

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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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 supramolecular polymers composed of achiral monomers

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

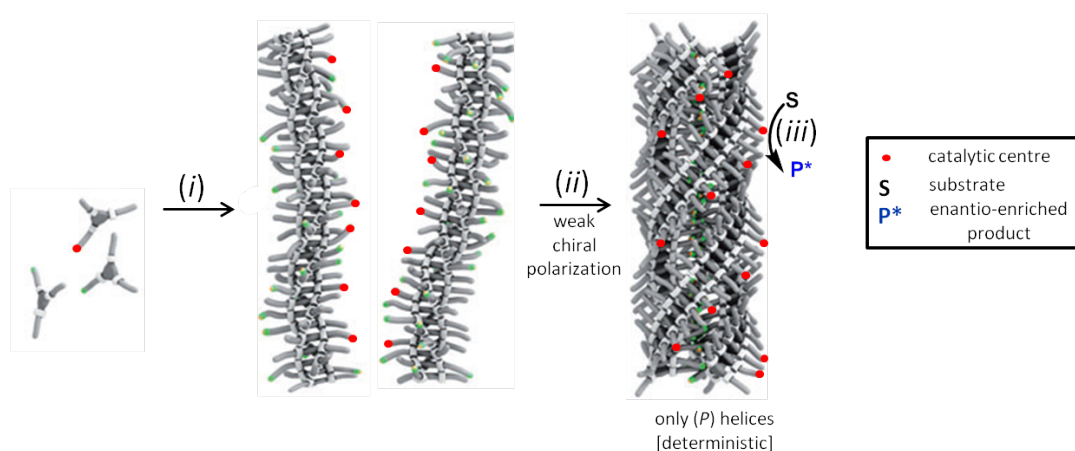
1. Description du projet / *Description of the project*

Asymmetric catalysis is the privileged route towards enantiopure compounds. The classical methods involve an enantiopure ligand (in metal catalysis) or an organic molecule (in organocatalysis) to induce a chiral bias to the chemical reaction. An obvious breakthrough would be to perform asymmetric catalysis without any chiral species in a rational manner. Recent work demonstrates that chiral assemblies, and notably supramolecular polymers, can be obtained from racemic or achiral molecules. Supramolecular polymers are composed of monomers linked together by means of non-covalent interactions. 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^[1] or amide^[2] groups. We recently located metallic centres at the periphery of the supramolecular polymers as well as chiral monomers in order to catalyse a reaction and control the chirality of the assemblies, respectively. The chirality is efficiently transferred to the

* 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).*

intrinsically achiral metal centres.¹³⁻⁵¹ The aim of this traineeship is to get asymmetric induction in the catalytic reaction without the use of chiral monomers. This can be envisaged by using the spontaneous chiral symmetry breaking phenomenon observed for supramolecular polymers which are structurally-similar to the ones used previously in the laboratory (Figure).¹⁶¹



2. Methods

The traineeship will contain the following tasks : (1) the synthesis of the monomers, (2) the determination of the conditions allowing spontaneous chiral symmetry breaking (use of circular dichroism spectroscopy), (3) the screening of ligand/monomer mixtures in metal catalysis (asymmetric copper hydrosilylation) and (4) 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. References

- [1] "Assembly via hydrogen bonds of low molar mass compounds into supramolecular polymers." L. Bouteiller **Adv. Polym. Sci.** 207, 79, **2007**.
- [2] "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**.
- [3] "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**.
- [4] "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**.
- [5] "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**.
- [6] "Macroscopic Chirality of Supramolecular Gels Formed from Achiral Tris(ethyl cinnamate) Benzene-1,3,5-tricarboxamides." Z. Shen, T. Wang, M. Liu, **Angew. Chem. Int. Ed.**, 53, 13424, **2014**.