doi.org/10.1021/cm901452z.

2. Scrosati, B.; Garche, J. Lithium Batteries: Status, Prospects and Future. J. Power Sources 2010, 195 (9), 2419–2430. https://doi.org/10.1016/j.jpowsour.2009.11.048.

P-07

Influence of crystallinity on the mechanical and gas barrier properties of polyethylene

Elena BOUVIER[1], Stéphane MARAIS[1], Nathalie MASSON[2], Laury LIVEMONT[2] and Kateryna FATYEYEVA[1]

[1]Université de Rouen Normandie, INSA Rouen Normandie, Polymères Biopolymères Surface (PBS) UMR 6270 CNRS, 76000 Rouen, France
[2]Unither Pharmaceuticals, 75009 Paris, France
elena.bouvier1@univ-rouen.fr ; https://www.pbs.cnrs.fr/

Keywords: low-density polyethylene; crystallinity; gas barrier properties; mechanical properties

Abstract: Polyolefins (including low-density polyethylene (LDPE)) are widely used in different manufacturing processes[1], such as food, cosmetic or pharmaceutical packaging. Raw materials are frequently modified to meet industrial requirements. In general, improving gas barrier properties is necessary.

To correlate the structure with gas barrier properties, LPDE films with different crystallinity (35% and 46%, measured by differential scanning calorimetry (DSC) and labelled as LDPE-35 and LDPE-46) were analyzed. It is known that crystallinity has a direct influence on the gas barrier properties by creating tortuosity and, therefore, preventing gas molecules from passing through the material[2].

LDPE films were obtained by extrusion using a twin-screw extruder. In order to study the influence of the extrusion direction, the mechanical analysis was performed in the transverse (TD) and machine (MD) directions. The obtained results show that whatever the direction of the film extrusion is, the Young modulus value of LDPE-46 is higher than that of LDPE-35 (Table 1), testifying to the film rigidity rising. Besides, higher gas permeation coefficient values were revealed for LPDE-35 than for LDPE-46. Indeed, the increase in film crystallinity slows down the gas molecules permeation through the LDPE film. However, the obtained gas selectivity values are rather similar for both films. This result confirms that selectivity depends mainly on the material chemical nature that is the same for both LDPE films. Consequently, an adequate balance between the gas barrier properties and mechanical behavior should be found in order to obtain a flexible gas barrier material.

Table 1 Mechanical and gas barrier properties of different LDPE grades

	Young modulus (MPa)		Permeability coefficient (Barrer)			Gas selectivity		
	MD	TD	N_2	O_2	CO_2	O_2/N_2	CO_2/O_2	CO_2/O_2
LDPE-35	110 ± 6	114 ± 8	1,49 ± 0,02	4,61 ± 0,01	20,66 ± 0,04	3,1	4,5	13,9
LDPE-46	225 ± 12	311 ± 11	0,92 ± 0,01	2,95 ± 0,01	13,1 ± 0,2	3,2	4,4	14,3

MD (Machine Direction), TD (Transverse Direction)

References:

1. Marechal, P. Polyéthylènes Basse Densité PE-BD et PE-BDL. *Techniques de l'ingénieur.* **2011**. https://doi.org/10.51257/a-v1-am3310.
2. Laragon, J.M.; Catala, R.;Gavara, R. Structural characteristics defining high barrier properties in polymeric materials. *Materials Science and Technology*. **2004**, *20(1)*, 1-7.

P-08

Polyisoprene depolymerisation *via* a photoinitiated process

Julien Renault[1], Yougourthen Boumelka[1], Isabelle Dez*[1]

[1]*Normandie Université, LCMT, ENSICAEN, UNICAEN, CNRS, 14000 Caen, France*
…
julien.renault@ensicaen.fr
https://www.lcmt.ensicaen.fr/

Keywords: Depolymerisation, Photoredox, Polyisoprene, Tire waste, Catalysis.

Abstract: Improving tire waste management presents a formidable environmental challenge, as conventional disposal methods often result in pollution and resource depletion.[1,2] Chemical recycling offers a promising alternative by repurposing waste tires into valuable chemical feedstocks. This study explores the application of photoredox catalysis for the depolymerization of tire rubber, offering a sustainable solution to this pressing issue. By using light-induced electron transfer processes, we can cleave polydiene bonds into functionalized oligomers offering a promising solution for waste reduction and resource optimization. This approach consists in using a vinyl ether initiator, a chain transfer agent for functionalization and an organic dye activated under blue light irradiation to depolymerize polyisoprene as a polydiene model. This innovative method enables the synthesis of smaller, functionalized polymers that can be reincorporated into further polymerization processes, contributing to a circular economy model.

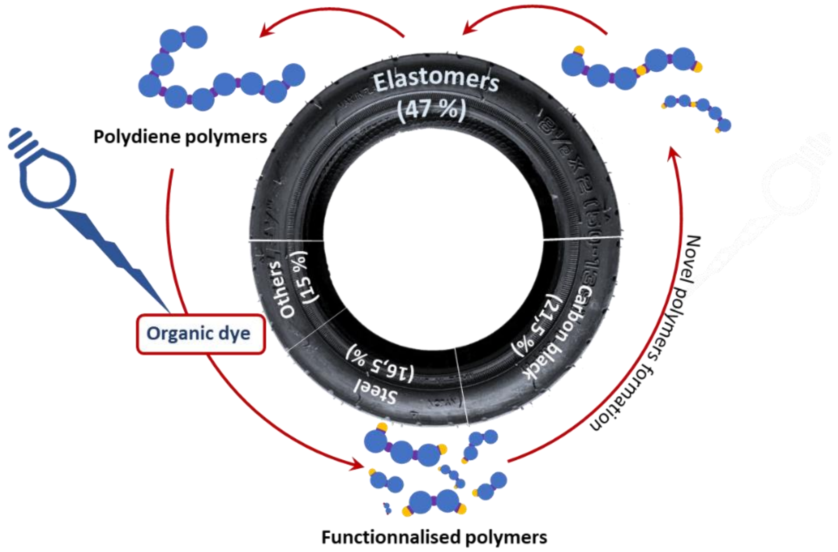


Figure 4 : The (he)art of recycling polymer through photoredox initiated depolymerisation.

References:
1. ADEME ; *Observatoire Pneumatiques Usagés.* **2020**
2. Aliapur, *Le devenir des pneumatiques.* **2018**

P-09

Amylopectin chain length distribution (CLD) by Fluorescence-assisted Capillary Electrophoresis (FACE) down to single starch granules

Isabelle Fabrizi[1,*], Christian Rolando[1], Nicolas Szydlowski[2], Fabrice Bray[1]

[1]*Minitaturisation pour la Synthèse l'Analyse et la Protéomique (MSAP, UAR 3290 CNRS), Université de Lille, Villeneuve d'Ascq, France*
[2]*Unité de Glycobiologie Structurale et Fonctionnelle (UGSF, UMR 8576 CNRS), Université de Lille, Villeneuve D'Ascq, France*
*Presenting author: Isabelle.fabrizi.etu@univ-lille.fr, https://msap-lab.fr/

Keywords: Starch, Single granule, Capillary Electrophoresis

Abstract: Starch is a main storage form of carbon for plants and is composed of glucose residues linked together by α-1,4 O-glycosidic linkages and branched through α-1,6 bounds [1]. The two polymers composing starch as amylose and amylopectin form water insoluble granules ranging from 1 to up to 100 µm in diameter depending of their botanical origin. Furthermore, a wide range of granule morphologies also exists regarding their origins (plant species, organs, tissues, cells) [2, 3]. In the present work, we developed a miniaturized method for determining amylopectin chain length distribution (CLD) by fluorescence-assisted capillary electrophoresis (FACE). The method relies on single granule entrapped with fused silica capillaries followed by starch gelatinization and debranching. Sample desalting on Hypersep™ Hypercarb™ tips following APTS-labelling and the use of nanovials allowed for the fluorescence analysis of undiluted samples.

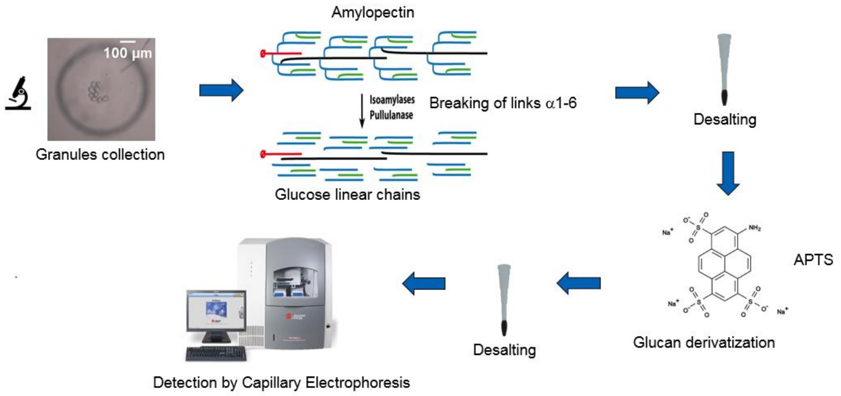


Figure 1 Methods for granules collection and glucans derivatization by APTS followed by Capillary Electrophoresis detection.

References:
1. Buleon A, Colonna P, Planchot V, Ball S. Starch granules: structure and biosynthesis. *Int. J. Biol. Macromol.* 1998;23(2), 85-112.
2. Verbeke J, Penverne C, D'Hulst C, Rolando C, Szydlowski N. *Carbohydr. Polym.,* **2016**, 152, 784-91.
3. Helle S, Bray F, Putaux J-L, Verbeke J, Flament S, Rolando C, et al. Intra-Sample Heterogeneity of Potato Starch Reveals Fluctuation of Starch-Binding Proteins According to Granule Morphology. *Plants*, **2019**, 8(9), 324.

P-10

Polysaccharide nanocrystals as pollutant adsorbents for textile industry

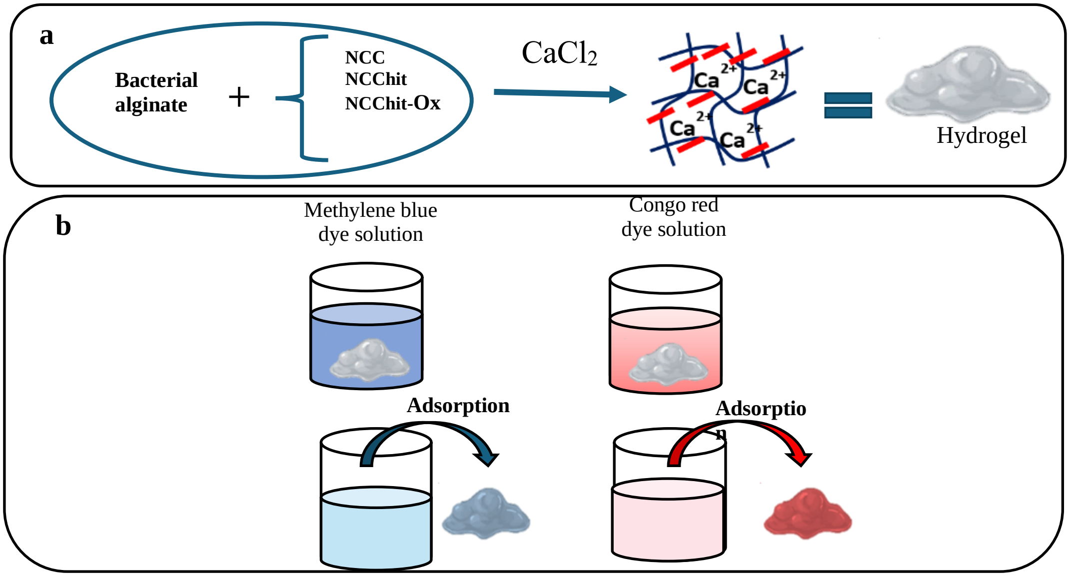
Daniela Duarte Serrano[1 2], Aurélie Vallin[1 2], Caroline Hadad[1 2] and Albert Nguyen Van Nhien[1 2]

[1] *Laboratoire de Glycochimie, des Antimicrobiens et des Agroressources, UR 7378, Université de Picardie Jules Verne, 33 rue Saint Leu, UFR des Sciences, 80039 Amiens cedex, France*

[2] *Institut de Chimie de Picardie FR 3085, 80039 Amiens, France*
daniela.duarte.serrano@u-picardie.fr web: https://www.u-picardie.fr/labo/LG/

Keywords: Biopolymers; chitin and cellulose nanocrystals; bacterial alginate; hydrogels; dyes; water pollution.

Abstract: Textile industry has a significant impact on water contamination because of the large amounts of heavy metals, toxic dyes, organic, and inorganic pollutants which generates several environmental problems.[1] Cost-effective polymers as absorbents can reduce the cost of the remediation process. Composites of biopolymers exhibit interesting properties such as improved durability, processing capability, high functionality, a large surface area, and recyclability[2]. Therefore, biopolymers based hydrogels have been investigated in recent years for the sorption of heavy metals and dyes[3]. In this study, we are focusing on dye adsorption such as Congo red (CR) and methylene blue (MB) used in textile industry. Surface-modified nanocrystals from chitin and cellulose are studied for their ability to remove those dyes from water during hydrogel preparation with bacterial alginate. These findings contribute to a better understanding of the potential applications and performance of the nanocrystals in dye-related systems.



Scheme 1. (a) polysaccharide-based hydrogels formation and (b) adsorption of Congo red and methylene blue by hydrogel.

References:

1. Ahmad, R.; Ansari, K. Comparative Study for Adsorption of Congo Red and Methylene Blue Dye on Chitosan Modified Hybrid Nanocomposite. *Process Biochemistry* **2021**, *108*, 90–102.

2. Udayakumar, G. P.; Muthusamy, S.; Selvaganesh, B.; Sivarajasekar, N.; Rambabu, K.; Sivamani, S.; Sivakumar, N.; Maran, J. P.; Hosseini-Bandegharaei, A. Ecofriendly Biopolymers and Composites: Preparation and Their Applications in Water-Treatment. *Biotechnology Advances* **2021**, *52*, 107815.

3. Malatji, N.; Makhado, E.; Modibane, K. D.; Ramohlola, K. E.; Maponya, T. C.; Monama, G. R.; Hato, M. J. Removal of Methylene Blue from Wastewater Using Hydrogel Nanocomposites: A Review. *Nanomaterials and Nanotechnology* **2021**, *11*, 184798042110394.

Palladium-Catalyzed Hydrosilylation of *gem*-Difluoroallenes

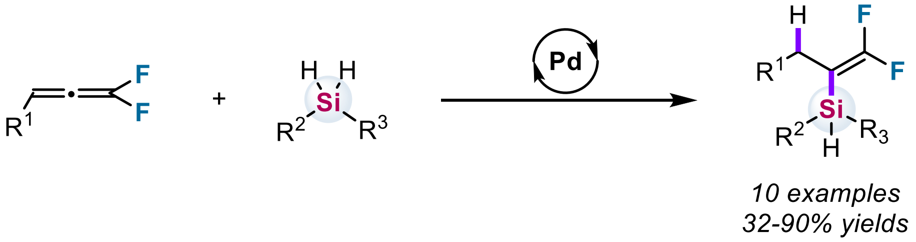
Xinlong Yu,[a,b] Philippe Jubault,[a] Samuel Couve-Bonnaire,[a] Li-Wen Xu*[b] and Jean-Philippe Bouillon*[a]

a Normandie Université, INSA Rouen, UNIROUEN, CNRS, COBRA (UMR 6014), 76100 Rouen, France
b College of Material, Chemistry and Chemical Engineering, Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, Key Laboratory of Organosilicon Material Technology of Zhejiang Province, Hangzhou Normal University, Hangzhou 311121, P. R. China

jean-philippe.bouillon@univ-rouen.fr; Web: lab-cobra.fr
liwenxu@hznu.edu.cn; Web: yjg.hznu.edu.cn

Keywords: Palladium; hydrosilylation; *gem*-difluoroallenes; vinylsilanes

Abstract: On the one hand, *gem*-difluoroallenes, due to their unique electronic properties and hydrophobicity, are widely used in medicinal chemistry, in pesticide development, and for the preparation of high-performance materials. On the other hand, organosilicons have become increasingly significant in organic synthesis. Their unique properties, coupled with the low toxicity of silicon atom, have led to their widespread application not only in organic synthesis but also in medicinal chemistry.[1-3] Herein, we reported palladium-catalyzed highly regioselective hydrosilylation of *gem*-difluoroallenes for the synthesis of disubstituted vinylsilanes (racemic version).



References:

[1] a) K. Takai, *et al. ACS Catal.* **2016**, *6*, 3387−3395. b) Y. H. Xu, *et al. J. Am. Chem. Soc.* **2022**, 144, 5535−5542. c) S. Ge, *et al. Nat. Commun.*, **2017**, *8*, 2258. d) X. Shen, *et al. Nat. Commun.*, **2022**, *13*, 3691. e) S. Ma, *et al. Org. Chem. Front.*, **2017**, *4*, 1829−1832. f) Y. H. Xu, *et al. Org. Lett.* **2022**, *24*, 6054−6059.
[2] a) Z. P. Zhan, *et al. Org. Chem. Front.*, **2020**, *7*, 1132−1136. b) Z. P. Zhan, *et al. Adv. Synth. Catal.* **2020**, *362*, 2360−2366. c) A. R. Schmidt, *et al. Chem. Commun.* **2015**, *51*, 5943−5946. d) Z. P. Zhan, *et al.* Chem. Commun., **2020**, *56*, 1597-1600. e) W. Tang, *et al. Green Synthesis and Catalysis*, **2020**, *1*, 171−174.
[3] a) Y. Yamamoto, *et al. J. Org. Chem.* **1999**, *64*, 2494-2499. b) M. Stratakis, *et al. Org. Lett.* **2015**, *17*, 4538−4541. c) J. Montogomery, *et al. Angew. Chem. Int. Ed.*, **2015**, *54*, 9088−9091. d) J. Montgomery, *et al. J. Am. Chem. Soc*. **2013**, *135*, 15282−15285. e) J. Montgomery *et al. Org. Lett.* **2014**, *16*, 5486−5489.

P-12

Enantioselective synthesis of cyclopropanes from ethyl diazo pyruvate and dienes catalyzed by Ru(II)Pheox

Zoé WEBER, Raphaël DOLLET, Thomas POISSON, and Philippe Jubault

BioSynF team, COBRA, Rouen, France

zoe.weber@insa-rouen.fr, https://www.lab-cobra.fr/

Keywords: cyclopropanation; enantioselective synthesis; dienes; Ru(II)Pheox.

Abstract: The cyclopropane is the smallest and the most constrained cycloalkane, and its introduction into bioactive molecules can affect their conformation, and hence their biological properties. The cyclopropyl ring is one of the most encountered cycles in the drugs structure approved by the FDA.[1] In this context, the development of new synthesis strategies is essential to access to new cyclopyl-containing scaffolds. The most efficient approach and the one described herein is the [2+1] cycloaddition, i.e. the cyclopropanation of alkenes.[2] The first enantioselective cyclopropanation reaction was reported by Nozaki using a copper(II)-catalyst, styrene, and ethyl diazoacetate.[3] Since then, new catalysts and reaction conditions have been developed to obtain outstanding enantiomeric excess. In the literature, there are several cyclopropanations based on the reaction between diazoacetates and dienes. During the last four decades, different catalysts were used to promote the synthesis of cyclopropanes from 2-substituted 1,3-butadienes such as rhodium(II) acetate, copper, or palladium[4]. Only three publications in the literature report the synthesis of this kind of cyclopropanes, based on the synthesis method of Mueller[5]. On the other hand, the diazo pyruvates were rarely used for cyclopropanation, especially with dienes. In this context, we decided to develop an enantioselective synthesis strategy of cyclopropanes from the ethyl diazo pyruvate and dienes. To catalyze the reaction, the Ru(II)Pheox is used, a highly stereoselective catalyst developed by Iwasa[6].

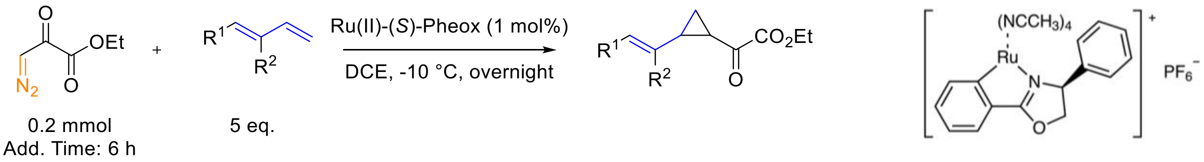


Figure: synthesis scheme of dienes cyclopropanation with the Ru(II)Pheox structure

References:

1. Taylor, R. D.; MacCoss, M.; Lawson, A. D. G. *J. Med. Chem.* **2014**, *57* (14), 5845-5859.
2. Lebel, H.; Marcoux, J.-F.; Molinaro, C.; Charette, A. B. *Chem. Rev.* **2003**, *103* (4), 977–1050.
3. Nozaki, H.; Moriuti, S.; Takaya, H.; Noyori, R. *Tetrahedron Lett.* **1966**, *7* (43), 5239–5244.
4. Kastrati, A.; Jaquier, V.; Garbo, M.; Besnard, C.; Mazet, C. *ACS Org. Inorg. Au* **2023**, *3* (5), 291–298.
5. Mueller, L. G.; Lawton, R. G. *J. Org. Chem.* **1979**, *44* (25), 4741–4742.
6. Chanthamath, S.; Iwasa, S. *Acc. Chem. Res.* **2016**, *49* (10), 2080–2090.

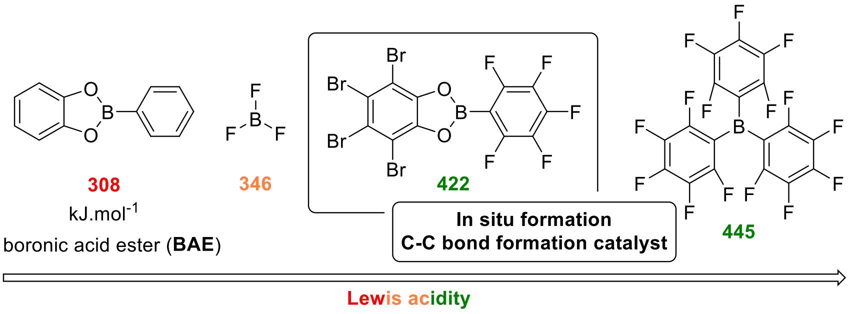
Revisiting the Lewis Acidity and Reactivity of Boronic Acid Esters.

Ava Bousselat, [1] Pr. Jacques Rouden [1] and Dr. Jérôme Blanchet [1]*

[1]*Calvados, Laboratoire de chimie moléculaire et thioorganique (LCMT), Caen, France*
ava.bousselat@ensicaen.fr ; https://www.lcmt.ensicaen.fr/

Keywords: Lewis acidity; Catalyse; Organic Chemistry; Boronic acid ester.

Abstract: Lewis acids, essential elements in the realm of organic chemistry, exhibit a spectrum of applications spanning pharmaceuticals, agrochemicals, and materials science. Particularly within the domain of main-group chemistry, Lewis acids present alternatives to transition metals, thereby driving this exploration into halogenated boronic acid esters (BAEs). Despite the well-known role of BAEs as fundamental building blocks, their catalytic capabilities have remained underexamined. Through an investigation into their Lewis acidity, our results uncovered strengths comparable to recognized boron trifluoride and tris(pentafluorophenyl)borane. Additionally, we delved into the catalytic efficacy of BAEs in the Hosomi-Sakurai allylation of aldehydes, revealing superior performance when compared to boron trifluoride. This research lays the groundwork for further advancements in this fields.[8]



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[8] Bousselat, A.; Rouden, J.; Blanchet, J.; *J. Org. Chem.* **2024**, Soumise.

P-14

Vinyl Radical-Mediated Bifunctionalization of Thioalkynes through Photoinduced $C(sp^3)$-H Activation *via* 1,5-HAT

Ramesh Balu, Vincent Herrera, Tatiana Besset

INSA Rouen Normandie, Univ Rouen Normandie, CNRS, Normandie Univ, COBRA UMR6014, INC3M FR 3038, F-76000 Rouen, France

tatiana.besset@insa-rouen.fr
www.lab-cobra.fr

Keywords: Vinyl radical-assisted functionalization; Hydrogen Atom Transfer (HAT); Organo photocatalysis; γ-imino thioalkenes.

Abstract: The selective modification of distant aliphatic $C(sp^3)$-H bonds is crucial for efficiently crafting intricate molecules with fewer steps.[9] Among the various methods, one promising approach involves utilizing photocatalyzed radical translocation through intermolecular hydrogen atom transfer (HAT). This method allows for the functionalization of distal $C(sp^3)$-H bonds under mild conditions, employing a 1,5-hydrogen atom transfer mechanism.[10, 11] However, compared to heteroatom-assisted transformations, there has been less exploration into carbon-radical mediated remote functionalization, particularly regarding vinyl radical-induced alterations to remote $C(sp^3)$-H bonds. Recently, there has been growing interest in employing bifunctional reagents as a sustainable means of modifying unsaturated compounds, facilitating the synthesis of crucial structural frameworks in a step-efficient manner.[12] Nevertheless, the coupling of vinyl radical-mediated distal $C(sp^3)$-H bond functionalization with bifunctional reagents via a 1,5-HAT process remains largely unexplored, with only a few instances reported to this day.[13] Therefore, we investigated into an innovative photocatalytic approach for the 1,4-bifunctionalization of thioalkynes, presenting a novel pathway for synthetic exploration.[14]

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[9] a) H. Chena, S. Yu, *Org. Biomol. Chem*. **2020**, *18*, 4519-4532; b) C. He, W. G. Whitehurst, M. Gaunt, *Chem*. **2019**, *5*, 1031–1058; c) S. Saha, J. Das, S.A. Al-Thabaiti, S.M. Albukhari, Q.A. Alsulami, D. Maiti, *Catal. Sci. Technol*. **2023**, *13*, 11–27.

[10] a) M. E. Wolff, *Chem. Rev*. **1963**, *63*, 55–64; b) A. W. Hofmann, *Chem. Ber*. **1883**, *16*, 558–560; c) K. Lçffler, C. Freytag, *Chem. Ber*. **1909**, *42*, 3427–3431; d) W. Guo, Q. Wang, J. Zhu, *Chem. Soc. Rev*. **2021**, *50*, 7359–7377; e) E. Nobile, T. Castanheiro, T. Besset, *Angew. Chem. Int. Ed*. **2021**, *60*, 12170–12191; f) X.-Q. Hu, J.-R. Chen, W.-J. Xiao, *Angew. Chem. Int. Ed.* **2017**, *56*, 1960–1962; *Angew. Chem*. **2017**, *129*, 1988–1990; g) L. M. Stateman, K. M. Nakafuku, D. A. Nagib, *Synthesis* **2018**, *50*, 1569–1586; h) G. Kumar, S. Pradhan, I. Chatterjee, *Chem. Asian J*. **2020**, *15*, 651–672; i) N. Goswami, D. Maiti, *Isr. J. Chem*. **2020**, *60*, 303–312.

[11] a) Y. Zhou, Z. Gu, Y. Hong, H. Chen, J. Luo, H. Zheng, G. Zhu, *Org. Chem. Front.* **2024**, *11*, 1232-1250; b) L-X. Li, K. Hu, *Tetrahedron* **2023**, 130, 133172.

[12] a) H-M. Huang, P. Bellotti, J. Ma, T. Dalton, F. Glorius, *Nat Rev Chem.* **2021**, *5*, 301–321; b) S. Dutta, J. E. Erchinger, F. Strieth-Kalthoff, R. Kleinmans, F. Glorius, *Chem. Soc. Rev.* **2024**, *53*, 1068–1089; c) J. Zhang, M. Zhang, M. Oestreich, *Chem Catalysis*. **2024**, *4*, 100962.

[13] a) Z. Xiong, F. Zhang, Y. Yu, Z. Tan, G. Zhu, *Org. Lett.* **2020**, *22*, 4088–4092; b) M. Luo, S. Zhu, C. Shi, Y. Du, C. Yang, L. Guo, W. Xia, *Org. Lett.* **2022**, *24*, 6560–6565; c) Z. Chen, Y. Duan, S. Sun, B. Lin, X. Liu, P. Liu, *J. Org. Chem.* **2023**, *88*, 4687–4693.

[14] B. Ramesh, V. Herrera, T. Besset, (Unpublished result).

Synthesis of α-chloroarylacetic acid *via* electrochemical carboxylation of α,α-dichloroarylmethane derivatives

Corentin Maret,[1] Nicolas David,[1] David Pierrot,[1] Eric Léonel,[2] Vincent Levacher,[1] Jean-François Brière,[1] Sylvain Oudeyer[1]
[1]*COBRA laboratory, Normandie Univ, UNIROUEN, INSA Rouen, CNRS, 76000 Rouen, France*
[2]*Electrosynthèse, Catalyse et Chimie Organique Université Paris-Est Créteil, CNRS, ICMPE, UMR 7182 2 rue Henri Dunant, 94320 Thiais, France*
sylvain.oudeyer@univ-rouen.fr

Keywords: Electrochemistry; carboxylation; electrocarboxylation

Abstract: α-chlorophenylacetic acids **1** are versatile synthetic intermediates involved in the synthesis of several drugs.[15] Therefore, several methods were reported to synthesize α-chlorophenylacetic acids including chemical (mainly oxidation of α-chloroaryl acetaldehydes[16] or chlorination of α-hydroxyarylacetic acid[17]) or electrochemical approaches but none of them proved to be general. As far as electrochemical approaches are concerned, the electrocarboxylation reaction of α-chloroaryl derivatives have been extensively studied.[18] On the other hand, electrocarboxylation of α,α-dichloro species remains elusive.[19] To the best of our knowledge, only one example has been described (R^1 = H, Ar = Ph) with low yield and selectivity (Cl *vs* H).

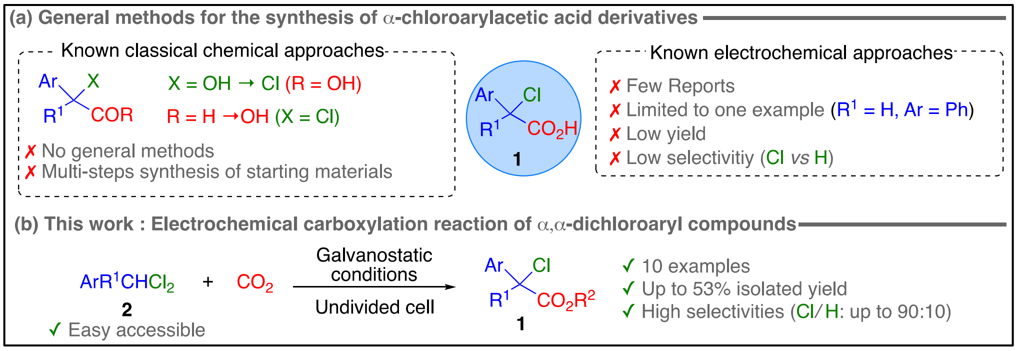

Figure 5 General approach and our approach towards chloroaryl compounds

We would like to report herein our contribution to the electrocarboxylation reaction of α,α-dichloroarylmethane **2** derivatives in order to provide an efficient and selective synthesis of chloroarylacetic acid derivatives **1** (Scheme b).[20]

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[15] For examples, see: (a) Frank, R.; Bahrenberg, G.; Christoph, T.; Schiene, K.; DeVry, J.; Damann, N.; Frormann, S.; Lesch, B.; Lee, J.; Kim, Y.-S. and Kim, M.-S. (2010) PCT International Application WO2010/127856. (a) Murakami, K.; Ohashi, M.; Matsunaga, A.; Yamamoto, I.;Nohira, H. *Chirality* **1993**, *5*, 41–48.

[16] For an example, see: Paraskevas, S. M.;Paraskevas, M. S. *Catal. Commun.* **2004**, *5*, 687–690.

[17] For an example, see: Carnell, A. J.; Kirk, R.; Smith, M.; McKenna, S.; Lian, L. Y.;Gibson, R. *ChemMedChem* **2013**, *8*, 1643–1647.

[18] For examples, see: Murtaza, A.; Qamar, M. A.; Saleem, K.; Hardwick, T.; Zia Ul, H.; Shirinfar, B.;Ahmed, N. *Chem Rec* **2022**, *22*, e202100296 and references therein.

[19] (a) Silvestri, G.; Gambino, S.; Filardo, G.; Greco, G.;Gulotta, A. *Tetrahedron Lett.* **1984**, *25*, 4307–4308. (b) Silvestri, G.; Gambino, S.; Filardo, G.; Tiitta, M.; Sjöström, M.; Wold, S.; Berglind, R.;Karlsson, B. *Acta Chem. Scand.* **1991**, *45*, 987–992.

[20] C. Maret, N. David, D. Pierrot, E. Léonel, V. Levacher, J.-F. Brière, S. Oudeyer, *Molecules* **2023**, *28*, 6704

Highly Regioselective Metal-Free Arylation of Planar Chiral Sulfur-Based [2.2]Paracyclophanes

Warren Lhuillier,[1] Vincent Tognetti,[2] Annie-Claude Gaumont[1] and Stéphane Perrio[1]

[1] *Normandie Univ, ENSICAEN, UNICAEN, CNRS, LCMT, 14000 Caen, France*
[2] *COBRA laboratory, Normandie Univ, UNIROUEN, INSA Rouen, CNRS, 76000 Rouen, France*
warren.lhuillier@unicaen.fr

Keywords: [2.2]Paracyclophane; Sulfoxide; Sulfonium; Phenol; Pummerer; Arylation

Abstract: [2.2]paracyclophane ([2.2]PCP) is an original 3D carbon architecture consisting in two benzene rings opposite to each other and covalently linked at the *para* positions by CH_2–CH_2 groups.[1] [2.2]PCP derivatives are characterized by a high rigidity, strong π-π interactions and planar chirality (a single substituent is enough to have enantiomers). In the last few years, [2.2]PCP chemistry has progressed tremendously, in terms of functionalization and applications (bio- and materials science). However, examples of sulfur-containing building blocks remain scarce.

We wish to present in this communication an innovative and metal-free approach to functionalize, in a highly regioselective manner, planar chiral sulfur-based [2.2]paracyclophanes **(Figure 1)**.[2] The methodology we developed is based on the use of readily available [2.2]PCP sulfoxides[3] and phenols as starting materials. Under the conditions of an interrupted Pummerer reaction, an aryloxy sulfonium salt is generated and further isomerizes to form a [2.2]PCP–aryl bond. The optimization of the operating conditions, the study of the scope and limitations of the process will be highlighted. A mechanistic proposal, supported by theoretical calculations using DFT, will be also presented.[4]

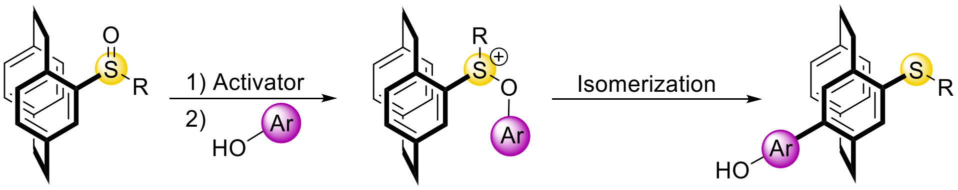


Figure 1 Reaction investigated from sulfinyl substituted [2.2]PCP in this study

References:

1.(a) Hassan, Z.; Spuling, E.; Knoll, D. M.; S. Bräse, *Angew. Chem. Int Ed.* **2020**, *59*, 2156–2170. (b) Weiland, K. J.; Gallego, A.; M. Mayor, *Eur. J. Org. Chem.* **2019**, 3073–3085.

2. For literature precedents, see for example: (a) Enders, M.; Friedmann, C. J.; Plessow, P. N.; Bihlmeier, A.; Nieger, M.; Klopper, W.; Bräse, S. *Chem. Commun.* **2015**, *51*, 4793–4795. (b) Rowlands, G.; Seacome, R. J. *Org. Biomol. Chem*. **2005,** *3*, 3873–3876**.**

3. Lohier, J.-F.; Foucoin, F.; Jaffrès, P.-A.; Garcia, J. I.; Sopková–de Oliveira Santos, J.; Perrio, S.; Metzner, P. *Org. Lett.* **2008**, *10*, 1271–1274.

4.(a) Yanagi,T.; Yorimistu, H. *Chem. Eur. J.* **2021**, *27*, 13450–13456. (b) Bisht, R.; Popescu, M. V.; He, Z.; Ibrahim, A. M.; Crisenza, G. E. M.; Paton, R. S.; Procter, D. J. *Angew. Chem. Int. Ed.* **2023**, e202302418.

Synthesis of Pyrano[2,3-c]pyrroles from vKAMAs

Mariia Savchuk,[1] Giang Vo-Thanh,[2] Sylvain Oudeyer,[1] Hélène Beucher[1] and Jean-François Brière[1]

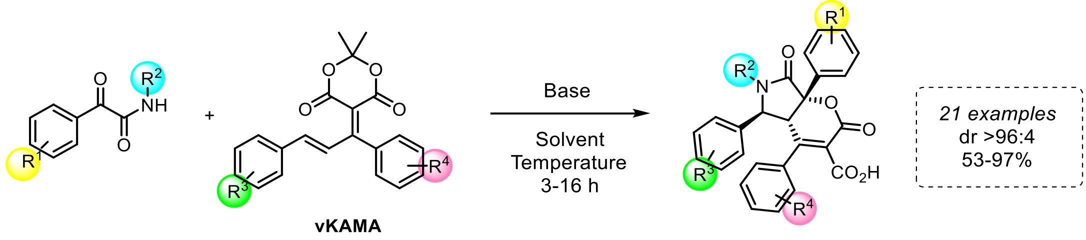
[1]INSA Rouen Normandie, Univ Rouen Normandie, CNRS, Normandie Univ, COBRA UMR 6014, INC3M FR 3038, F-76000 Rouen, France.
[2]Institut de Chimie Moléculaire et des Matériaux d'Orsay. CNRS UMR 8182, Université Paris Saclay, 91405 Orsay Cedex, France.

mariia.savchuk@univ-rouen.fr; https://www.lab-cobra.fr/equipes/heterocycles/

Keywords: Organic synthesis; Alkylidene Meldrum's acids (AMAs); Catalysis; Aza-Michael addition; Domino process; Vinylogy; Diastereoselectivity; Stereoselectivity; Cyclization

Abstract: Pyrrolidine is one of the most common heterocycle in organic synthesis and pharmaceuticals (more than 37 medicaments known).[1] Bicyclic pyrrolidines such as pyrano[2,3-c] pyrrole derivatives are valuable molecules, because of their conformational restriction may be useful for better bio-target interections (Scheme below).[2] On the other hand, vinylogous ketone-derived alkylidene Meldrum's acids (vKAMA) proved to be versatile platform molecules involved in the various 1,6-conjugate additions involving C-C bond formation, and were recently applied in the thio-Michael addition reaction by our group to obtain thiochromanes.[3] Thus, we decided to challenge the aza-Vinylogue-Michael-Aldol-Cyclocondensation (aza-VMAC) reaction with α-ketamides as readily available substrates to lead to an unprecedented C-N bond formation with this type of substrate.

To our delight, the vKAMAs showed an excellent performance in the aza-VMAC reaction affording a new entry to pyrano[2,3-c]pyrrole derivatives, encompassing the relative control of three contiguous stereocenters in an excellent diastereoselectivity and good to excellent yields (21 examples, 53-97% isolated yields, >96:4 dr).[4]



Domino aza-VMAC reaction with vKAMAs

References:
1. Taylor, R.D.; MacCoss, M.; Lawson, D.J. *J. Med. Chem.* **2014**, 5845–5859.
2. Savych, A.; Mykhalchuk, V.; Melnychuk, P.; Isakov, A.; Savchuk, T.; Timoshenko, V.; Siry, S.; Pavlenko, S.; Kovalenko, D.; Hryshchuk, O.; Reznik, V.; Chalyk, B.; Yarmolchuk, V.; Rusanov, E.; Mykhailiuk, P. *J. Org. Chem.* **2021**, 13289–13309.
3. Milbeo, P.; Lebrêne, A.; Savchuk, M.; Vo-Thanh, G.; Oudeyer, S.; Beucher, H.; Brière, J.-F. *Chem. Eur. J.* **2023**, 29, e202301311.
4. Savchuk, M.; Vo-Thanh, G.; Oudeyer, S.; Beucher, H.; Brière, J.-F. *Org. Biomol. Chem.* **2024**, 2948-2952.

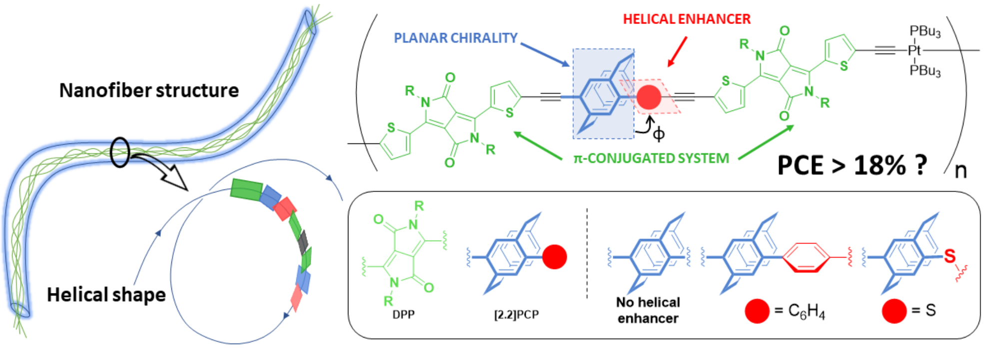
[2.2]Paracyclophane-based Stereoregular [Pt] Conjugated Oligomers for Solar Cells Applications

Arthur LE COZ,[1] Pierre D. HARVEY,[2] Ganesh D. SHARMA,[3] Cyprien LEMOUCHI,[1] Stéphane PERRIO[1]

[1] Normandie Univ, ENSICAEN, UNICAEN, CNRS, LCMT, 14000 Caen, France
[2]Département de Chimie, Université de Sherbrooke, 2550 Boulevard de l'Université, Sherbrooke, Quebec, Canada
[3]Department of Physics, The LNM Institute of Information Technology, Jamdoli, Jaipur, Rajasthan 302031, India
arthur.le-coz@ensicaen.fr

Keywords: [2.2]paracyclophane; [Pt]-oligomers; planar chirality; helicity; solar cells

Abstract: Organic solar cells offer a number of advantages light weight and a good flexibility. However, their power conversion efficiencies (PCE) are still well below those of silicon-based cells (PCE 25-26%).[1] Platinum oligomers are suitable donors, mixed with an acceptor, a PCE off 15% have been achieved, close to international record of 19.2% reached with conjugated polymers.[2] Their performance can be improved (objective, PCE > 18%) by preparing fiber-shaped stereoregular [Pt]-oligomers to promote charge transport and nanosegregation of the active layer. By now, none fiber have been obtained with [Pt]-oligomers, the aim of our work is to promote their formation with the insertion of a planar chiral [2.2]paracyclophane ([2.2]PCP) platform[3] in diketopyrrolopyrrole (DPP) containing conjugated ligand. The use of enantiomerically pure [2.2]PCP should produce the first stereoregular [Pt]-oligomers, while the insertion of a helical enhancer should increase the dihedral angle (ϕ) and promote helicoidal structure for the preparation of the fibers. Initial results, including the synthesis aspects and first target characterizations, will be presented in this communication.



References:

1. Yoshikawa, K.; Kawasaki, H.; Yoshida, W.; Irie, T.; Konishi, K.; Nakano, K.; Uto, T.; Adachi, D.; Kanematsu, M.; Uzu, H.; Yamamoto, K. *Nature Energy* **2017**, *2*, 17032.
2. Qassab, M.; Lohier, J.-F.; Marineau-Plante, G.; Wayzani, A. A.; Herbinet, R.; Durandetti, M.; Hardouin, J.; Karsenti, P.-L.; Pluart, L. L.; Harvey, P. D.; Lemouchi, C.; Sharma, G. D. *ACS Appl. Energy Mater.* **2023**, *6*, 12452–12467.
3. Lohier, J.-F.; Foucoin, F.; Jaffrès, P.-A.; Garcia, J. I.; Sopková–de Oliveira Santos, J.; Perrio, S.; Metzner, P. *Org. Lett.* **2008**, *10*, 1271–1274.

P-19

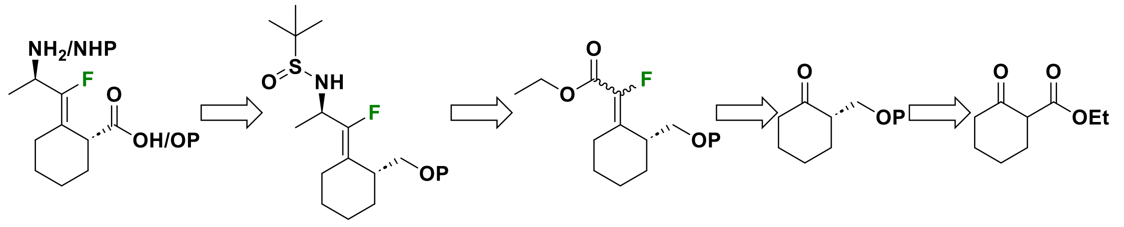
Synthesis of a Novel Fluorinated Pseudodipeptide

Frédérique Parfait[1], Soma Keszei[2], David Aitken[3], Thomas Castanheiro[1*], Samuel Couve-Bonnaire[1*]

[1] *COBRA UMR 6014, Univ Rouen Normandie, INSA Rouen Normandie, CNRS, Normandie Univ, 76000 Rouen, France*
[2] *Nanostructures Department, Centre for Energy Research, Konkoly-Thege Miklós út 29-33, H-1121, Budapest, Hungary*
[3] *ICMMO UMR 8182, Université Paris-Saclay, CNRS, 91400 Orsay, France*
*thomas.castanheiro-matias@univ-rouen.fr; samuel.couve-bonnaire@insa-rouen.fr
www.lab-cobra.fr

Keywords: fluoroalkene; peptide; multistep synthesis; foldamer

Abstract: Fluorine chemistry has been extensively studied for decades, due to its wide set of applications (medicinal chemistry, medical imaging, materials, agrochemicals…). In this context, fluoroolefins have proven to be good mimics of the peptide bond, owing to their similar steric and electronic properties.[1] The strength of the C–F bond also imparts a better stability (i.e., towards peptide cleavage and isomerisation). Fluoropeptidomimetics have been synthesised using various methods[2] and have a broad range of applications such as bioactive substances (e.g., anti-cancer agents).[1b] Although the folding of oligomers of these pseudopeptides into well-defined three-dimensional structures (foldamers) has been studied for *γ*-peptides and theoretical studies on *δ*-peptides have been carried out[3], however no experimental studies of *δ*-peptide foldamers has been reported to date, up to our knowledge. Therefore, herein, we report the synthesis of a novel *δ*-pseudodipeptide, whose foldamer studies are underway.



P = Protecting group 1 2 3 4

Figure 1 Retrosynthetic pathway for the synthesis of a novel *δ*-pseudodipetide

References:

1. a) Meanwell, N. A. *J. Med. Chem.* **2018**, *61* (14), 5822–5880. b) Osada, S.; Sano, S.; Ueyama, M.; Chuman, Y.; Kodama, H.; Sakaguchi, K. *Bioorganic & Medicinal Chemistry* **2010**, *18* (2), 605–611.
2. a) Pierry, C.; Couve-Bonnaire, S.; Guilhaudis, L.; Neveu, C.; Marotte, A.; Lefranc, B.; Cahard, D.; Ségalas-Milazzo, I.; Leprince, J.; Pannecoucke, X. *ChemBioChem* **2013**, *14* (13), 1620–1633. b) Villiers, E.; Couve-Bonnaire, S.; Cahard, D.; Pannecoucke, X. *Tetrahedron* **2015**, *71* (38), 7054–7062.
3. a) Legrand, B.; Maillard, L. T. *ChemPlusChem* **2021**, *86* (4), 629–645. b) Baldauf, C.; Günther, R.; Hofmann, H.-J. *J. Org. Chem.* **2004**, *69* (19), 6214–6220.

P-20

Terminal Alkyne Carboxylation via Mechanocatalysis under Reactive CO_2 Atmosphere

Sawssen Nasri, Anne Ponchel, and Stéphane Menuel

Univ. Artois, CNRS, Centrale Lille, Univ. Lille, UMR 8181, Unité de Catalyse et Chimie du Solide (UCCS)
rue Jean Souvraz, SP 18, 62300 Lens, France

sawssen.nasri@univ-artois.fr

Keywords: mechanochemistry, catalysis, carboxylation

Abstract: In the context of reducing the energy and environmental impact of organic chemistry processes, mechanochemistry emerges as a promising alternative[1]. Mechanochemistry involves the use of mechanical energy to activate a chemical reaction. Energy is supplied by moving beads (vibratory mills or planetary mills). Furthermore, mechanochemistry enables solvent-free reactions with significant reductions in reaction times[2].

The carboxylation of unsaturated compounds via mechano-catalysis under a reactive CO_2 atmosphere holds significant promise for the valorization of synthons and the synthesis of high-value carbonyl compounds[3]. Additionally, the direct carboxylation of aromatic compounds aligns with the approach of CO_2 valorization by utilizing it as a carbon source through the development of eco-friendly technologies. (Figure 1)

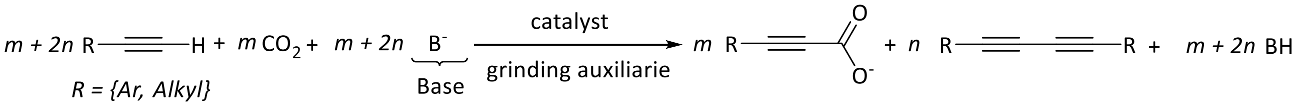


***Figure 1** carboxylation and carbon-carbon coupling are competing reactions in this study*

We will present the results obtained using phenylacetylene as a model substrate. We will demonstrate the significance of grinding auxiliaries on the obtained results. We will discuss the mechanical influence of grinding auxiliaries, particularly auxiliaries on the catalyst reactivity as well as the selectivity of the obtained products. Additionally, we will present the impact of grinding on the abrasion phenomena of reactors and beads.

References:

1. S. L. James, C. J. Adams, C. Bolm, D. Braga, P. Collier, T. Friščić, F. Grepioni, K. D. M. Harris, G. Hyett, W. Jones, A. Krebs, J. Mack, L. Maini, A. G. Orpen, I. P. Parkin, W. C. Shearouse, J. W. Steed, D. C. Waddell, *Chem. Soc. Rev.* **2012**, *41*, 413–447. DOI: 10.1039/C1CS15171A.
2. S. Menuel, B. Doumert, S. Saitzek, A. Ponchel, L. Delevoye, E. Monflier, F. Hapiot, *J. Org. Chem.* **2015**, *80*, 6259–6266. DOI: 10.1021/acs.joc.5b00697.
3. I I. C. Tommasi, *Catalysts* **2019**, *9*, DOI 10.3390/catal9010037. DOI: 10.3390/catal9010037

Iron Homogenous Catalysis for a suitable polyols valorization

Fabian Cuffel, Antoine Lancien, Sébastien Comesse* and Laure Benhamou*

URCOM, Normandy Le Havre University (UNILEHAVRE FR 3038 CNRS), Le Havre, France

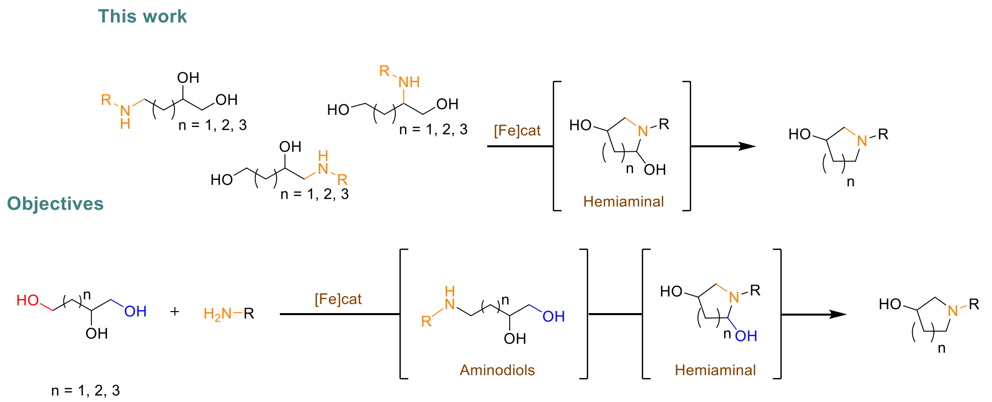
Fabian.Cuffel@univ-lehavre.fr

Keywords: Catalysis, hydrogen borrowing, Iron.

Abstract: Polyols valorization traditionally relies in a protection/deprotection strategies. Despites its bio-sourced origin, those methods bring many wastes and are not optimum. As a solution, our group recently developed a straightforward catalytic method for the selective oxidation of polyols using Iron Complex leading to lactones.

This method leans on the Iron complex capacity to do Hydrogen Borrowing. In 2014, Barta et al. demonstrate the possibility to do reductive amination of an alcohol using Iron Complex, having water as the exclusive side product[1]. Recently, a polyol (1,2,4-butantriol) has been cyclized with aromatic amines using Ruthenium Complex[2].

We are developing a method to understand and optimize the reductive amination of aminopolyols using Iron Complex. This preliminary work opens the way to iminosugars formation using Iron Homogenous Catalysis on polyols. Noticing that iminosugars are broadly represented in pharmaceuticals industry.



References:

1. Tao Yan; Tao Yan; Yan, T.; Feringa, B.; Bernard Feringa; Feringa, B.; Barta, K. *Nature Communications* **2014**, 5 (1), 5602.
2. Xu, Q.-S.; Li, C.; Xu, Y.; Xu, D.; Shen, M.-H.; Xu, H.-D. *Chinese Chemical Letters* **2020**, 31 (1), 103–106.

P-22

Adsorption and immobilization of cesium and strontium ions on zeolites synthesized from brick residues

Gildas Doyemet (1,2), Nicole Poumaye [2], Baghdad Ouddane[1], Oscar Allahdin (1,2), Abdel Boughriet [1] and Michel Wartel[1]

[1] *Université de Lille, Faculté des Sciences, CNRS, UMR 8516-LASIRE, Laboratoire Avancé de Spectroscopie pour les Interactions, la Réactivité et l'Environnement F-59000 Lille, France*

[2] *Université de Bangui, Faculté des Sciences, Chaire Unesco sur la Gestion de l'eau», Laboratoire Hydrosciences Lavoisier, B.P. 908, Bangui, Central African Republic*

Keywords: Brick, zeolites, Adsorption, immobilization, cesium and strontium

Abstract: The aim of this work was to study the adsorption of radioactive ions from their stable isotope (caesium and strontium) on brick residues whose metakaolinite has been transformed into zeolites by reaction with sodium hydroxide, as well as the immobilization of these cations on the adsorbent after heat treatment. Column adsorption and kinetic studies of Cs+ and Sr^{2+} ions on the adsorbent (zeolite-activated brick) were carried out. Column adsorption results were interpreted according to the Thomas model, and kinetic results were interpreted according to the Weber and Morris model. Ion immobilization was achieved by vitrification of the composite after heat treatment (600°C, 800°C and 1000°C) followed by acid leaching (HCl, 1mol/L) to assess the stability of the fixed metal. The results obtained show that adsorption onto zeolites takes place via the departure of the sodium constituting the zeolites: the amount of sodium released is proportional to the valency of the cation to be eliminated. The amount of strontium (37%) eliminated is greater than that of caesium (27%), although the rate of caesium uptake is greater than that of strontium. Next, leaching results show that Cs+ cations are more stable than Sr2+ cations when the composite is calcined at 1000°C. Finally, SEM-EDS images show a morphological transformation of zeolites proportional to calcination temperature. Studies by DRX, SIMs and NMR are currently underway to characterize the calcined complex (composite-metal).

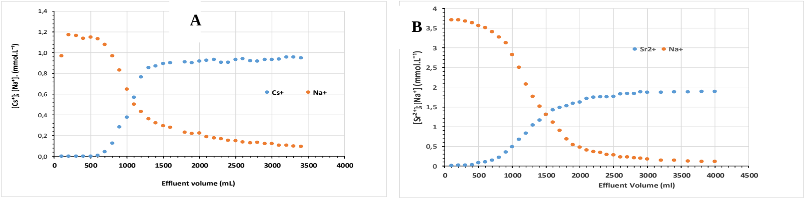


Figure : Adsorption mechanism of cesium(A) and strontium (B ions by zeolites synthesized from brick residues

References

1. Sama M. Al-Jubouri, Stuart M. Holmes Immobilization of cobalt ions using hierarchically porous 4A zeolite-based carbon composites: Ion-exchange and solidification, jwpe 33 (2020) 101059, https://doi.org/10.1016/j.jwpe.2019.101059
2. Jain, S.; Banthia, N.; Troczynski, T. Leaching of immobilized cesium from NaOH-activated fly ash-based geopolymers. Cem. Concr. Compos. 2022, 133, 104679.

P-23

Measurement of lactate and pyruvate in cells using LC-MS/MS

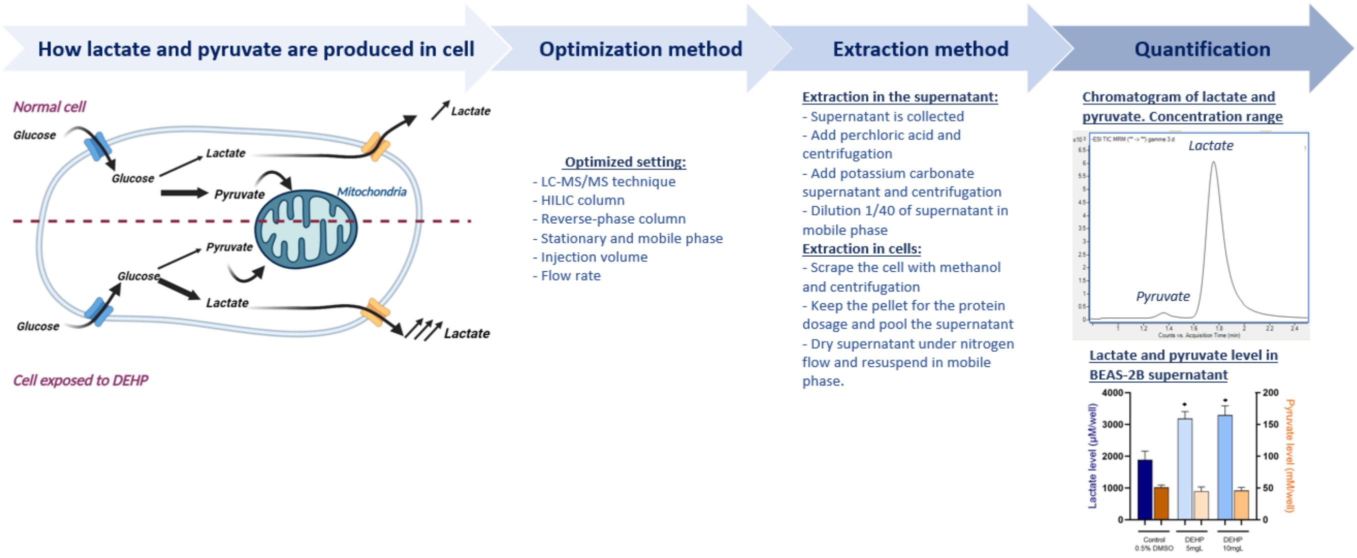
Lyse Szymanski[1], Margueritta Al Zallouha[1], Edwige Votier[1], Christelle Monteil[1] and Tiphaine Rogez-Florent[1]

[1] *Univ Rouen Normandie, Université Caen Normandie, Normandie Univ, ABTE UR 4651, F-76000 Rouen, France*
lyse.szymanski@univ-rouen.fr

Keywords: LC-MS/MS; Lactate; Pyruvate; HILIC; Validation, Metabolic

Abstract: Lactate and pyruvate are metabolites of interest used as indicators of the metabolic status of cells. Existing techniques to quantify these metabolites are based on colorimetric assays. However, commercially available kits are expensive for an application on a large number of samples. A new Liquid Chromatography-tandem mass spectrometry (LC-MS/MS) method for the simultaneous quantitative analysis of lactate and pyruvate was optimized and validated. To measure analytes such as lactate and pyruvate, hydrophilic interaction liquid chromatography (HILIC) and reversed-phased chromatographic were evaluated. Many parameters were optimized: the stationary phase, the mobile phase, the injection volume, the flow rate. The developed technique was applied to extract and quantify these two analytes after human bronchial epithelial cells (BEAS-2B) exposure to pollutants. The average concentrations of extracellular lactate and pyruvate in BEAS-2B were 2.02 mM and 59 µM respectively.

Figure 1: Graphical abstract



Optimized setting:
- LC-MS/MS technique
- HILIC column
- Reverse-phase column
- Stationary and mobile phase
- Injection volume
- Flow rate

Extraction in the supernatant:
- Supernatant is collected
- Add perchloric acid and centrifugation
- Add potassium carbonate supernatant and centrifugation
- Dilution 1/40 of supernatant in mobile phase

Extraction in cells:
- Scrape the cell with methanol and centrifugation
- Keep the pellet for the protein dosage and pool the supernatant
- Dry supernatant under nitrogen flow and resuspend in mobile phase.

Chromatogram of lactate and pyruvate. Concentration range

Lactate and pyruvate level in BEAS-2B supernatant

Atmospheric fate of Myrtenal: study at the single particle scale

Jad Baltaji, Myriam Moreau, Yeny Tobon,

Univ. Lille, CNRS, UMR 8516-LASIRE– Laboratoire de Spectroscopie pour Les Interactions, La Réactivité et L'Environnement, F-59000, Lille, France.[2]Lasire, University Lille, Lille, France
…
jad.baltaji.etu@univ-lille.fr

Keywords: myrtenal; atmospheric aerosols, single particles, atmospheric chemistry.

Abstract: Terpenes are abundantly emitted from vegetation into the troposphere. They react readily with atmospheric species, such as H_2O, ozone, OH, and NO_3 radicals, and with light, resulting in several first-generation terpene oxidation products (FGTOP).[1] These products, having a brief existence in the atmosphere, swiftly undergo oxidation reactions, generating secondary oxidation products.[2] In this context, we present the research conducted on Myrtenal, a FGTOPgenerated mainly from the oxidation of α-pinene[1]. The gas phase reaction of some atmospheric species with myrtenal has been addressed in the literature[1,2]. However, studies on the chemical behavior of myrtenal in the condensed phase are lacking in the literature. This study intends to understand the behavior of single droplets containing myrtenal when particles are exposed to various environmental circumstances. To observe their behavior, we employed an innovative setup combining an acoustic levitation system with a Raman microspectrometer that includes a high-speed video camera (figure 1). This allowed us to monitor the changes in particle composition and morphology over time as the reactions progressed. Research on myrtenal revealed significant differences in reactivity between individual particles and bulk conditions. Additionally, we investigated the hygroscopic properties of the particles before and after reactions. Interestingly, the products formed from myrtenal oxidation did not alter the particles' hygroscopicity.

References:
Mutzel, A., Rodigast, M., Iinuma, Y., Böge, O., Herrmann, H., *Atm. Env.* **2016.** 130, 136-144.
Fakih, M., Roth, E., Tomas, A., Chakir, A., *Int. J. Chem. Kin*. **2023**. *55,* 751-759

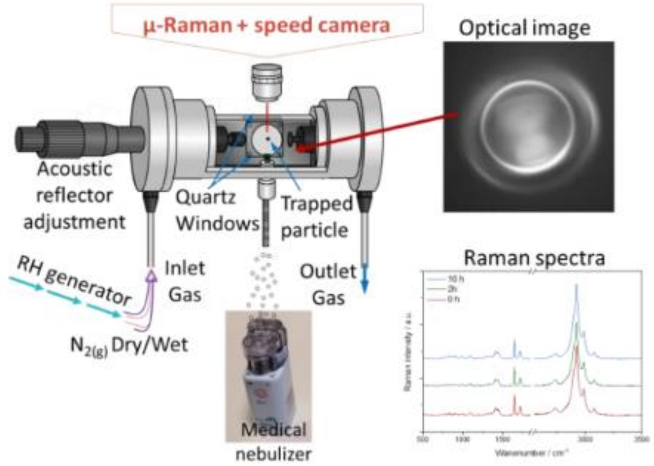


Figure 1 Schematic illustration of the environmental acoustic levitation cell coupled to

P-25

Electrochemical carbo-alkoxy-functionalization of 1,3-dienes

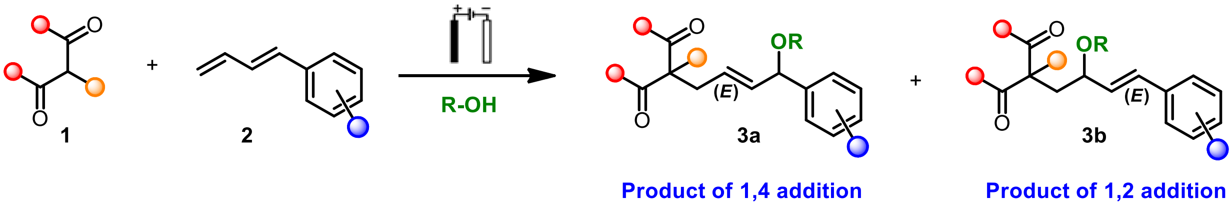
Ophélie Montiège,[1] Marion Siccardi,[1] Hélène Beucher,[1] Jean-François Brière,[1] Cédric Schneider[1]

[1]*INSA Rouen Normandie, Univ Rouen Normandie, CNRS, Normandie Univ, COBRA UMR 6014, INC3M FR 3038, F-76000 Rouen, France.*
Ophelie.Montiege@insa-rouen.fr, https://www.lab-cobra.fr/equipes/heterocycles

Keywords: Carbo-alkoxy-functionalization; 1,3-dienes; 1,3-dicarbonyls; radical-polar crossover reaction; metal-free; electrochemistry, MCR.

Abstract: From an economic and environmental perspective, the development of efficient reaction for the synthesis of structurally complex architectures through the difunctionalization of 1,3-dienes has attracted increasing interest of the industrial and academic communities.[1] Whereas the development of a radical cascade process has emerged as a powerful tool for the difunctionalization of 1,3-dienes, this strategy under electrochemical conditions and metal free remains limited to only few examples[2] and represents a major challenge in synthetic organic chemistry.

In this context (Scheme below), we report here a novel, metal-free, oxidant-free and electro-mediated methodology for the regio- and stereoselective carbo-alkoxy-functionalization of 1,3-dienes, which provides an eco-efficient multicomponent reaction (MCR) towards various valuable (*E*)-polyfunctionalized alkene products. More than 25 compounds have been synthesized with a regioselectivity for the 1,4 adduct reaching up to 95:5. The method exhibits a great tolerance towards functional groups, when starting with substituted-1,3-dicarbonyls **1** and dienes **2** substrates.



27 examples synthesized
Ratio (1,4 addition : 1,2 addition) up to 95:5

Electrochemical carbo-alkoxy-functionalization of 1,3-dienes.

References:

1. a) Wu Zhengxing, Z. W. *Chin. J. Org. Chem.* **2017**, *37*, 2250. b) Xiong, Y.; Sun, Y.; Zhang, G. *Tetrahedron Lett.* **2018**, *59*, 347. c) Herrmann, N.; Vogelsang, D.; Behr, A.; Seidensticker, T. *ChemCatChem* **2018**, *10*, 5342. d) Wu, X.; Gong, L.-Z. *Synthesis* **2019**, *51*, 122. e) Huang, H.-M.; Garduño-Castro, M. H.; Morrill, C.; Procter, D. J. *Chem. Soc. Rev.* **2019**, *48*, 4626. f) Li, G.; Huo, X.; Jiang, X.; Zhang, W. *Chem. Soc. Rev.* **2020**, *49*, 2060.

2. a) Zhang, H.; Guo, L.; Yang, C.; Xia, W. *Synthesis* **2023**, *55*, 3033. b) Sheta, A. M.; Mashaly, M. A.; Said, S. B.; Elmorsy, S. S.; Malkov, A. V.; Buckley, B. R. *Chem. Sci.* **2020**, *11*, 9109. c) Ren, S.-Y.; Zhou, Q.; Zhou, H.-Y.; Wang, L.-W.; Mulina, O. M.; Paveliev, S. A.; Tang, H.-T.; Terent'ev, A. O.; Pan, Y.-M.; Meng, X.-J. *J. Org. Chem.* **2023**, *88*, 5760.

Liste des participants

	Nom	Prénom	Adresse e-mail
1	Achour	Roukaya	Roukaya.achour1@centralelille.fr
2	Alameddine	Souraya	souraya.alameddine@insa-rouen.fr
3	Alameri	Abdulrahman	Abdulrahman.alameri.etu@univ-lille.fr
4	Almasri	Bayan	bayan.almasri1234@gmail.com
5	Antoine	Méline	meline.ac@free.fr
6	Baltaji	Jad	jad.baltaji.etu@univ-lille.fr
7	Batista Peguero	Patricia	patricia.batista@insa-rouen.fr
8	Bazille	Djemel-Dine	djemel-dine.bazille@insa-rouen.fr
9	Benmammar	Rachida	rachida.benmammar@univ-lille.fr
10	Bigard	Edma	edma.bigard@ensicaen.fr
11	Biniek	Laure	laure.biniek@ics-cnrs.unistra.fr
12	Bonnet	Véronique	veronique.bonnet@u-picardie.fr
13	Bousselat	Ava	ava.bousselat@ensicaen.fr
14	Bouvier	Elena	elena.bouvier1@univ-rouen.fr
15	Brière	Jean-François	jean-françois.briere@insa-rouen.fr
16	Brocardo Ferreir	Bruna	bbrocardoferreira@insa-rouen.fr
17	Burel	Fabrice	fabrice.burel@insa-rouen.fr
18	Chailly	Ludvina	ludvina.chailly@insa-rouen.fr
19	Colombani	Olivier	Olivier.Colombani@univ-lemans.fr
20	Cormier	Gabriel	gabriel.cormier@universite-paris-saclay.fr
21	Cuffel	Fabian	Fabian.Cuffel@univ-lehavre.fr
22	Dalla	Vincent	vincent.dalla@univ-lehavre.fr
23	David	Nicolas	nicolas.david@insa-rouen.fr
24	Decourval	Flavien	flavien.decourval@ensicaen.fr
25	Delacotte	Emma	emmadelacotte15@gmail.com
26	Delaporte	Adeline	adeline.delaporte@doct.univ-lehavre.com
27	Delegue	Louis	louis.delegue.etu@univ-lille.fr
28	Delort	Geoffrey	geoffrey.delort@insa-rouen.fr
29	Demily	Guillaume	guillaume_demily@ens.univ-artois.fr
30	Desilles	Nicola	nicolas.desilles@insa-rouen.fr
31	Dez	Isabelle	isabelle.dez@unicaen.fr
32	Ding	Bao	bao.ding@insa-rouen.fr
33	Doyemet	Gildas	gildasgaelgervil.doyemet.etu@univ-lille.fr
34	Duarte Serrano	Daniela	daniela.duarte.serrano@u-picardie.fr
35	Elmouhinni	Mohamed	mohamed.elmouhinni@u-picardie.fr
36	Fabrizi	Isabelle	Isabelle.fabrizi.etu@univ-lille.fr
37	Fensterbank	Louis	louis.fensterbank@college-de-france.fr
	Nom	**Prénom**	**Adresse e-mail**

38	Fratoddi	Ilaria	ilaria.fratoddi@uniroma1.it
39	Gemelli	Giulia	giulia.gemelli.etu@univ-lille.fr
40	Harb	Jana	Jana.Harb@univ-lemans.fr
41	Henn	Mathieu	mathieu.henn.etu@univ-lille.fr
42	Herrera	Vincent	vincent.herrera@insa-rouen.fr
43	Jastak	Klara	klara.jastak@insa-rouen.fr
44	Kebir	Nasreddine	nasreddine.kebir@insa-rouen.fr
45	Khol	Bator	bator.khol@univ-artois.fr
46	Kichibayov	Azad	a.kichibayov@ufaz.az
47	Le Coz	Arthur	arthur.le-coz@ensicaen.fr
48	Le Pluart	Loic	loic.le_pluart@ensicaen.fr
49	Lecamp	Laurence	laurence.lecamp@insa-rouen.fr
50	Lhuillier	Warren	warren.lhuillier@unicaen.fr
51	Lopes	Chrystal	chrystal.lopes1@univ-rouen.fr
52	Montembault	Veronique	veronique.montembault@univ-lemans.fr
53	Montiege	Ophélie	Ophelie.Montiege@insa-rouen.fr
54	Morandi	Gaëlle	gaelle.morandi@insa-rouen.fr
55	Moustapha	Mahamat Tahir	Mahamat_tahir.moustapha.etu@univ-lemans.fr
56	Muyronova	Veronika	veronika.myronova@univ-rouen.fr
57	Nasri	Sawssen	sawssen.nasri@univ-artois.fr
58	Nguyen	Thi Mo	thi-mo.nguyen@univ-rouen.fr
59	Nunez	Luis	luis.nunez@insa-rouen.fr
60	OREVE	Vincent	vincent.oreve1@univ-rouen.fr
61	Otuszewski	Pierre	pierre.otuszewski.etu@univ-lille.fr
62	Palio	Laurenzo	lorenzo.palio@univ-lille.fr
63	Parfait	Frédérique	frederic.parfait@insa-rouen.fr
64	Perrio	Stéphane	stephane.perrio@unicaen.fr
65	Perrot	Alexis	alexis.perrot@ensicaen.fr
66	Renault	Julien	julien.renault@ensicaen.fr
67	Riaz	Qurat-Ui-Ain	quratulain.riaz.etu@univ-lille.fr
68	Richard	Floriane	floriane.rischard@doct.univ-lehavre.fr
69	Rieger	Jutta	jutta.rieger@sorbonne-universite.fr
70	Savchuk	Mariia	mariia.savchuk@univ-rouen.fr
71	Seaali	Bochra	ochra.seaali@cnrs-orleans.fr
72	Sensan	Tharin	tharin.sensan.etu@univ-lemans.fr
73	Sinturel	Christophe	christophe.sinturel@univ-orleans.fr
74	Szymanski	Lyse	lyse.szymanski@univ-rouen.fr
75	Vaillant	Maxime	maxime.vaillant@ensicaen.fr
76	Verger	Marine	marine_verger@ens.univ-artois.fr
77	Weber	Zoé	zoe.weber@insa-rouen.fr
78	Yu	Xinlong	liwenxu@hznu.edu.cn
79	Zerini	Hadjer Asmaa	zerinihadjer@gmail.com
	Nom	**Prénom**	**Adresse e-mail**

80	Zguir	Rihab	Rihab.Zguir.Etu@univ-lemans.fr
81	Zoghlami	Wala	wala.zoghlami.etu@univ-lille.fr

Comité d’organisation

Nom	Prénom	Adresse e-mail
Bouillon	Jean-Philippe	jean-philippe.bouillon@univ-rouen.fr
Castanheiro-matias	Thomas	thomas.castanheiro-matias@univ-rouen.fr
Deniau	Elise	Elise.Deniau@univ-lemans.fr
Follain	Nadege	nadege.follain@univ-rouen.fr
Gaillard	Sylvain	sylvain.gaillard@ensicaen.fr
Guillet	Remy	remy.guillet-nicolas@ensicaen.fr
Hespel	Louise	louise.hespel@univ-rouen.fr
Lemouchi	Cyprien	cyprien.lemouchi@ensicaen.fr
Lepoittevin	Benedicte	benedicte.lepoittevin@ensicaen.fr
Rogez	Thiphaine	tiphaine.rogez@univ-rouen.fr
Vuluga	Daniela	daniela.vuluga@insa-rouen.fr