

MASTER DE CHIMIE DE PARIS CENTRE - M2S2

Proposition de stage 2018-2019

Internship Proposal 2018-2019

Spécialité(s) / Specialty(ies) :

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

Laboratoire d'accueil / Host Institution

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

Adresse / *Address* : UPMC, 4 place Jussieu, Paris

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

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Equipe d'accueil / Hosting Team : Chimie des Polymères

Adresse / *Address* : UPMC, 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 2018

Gratification / *Salary* : 554€/mois

Asymmetric catalysis with supramolecular polymers composed of achiral monomers

Scientific project :

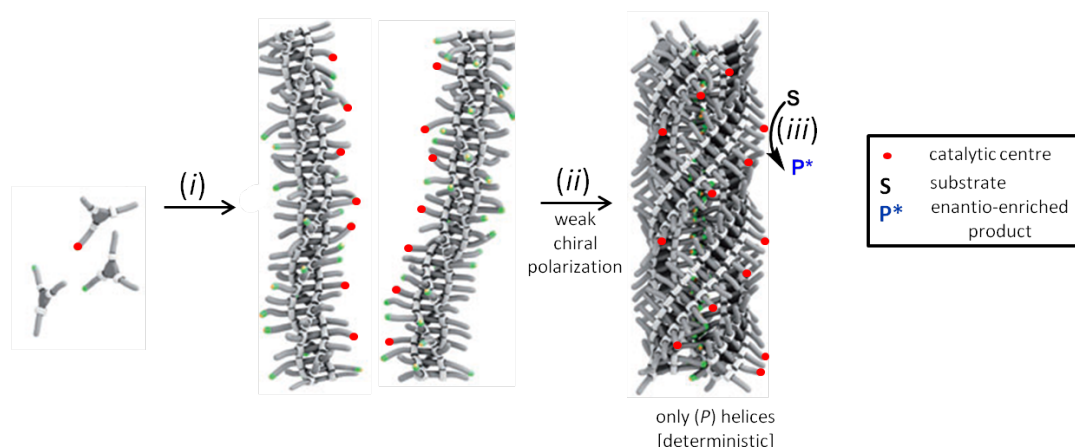
1. Presentation and description of the project

Asymmetric catalysis is the privileged route towards enantiopure compounds. The classical methods involve an enantiopur ligand (in metal catalysis) or 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, could 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 intrinsically achiral metal centres.^[3-6] 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

* 5 mois à partir du 26 janv 2018 / *5 months not earlier than January, 26th 2018*

** Fin du premier semestre M2S1: 19/01/2018; Soutenances des stages M2S2, 1ere session du 29/6-3/7/2018/
End of the 1st semester M2S1: 19/01/2018. Master Defense (1st session of M2S2) from 29/06 to 3/07/2018.

the spontaneous chiral symmetry breaking phenomenon observed for supramolecular polymers which are structurally-similar to the ones used previously in the laboratory (Figure).⁷¹



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. Références

- [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] "Real-time control of the enantioselectivity of a supramolecular catalyst allows selecting the configuration of consecutively formed stereogenic centres." J. M. Zimbron, X. Caumes, Y. Li, C. M. Thomas, M. Raynal, L. Bouteiller, **Angew. Chem. Int. Ed.**, 56, 14016, **2017**.
- [6] "Modulation of catalyst enantioselectivity through reversible control of the length of supramolecular helices." Y. Li, X. Caumes, M. Raynal, L. Bouteiller, *submitted*.
- [7] "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**.