LABORATOIRE DE CHIMIE ENS DE LYON

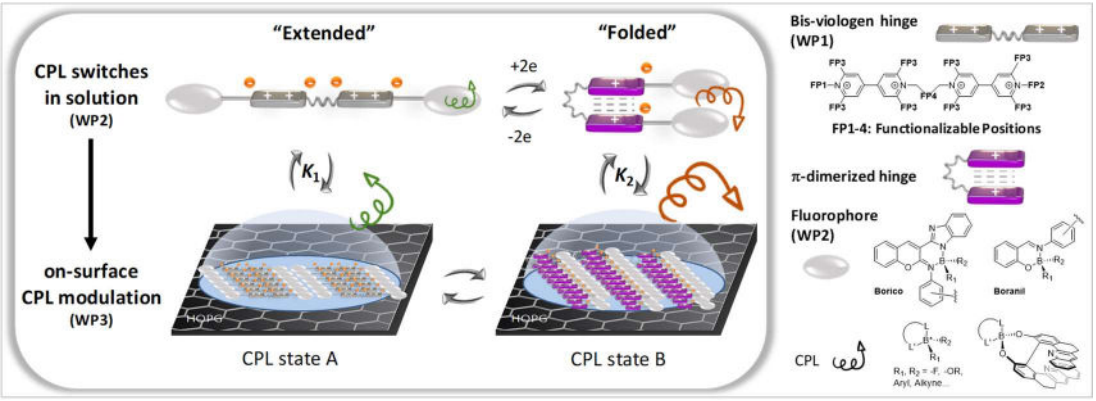
PhD 2023-2026 at ENS Lyon, France

Metamorphic Approaches for On-surface Switching of Chiroptical Properties

SCIENTIFIC CONTEXT AND OBJECTIVES

One great challenge nanoscience is facing is the difficulty to transpose molecular-scale phenomena into macroscopic properties finding application in everyday-life devices. A way to address this issue is to develop *metamorphic* molecular systems for which an external stimulus triggers a drastic structural reorganization. By controlling supramolecular self-assembly of *metamorphic* building blocks it is indeed possible to develop responsive materials for which properties at the macroscopic level can be modulated. Based on this strategy this project will bridge the gap between chiroptical properties observed in solution for Circularly Polarized Luminescence (CPL) switches[1] and their use in device-like systems. Despite being crucial steps toward application in photonics and optoelectronics, modulation of CPL properties has rarely been achieved on-surface and switches responding to an electric stimulation remain almost unexplored. Here we propose to develop responsive supramolecular assemblies for which *metamorphism* will be associated with modulation of chiroptical properties. The main objective of this project is to design responsive chiroptical building blocks whose self-assembly at the liquid–solid interface can be controlled with optical or electrical stimulations.

This PhD position is opened at the Chemistry Laboratory of ENS de Lyon and funded for three years by the French ANR in the frame of the project ChiroSwitch: *metamorphic approaches for on-surface switching of chiroptical properties*. The work will be focus on the synthesis and investigation of new boron-based chiral fluorophores[2-4] and to their implementation on bis-viologen hinges to create stimuli-responsive CPL switches with *metamorphic* properties (see the scheme below for representative structures). In solution, the photo- or electro-triggered motion of the building blocks[5,6] will result in restriction of the fluorophores rotation associated with changes in their respective orientation, polarization and/or chiral environment leading to two states with different chiroptical properties. The adsorption at the liquid–solid interface of these building blocks will be investigated using scanning tunnelling microscopy (STM) and CPL confocal microscopy. Reorganization of the self-assembled monolayers upon exposure to light or electrical stimuli will bring the two fluorophores close to each other. Depending on the molecular structure and on the choice of fluorophores, interesting phenomenon arising from their close proximity imposed in the folded conformation, such as excimer and charge or energy transfer, should affect drastically CPL properties (fluorescence shifts, enhanced CPL, inversion of polarization).



REQUESTED PROFILE

The recruited student will be trained and involved in a large variety of tasks (synthesis, NMR, fluorescence and UV-Vis. spectroscopy, ECD/CPL, STM, electrochemistry…). The applicant will thus ideally have a multidisciplinary background in organic synthesis and supramolecular chemistry with an interest for physical chemistry and surface sciences.

CONTACT

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(1) Ma, J.-L.; Peng, Q.; Zhao, C.-H. *Chem. Eur. J.* **2019**, *25* (68), 15441–15454. (2) Frath, D.; Massue, J.; Ulrich, G.; Ziessel, R. *Angew. Chem. Int. Ed.* **2014**, *53* (9), 2290–2310. (3) Frath, D.; Poirel, A.; Ulrich, G.; De Nicola, A.; Ziessel, R. *Chem. Commun.* **2013**, *49* (43), 4908–4910. (4) Frath, D.; Azizi, S.; Ulrich, G.; Retailleau, P.; Ziessel, R. *Org. Lett.* **2011**, *13* (13), 3414–3417. (5) Roizard, C.; Andrieux, V.; Shehimy, S. A.; Chowdhury, S.; Reynard-Feytis, Q.; Kahlfuss, C.; Saint-Aman, E.; Chevallier, F.; Bucher, C.; Gibaud, T.; Frath, D. *ECS Adv.* **2022**, *1* (2), 020502. (6) Chowdhury, S.; Nassar, Y.; Guy, L.; Frath, D.; Chevallier, F.; Dumont, E.; Ramos, A. P.; Demets, G. J.-F.; Bucher, C. *Electrochim. Acta* **2019**, *316*, 79–92.

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