Master 2 internship 2021-2022 at ENS Lyon (France)

Metamorphic Approaches for On-surface Switching of Chiroptical Properties

SUPERVISORS

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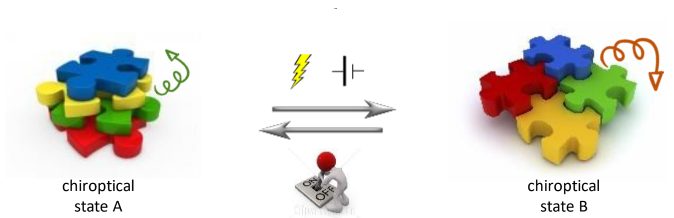
SCIENTIFIC CONTEXT AND OBJECTIVES

The key elements in the development of nanoscience are to observe, modify and control matter at the nanoscale. One strategy proposed to meet these immense challenges is to develop responsive molecular systems for which an external stimulus triggers a drastic structural reorganization. This phenomenon is known as molecular "*metamorphism*".[1-3] analogous to the term used in geology. Systems that endure structural changes leading to major modification of macroscopic properties are of great interest for molecular electronics, the controlled capture and release of guest molecules, or the development of molecular machines. The importance and growing interest in this research area was highlighted in 2016 with the Nobel Prize in Chemistry awarded to Jean-Pierre Sauvage, J. Fraser Stoddart, and Ben L. Feringa. Despite the progresses made since their pioneering works, exploitation of the motion of artificial molecular systems remains highly challenging both from a conceptual and technological point of view. In that context, strategies are needed to take advantage of *metamorphic* processes in the development of "smart" molecular materials for which macroscopic-level properties can be modulated using an external stimulus.

A *metamorphic* approach could potentially be applied in devices that address one of the major challenges the world will be facing during the 21st century: the exponential growth of numerical data requiring secure processing and storage. Recently, the chiroptical phenomenon known as Circularly Polarized Luminescence (CPL) was developed with promising application in cryptography, memory and computing based on quantum mechanics. To prompt the development of CPL application, this field would benefit from efficient materials for which CPL properties can be modulated.

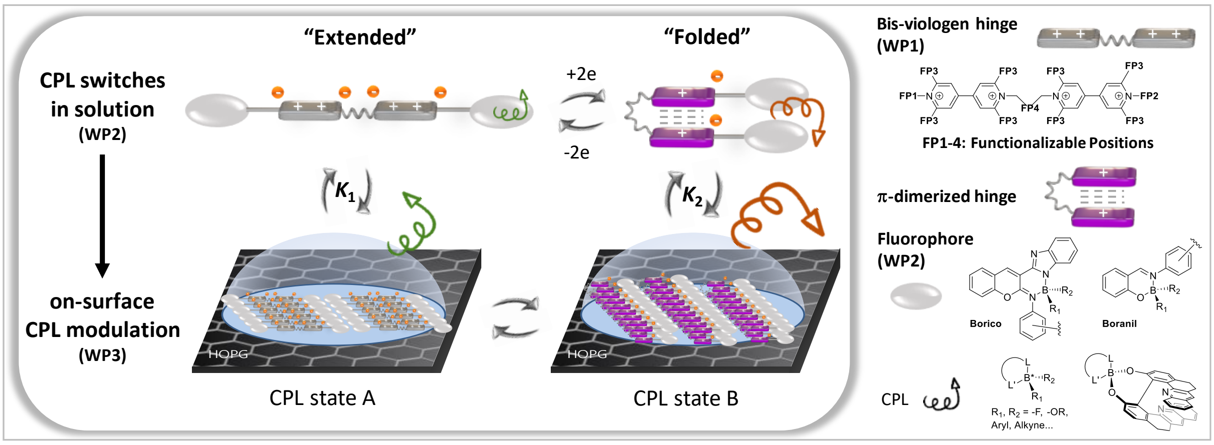
The major breakthrough of our project relies on the hypothesis that *metamorphic* processes in supramolecular assemblies can be used to **achieve on-surface modulation of chiroptical properties,** a field that remains **unexplored despite tremendous potential applications** envisioned in photonics and optoelectronics. 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 metal-free 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[1-3] 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).
Theoretical studies carried out on the targeted CPL emitters and CPL switches will be very useful to better understand and rationalize structure/properties relationship. Modeling of building block optical properties, both in the “extended” and “folded” geometries will be done at the (TD-)DFT level, after MD simulations to infer energies. Changes induced by the folding on spectroscopic properties will be considered with the aim to propose, *in silico*, new functionalization such as improving the emission intensity from the excitonic excited states generated by the supramolecular arrangement of the folded geometry.



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 mainly be involved in the experimental work supervised by D. Frath (synthesis, NMR, fluorescence and UV-Vis. spectroscopy, electrochemistry) but will also run computational studies under the supervision of E. Dumont. The applicant will thus ideally have a multidisciplinary background in organic and physical chemistry with an interest for theoretical chemistry.

REFERENCES

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