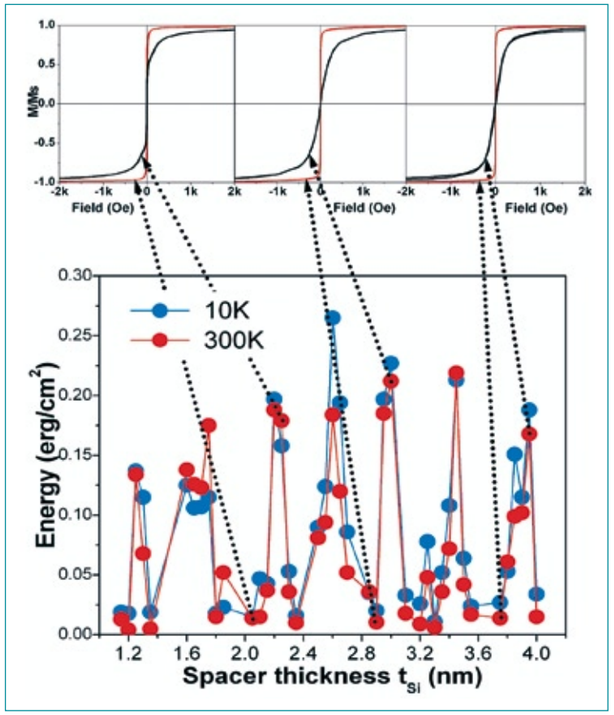
• Short period magnetic coupling oscillations in Co/Si multilayers

The discovery of the exchange coupling and giant magnetoresistance effect (GMR) between ferromagnetic layers, separated by nonmagnetic metallic interlayers, has focused the attention toward magnetic multilayers. Since then, intensive work has been performed on the magnetic and electronic properties of multilayered systems. More recently, in order to develop Magnetic Random Access Memories (MRAM), the non-magnetic metallic spacers have been replaced by non-metallic spacers (insulators or semiconductors). While interesting results were obtained with insulator layers (tunnel magnetoresistance), the results obtained with semiconductor spacers are much more controversial. Indeed, when one elaborates nanostructures with ferromagnetic metals and semiconductors, a large mixing of metal and semiconductor atoms occurs at the interfaces between them. This interfacial mixing influences strongly their magnetic properties. For instance, while Enkovaara et al *(Phys. Rev. B 2000)* have predicted the presence of magnetic coupling oscillations between the cobalt layers, through the silicon spacer, they were never observed experimentally up to now.

In order to reduce the interfacial mixing during the growth process, we have prepared cobalt/silicon multilayers at low temperature (90 K). The structural analyses show that low temperature deposition allows reducing the interfacial mixing to about 1 nm, to be compared to the 5-10 nm for room temperature elaboration. This allowed us to observe, for the first time, short period magnetic coupling oscillations through the silicon spacer as predicted by Enkovaara et al. Examples of our samples magnetization curves are given in the figure (top panel). Within few tenth of a nanometer, the samples show low and high saturation fields. These saturation fields oscillate with the increase of the silicon spacer thickness with a period of about 0.4 nm. This is shown in the bottom panel where the energy needed to saturate the samples (integral of HdM) is plotted versus the Si thickness. These oscillations are due to the modification of the Si electronic structure when a thin layer is embedded between two ferromagnetic Co layers. These oscillations are consistent with the coupling oscillations predicted by Enkovaara et al. and confirmed by our own computations. It may be noticed that these oscillations are as strong at room temperature as at low temperature. These results should initiate new research work in the field of semiconductors and ferromagnetic metals and might promote new technological developments in silicon electronics. ■

N. Yaacoub, C. Meny, O. Bengone, and P. Panissod, Phys. Rev. Lett. **97**, 257206 (2006)

Contact:
christian.meny@ipcms.u-strasbg.fr



Magnetic properties of the Co/Si multilayers versus the Si spacer thickness.
Top panel: examples of magnetization curves.
Bottom panel: magnetic energy needed to saturate the samples.

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- **Publisher:** Marc Drillon - **Coordination:** Daniel Guillon
- **Redaction committee:** Jean-Yves Bigot, Jean-Paul Kappler, Geneviève Pourroy.

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Design atelierc.com

I.P.C.M.S
23 rue du Loess - B.P. 43
F-67034 Strasbourg cedex 2, France
Tél: +33 38-810-7141
Fax: +33 38-810-7250

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Summary

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Editorial

This issue spotlights the last achievements of the Institute in the design and construction of nanoscaled architectures with controlled properties in the field of magnetism and optics.
New developments have been achieved in the exciting areas of quantum magnetoresistance, by measuring the ballistic conductance of cobalt electrodeposited nanocontacts, the periodic oscillations in cobalt/silicium multilayers which may promote new technological devices, and chiral molecule-based ferromagnetic materials. Furthermore, the self-organization of phosphorescent materials is reported in liquid crystals, induced by Pt-Pt and π-π interactions. These contributions cover diverse areas of sciences and engineering, from spintronics to sensors and materials for energy.

The scientific meeting "***Trends in Materials and Nanosciences***" (*TMN 2006*), held last November in Strasbourg, gathered more than 250 participants including high ranking international speakers. They debated on the hot new topics appearing in the fields of optics and plasmonics, molecular and self-organized materials, magnetic nanostructures, bio-related materials, and last on nanomaterials and energy.

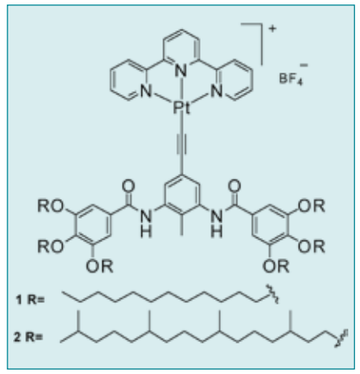
Next fall, **IPCMS** will organize in the framework of the French clusters on nanotechnology, C'nano, the 7th France-Japan workshop on Nanomaterials and Nanosciences in Alsace on October 24-26th.

Marc Drillon
Director


Nobel Prizes Claude Cohen-Tannoudji and Jean-Marie Lehn during their presentations at TMN 2006.

• Liquid-crystals induced by Pt...Pt and π-π interactions

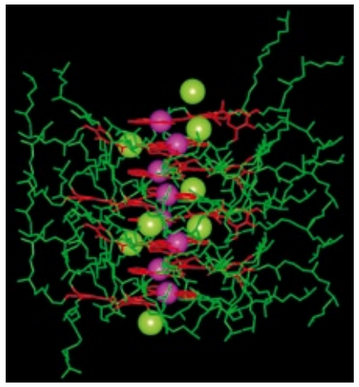
The construction of well-organized phosphorescent architectures is an important issue, that may be mastered by means of: (i) heavy metals to favour spin-orbit coupling for phosphorescence, (ii) ligand tailoring to facilitate intermolecular interaction through hydrogen bonding (*e.g.* amide vectors) or π-π interactions through polyaromatic and/or polyimine fragments, (iii) d^8 transition metals known to favour square-planar structures facilitating metal...metal interactions.



The above molecules with R being **1** and **2** lead to such architectures. For **2**, a liquid crystalline phase is observed over a large temperature range. The recorded XRD patterns between 20 and 200 °C are identical, and show several sharp and intense small-angle reflections according to an hexagonal 2D lattice with parameter $a = 4.2$ nm (at $T = 160$°C). The presence of higher order features indicates that the columnar structure extends over large distances.

The molecules are stacked almost perpendicular to the columnar axis in an alternated fashion, in order to fill the available space between neighbours. This is confirmed by molecular dynamics (MD) simulations which show a good space filling of the available volume as well as the enhancement of the microsegregation over the entire simulation time, contributing to the cohesion of the columnar structure. Additionally, amide functions are engaged in hydrogen bonding which accounts for additional stabilisation of the entire edifice. Moreover, the model shows that the cohesion of the columns is further reinforced by metal-metal interactions, also evidenced by the sharp low angle signal. The BF_4 anions are located between the complexes. A snapshot of the MD simulation accounting for the excellent molecular packing of **2** in the Colh phase is shown in the following figure. The size of the central rigid core is around 2 nm.

Finally, the organization of these fibrilar superstructures on surfaces was also investigated. A diluted gel (0.08 mmol l^{-1}) of **1** was deposited by drop casting at room temperature on a mica substrate. Random orientation of fibers having serpentine forms and an average thickness of 2 nm is clear. The thickness matches the width obtained by molecular dynamics simulations. These 2 nm fibers can be viewed as made of single molecular wires lying flat on the surface. The core of the molecule is 1.5 nm thick, the additional 0.5 nm being attributed to kinking of the molecules to allow the alkyl chains to interact with the surface. Thus, this kind of fiber alignment achieved also on HOPG is auspicious for charge separation devices. ■



*MD simulation showing the molecular self-assembly of **2** into columns (side view)*

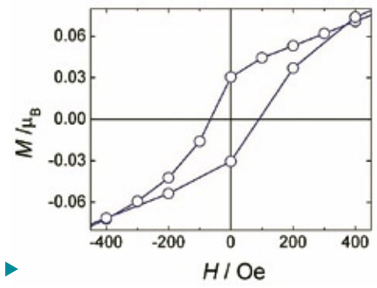
This work is a part of an exemplary collaboration between IPCMS, ECPM *(laboratoire de chimie moléculaire)* and ICS *(institute Charles Sadron)*.

F. Camerel, R. Ziessel, B. Donnio, C. Bourgogne, D. Guillon, M. Schmutz, C. Iacovita, J.P. Bucher, Angew. Chem. Int. **46** (2007) 2659-2662.

Contact: bdonnio@ipcms.u-strasbg.fr

• Chiral magnets based on transition metal carboxylates

Chiral carboxylate-bridged complexes of transition metals were synthesized by reaction of M^{II} salts with L-malate under hydrothermal conditions. These complexes have been fully characterized structurally, thermally and magnetically. The crystal structures of the new chiral compounds, $[M^{II}(L\text{-mal})(H_2O)]$ with M = Mn, Fe, Co, Zn and that of the bimetallic analogues $[Mn_{0.63}Co_{0.37}(L\text{-mal})(H_2O)]$ and $[Mn_{0.79}Ni_{0.21}(L\text{-mal})(H_2O)]$ have been solved by single crystal X-ray diffraction. These L-malate monohydrates crystallize in the chiral space group $P2_12_12_1$ and consist in a 3-dimensional network of metal(II) ions in octahedral sites formed by oxygen atoms. This structure was compared to that of the chiral trihydrate compounds $[M^{II}(L\text{-mal})(H_2O),2H_2O]$, which shows helicoïdal chains, and that of DL-malate $[M^{II}(DL\text{-mal})(H_2O), xH_2O]$ x=1 or 2

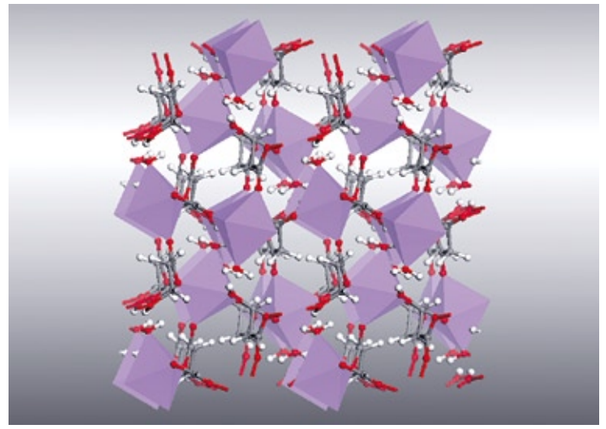


Magnetization versus field of $[Mn_{0.79}Ni_{0.21}(L\text{-mal})(H_2O)]$ at 1.8 K. ▶

highlighting the great flexibility of the coordination by the malate ligand. Extensive magnetic characterization of each homologous series indicates Curie-like antiferromagnetic, ferromagnetic or weak ferromagnetic behaviours related to the structural features. The bimetallic compounds described above represent new examples of chiral magnets. ■

A. Beghidja, P. Rabu, G. Rogez, R. Welter, Chem. Eur. J. **12** (2006) 7627-7638.

Contact: pierre.rabu@ipcms.u-strasbg.fr



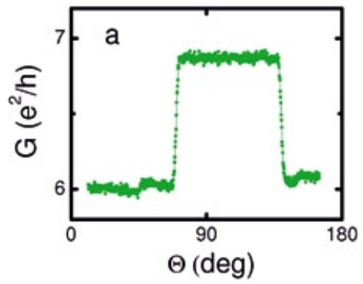
Structure of the mixed L-malate monohydrates. ▶

• Quantum magnetoresistance

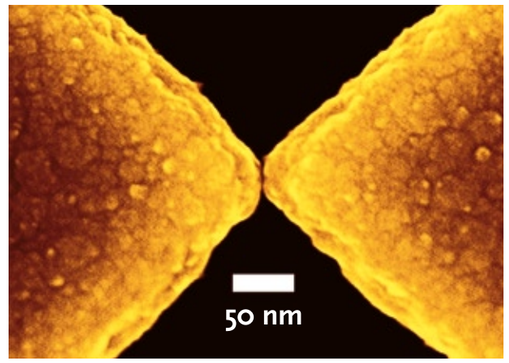
Anisotropic magnetoresistance (AMR), i.e. the change in the electrical resistance of ferromagnetic bulk metals with magnetization direction, has been known since the middle of the 19th century. The importance of this phenomenon was recognized more than a century later, in the 1970s, after the development of thin films technology, when AMR sensors were exploited for magnetic recording. Constant increase in storage density requires reading sensor to follow the miniaturization trend. Scaling such devices down to sub-nanoscale leads to effects which are different from those traditionally observed in bulk materials.

The nature of AMR in atomic-size conductors is profoundly different, due to a ballistic electron transport occurring in the absence of scattering. By measuring *in-situ* the ballistic conductance of Co electrodeposited nanocontacts, the conductance changes in a step-wise fashion when the saturation magnetic field changes its direction. This behavior is the signature of a Ballistic Anisotropic Magnetoresistance (BAMR) effect which stems from the spin-orbit coupling and conductance quantization. When dimensions of a metallic conductor are comparable with the electron's wave length, the conductance becomes quantized, reflecting the discrete number of electronic bands crossing the Fermi level. Due to the spin-orbit interaction, which couples the electron's spin and orbital momenta, varying the magnetization direction changes the number of bands at the Fermi energy and hence the magnitude of the quantized ballistic conductance.

Although quantum ballistic transport attracted a lot of attention in the last 5 years, it is widely accepted by the scientific community that traditional 'lithography made' samples suffer from a number of artifacts and are not adequate for a clear interpretation of their magnetic properties. The combination of focused ion beam and electroplating technique drastically reduces previously claimed uncertainties and allows us to get better insight into electron transport of such a fragile construction as an atomic-size contact.



Conductance value (in units of the quantum of conductance e^2/h) of a Co nanocontact as a function of angle between saturation magnetization and current direction.



SEM picture of a Ni nanocontact.

These experiments clearly demonstrate a new quantum effect at the atomic scale. At the moment, it is difficult to predict what will be the consequences of this discovery for technology in the growing field of spintronics. BAMR may be appealing for the future generation of ultra-small electronic devices, such as ultra small magnetic read heads, quantum switches and logic circuits, due to the possibility to control the quantized conductance by applied magnetic fields. A key difficulty is the reproducibility of the effect which requires controllable fabrication of structures consisting of a few atoms. ■

This work has been done in collaboration with the Nebraska Center for Materials and Nanoscience (University of Nebraska, USA).

A. Sokolov et al, Nature Nanotechnology **2**, 171 - 175 (2007).

Contact: bdoudin@ipcms.u-strasbg.fr