

PhD application at ENS-Lyon (2021-2024)

Supramolecular Metamorphism in Stimuli-Responsive Soft-materials

SUPERVISORS

Dr. Denis Frath (CR CNRS), denis.Frath@ens-lyon.fr

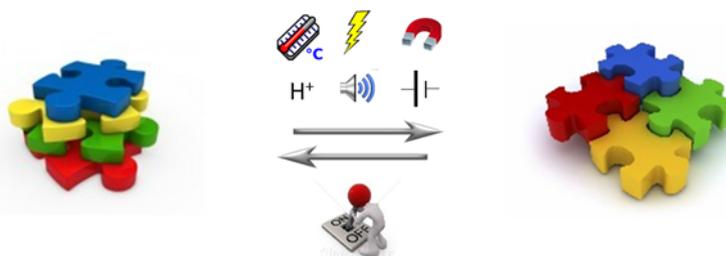
Dr. Christophe BUCHER (DR CNRS), christophe.bucher@ens-lyon.fr

Ecole Normale Supérieure de Lyon-France (<http://www.ens-lyon.eu/>)

« Supramolecular Chemistry Group » (<http://www.ens-lyon.fr/CHIMIE/recherche/Teams>)

SCIENTIFIC CONTEXT AND OBJECTIVES

Stimuli-responsive self-assembled molecular materials are currently subject to intense research activity.¹⁻⁴ The ability to control the organization of molecules within molecular materials has indeed emerged in the past decade as a major scientific objective that is mainly motivated by exciting foreseeable applications in areas ranging from electronics and catalysis to medicine. In this field, one key objective is to achieve a control over the organization or over the association/dissociation of molecular tectons (tecton=monomer) within self-assembled materials using an external stimulus (temperature, light, electricity, chemicals, magnetic field...).



Enormous technologic interests are indeed at stake in being able to control and exploit the properties of self-assembled materials built from monomers held together by reversible and directional interactions. This particular field can lead to applications in various domains as (i) molecular electronics, with the development of molecular wires and devices for data storage, (ii) in analytic science, with materials allowing the controlled binding/release of pollutants or drugs, (iii) in materials science with the development of self-healing and adaptive supramolecular polymers that could respond to well defined and controlled external stimuli by changes in structure and function.

In this context, the aim of this project is to explore a new concept of organic tectons whose self-assembly and disassembly could be controlled externally, by photo/electroreduction of bipyridinium units.⁵⁻⁸ The strategy which will be used to allow an electronic control over soft-materials (gels, liquid-crystals)^{3,4} will rely on the formation of coordination polymers or of fully organic supramolecular assemblies based on photo/redox-responsive π -dimerizable bipyridinium-based tectons.⁶⁻⁸ Association/dissociation will be actuated upon changing the redox state of bipyridinium units involved in the tectons from their dicationic state to their radical cation state, the driving force of the process being the non-covalent and fully reversible dimerization occurring between bipyridinium cation radicals.⁶⁻⁸ This strategy will be used to control luminescent properties conferred by boron based fluorophores to the targeted soft-materials.⁹

This multidisciplinary project is at the interface between organic, supramolecular and physical chemistry. The applicant will ideally have a multidisciplinary background with strong expertise in synthetic chemistry and physical characterizations.

REFERENCES

- 1) *Adaptive soft molecular self-assemblies*. *Soft Matter*, **2016**, *12*, 337 ([Link](#)).
- 2) *Stimuli-Responsive Metal–Ligand Assemblies*. *Chem. Rev.* **2015**, *115*, 7729 ([Link](#)).
- 3) *Functional Liquid Crystals towards the Next Generation of Materials*. *Angew. Chem., Int. Ed.* **2018**, *57*, 4355 ([Link](#)).
- 4) *Gels with sense: supramolecular materials that respond to heat, light and sound*. *Chem. Soc. Rev.* **2016**, *45*, 6546 ([Link](#)).
- 5) *Ultrafast Photoinduced Electron Transfer in Viologen-Linked BODIPY Dyes*. *ChemPhysChem*, **2013**, *14*, 3348 ([Link](#)).
- 6) *Electron-Triggered Metamorphism in Porphyrin-Based Self-Assembled Coordination Polymers*. *J. Am. Chem. Soc.*, **2016**, *138*, 15234 ([Link](#)).
- 7) *Redox-Induced Molecular Metamorphism Promoting a Sol/Gel Phase Transition in a Viologen-Based Coordination Polymer*. *Chem. Eur. J.*, **2018**, *24*, 13009 ([Link](#)).
- 8) *Photo/Redox-Responsive 2D-Supramolecular Assembly Involving Cucurbit[8]uril and a Star-Shaped Porphyrin Tecton*. *Electrochim. Acta*, **2019**, *316*, 79 ([Link](#)).
- 9) *Luminescent Materials: Locking π -Conjugated and Heterocyclic Ligands with Boron(III)*. *Angew. Chem., Int. Ed.* **2014**, *53*, 2290 ([Link](#)).