



PhD offer

Confinement effects on the multi-stimulus response of bridged binuclear metal complexes

The study of nanoscale systems is an area of research with great potential at both the fundamental and applied levels. This involves the development of synthetic methodologies capable of generating highly complex but controlled molecular structures, and the emergence of sophisticated experimental methods capable of studying and positioning these materials down to the single molecule level. A particularly important target has been the construction and characterization of single-molecule electronic devices, as these represent the ultimate limit of miniaturization.

Electrochromic materials are known to undergo changes in their electronic absorption bands in a reversible manner due to interconversion between two or more redox states in response to applied potentials. [1-4] The development of new electrochromic materials with good operational stability, optical contrast, coloring efficiency, and fast response time has seen significant progress for potential applications such as information storage and optical storage, smart windows, and color displays. The most frequently studied electrochromic molecules are conductive organic polymers [5-8] which can be optionally modified with organic side functions contributing to improve their optical properties. [9]

Iron(II) polypyridyl complexes are of great interest for the construction of electrochromic materials due to their chromophoric character (absorption bands in the visible range, variable depending on the oxidation state of the transition metal) as well as their exceptional stability. However, their structuring at the nanoscale remains a challenge and some binuclear polypyridyl iron(II) complexes simply cannot be formed in solution (unlike similar ruthenium-based complexes) due to ligand exchange. Thus, obtaining ideal structures consisting of individual molecular wires ensuring fast electronic communication remains difficult and becomes extremely important in this context. The phenomenon of polychromism induced by redox processes and the fabrication of these materials in a practical configuration are related challenges. Accurately aligning donor-acceptors (D-A) is an important target in materials development for improved device performance. For example, mutual D-A orientation can promote unidirectional charge and energy transfer, enabling better control of the electrical and optical properties of the materials. [10]

The objective of this thesis will be to design, fabricate and characterize photo-/electrochromic devices based on multinuclear metal polypyridyl complexes confined within oriented mesoporous films prepared by combining electrochemistry and click chemistry. The targeted molecular platforms will involve the immobilization of terpyridine ligands in the mesoporous channels followed by a derivatization exploiting, on the one hand, the ability of these ligands to form coordination complexes with transition metals and, on the other hand, the use of polypyridyl bridging ligands in order to modulate the strength of the metal-metal interactions through the conjugated ligand and thus control the degree of electron delocalization.

We will thus obtain nanostructured thin films with oriented porosity presenting (photo-)electrochromic properties modulated by the applied potential and/or light.

The thesis work will include three important parts:

- 1) Synthesis of organic ligands and metal complexes.
- 2) Characterization: The classical characterization methods (NMR, IR.) will be used. The optical and electrochemical properties of the synthesized compounds will also be studied by absorption spectrometry (UV-visible) and cyclic voltammetry.
- 3) Preparation and functionalization of vertically-oriented mesoporous silica films.

The host group, localized at the Laboratoire de Chimie Physique et Microbiologie pour les Matériaux et l'Environnement at the Université de Lorraine possesses recognized experience in preparation and functionalization of mesoporous materials and electrode surfaces. This thesis will be supervised by Dr. Neus Vila (MdC-UL), ELAN group of the LCPME.

Required skills: The candidate is expected to have skills in organic synthesis as well as experience in the use of classical characterization and analysis tools (NMR spectro, mass, etc). Moreover, an interest in the field of electrochemistry will be appreciated.

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Applications (CV + cover letter) can be sent to neus.vila@univ-lorraine.fr.

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