PhD Thesis Proposal - École Doctorale de Chimie de Lyon

Redox-Responsive Molecular and Supramolecular Switchable Magnetic Systems

Systèmes Commutables Magnétiques Moléculaires et Supramoléculaires Rédox-Répondants

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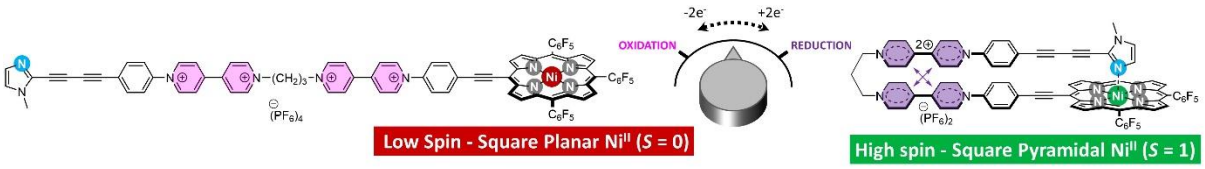
The essential roles played by molecular movements in numerous biological processes (e.g., photosynthesis, DNA replication, ATP and protein biosynthesis) has been a powerful source of inspiration for chemists, and has led for instance to the development of artificial molecular-level machines and switches.[1] These synthetic systems, designed to produce mechanical movements in response to specific stimuli, have proved useful in many areas such as molecular electronics,[2] drug delivery,[3] and catalysis.[4] In recent years, controlling reversible molecular motions with external stimuli has emerged as a promising approach to tune the magnetic activities of discreet switchable architectures.[5]

In such context, the objective of this thesis will be to develop metal-organic molecular systems for which large amplitude and reversible mechanical motions, actuated by electron transfer centered on remote key organic fragments, can be used to control the spin-state of a metal using coordination number or coupling interaction modulation.

This project builds on our recent achievements in the field of redox-responsive molecular structures,[6] especially the development of a redox-responsive tweezer-like molecule featuring a Ni(II)-porphyrin tethered to an imidazole ligand through a flexible mechanical hinge capable of undergoing folding motion under the effect of electrical stimulation.[7] This redox-triggered movement was exploited to force the axial coordination of the appended imidazole ligand onto the square-planar Ni(II) center, resulting in a change in its spin-state from low spin (S = 0) to high spin (S = 1).



The proposed strategy to achieve magnetic switching relies on the π-dimerization of viologen cation radicals as the driving force of structural reorganizations. In such diamagnetic π-dimers, non-covalent bonding arises from overlaps between two SOMOs centered on two π-radicals.[8]

The main concepts that will be developed in this thesis aim at achieving an electrochemical control over the distance between a metal complex and a ligand (coordination induced spin-state switching), or between two metal centers (coupling interactions between two spin centers). The targeted spin-state control processes will be triggered either by intramolecular folding processes, by the formation of CB[8]-assisted[9] supramolecular assemblies or by intermolecular coordination processes controlled by the redox state of carefully selected ligands or substituents.

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