

## PhD offer in Chemistry - Material Science / 2023-2026

### Preparation of a sequential microcolumn made of macroporous polymer monoliths combined with metal-organic frameworks for catalysis in continuous flow

- **Context**

Microsystems constitute a unique opportunity to achieve industrial technological breakthroughs. In particular, continuous flow microreactors with channels hydraulic diameters below 1 mm allow for improved heat and mass transfer owing to the increased surface area to volume ratio.<sup>1</sup> Other benefits over traditional batch procedures include a precise temperature control, efficient mixing, reduction of the environmental burden and increased process safety through the minimization of reagent and solvent quantities. The precise control of reaction parameters by in-line monitoring may also be accomplished with such systems enabling to obtain a large amount of information in real-time about the reaction progress, catalytic activity and stability. Regarding catalysis, continuous-flow processes also allow for the easy recovery of the products from the catalysts and minimizing catalyst poisoning. Furthermore, many operating parameters such as temperature, pressure, and feed concentrations can be easily and quickly varied in flow microreactors.

- **Objective**

The aim of this project is to create an innovative sequential microreactors, composed of connected catalysis and separation microcolumns based on the combination of macroporous polymer monoliths (MPM)<sup>2,3</sup> and chiral metal-organic framework (CMOFs), a class of highly porous hybrid materials built from the assembly of multifunctional organic linkers and metal ions. In both microcolumns, MPM will allow performing both catalytic and separation processes *at high flow rates and low back-pressures*. The MPM surface of the catalysis microcolumn will be covered with CMOF nanocrystals, *providing the adequate chiral environment within which a high density of catalytic sites will be located*. The separation column will be composed of MPM whose surface will be functionalized with surface chiral functions (Fig. 1).

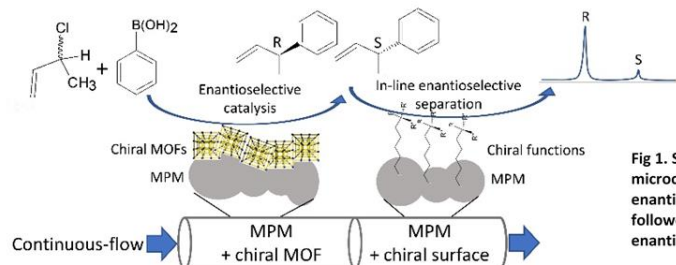


Fig 1. Scheme of the polyvalent microcolumn capable of enantioselective catalysis followed by an in-line enantioselective separation.

The methodological approach will be : (1) the synthesis of the MPM/MOF hybrid microcolumn *via* the MPM synthesis and surface functionalization followed by the *layer-by-layer* CMOF growth from the MPM surface, (2) monitoring of the continuous flow catalysis, (3) Synthesis and coupling of the separation section. The

hybrid microcolumns will be characterized by different physico-chemical techniques, among which: Infrared and Raman spectroscopy, powder X-ray diffraction, X-ray photoelectron spectrometry. The texture and porosity of the samples will be assessed by N<sub>2</sub> and Kr volumetric gas adsorption and electron microscopy.

- **Profil and environment**

We are seeking candidate with a background in material chemistry and a strong interest (and already some knowledge about) for the synthesis and physico-chemical characterization of porous materials. Openness and curiosity, as well as motivation, autonomy and rigour are required. The work will be carried out in the frame of a collaborative ANR project between the **Institut de Chimie et des Matériaux Paris-Est (ICMPE)**, research group expert in the field of polymer science and continuous flow processes<sup>2,3</sup> and the **Laboratoire de Réactivité de Surface (LRS)**, a research group expert in the field of heterogeneous catalysis and MOF.

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<sup>1</sup> M. B. Plutschack *et al.* Chem. Rev. 2017, 117, 18, 11796–11893 (<https://doi-org.inc.bib.cnrs.fr/10.1021/acs.chemrev.7b00183>)

<sup>2</sup> M. Guerrouache *et al.* Macromol. Rapid Commun. 2009, 30, 109-113 (<https://doi.org/10.1002/marc.200800584>)

<sup>3</sup> AM. Khalil *et al.* Polymer 2015, 77, 218-226 (<https://doi.org/10.1016/j.polymer.2015.09.040>)