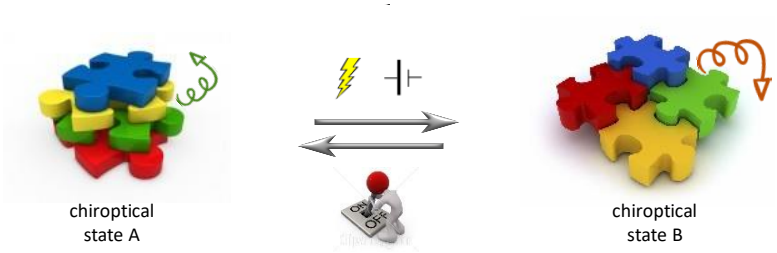
LABORATOIRE
DE CHIMIE
ENS DE LYON

Master 2 internship 2022-2023 at ENS Lyon, France

Metamorphic Approaches for On-surface Switching of Chiroptical Properties

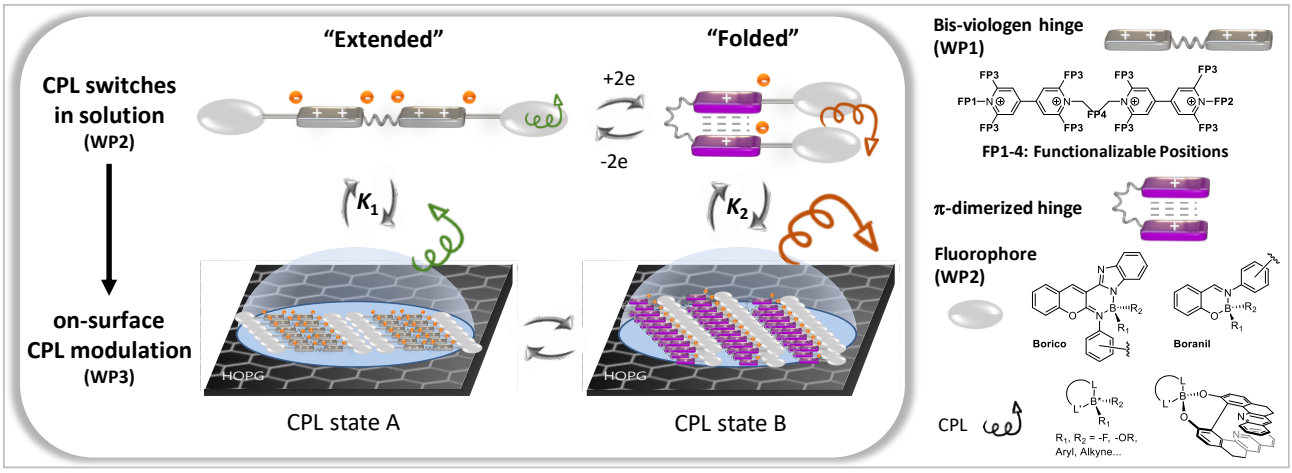
SCIENTIFIC CONTEXT AND OBJECTIVES

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 and their use in device-like systems.[1] 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 (Scheme 1). 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.



Scheme 1. Schematic representation of metamorphic processes associated with modulation of chiroptical properties.

The internship will focus on the synthesis and investigation of new chiral boron-based fluorophores and to their implementation on bis-viologen hinges to create stimuli-responsive CPL switches with *metamorphic* properties (see Scheme 2 for representative structures). The photo- or electro-triggered folding motion of the building block[2,3] will result in restriction of fluorophores rotation associated with changes in their respective orientation, polarization and/or chiral environment leading to two states with different chiroptical properties. 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. The targeted chiral molecular structures will be based on fluorescent boron complexes,[4] known as *Boranils* and *Boricos*,[5,6] that have very interesting advantages: easy access to large scale in few synthetic steps, high chemical and photochemical stabilities, synthetic versatility and excellent optical properties (high quantum-yield of fluorescence up to 80-90%, intense absorption, large Stokes shift, solid-state emission, intramolecular charge transfer).



Scheme 2. General concept of on-surface CPL modulation based on the control of *metamorphic* properties of bis-viologen/boron-based emitters CPL switches.

REQUESTED PROFILE

The recruited student will be trained and involved in a large variety of tasks (synthesis, NMR, fluorescence and UV-Vis. spectroscopy, 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.
PhD funding will be available on the same project at the end of the internship. Applicant willing to enroll in a doctoral course will be considered favorably.

CONTACT

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REFERENCES

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