

## ♦ A very strong ferromagnetic interaction in a new binuclear Mn<sup>III</sup> complex

We have recently started to explore the coordination chemistry of a new multidentate ligand, 2-salicyloylhydrazono-1,3-dithiolane (H<sub>2</sub>L) capable of providing interesting high spin polymeric complexes. In the course of our investigations, we have synthesized and structurally characterized a new high-spin binuclear manganese (III) complex Mn<sub>2</sub>(μ-OCH<sub>3</sub>)<sub>2</sub>(HL)<sub>4</sub>.

The molecular structure consists in a neutral asymmetric complex which presents an unexpected non-symmetrical environment for both Mn(III) ions due to two intramolecular non-classical H-bonds.

This binuclear complex exhibits the highest intramolecular ferromagnetic coupling ever reported for a Mn(III) dimer:  $J = 28.3$  K. The ferromagnetic interaction is further supported by first-principles Density Functional Theory (DFT) calculations carried out using the Naval Research Laboratory Molecular Orbital Library program package ( $J = 26.1$  K). Further magnetic investigation, there again confirmed by DFT calculations, has provided the anisotropy parameters (Zero Field Splitting) of the  $S = 4$  ground state:  $D_{S=4} = -1.22$  K and  $E_{S=4}/|D_{S=4}| = 0.21$ .

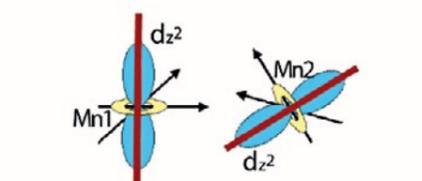
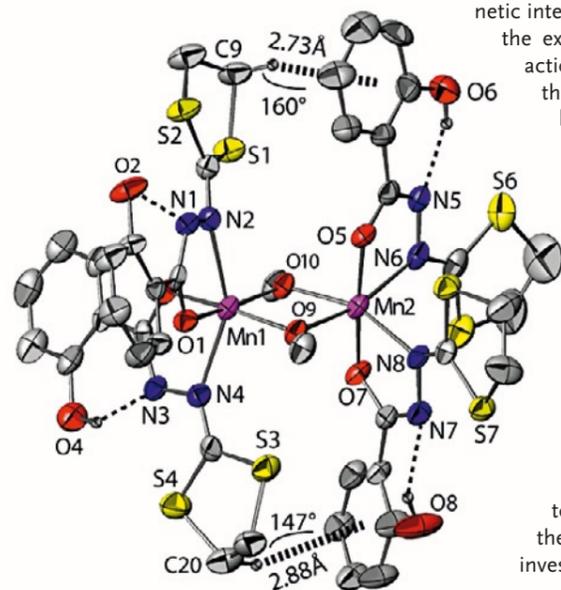
We have shown that the strong ferromagnetic interaction is most probably due to the existence of ferromagnetic interaction pathways which arise from the efficient "crossed interaction" between the singly occupied  $d_{xy}$  orbital on the left fragment and the empty  $d_{x^2-y^2}$  on the right fragment. This interaction leads to four additional positive contributions and thus contributes to a positive overall exchange constant between the two magnetic centres.

The influence of the nature of the bridges between the magnetic centres and of the relative orientation of the distortion axis on the magnitude of the interaction is currently being investigated.

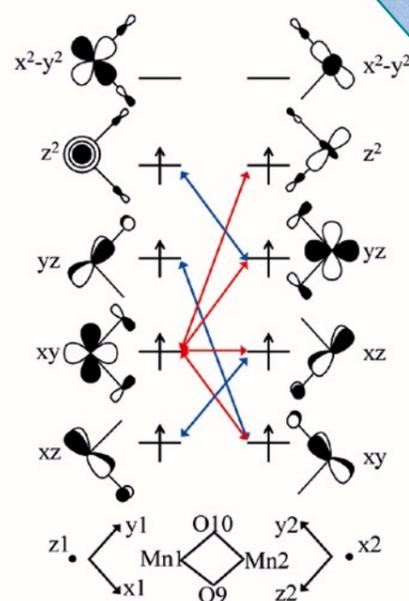
Finally, this binuclear complex, possessing a high-spin ground state well separated from the excited ones with a strong axial magnetic anisotropy, opens promising perspectives in the challenging issue of single molecule magnets characterized by a quantum tunnelling of magnetization. ■

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ORTEP view of the binuclear Mn(III) complex showing specific intramolecular hydrogen bonds and indication of the relative orientation of Jahn-Teller elongated ( $d_{z^2}$ ) axes around both Mn(III) atoms.



Simplified scheme of natural magnetic orbitals and dominant exchange pathways. Blue lines symbolize AF coupling while red lines stand for F coupling.

**TMN 2006**

### Trends in Materials and Nanosciences

The conference TMN 2006 will be held in Strasbourg, on November 21-24. It will focus on optics and plasmonics, magnetic nanostructures, self organized molecular materials, biological materials and materials for energy. A special session will be devoted to a tribute to our former colleague François Bardou for his achievements in Physics. The programme and inscription form are available on the website: [www-ipcms.u-strasbg.fr/TMN2006/](http://www-ipcms.u-strasbg.fr/TMN2006/)

## Summary

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## Editorial

In this second issue of *IPCMS International Newsletter*, the emphasis is put on some important results obtained in the fabrication and study of new materials – nanoparticles, nanostructures, molecular materials - for optical or magnetic applications, in the control of spin transfer upon reflection from a ferromagnet - for spintronics applications - and in the instrumental development for studying ultrafast biomolecular processes. Most of these advances rely on strong collaborations between chemists and physicists, experimentalists and theorists.



IPCMS has strengthened its partnerships with foreign institutions, in particular with Korea and Japan.

A visit of the IPCMS staff in Korea, in Mars 2006, has been enlightened by the signature of a collaborative research agreement with Hannam University, Daejeon, which conducts an important research program in the field of nanotechnologies.

This agreement promotes the exchange of graduate students and researchers for a period of 5 years.

Furthermore, the partnership with the National Institute for Materials Science (NIMS) in Japan will be deepened. After the sixth France-Japan Workshop on Nanomaterials held in Sapporo, Japan on March 6-8, 2006 a visit of a group of scientists from IPCMS at the NIMS research centre in Tsukuba has allowed to identify common projects in nanosciences. As a result of the fruitful discussions that took place during the meeting, the next France-Japan Workshop on Nanomaterials will be organized in Alsace in 2007.

Marc Drillon  
Director

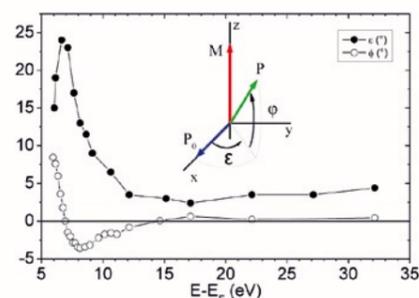
## ♦ Electron-spin transfer upon reflection from a ferromagnet

In the course of developing new devices based on the use of spin polarized electrons (spintronics), it is very important to understand their interaction with thin film magnets.

Along this line, it has been shown in the past that high current densities of spin-polarized electrons can cause the reversal of a magnetic "bit" by transfer of spin-angular momentum from the incident electrons to the ferromagnet without the need of applying a magnetic field. In order to controllably utilize this effect, it is therefore necessary to achieve a better understanding of the spin-induced torques.

We performed a study on several model systems, which answers the question about how the reflection of electrons at a ferromagnetic surface influences the spin motion of the electrons and therefore the transfer of spin-angular momentum from the incident electrons to the ferromagnet. To get the maximal spin motion of the reflected electrons, it is necessary to choose the direction of the incident spin polarization  $P_0$  to be perpendicular to the direction of the magnetization  $M$  of the fer-

romagnetic film. The observed spin motion consists of two contributions, namely a precession of the spin polarization  $P$  around  $M$  by an angle  $\epsilon$  and a rotation by an angle  $\phi$  in the plane spanned by  $P$  and  $M$  (see inset in the figure). While the two spin motion angles do not vary much at high energies (see figure), the behavior at low energies is quite different. Both the strong increase in  $\epsilon$  and the plus/minus structure in  $\phi$  can be attributed to the presence of a spin-depend-



The spin motion angles  $\epsilon$  and  $\phi$  are shown as a function of the electron energy for a 10 nm thick Co film. The inset shows the two angles  $\epsilon$  and  $\phi$  which determine the spin motion.



ent band gap in the electronic structure of the ferromagnet.

The observation of a spin precession of the reflected electrons has an important consequence. Because of total angular momentum conservation, the spin precession of the electrons results in a change of the angular momentum of the ferromagnet. Thus, we find that for ferromagnetic film thicknesses of the order of the inelastic mean free path (typically 1 nm at energies just above the vacuum level), a significant angular momentum - comparable to that found in transmission - is transferred at low electron energies from a reflected electron to the ferromagnetic film. ■

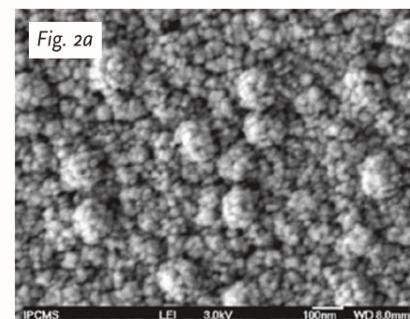
L. Joly, J.K. Ha, M. Alouani, J. Kortus, W. Weber, Phys. Rev. Lett. **96**, 137206 (2006)

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## ♦ Electrodeposition of silver and gold nanoparticles from ionic liquid-crystal precursor

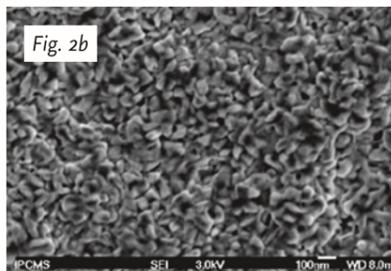
We present a strategy for a versatile exploitation of liquid-crystal-template effects illustrated by the electrolysis of imidazolium liquid crystals containing dicyanoargentate(I) and dicyanoaurate(I) anions to create silver and gold nanoparticles. The key to this approach is the coupling of the self-organisation of the imidazolium metallate to the use of electrochemical reduction, the latter providing the means to control the particle size and form of the electrodeposited metals by variation of parameters such as the potential and the current density.

In the isotropic liquid, the particles formed by electrodeposition have the shape of nanodots (20 to 30 nm) aggregated in spheres or multiglobular objects (100 nm) (Fig. 2.a).



Electrodeposition from isotropic liquid.

In contrast, the morphology of the nanoparticles deposited from the liquid crystal state at 111° C is completely different and shows leaf-like forms interlocked in rosettes (Fig. 2.b).



Electrodeposition from liquid crystal phase.

Of particular significance in the present work is the demonstration that the supramolecular structure of the liquid crystal phase can be used to influence the morphology of metal nanoparticles deposited by electrochemical reduction and provides a new route to synthesize silver and gold nanoparticles. ■

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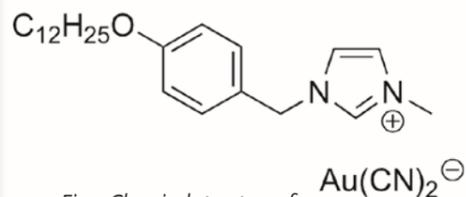
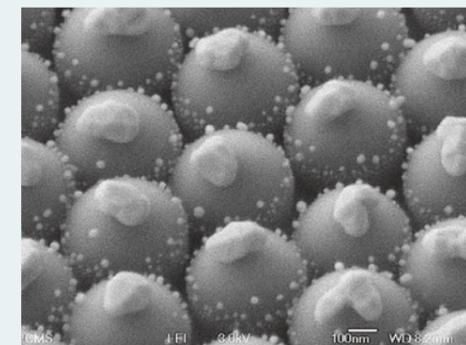


Fig. 1 Chemical structure of  $[Au(CN)_2]^-$  [1-(4-dodecyloxybenzyl)-3-methyl-1H-imidazol-3-ium].

## Self organized magnetic nickel-nanocrystals arrays

A large program of study of the magnetic and optical properties of ordered nanometric objects has been developed at the IPCMS. In this framework we present the most recent advances that were made when using silica spheres that are prepared using a well-controlled Stöber chemical reaction.

A homemade automaton allows the deposition of monolayers of silica beads on glass substrates. Self-organization of the beads as a compact two-dimensional array is the result of a competition between capillary forces and gravity at the time the substrate is extracted from the colloidal suspension that contains the silica beads. A thin, 5nm thick, layer of nickel is MBE deposited on these 2D-self-organized arrays of silica beads, 400 nm in diameter. The beads array that acts as a template is then submitted to a heat treatment. In the process 50 nm nanocrystals do form on top of the silica beads (See Fig.). This is the result of a dewetting process taking place during the cooling phase of the material in which the Ni film is first fragmented and then undergoes a migration and growing process toward the top of the silica beads. Using dichroic magnetization measurements it has been shown that the nickel nanocrystal, 200x100 nm in size, remain stable in air for at least several months. These nanocrystalline magnetic arrays have a great potential of applications in the field of magnetic recording.



SEM image of a self-organized 2D-array of silica beads supporting an array of nickel nanocrystals, scale is 100 nm.

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## ♦ Photoreceptor proteins and femtosecond spectroscopy

IPCMS has received a new femtosecond laser system, providing 35 fs high energy pulses for the study of important ultrafast biomolecular processes involved in vision and primitive photosynthesis.

Spectroscopic experiments with ultrashort pulses in the VIS or near-UV allow to "watch" molecules move. As a matter of fact, the frequencies of vibrations in organic molecules range from ≈20 fs (ethylene stretch) to a few hundreds of femtoseconds (twist and torsion). The motion of atoms in molecules then modulates the properties like absorption and fluorescence giving rise, in some experiments, to periodic oscillations of the signal measured. The central instrument that allows reaching such high time resolution is the laser source. Amplitude Technologies (Évry, France) has now delivered such a source to the BIODYN team of the optics group, providing 35 fs pulses of > 0.5 mJ energy at 5 kHz with an excellent pulse-to-pulse stability (see picture). The system will be used for the study of the internal, laser-excited motion of vitamins and proteins, but also to investigate tiny molecular fluctuations in complexes made up of proteins and RNA's.

Recent results obtained in collaboration with the Laboratory of ultrafast spectroscopy at the Swiss EPFL have shown that very large transient electric fields are generated in photo-sensitive proteins upon absorption of light<sup>1,2</sup>. Using bacteriorhodopsin, a retinal protein very similar to the photoreceptor of vision (rhodopsin), the dynamics of these electric fields has been measured for the first time by ultrafast spectroscopy. The observation of the underlying charge

translocation is very important, as it is suspected to be the driving force for the isomerization of retinal in these proteins. Isomerization is a fundamental motif often used by photo-receptor proteins, defining the starting point for a complex cascade of biochemical reactions, which in the case of vision, ultimately leads to the nerve impulse, signalling the presence of light. Other examples are the photoactive yellow protein (PYP) or phytochrome, an important near-infrared photoreceptor regulating the light-dependent growth of plants. It is known that the isomerisation speed and efficiency depend very much on the electric fields supported by protein environment. Femtosecond monitoring of the photocatalytic action of the protein is therefore

not only important for deepening our understanding, but it may also trigger the design of artificial nanosystems mimicking the natural photo-receptor proteins. ■

<sup>1</sup> S. Schenk, F.van Mourik, S. Haacke, G. van der Zwan, M. Chergui, Science **309**, 917-921 (2005).

<sup>2</sup> S. Schenk, F. v. Mourik, N. Friedman, M. Sheves, S. Haacke and M. Chergui, Proc. Nat. Acad. Sci. USA, **103**, 4101-4105 (2006).

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