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# *Molecular engineering of cyanide-bridged cubic complexes for molecular materials*

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# Thesis overview

Molecular switches are a class of molecules capable of reversibly transitioning between two or more states with different physical properties upon the application of a stimuli (temperature, light, pressure, electricity). This peculiar property makes them very interesting for a number of applications, from sensors to molecular electronics devices. However, the integration of the switches into a material is challenging, as a loss of properties is often seen. New types of molecular switches designed for material integration thus need to be designed.

In the recent years, molecular Prussian Blue Analogues have emerged as a promising type of cyanide-bridged polymetallic complexes showing strong magnetic and redox switching properties thanks to the electronic communication mediated by the cyanide linker. In particular, octanuclear cubic complexes of general formula $A\subset\{[M(L)(CN)_3]_4[M'(L')]_4\}$ are interesting as they form a cavity capable of encapsulating a cationic host. The ERMMES team has been involved in those research efforts and have developed different cubes bearing scorpionate ligands. Their properties are varied depending on the ligands and the metal pair used, from light-induced ETCST to electrochromism.

The aim of this work was thus to synthesize new types of cubic molecular switches that can be integrated into molecular materials. To this end, two pathways were explored: surface grafting and the formation of supramolecular coordination networks.

The **first part** of this thesis is focused on the integration of the cubes on surfaces by covalent grafting. **Chapter I** describes our efforts to synthesize new scorpionate ligand bearing an amino or nitro moiety, that could be transformed into a diazonium salt and electrochemically grafted on a surface.

**Chapter II** introduces a new family of cyanide-bridged cube, where the M' metal ion is capped by a monodentate and a bidentate ligand instead of the classical tridentates. Three new cubes bearing an aminopyridine are described, and the flexibility of this approach is discussed.

Another type of grafting is explored in **Chapter III**: the self-assembly of thiol moieties on gold surface. Using the synthetic approaches described in the first two chapter, four new cubes are described: two with a novel thiol-bearing heteroscorpionate on the M' metal ion (with M' = Co or Ni), and two with a monodentate-bidentate capped M' where the monodentate is a thioether-pyridine. Preliminary results of their assembly on a gold surface are also discussed.

In a **second part**, this thesis will be focused on the formation of supramolecular coordination assemblies of $A\subset\{[Fe(L)(CN)_3]_4[M'(Tpms)]_4\}$ (with L = Tp or pzTp and M' = Co or Ni) cubes. The Tpms ligand bears a sulfonate moiety capable of forming coordination bonds with different cations, thus linking the cubes in an extended assembly.

**Chapter IV** delves into the 3D supramolecular architecture obtained by this approach. The possibility of modifying the monomeric cubic unit to form different switching network will be discussed in-depth.

Finally, **Chapter V** describes the other supramolecular architecture that can be obtained with Tpms-based cube assemblies, such as chains and layers. A discussion aimed to rationalize the formation of the assemblies will conclude this second part.