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News

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Editorial

Recent technological developments reveal the huge potential of nano-matter, and accordingly controlling the properties of nanomaterials is a major purpose for many scientists worldwide. This issue of IPCMS News puts the spotlights on some new achievements in our institute.

First, it is reported that by using femtosecond laser pulses, it is possible to control the magnetization of a ferromagnet at a timescale unimaginable with classical magnetic sensors, and thus storage and data access on hard discs could be accelerated by up to 100,000 times. Research in spintronics is progressing as well with the discovery of a novel period of oscillation in the interlayer exchange coupling of Fe/Cr/Fe multilayers, due to spin-dependent confinement of electrons in the Cr layer. Quantum effects are also discussed in molecule-based magnets involving [Co₄] clusters that show a slow relaxation of the magnetization.

The creation of robust junctions between metal crystals and carbon nanotubes is reported for the first time by using electron irradiation, and thus efficient covalent interconnects become conceivable. These are a prerequisite for the applicability of carbon nanotubes in electronic devices.

Another highlight deals with the synthesis of new dendritic Mn(II) and Gd(III) complexes for application as contrast agent in magnetic resonance imaging in order to improve diagnostic in medicine. Finally, it is shown that tryptophan amino-acids can be used as probes to figure out the ultrafast functional electric changes in the retinal proteins. The results accredit the hypothesis that proteins store energy in form of electrostatic energy, which is released later on timescale that is much longer than the initial photo-isomerization.

Partnerships with academic research centres in South Korea and China are being developed. A France-Korea workshop on "Functional nanostructured materials for magnetic and opto-electronic applications" held at Strasbourg last July. Further, we have organized a graduate school in "Photonics and laser science" in collaboration with Wuhan National Laboratory for Optoelectronics to promote common projects and joint PhD programmes.

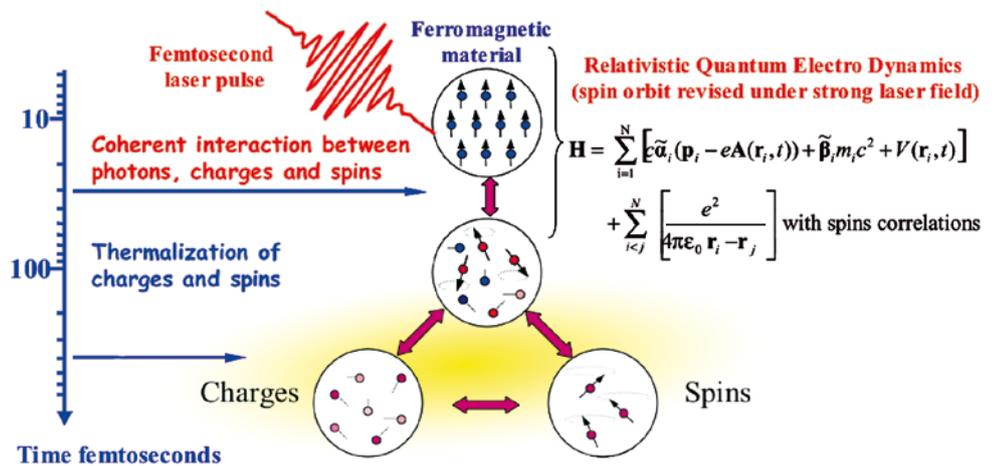
Marc Drillon
Director

◆ Coherent interaction between the spins of ferromagnets and femtosecond laser pulses

How fast can one modify the magnetization of a ferromagnet, constituted of ordered interacting electronic spins, and how can the corresponding change be measured? This question has been at the origin of a new field in modern magnetism that is referred to as femtosecond magnetism. It makes use of femtosecond laser pulses to induce a sudden variation of the magnetization, resulting in a net decrease of the modulus and re-orientation of the magnetization vector. Our team, which is at the forefront of fundamental studies in that research field, has gone one step further recently by investigating how an ultrashort laser pulse couples to the spin of electrons in ferromagnetic metals [1].

We have shown that a single 50-fs laser pulse couples efficiently to a ferromag-

netic film during its own propagation. This result indicates that the material polarization induced by the photon field interacts coherently with the spins. The corresponding mechanism has its origin in relativistic quantum electrodynamics, beyond the spin-orbit interaction involving the



▲ Fig.1: Sketch of interaction mechanisms occurring in the ultrafast magnetization dynamics.

French physicists claim breakthrough in ultra-fast data access

News item from French Press Agency (AFP)
May 31, 2009

French physicists report that they had used ultra-fast lasers that could accelerate storage and retrieval of data on hard discs by up to 100,000 times, pointing the way to a new generation of IT wizardry.

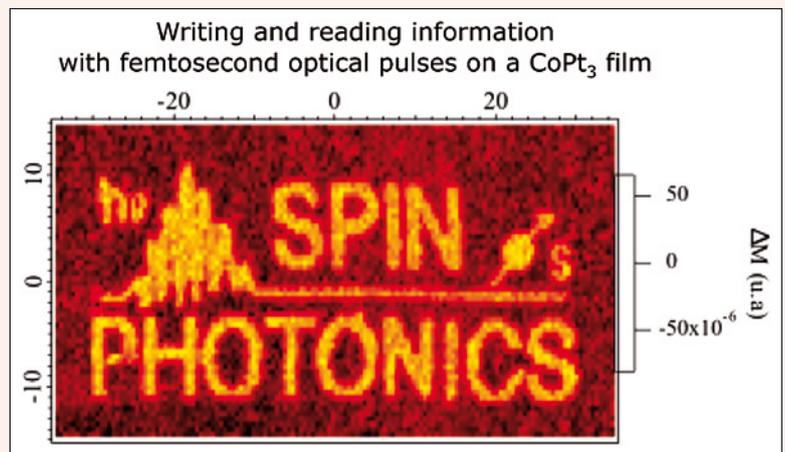
The research builds on achievements that earned the 2007 Nobel physics prize for Albert Fert of France and Peter Gruenberg of Germany, who ushered in a revolution in miniaturised storage in the 1990s. Fert and Gruenberg discovered that tiny changes in magnetic fields can yield a large electric output. These differences in turn cause changes in the current in the readout head that scans a hard disk to spot the ones and zeroes in which data is stored.

That discovery opened the way to «spintronics», a form of electronics that uses not only electrical charge but also the spin of electrons in individual atoms to provide a more compact, denser storage on hard drives. But reading and writing data through spintronics has been hampered by the relative slowness of magnetic sensors.

In a study published in the specialist journal Nature Physics, a team led by Jean-Yves Bigot of the Institute of Materials Physics and Chemistry in Strasbourg employed a «femtosecond» laser, using ultra-fast bursts of laser light, to alter electron spin and thus speed up retrieval and storage.

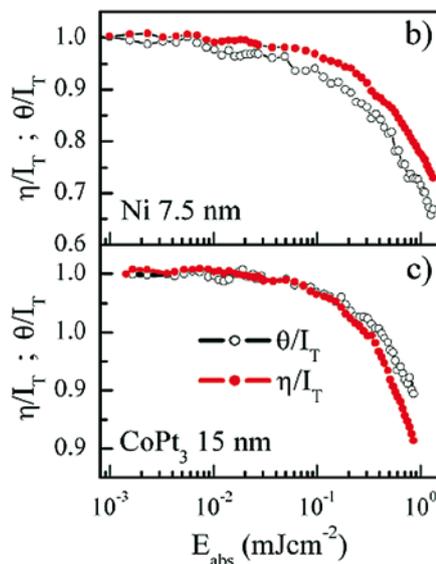
«Our method is called the photonics of spin, because it is photons [particles of light] that modify the state of the electrons' magnetisation» on the storage surface, Bigot told AFP. Data is retrieved with a burst that lasts just a millionth of a billionth of a second, said Bigot. Femtosecond lasers currently measure around 30 centimetres (12 inches) by 10 centimetres (four inches) which means they are too big for consumer electronics, he cautioned. Bigot added, though, that their miniaturisation is likely to be achieved over the next decade.

IBM, Hitachi and other corporations are «extremely interested» by the research, Bigot said.



ionic potential. In addition, this coherent interaction is clearly distinguished from the incoherent ultrafast demagnetization associated with the thermalization of the spins. In figure 1 we have sketched the several steps which are involved during the demagnetizing and re-magnetizing process. The main aspect of our breakthrough is emphasized by the initial step (coherent interaction processes) sketched in figure 1.

We carried two different experiments that show the coupling between the electromagnetic field and the spins in magnetized ferromagnetic thin films. First we have measured the Kerr or Faraday magneto-optical response of Nickel (7.5 nm thick) and CoPt₃ (15 nm thick) films shined by 48 fs laser pulses. The experiment can be considered as single pulse because we use only one laser beam (Ti:Sapphire with 800 nm centered wavelength, amplified at 5 kHz). Figure 2 shows the variation of the rotation and ellipticity as a function of the light density of energy. The accuracy of the set-up has been worked out so that we can cover four decades of the absorbed density of laser energy (the laser beam is focused onto a spot of 30 μm diameter on the samples). These results show the coherent nature of the underlying physical mechanism. Indeed, the decrease of the rotation and ellipticity versus energy density E_{abs} , clearly answers a basic question: yes, self-induced magnetic changes are present on the timescale of a femtosecond laser pulse (note that the maximum relative changes are as large as 30% for nickel and 10% for CoPt₃). The mechanism that we propose to explain these results is a coherent coupling



▲ Fig.2: Single-femtosecond-pulse Faraday experiment. Normalized rotations θ/I_T and ellipticities η/I_T of a single beam 48 fs pulse, represented as a function of the density of absorbed energy E_{abs} (in logarithmic scale). Both θ and η are normalized to the transmitted energy I_T and differentiated with respect to their values obtained for the lowest excitation density.

between the electromagnetic field and the spins in the ferromagnetic material. It has its origin in nonlinear relativistic quantum electrodynamics. The spin-orbit interaction includes here a nonlinear interaction between the laser pulses and the spins. The polarization induced in the material couples to the spins. In other words, an anisotropy is induced in the electronic potential, via the polarization set by the linearly polar-

ized laser pulse, which in turns modifies the spin-orbit interaction.

Such results are confirmed with two beam pump-probe measurements where a first 48 fs pulse modifies the magnetization and the second one probes the magnetic state. As developed in reference [1], the coherent component of the magnetization is then deduced by measuring the rotation and ellipticity for several pump-probe configurations and orientations of a static magnetic field.

In conclusion, we have shown the existence of a coherent coupling between a femtosecond laser pulse and the magnetization of Ni and CoPt₃ ferromagnetic thin films. The underlying interaction involves a laser-dependent spin-orbit interaction that must take into account the coherent polarization set by the femtosecond pulses. We forecast that the corresponding coherent self-induced processes are the dawn of a new era for future research in magnetism. It might indeed raise a strong interest for investigating the magnetization dynamics with attosecond laser pulses. Let us emphasize that such new researches would be interesting equally for the temporal duration and for the spectral components constituting the attosecond pulses. ■

[1] J.-Y. Bigot, M. Vomir, E. Beaurepaire Nature Physics 5, 515 - 520 (2009)

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◆ Junctions between carbon nanotubes and metal crystals

A way of creating junctions between nanometer-sized metal crystals and carbon nanotubes was discovered by an international research team, led by researchers at the Institut de Physique et Chimie des Matériaux in Strasbourg. The development of a technique for establishing strong covalent bonds between the end of a carbon nanotube and a metal has just been published.

The generation of junctions between carbon nanotubes and metal crystals was achieved by electron irradiation of composites of carbon nanotubes and nanocrystals of transition metals such as iron, cobalt, or nickel. The experiments were carried out with a new transmission electron micro-

scope that has recently been installed in Strasbourg. Using *in-situ* electron microscopy, where manipulations of the objects can be done while observing them at high resolution, it was shown that strong covalent bonds were established between carbon and metal atoms at the interface and hold the two materials together. By correlating the *in-situ* observations with density functional calculations, the covalent bonding between carbon and metal as well as a high charge density at the interface is confirmed. Delocalization of charge at the interface leads to a metallic nature of the contact. Electrical measurements show that these junctions are of an ohmic type and have excellent electrical properties for applications as contacts. The electron

transport through these junctions occurs with a large transmission amplitude. For the first time, the nature of bonding between graphitic structures and metals has been studied experimentally and at the atomic scale.

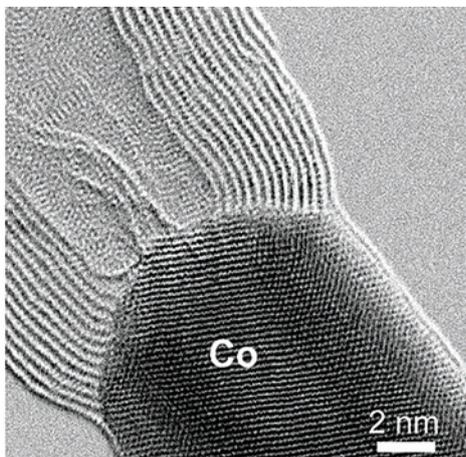
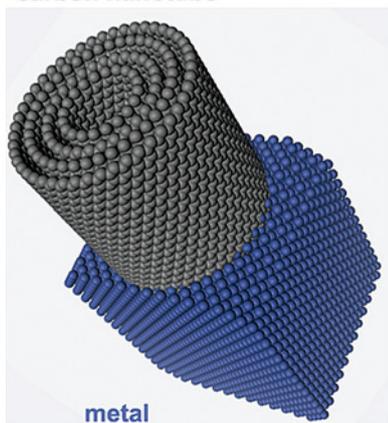
Metal-nanotube junctions are of high importance for both nanoelectronics and mechanical applications of carbon nanotubes. The construction of electronic devices is becoming more and more demanding and complex at the nanometer scale. Although some control in the production of nanotubes, nanowires and nanorods has been achieved in recent years, only little research on the fabrication of efficient covalent interconnects, crucially ■■■

important for the construction of functional nanodevices, has been conducted or in fact reported. Attaching carbon nanotubes reliably to other materials such as metal contacts is an important prerequisite for the applicability of nanotubes in electronic devices or mechanical components. The outstanding mechanical prop-

erties of carbon nanotubes, such as the extreme resistance against failure under axial load and their high elasticity, can only be applied if nanotubes can be attached firmly to metals or other supports. The application of ultra-strong ropes of nanotubes relies on a technique of «holding» them firmly. The fabrication of robust met-

al-nanotube composite networks is now coming in sight since it became clear that reliable interconnects exist and how they can be made. Such junctions are also ideal model systems for studying the formation and characteristics of metal-carbon interfaces. Follow-up studies are just showing that the metal-nanotube junctions have indeed a high strength against failure, being of the order of the tensile strength of bulk metals. ■

carbon nanotube



J.A. Rodriguez-Manzo, F. Banhart, M. Terrones, H. Terrones, N. Grobert, P.M. Ajayan, B.G. Sumpter, V. Meunier, M. Wang, Y. Bando and D. Golberg, PNAS **106**, 4591 (2009)

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◀ A carbon nanotube is attached by covalent bonds to a metal crystal. The electron microscopy image shows the example for a junction between a cobalt crystal and a multi-wall carbon nanotube.

◆ New dendritic contrast agents for Manganese Enhanced MRI

The development of the current scientific techniques improves day by day the quality of human health and life. The field of medicine in particular, brought considerable improvement. Indeed, Magnetic Resonance Imaging (MRI) is one of the most powerful diagnostic imaging tool in medicine since it provides not only images with excellent anatomical details based on soft-tissue contrast, but also functional information in a non-invasive and real-time monitoring manner.

Shortly after the development and market introduction of magnetic resonance imaging contrast media in 1988, their use became a worldwide established tool for improved medical diagnosis. Nowadays developing effective, non-toxic and organ-specific contrast agents (CAs) for *in vivo* image enhancement is a great current area of research. Although most CAs are based on extracellular, low molecular weight gadolinium(III) chelates due to the seven unpaired electrons and relatively slow electronic relaxation of Gd(III), a

number of novel and more specific MRI contrast media (MRI-CM) containing other metals (Mn(II) chelates or iron oxide nanoparticles) have been introduced. Notably, Mn(II) based MRI-CM

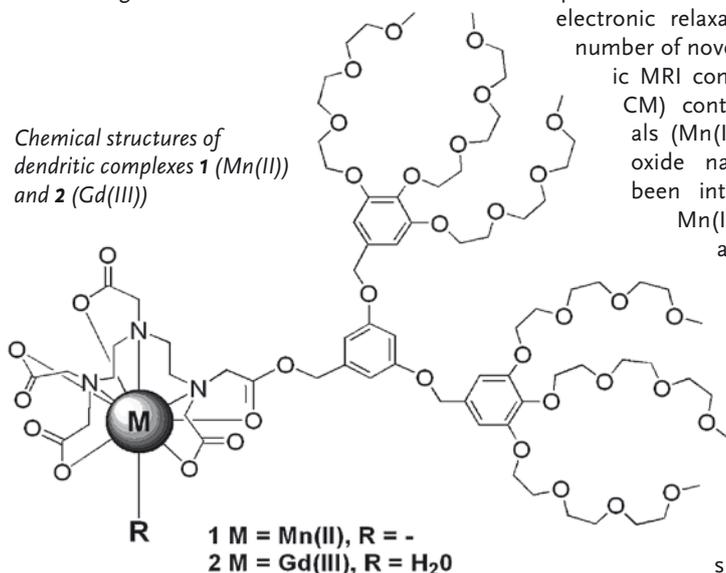
are of great interest and especially in neuroscience research since manganese has a natural human biochemistry which may allow the design of target-specific CAs thanks

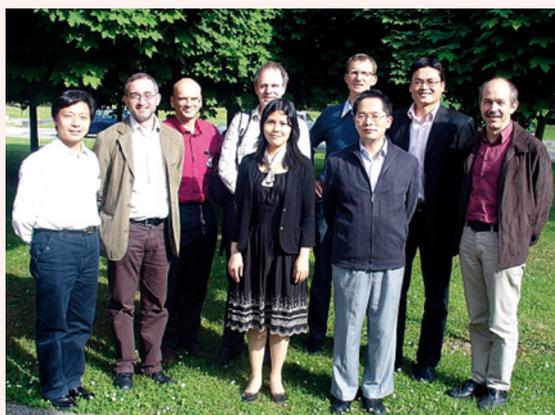
to known biochemical uptake mechanisms. A possible strategy to reduce the *in vivo* toxicity of manganese(II) is to deliver Mn²⁺ to a specific site at an appropriate concentration (greatly reduce its concentration) and via a time-efficient manner (maintain a long diffusion).

With such aim, a dendritic manganese(II) chelate **1** has been evaluated by *in vivo* (relaxivity) and *in vitro* (toxicity and relaxivity) experiments as a Manganese Enhanced Magnetic Resonance Imaging (MEMRI) contrast agent. Also, a comparison with its corresponding gadolinium(III) homologue **2** and the commercially available MEMRI agent MnDPDP (Teslascan, Amersham Health) was achieved in order to determine respectively the real influence of the paramagnetic ion in terms of toxicity and relaxivity for this precise tree-like structure and the potential of **1** to be a favourable candidate for brain-targeting MRI. Complexes **1** and **2** displayed high hydrosolubility (0.1M) and revealed no *in vitro* neuronal toxicity at concentrations as high as 1 mM.

Considering manganese(II) complex **1**, the *in vivo* non-toxicity at 20 mM (100% rats survival) is very likely due to a slow diffusion of the compound, meaning a controlled release of the paramagnetic ions. Finally, T₁-relaxivity of 4.2 mM⁻¹.s⁻¹

Chemical structures of dendritic complexes **1** (Mn(II)) and **2** (Gd(III))





Kick-off meeting for the French Chinese Graduate School in Photonics and Laser Science



The «China Optics Valley» is located in central China in the Hubei region. Its capital Wuhan is home to more than 6000 companies and enterprises producing devices and systems for optical communications, mobile communications, lasers, **LED lighting**, etc.

It is often said that at least every second laser produced in China comes from Wuhan. The Wuhan National Laboratory for Optoelectronics (WNLO) was created by the Chinese central government in 2003 with the

aim of fostering state-of-the-art scientific and technologic know-how and thus to significantly back-up the industrial landscape via technology transfer.

Today, the Hubei region can look back on already 20 years of history in Chinese-French industrial relations and partnerships. A few big French companies related with the automobile industry run a number of factories in the Wuhan area: PSA, Hutchinson and Valeo, to mention just a few.

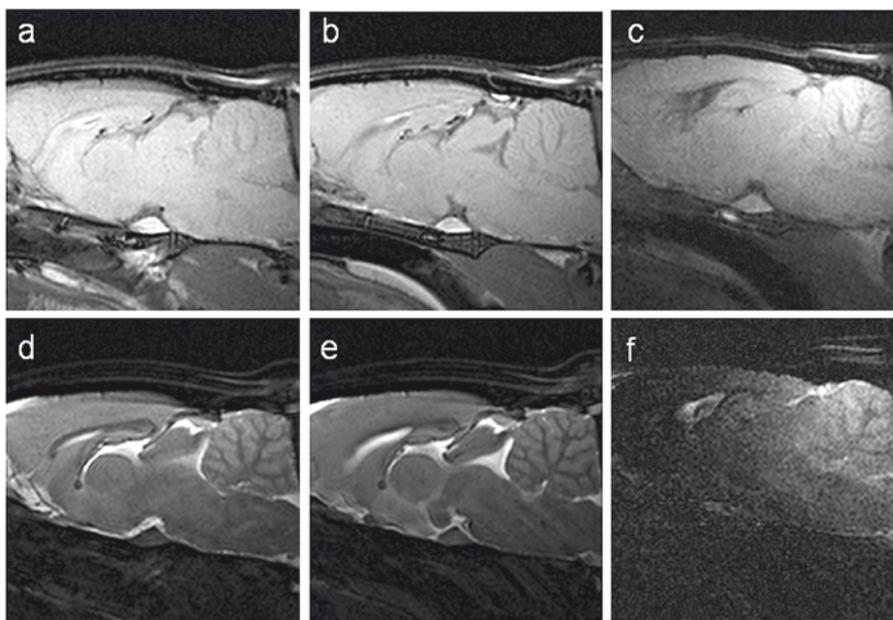
In November 2008, the French Consulate in Wuhan invited about a dozen of French researchers and University faculty members for a workshop organized by WNLO, with the aim of promoting scientific collaborations and student exchange in various areas of photonics: optical signal processing, biophotonics, ultrafast laser science and material engineering, etc.

The partners agreed to form a network, called the French-Chinese Graduate School for Photonics and Laser Science, wherein common projects are defined on a bilateral basis, and joint PhD programmes are being proposed to the students of both nationalities. Projects are currently emerging in different areas ranging from the fabrication and investigation of novel functional materials for photonics to the development of new laser spectroscopy methods for the study of living matter. The French partners are POMA-Angers University, IEF- University Paris-Sud, LASIM – University Claude Bernard Lyon 1 and IPCMS – Strasbourg University.

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for **2** and T_2 -relaxivity of $17.4 \text{ mM}^{-1} \cdot \text{s}^{-1}$ for **1** at 4.7 T were measured and are higher than those of the commercial MRI contrast agents GdDTPA and MnDPDP respectively.

All these data support the view that, in spite of the lower effective magnetic moment of manganese, complex **1** and well designed Mn(II) complexes can therefore be considered as viable alternatives to the currently used gadolinium(III) complexes as contrast agents for MRI. Considering brain imaging, this is mainly due to the rich biochemistry of manganese allowing absorption and transport of Mn^{2+} to the brain: the uptake of extracellular Mn^{2+} by a neuron is directly coupled to its physiological activity and function. This suggests potential applications not only for basic neurosciences but also for managing clinical neurological diseases such as Alzheimer or Parkinson but also other diseases showing disturbances in neuronal cell structures without disturbing the Blood Brain Barrier. ■



▲ T_1 (a, b, c) and T_2 (d, e, f) MEMRI images obtained with complex **1**. a, d) 15 hours, b, e) 24 hours, c, f) 72 hours. Rat brain, at 0.4 mmol/kg , IP of a 20 mM solution of **1** in NaCl (150 mM); SMIS 4.7T, 1 mm thickness, resolution 256×256 , field of view 20 mm.

A. Bertin, J. Steibel, A.-I. Michou-Gallani, J.-L. Gallani, and D. Felder-Flesch, *Bioconjugate Chemistry*, **20**(4), 760-767, (2009).

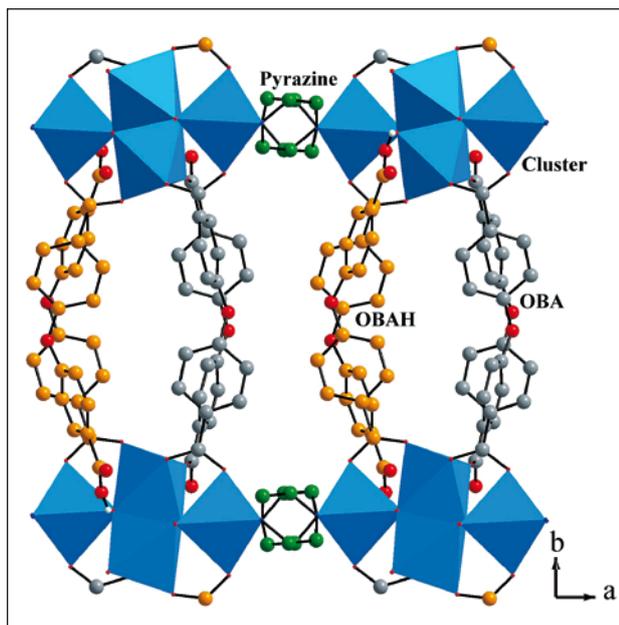
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◆ Slow Relaxation in a Metal Organic Network of $[Co_4]$ Clusters

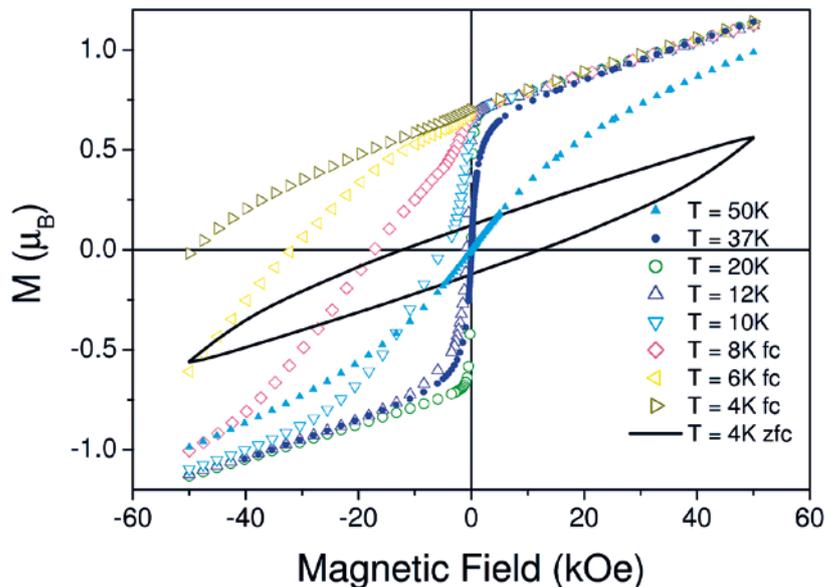
Since the early 90s, the current trend towards ever-smaller electronic devices, based on spintronics, pushes the scientists to exploit the fascinating properties of single-molecule magnets (SMMs). Their physical properties, which combine the macroscopic properties of classical magnets and the quantum ones of nanoscale species have fascinated scientists from across the disciplines.

While $[Mn_{12}]$ and $[Fe_8]$ clusters have been extensively studied, very few cobalt-based SMMs have been reported so far, likely due to the difficulties encountered to increase the nuclearity of the metal clusters. The recent advent of the Metal-Organic Frameworks (MOFs) has been a boon to synthetic chemists as it facilitates organizing unusual metal clusters. In that frame, we have reported a body centered network of $[Co_4]$ magnetic clusters, synthesized from the dicarboxylate ligand (4,4'-oxybis(benzoate)) (OBA) and pyrazine, which give rise to a new solid, $[Co_2(\mu_3-OH)(\mu_2-H_2O)(pyrazine)(OBA)(OBAH)]$.

The Co_4 clusters, $[Co_4(\mu_3-OH)_2(\mu_2-H_2O)_2]$, are connected by the pyrazine ligand forming two-dimensional layers, which are pillared by the OBA units giving the three-dimensional structure (see below). As can be noted, the $[Co_4]$ clusters are connected through four pyrazine and four OBA units to eight different $[Co_4]$ clusters, and thus form the first body centered (BC) structure involving transition metal clusters.



▲ Structure of $[Co_2(\mu_3-OH)(\mu_2-H_2O)(pyrazine)(OBA)(OBAH)]$ showing the connectivity between $[Co_4]$ clusters.



▲ $M(H)$ curves showing a Langevin like behavior for $T > 32$ K, a soft ferromagnetic behavior for 14 K $< T < 32$ K and a harder and harder ferromagnetic behavior for $T < 14$ K.

Different magnetic regimes are observed upon cooling the sample:

(i) As the temperature decreases, spin coherence builds up first inside the clusters through the oxygen bonds. The competing AF interactions make the cluster to adopt a non collinear spin configuration with a net magnetic moment of $1.4 \mu_B$

(ii) Below 80 K, the large increase of χT agrees with extended spin correlations which result from ferromagnetic exchange

couplings between the clusters. On close examination of the structure, it can be figured out that the pyrazine ligands favor a quasi 2D magnetic behavior. The exchange coupling through OBA between the planes is quite certainly much weaker.

(iii) Upon cooling further, the system exhibits a Berezinskii-Kosterlitz-Thouless transition at 32 K, which is evidenced by the stretched-exponential divergence of the magnetic susceptibility in low fields. BKT systems remain critical below the transition temperature and hence no hysteresis is observed in

the magnetization curves down to 14 K. A thermally activated relaxation is observed which is assigned to the hopping between two collective magnetic states with an energy barrier of ~ 500 K.

(iv) Below ca. 12 K, the relaxation slows down to characteristic times that are longer than the experimental time and a hysteretic behavior takes place with the coercive field reaching a value as high as 5 T at 4 K (see above).

Although the temperature dependence of the relaxation time could suggest either a superparamagnetic behavior of the powder particles or a Single Molecule Magnet (SMM) behavior of the clusters, none of these effects can explain quantitatively the value of the activation energy. The estimated anisotropy barrier for a single cluster (8 K) is, indeed, much too small and, oppositely, the volume of the smallest particles is too large. By contrast, the value of the activation energy lies in the estimated energy range (240-520 K) of the vortex-antivortex elementary excitations of an XY system. It is then concluded, tentatively, that the observed slow relaxation is associated with the thermally activated creation/annihilation of the elementary excitations of an XY system. ■

P. Mahata, S. Natarajan, P. Panissod and M. Drillon
J. Am. Chem. Soc. 2009, **131**, 10140–10150

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5th France-Korea workshop, July 1-4, 2009



The annual France-Korea workshop focused, this year, on «Functional nanostructured materials for magnetic and optoelectronic applications».

It has been held in Strasbourg at IPCMS on July 1-4. Invited lectures were given by Korean and French colleagues from different universities, and posters were presented by students from both countries. This workshop reinforces several bilateral collaborations between French and Korean teams since the start of this series of regular meetings. It appears also that a more formal framework for collaborations is needed to expand and deepen relationships between both countries. A project of an International Network of Korean and French Researchers has been submitted very recently for that purpose.



◆ Novel period of the oscillations in the magnetic coupling of the Fe/Cr/Fe(001) system

Researchers of the IPCMS have observed a new period in the magnetic coupling of the Fe/Cr/Fe system as a function of the chromium epilayer thickness. This well-known system has been extensively studied since the Interlayer Exchange Coupling (IEC) was discovered by P. Grünberg in 1988, but here, the coupling was strongly modified by MgO capping.

The Interlayer Exchange Coupling of ferromagnetic films across a non-magnetic metal was a key point for the discovery of Giant Magneto-Resistance effects. The strength of this coupling has been shown in many systems to oscillate as a function of the non magnetic metallic spacer (chromium in our case). This oscillation is due to spin-dependent confinement of electrons in the spacer layer, leading to quantum interference as a function of the thickness of this layer. It was proved in many theoretical works that the period of the oscillation is related to the topology of the Fermi surface of the non magnetic metal. In the case of chromium, two periods, at 2.1 and 12 chromium monolayers (ML) were experimentally observed in good agreement with this theory.

The figure shows the saturation field H_{sat} – proportional to the magnetic coupling – measured by Kerr effect on samples with a wedge shape for the chromium layer. By measuring the saturation field along this wedge, we can observe the oscillation of magnetic coupling as a function of the chromium layer thickness. When the capping is MgO (Fig. a), two periods are observed: one at 2.1 ML and another one at 3 ML. In the case of chromium capping, we

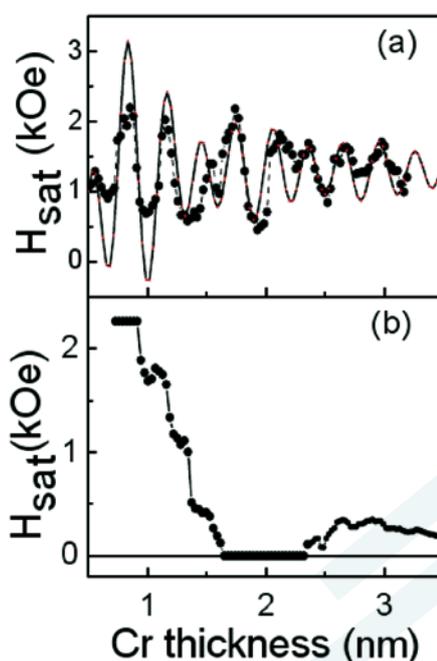
just observe (Fig. b) the well known periods at 12ML and 2.1 ML.

This 3ML period of the magnetic coupling is thus related to the MgO capping on top of the Fe layer. Indeed, MgO is an insulator, leading to a strong reflection coefficient at the Fe/MgO interface for electrons in the top Fe layer. It thus increases the confinement of electrons in this Fe layer and leads to the creation of a quantum well. This in turn modifies the density of states in this layer and subsequently the reflection coef-

ficient at the Cr/Fe interface. Therefore, the confinement of electrons in the chromium layer and the magnetic coupling are modified. That is why the 3ML period oscillation can be observed in the case of MgO capping. ■

D. Halley, O. Bengone, S. Boukari, W. Weber, Phys. Rev. Lett. **102**, 027201 (2009).

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◀ Saturation field H_{sat} measured along the chromium wedge in Fe(125 ML)/Cr(x ML)/Fe(14 ML)/capping samples. (a) with MgO capping. The continuous line is a fit taking into account the 2.1 ML and the 3ML periods. (b) with Cr capping.

◆ Tryptophans as ultrafast voltmeters in retinal proteins

Retinal proteins are small membrane proteins embedding a photoisomerizing molecule derived from vitamin A, namely retinal. These proteins are photodetectors almost universally spread, since they are found in all 3 domains of life (Eucarya, Bacteria, Archaea) with various functions in various organisms, but a very well conserved structure. For instance, rhodopsin (Rho) is the photoreceptor of human vision, as well as that of all known vision systems. Another example is bacteriorhodopsin (bR), which is a photoactivated proton pump, (e.g. a primary photosynthetic system), found in bacteria.

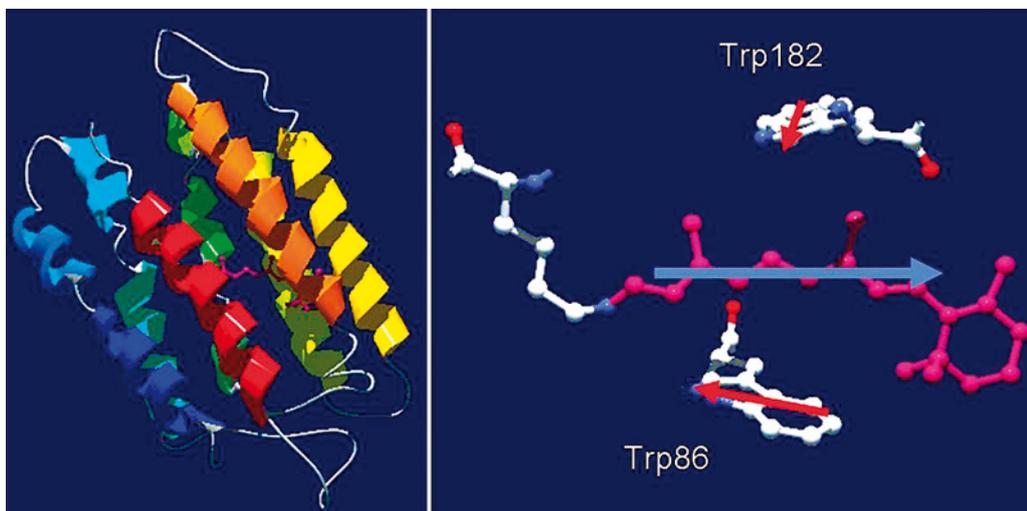
The biological function of all these proteins is triggered by the ultrafast photo-isomerization of retinal. The reaction is catalyzed

In a recent work [2] we use the photophysical properties of tryptophan amino-acids (Trp) as probes for their local electrical environment. Ultrafast spectroscopy of the Trp's lying close to retinal allows us to unravel the changes in the retinal dipole or in its electric environment. By comparing the wild type protein with 2 mutants in which a Trp residue is replaced by a spectroscopically silent phenylalanine, and on the grounds of a simple model describing the dipolar interaction between the retinal and the 2 Trp's, we show, that one of the two nearest Trp's undergoes a spectral Stark shift immediately after the retinal photoexcitation. This signal lasts over a time period much longer than the life time of the photoexcited retinal, indicating a sustain-

to conceive and synthesize biomimetic molecules which would isomerize as efficiently and quickly in solution as retinal does inside the protein. One of the goals is to develop new molecular photoswitches. The ultrafast photophysics of such biomimetic molecules is being investigated in S. Haacke's team (collaboration with M. Olivucci).

[2] J. Léonard, E. Portuondo-Campa, A. Cannizzo, F. van Mourik, G. van der Zwan, J. Tittor, S. Haacke, and M. Chergui, PNAS, vol. 106 p. 7718-7723, 2009.

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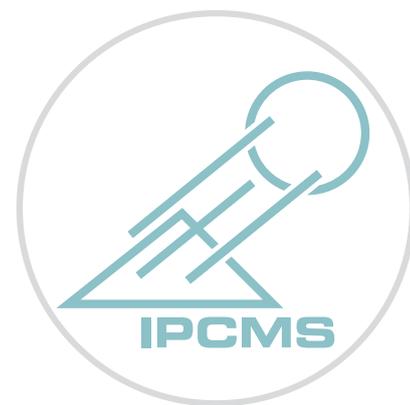


◀ Left: like in all retinal proteins, the bacteriorhodopsin is composed of seven alpha helices surrounding the retinal. Right: inside the protein, the retinal (purple) electric dipole moment interacts with that of the two nearest Trp's. Trp86 has a favourable relative orientation and undergoes a significant spectral Stark shift which is proportional to the local variations of the electric field.

by the protein since inside the protein the retinal photoisomerization is more efficient (66% quantum yield), faster (500fs in the case of bR) and more specific (all-trans to 13-cis for bR) than in any other environment (e.g. in solution) [1]. Besides, in its excited state and before isomerisation, the retinal undergoes a huge increase in electric dipole moment, which should induce a dielectric response from the protein. The electric interaction of the retinal and the protein is thus a key ingredient in understanding a) the exceptional photophysics of retinal inside the protein and b) the activation mechanism of the protein biological function.

able change in the retinal's electrostatic environment due to the protein response. These results show that Trp's can be used as probes for the ultrafast, functional electric changes in the retinal proteins. They also lend credence to the hypothesis that the protein stores energy in form of electrostatic energy which is released later in order to drive successive structural rearrangements so as to perform its function on time scales much longer (seconds) than the initial photoisomerization. ■

[1] This exceptional photophysics of retinal in the protein has triggered theoretical and experimental investigations in order



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