PhD Thesis proposal form

Discipline
(Chemistry)

Doctoral School
Ecole Doctorale de Chimie de Paris Sud

Thesis subject title: Supramolecular nano-objects for spintronic applications

- Laboratory name and web site: Laboratoire de Chimie Inorganique, Institut de Chimie Moléculaire et de Matériaux d’Orsay (UMR 8182), http://www.icmmo.u-psud.fr/Labos/LCI/

- PhD supervisor (contact person):
  - Name: Prof. Talal Mallah
  - Position: Professor
  - email: talal.mallah@u-psud.fr
  - Phone number: +33 1 69 15 47 49

- Thesis proposal (max 1500 words):

  The overreaching goal of this project is the self-assembly of metal-containing nano-objects towards the construction of spintronic devices. The project lies at the interface between inorganic chemistry, supramolecular chemistry, magnetic materials, surface science and physics. Due to the interdisciplinary nature of the project, the student selected will have the opportunity to work in different domains and acquire numerous skills (synthesis, coordination chemistry, molecular magnetism, surface chemistry and surface characterization). The highly innovative research topic will lead to numerous publications in high impact journals.

  In recent years, the field of spin electronics (spintronics) has received enormous attention. Devices that use the spin degree of freedom have revolutionized magnetic memory applications. One of the most fascinating examples is a spin valve. A giant change in the resistance is induced in the device upon the application of a magnetic field (Giant Magneto Resistance: GMR), which allows to detect tiny magnetic moments and thus decrease the size of the memory unit and increase the density of magnetic memories (Figure 1).
Figure 1. Schematic representation of a GMR device consisting of a pinned FM layer (green), a free magnetic layer (green or purple), and a metal or insulating separating layer. (a) The device is in the parallel mode and spin current flows; (b) the device is in the antiparallel mode and spin current does not flow.

Molecular spin valves will not replace the current devices present on the market however, they are attractive because they allow for the introduction of new functionalities that cannot exist in solid-state based devices. Molecule-based materials may be designed and tailored to attain specific properties, leading to bottom up fabrication, flexibility and low production costs. One important advantage of molecule-based spintronic devices is that spin information can be preserved over long periods of time in organic and organometallic materials, because of weak spin-orbit coupling. However before we can successfully assemble molecule-based spintronic devices, ways to systematically anchor them onto the surfaces are needed.

The basic question to be answered in the proposed research is: can we design supramolecular nano-objects suitable for spintronic applications? Transition metals act as excellent anchors around which molecular architectures can be built. The predictable geometry of metal-ligand bonds opens up the possibility of designing interesting intertwined geometries around metal ions. Examples of simple coordination geometries (up to coordination number 6) are shown in Figure 2.

Figure 2. Simple coordination geometries: a) linear with a 1+1 coordination geometry, b) square planar with a 2+2 coordination geometry, c) tetrahedral with a 2+2 coordination geometry, d) trigonal bipyramidal with a 2+3 coordination geometry, e) octahedral with either 3+3, 2+4 or 2+2+2 coordination geometry. Colored spheres represent metal ions, black sphere are the ligand donor atoms, and the colored lines are possible connectivities between the ligand atoms.

Initially paramagnetic transition metals (ex. Fe(II), Fe(III), Co(II), Ni(II), Cu(II)) will be employed. A question that comes to mind is: why molecules incorporating paramagnetic transition metals? The answer to this question is triple. Firstly, coordination chemistry in conjunction with supramolecular chemistry gives access to a large number of molecular complexes whose electronic properties may be tuned resulting in a control of the spin current as a function of the molecular spacer. Secondly, the use of paramagnetic complexes where in general the semi-occupied and the lowest unoccupied molecular orbitals are mainly d orbitals allows for a much better orbital overlap with the ferromagnetic electrodes than other materials, which in turn should increase the magnetoresistance effect and lead to more efficient devices. Thirdly, it is possible to use molecular complexes and tune their spin or charge state by an external perturbation as light or/and an electrical field opening up the possibility of controlling the intensity (and eventually the sign) of the spin current (Figure 3).
Subsequently, lanthanide-containing molecules will be synthesized, deposited onto the ferromagnetic metal-oxide surfaces and their spin transport capabilities will be tested. **Why molecules incorporating lanthanide ions?** Because it has been reported that lanthanide-containing molecules (Figure 3) may show single molecule magnetic (SMM) behavior, which is of particular interest for building new devices using the spin transfer concept, which allows a spin flip without the use of an external magnetic field. Therefore, a downscale of the density of information storage to molecular level becomes possible in such devices.4,5

The overreaching goal of this research project is to investigate the incorporation of different self-assembled magnetic molecules and nano-objects as materials for spintronic applications. The student will actively be involved in the different aspects of the project, which are listed below.

**Methodology**

*Design and synthesis of the supramolecular nano-objects.*

The synthesis of the supramolecular nano-objects will be carried out in three steps.

**Step 1:** Design and synthesis of the supramolecular entities: a) design of ligands; b) assembly and characterization of the nano-objects.

The nano-objects will be synthesized via two different routes, either by simultaneous condensation of an amine and an aldehyde around a metal ion template (Scheme 1a), or by pre-synthesis of the ligands followed by complexation with a metal ion (Scheme 1b).
Scheme 1. a) Metal ion templates self-assembly starting from an amine and an aldehyde; b) synthesis of a metal complex starting from a pre-synthesized ligand, two of the three ligands were omitted for clarity. Examples of M$^{2+}$: Fe(II), Fe(III), Ni(II), Co(II), Co(III), Co(II), Mn(II). R = see Scheme 4.

The two synthetic pathways will be investigated in parallel. A variety of ligands with different steric and electronic properties will be prepared. Simple mono-metallic architectures will be investigated first. We will explore the self-assembly around first row transition metals (ex. Fe, Ni, Co), then we will proceed to test lanthanide ions. The building blocks initially chosen will be simple, which will allow us to screen many different architectures at once.

The complexes will be studied by NMR, EPR, IR, MS, cyclic voltammetry, SQUID, X-ray crystallography and elemental analysis. The nano-structures that are the most thermodynamically stable will be investigate in step 2.

Step 2: Fundamental investigation of the self-assembly of the supramolecular nano-objects onto solid supports.

The student will focus on the adsorption of the molecules onto a solid support. The initial tests will be done on ferromagnetic LSMO (Lanthanum Strontium Manganese Oxide) substrates (Scheme 2). The solution containing the metal complexes will be spin-coated or dip-coated onto the support and the film thickness and quality will be characterized by ellipsometry, XPS, and AFM.

Once reproducible conditions for surface deposition are found we will proceed to step 3.

Scheme 2. Examples of functional groups that might anchor onto an LSMO surface: a) phosphonic acid; b) carboxylic acid; c) trimethoxy silane; d) chatecol. The yellow circle represents the nano-object.

Step 3: Fundamental investigation of the spin transport capabilities of these materials.

The materials will be employed in the assembly of a spin valve to test their spin transport abilities. The spin valves will be constructed in collaboration with the Unité Mixte de Physique and will be similar to those described by Barraud and collaborators.$^6$ It will consist of a LSMO electrode onto which the metal-complex will be deposited. An insulating layer and a Cobalt FM electrode will be
deposited as the final two layers. It is possible to indent the insulating layer and the OSC metal-complex layer to obtain a film of the desired thickness (Figure 5).

Figure 5. Schematic drawing of a spin valve. The device is composed of a LMSO substrate, a metal-complex thin film, an insulating layer and a Co electrode. The metal-complex thin film is scraped down until the desired thickness is obtained.

The magneto-resistance will be measured and the dependence of the film/interface quality will be investigated. SEM studies will be carried out to determine the interface quality.

Although we might not reach our ultimate goal of detecting spin transport through these supramolecular nano-objects, **the fundamental research that we will conduct will lead us closer to employing self-assembled metallasuprastructures in nonospintronic devices with the purpose of rendering the storage of information in a single magnetic entity a reality.**

**Key-words:** coordination chemistry, surface chemistry, molecular magnetism, single molecule magnets, molecular spintronics

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- **Publications of the laboratory in the field (max 5):**


- Specific requirements to apply, if any:

Master or equivalent degree in chemistry, materials science or engineering, this project is particularly well suited for and inorganic chemist who wishes to pursue more applications based research. Previous experience in synthesis is not a requirement but recommended. The candidate should have experience (or is willing to learn) surface science techniques, such as sample preparation and characterization. The candidate needs to possess excellent oral and written communication skills in English. Other contact person: Dr. Victoria E. Campbell (victoria.campbell@u-psud.fr)