

Offre de thèse

Conception et optimisation d'un réacteur photo-catalytique pour la synthèse organique

Context and objectives

Merging fundamental molecular chemistry and industrial standards plays a key role in drug manufacturing.¹ One current challenge is to develop sustainable synthetic pathways to rapidly exploit their potential for industrial applications.² In this context, *visible light photocatalysis* is attracting an increasing interest thanks to its potential to promote radical processes under mild conditions from sustainable energy sources.³ In the same vein, *continuous-flow chemistry* is a powerful tool to promote efficient, reliable and scalable chemical reactions under safe and space-saving conditions.⁴ Importantly, flow chemistry is perfectly suited for photochemical transformations because of the high surface-area-to-volume ratios typical of flow reactors, which allow for more efficient irradiation of a reaction mixture.⁵ However, the sustainability of flow photochemistry is only valid if the synthetic strategy avoid the use of transition metal complexes (Ru, Ir) and prevent the formation of chemical waste.⁶ These sustainability issues remain important limitations for the application of homogeneous photocatalysis in the chemical industry. To solve this, exploiting *heterogeneous organic photocatalysis in continuous-flow reactors* appears as an elegant alternative.⁷ Nonetheless, their application in fixed-bed continuous reactors remains difficult due to light penetration effects and mass transfer limitations, especially in the case of gas/liquid/solid reactions. Therefore, there is a high need for designing heterogeneous photocatalytic flow reactors in order to achieve truly sustainable photocatalytic transformations in continuous-flow with great potential for direct scale-up and industrial applications.

In this context, the main goal of this project is to achieve *heterogeneous photocatalysis in continuous-flow reactors* by means of *organic semiconductor photocatalysis*.⁸ Specifically, we will exploit the photocatalytic property of *π -conjugated porous polymers (CPP)* to enable the singlet oxygen-mediated formation of biologically active lactones from aliphatic ethers.⁹ This work will include *the synthesis and characterization of solid-state semiconductor photocatalysts and their immobilisation on transparent reactor supports (walls)* towards the conception of *efficient and scalable devices for triphasic photocatalytic reactions*. Capitalizing upon the expertise in heterogeneous photocatalysis of the ESPCI team and the know-how in process engineering and reactor design of the Chimie ParisTech team, we will develop conceptually new photocatalytic flow procedures and devices that could be easily transposable to the chemical industry.

Project organization

This project will be divided in two complementary and inter-connected parts organized between two PhD students. This will ensure a fruitful collaborative network between the PhD candidates and the two teams. **This offer concerns the PhD student in charge of the (i) conception, (ii) characterization in terms of irradiation efficiency and hydrodynamics and (ii) optimisation of the gas/liquid photocatalytic reactors.**

In this project the PhD student will compare two different reactor design strategies: the photocatalytic packed bed reactor and the micro-structured reactor with photocatalysts immobilized on the reactor wall.

¹ Q. Michaudel, Y. Ishihara, P. S. Baran, *Acc. Chem. Res.* **2015**, *48*, 712.

² E. H. M. Mors *et al.*, *Drug Discov. Today* **2014**, *19*, 1711.

³ M. H. Shaw, J. Twilton, D. W. C. MacMillan, *J. Org. Chem.* **2016**, *81*, 6898.

⁴ L. Vaccaro in *Sustainable Flow Chemistry: Methods and Applications (2017)*.

⁵ Y. Su, N. J. W. Straathof, V. Hessel, T. Noel, *Chem. Eur. J.* **2014**, *20*, 10562.

⁶ R. Gérardy *et al.*, *J. Org. Chem.* **2018**, 2301.

⁷ C. G. Thomson, A.-L. Lee, F. Vilela, *Beilstein J. Org. Chem.* **2020**, *16*, 1495–1549.

⁸ D. Franchi, Z. Amara, *ACS Sustainable Chem. Eng.* **2020**, *8*, 41.

⁹ A. Sagavan, K. C. Hwang, M.-D. Su, *Nat. Commun.* **2017**, *8*, 1812.

The micro-structured reactor with photocatalysts immobilized on the reactor wall will be designed and fabricated in the microfabrication platform of the Institut Pierre Gilles de Gennes pour la microfluidique et ses applications.

https://www.institut-pgg.fr/Presentation-de-l-IPGG_3.html

Location:

The PhD student will be based in the institute de Recherche de Chimie de Paris, Paris 5ème.

<https://www.chimieparistech.psl.eu/recherche/les-laboratoires/ircp/>

Candidate:

The PhD candidate should have a strong background in chemical engineering with knowledges in reactor design, hydrodynamics and mass transfer.

Procedure:

Please send a CV and motivation letter to:

Stephanie.ognier@chimieparistech.psl.eu