

MASTER DE CHIMIE DE PARIS CENTRE - M2S2

Proposition de stage 2020-2021

Internship Proposal 2020-2021

Parcours type(s) / Specialty(ies) :

- Chimie Analytique, Physique et Théorique / *Analytical, Physical and Theoretical Chemistry* :
- Chimie Moléculaire / *Molecular Chemistry* :
- Chimie et Sciences Du Vivant / *Chemistry and Life Sciences* :
- Chimie des Matériaux / *Materials Chemistry*:
- Ingénierie Chimique / *Chemical Engineering*:

Laboratoire d'accueil / Host Institution

Intitulés / *Name* : Institut Parisien de Chimie Moléculaire (IPCM), UMR 8232

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Directeur / *Director (legal representative)* : Louis Fensterbank

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Equipe d'accueil / Hosting Team : Equipe Chimie des Polymères

Adresse / *Address* : tour 43-53, 5^{ème} étage, 4 place Jussieu, Paris

Responsable équipe / *Team leader* : Laurent BOUTEILLER

Site Web / *Web site* : <http://www.ipcm.fr>

Responsable du stage (encadrant) / *Direct Supervisor* : Matthieu RAYNAL

Fonction / *Position* : Chargé de Recherche

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Période de stage / *Internship period* : janvier-juin ou juillet 2021

Asymmetric catalysis with minute amount of chiral species

Projet scientifique (1 page maximum) / Scientific Project (maximum 1 page):

1. Description du projet / *Description of the project*

The preparation of enantiopure compounds from achiral feedstock with minute amount of chiral species is a topic of considerable interest in chemical sciences given its connexion with the emergence of homochirality on Earth and its potential applications for the elaboration of synthetic methods. A fundamental requirement for addressing this challenge is to design helical assemblies possessing extremely high chirality amplification properties. Here, chirality amplification refers to the control of the main chain helicity of the macro/supramolecule by means of cooperative (minute) conformational biases induced by the monomers. It can notably be achieved by a minor amount of a chiral monomers able to impose their preferred handedness to an excess of achiral monomers. The incorporation of catalytic sites on extremely chirally amplified helical assemblies may allow the preparation of any types of enantiopure compounds with a minute amount of chiral monomers or inducers (see figure).⁽¹⁾

* min. 5 mois à partir du 18 janv 2021 / *min. 5 months not earlier than January, 18th 2021.*

Fin de stage au plus tard le 16/07/2021 ou le 30/09/2021 (dates de validation de diplôme). / *End of internship at the latest July 16, 2021 or Sept. 30, 2021 (dates of graduation).*

Our team has a strong expertise in the preparation and characterization of hydrogen-bonded supramolecular polymers. The monomers are structurally-simple and easily functionalizable as they contain a central aromatic ring connected to three urea^[2] or amide^[3] groups. We recently located metallic centres at the periphery of a chiral supramolecular polymer. The chirality is efficiently transferred to the intrinsically achiral metal centres and to the product of the catalysis.^[4-6] The aim of this project is to improve the chirality amplification properties of the helices supporting the catalytic sites. It can be envisaged by finely tuning the structure of the monomers.

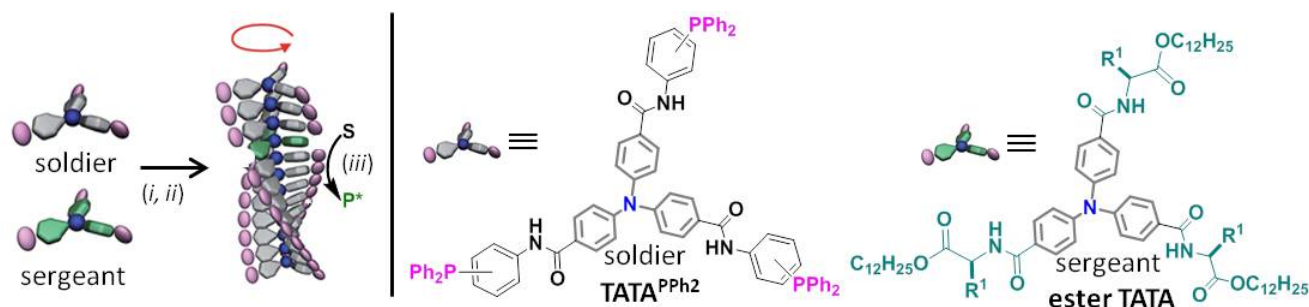


Figure Left: schematic representation of highly chirally amplified helices supporting catalytic sites: (i) co-assembly between catalytic active achiral monomers and enantiopure monomers, (ii) formation of a homochiral helix through chirality amplification and (iii) asymmetric reaction. Right: chemical structures of the monomers.

2. Techniques ou méthodes utilisées / *Specific techniques or methods*

The project will contain the following tasks: (1) the synthesis of the monomers, (2) their evaluation in a catalytic reaction of reference, and (3) the correlation of the catalytic results with the structure of the supramolecular assemblies by means of various characterization techniques (FT-IR, viscosimetry, circular dichroism, small angle neutron scattering, calorimetry).

3. Références / *References*

- [1] "Catalysts supported by homochiral molecular helices: a new concept to implement asymmetric amplification in catalytic science."
Y. Li, L. Bouteiller, M. Raynal **ChemCatChem** 11, 5212, **2019**.
- [2] "Assembly via hydrogen bonds of low molar mass compounds into supramolecular polymers."
L. Bouteiller **Adv. Polym. Sci.** 207, 79, **2007**.
- [3] "Benzene-1,3,5-tricarboxamide: a versatile ordering moiety for supramolecular chemistry."
S. Cantekin, T. F. A. de Greef and A. R. A. Palmans **Chem. Soc. Rev.** 41, 6125, **2012**.
- [4] "Tunable asymmetric catalysis through ligand stacking in chiral rigid rods."
M. Raynal, F. Portier, P. W. N. M. van Leeuwen, L. Bouteiller **J. Am. Chem. Soc.** 135, 17687, **2013**.
- [5] "Correlation between the selectivity and the structure of an asymmetric catalyst built on a chirally amplified supramolecular helical scaffold."
A. Desmarchelier, X. Caumes, M. Raynal, A. Vidal-Ferran, P. W. N. M. van Leeuwen, L. Bouteiller **J. Am. Chem. Soc.** 138, 4908, **2016**.
- [6] "Emergence of homochiral benzene-1,3,5-tricarboxamide helical assemblies and catalysts upon addition of an achiral monomer."
Y. Li, A. Ahmoud, L. Bouteiller, M. Raynal **J. Am. Chem. Soc.** 142, 5676, **2020**.