

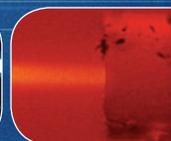


IPCMS

International Newsletter

News

December 2016



No. 20

Summary

How to recycle a chiral molecular catalyst p. 2

Surface Engineering of a Magnetic Organometallic Nanowire p. 2

Interface-mediated Magnetoelectric Coupling in Co/Pb(Zr,Ti)O₃ p. 3

Optical writing of magnetic properties by remanent photostriction p. 4

Towards liquid optoelectronics p. 5

High Spin Polarization at Ferromagnetic Metal–Organic Interfaces p. 5

Dynamical torque in Co_xFe_{3-x}O₄ nanocube thin films characterized by femtosecond magneto-optics: a π -shift control of the magnetization precession p. 6

Awards and distinctions p. 7

www.ipcms.unistra.fr

Editorial

A substantial part of the present issue of IPCMS news focuses on results for various interface nanostructured systems together with their peculiar structural, electronic and magnetic properties. These accomplishments demonstrate the strong interplay between fundamental and applied sciences that fosters IPCMS research activities. Within a multi-national effort involving teams of three different countries (France, Germany and Spain), interface magnetoelectric couplings have been highlighted in CoPbZr_{0.2}Ti_{0.8}O₃ bilayers, showing that these interface effects can be used to optimize the performances of memory devices in terms of stability and dissipation (ACS Appl. Mater. Interfaces **2016**, 8, 7553-7563).

The paper by W. Weber and coworkers is based on spin-resolved photoemission spectroscopy measurements. This technique can shed light on the general character of highly spin-polarized states observed when an interface between a ferromagnetic metal and a molecule is formed. The existence of these states does not depend on the strict chemical nature of the ferromagnetic substrate and of the adsorbed molecular species (J. Phys. Chem. Lett. **2016**, 7, 2310-2315).

In the contribution by L. Limot and coworkers (Nano Lett. **2016**, 16, 588-593) the emphasis is on a general method for modifying the structure and magnetic moment of a metallocene molecule by coupling it to a single atom. This result opens a path to create and study a whole new family of metallocene nanowires coupled to metal electrodes. A breakthrough example in the area of coupling optical, mechanical and magnetic properties is provided by the optical modification of magnetic properties achieved via a photostriction effect at the interface BiFeO₃/Ni. This exemplifies the tremendous potential applications of light-mediated straintronics (Phys. Rev. Lett., **2016**, 177, 107403).

Turning to an outstanding example of ultrafast magneto-optics, the results of J.Y. Bigot team, (Nano Lett. **2016**, 16, 5291-5297) relative to the torque acting on magnetization, bring valuable insights into the understanding of magnetization dynamics in confined magnetic nanosystems. These findings are useful for applications in data storage and local magnetic sensing. Also in the area of optics, this time in connection with organic materials, excellent performance for photophysical and charge transport properties were found in a novel non-volatile room temperature liquid fluorene derivatives functionalized with siloxane chains (Chem. Commun., **2016**, 52, 3103-3106).

Finally, as an example of advance in the area of nanochemistry, the production of a highly efficient robust and recyclable enantioselective catalyst is described. This is obtained through the simple chemical modification of a chiral diamine ligand (Adv. Synth. Catal. **2016**, 358, 1982-1988).

Stefan Haacke, *Director*



◆ How to recycle a chiral molecular catalyst

As it combines unique ecological and economic aspects, asymmetric catalysis has become essential in chemistry. Thus, research to replace predominant stoichiometric processes through shortened catalytic procedures is particularly important. However, asymmetric catalysis is a process that suffers from a major disadvantage which is the non-recyclability of the catalyst. Many strategies have been investigated to develop recyclable chiral catalysts but all these systems have drawbacks that make them still limited and unsatisfactory.

We recently demonstrated that *dynamic* self-supported catalysis is a promising alternative and that this new strategy cir-

cumvents many limitations of classical immobilized catalysts.

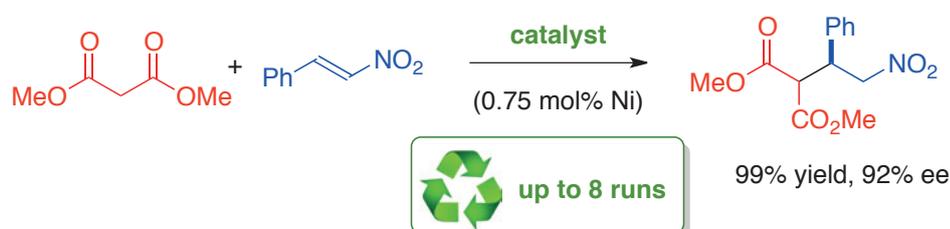
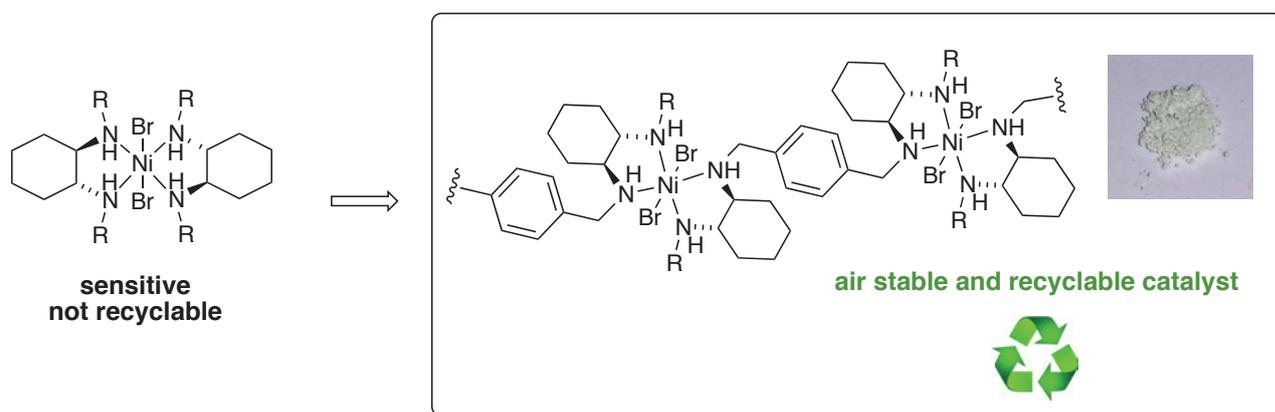
Indeed, a simple chemical modification of a chiral diamine ligand may produce a robust and recyclable enantioselective catalyst. Metallo-polymers based on chiral cyclohexyl-diamine-containing ditopic ligands and nickel (II) complexes have been readily prepared and applied in catalytic enantioselective Michael addition of 1,3-dicarbonyl to nitro-alkenes. High yields and good enantioselectivities have been obtained and the catalytic systems have been recycled up to 11 times without loss of activity and enantioselectivity at a low catalyst loading of 0.75 mol%. Moreover,

the nickel metallopolymers were found air and moisture stable, which enabled this chemistry to be carried out on the bench with no use of any air-free techniques and with nondegassed solvents.

Considering these promising results, it is reasonable to predict that further systems based on this strategy will be developed in the coming years. ■

D. Bissessar, T. Achard, S. Bellemin-Laponnaz, *Adv. Synth. Catal.* **2016**, 358, 1982-1988.

Contact: bellemin@unistra.fr



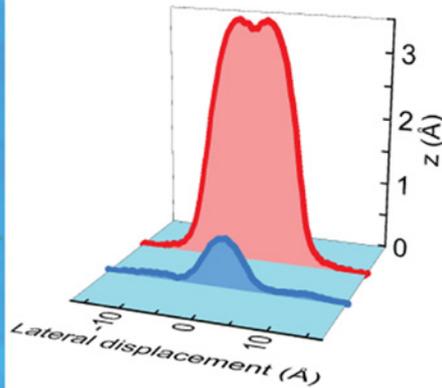
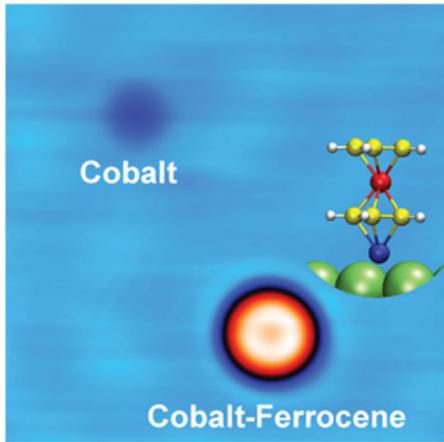
◆ Surface Engineering of a Magnetic Organometallic Nanowire

The ability to manipulate the magnetic properties and the spin-polarized current through single molecules is at the basis of molecular spintronics. The spin and the electronic structure of the molecule near the Fermi level critically influence the spin-polarization of the current, opening up the tantalizing prospect of tuning the spin polarization through a custom-made chemistry of the molecule and an accurate choice of the electrode material. Within

this context, the investigation of single molecules with built-in magnetic moments that are coupled to ferromagnetic, or more generally, to metallic electrodes represents a model playground for exploring novel spintronic concepts.

Many experimental investigations have reported on the possibility of manipulating the molecular spin by metallizing or altering the chemical environment of porphyrin-

based, phthalocyanine-based molecules adsorbed on metallic surfaces, or of cobalt complexes coupled to metallic electrodes. Experimental studies of this kind on single metallocenes (MCp₂ where Cp = C₅H₅ and M = Fe, Co, Ni etc., see Figure) remain instead limited, despite numerous studies have predicted that metallocene-based nanowires (M-Cp-M-Cp-...) could produce highly spin-polarized charge carriers. The efficiency of this process is influenced by



STM image and line profile of a CoFc molecule and of a Co atom. Inset: Chemical structure of CoFc; white, yellow, and red balls represent H, C, and Fe atoms of the Fc molecule respectively, and green balls represent the Cu atoms of the Cu(111) surface.

the metallic constituents of the nanowires, the wire length, and by the geometry of the metal-wire contact. Progress in this area is hampered by the difficulty encountered in synthesizing these molecules in the correct molecular-device environment. The demand for elaborating a prototypical system with atomic-scale control is therefore strong.

In a recent study we published in *Nano Letters* (*cf. reference below*), we present a general method for modifying the structure and magnetic moment of a metallocene molecule by coupling it to a single atom. The method is exemplified by using a ferrocene molecule (FeCp₂, noted Fc hereafter)

and a cobalt atom adsorbed onto a copper surface. By manipulating ferrocene and cobalt with the tungsten tip of a low-temperature scanning tunneling microscope (STM) and forcing them to interact with each other, we show that we can produce a small nanowire consisting of Co-Cp-Fe-Cp (noted CoFc hereafter; see Figure). The upstanding geometry obtained for CoFc on the surface is ideal for elaborating a single-molecule device, for example by a subsequent connection of the nanowire to a top electrode. Through a combined STM and density functional theory (DFT) study, we then show that CoFc exhibits a magnetic moment revealing a change on the spin state of Fc. These results are a sub-

stantial advance upon existing studies devoted to metallocene nanowires as, to date, the production and magnetic characterization of these systems are restrained to the gas-phase. Our findings can be easily generalized to other metallocenes and to ferromagnetic surfaces. ■

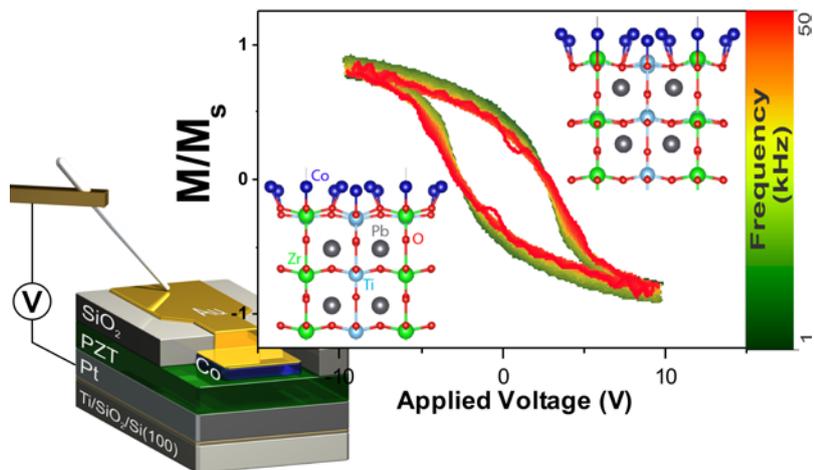
M. Ormaza, R. Robles, N. Bachellier, P. Abufager, N. Lorente, L. Limot, "On-surface engineering of a magnetic organometallic nanowire", *Nano Lett*, 2016, 16, 588-593

Contact: Laurent.Limot@ipcms.unistra.fr

IPCMS News

◆ Interface-mediated Magnetoelectric Coupling in Co/Pb(Zr,Ti)O₃

Modern research on spin electronics has been strongly influenced by the discovery of alternative means to control the magnetization, *i.e.*, other than by applying a magnetic field. An outstanding achievement of this research is the electric-field control of magnetic states, offering important advantages in terms of energy consumption, speed and reliability. Ferromagnetic and ferroelectric composite systems provide a particularly promising pathway towards the efficient electric-field control of the magnetization, owing to a strong magnetoelectric coupling (MEC). In ferroelectric/ferromagnetic bilayers, the coupling occurs either through strain-mediated mechanisms (converse piezoelectric effect and magneto-elastic interaction) or via interface-related effects (electronically-driven).



Electric-field control of the magnetization, switching between two nonvolatile states in Co(7 nm)/PZT. Each magnetization state is connected to two opposite ferroelectric polarization orientations, as shown by the atomic structure derived from DFT calculations (see figure inset).

■■■ The latter case is particularly interesting for applications since it involves a two-state nonvolatile magnetization, as demonstrated in this study (see Figure).

We have recently evidenced room temperature multiferroicity and interface MEC in Co/PbZr_{0.2}Ti_{0.8}O₃ (Co/PZT) bilayers. The statics and the dynamics of the interface MEC were explored in the kHz regime by means of electric-field dependent optical measurements. The measurements demonstrate a mixed linear and quadratic optical response to the electric field in Co(5-10nm)/PZT bilayers, which results from a magneto-electro-optical effect. We have developed a decomposition method of the

optical signal to discriminate between different components involved in the electric field-induced polarization rotation of the reflected light. This allowed us to extract the magneto-optical signal that we can ascribe to interface magnetoelectric coupling. The coupling mechanism was further demonstrated by complementary methods based on polarized X-ray absorption spectroscopy measurements (performed at DEIMOS beamline, Soleil) and density functional theory calculations (conducted by collaborators at CEMES, Toulouse). A coupling constant of $1.5 \cdot 10^{-10}$ Gcm²/V is obtained when the electric field is swept at 1-50 kHz. This remarkably stable coupling shows the potential of exploiting interface

coupling with the prospect of optimizing the performance of magnetoelectric memory devices in terms of stability and dissipationless operation. ■

O. Vlasin, R. Jarrier, R. Arras, L. Calmels, B. Warot-Fonrose, C. Marcelot, M. Jamet, P. Ohresser, F. Scheurer, R. Hertel, G. Herranz, and S. Cherifi-Hertel, "Interface Magnetolectric Coupling in Co/Pb(Zr,Ti)O₃". ACS Appl. Mater. Interfaces, **2016**, 8, 7553-7563.

Contact:
Salia.Cherifi@ipcms.unistra.fr

IPCMS News

◆ Optical writing of magnetic properties by remanent photostriction

The emergent field of 'straintronics', taking advantage of elastic properties of materials, is aiming at realizing new low-power multi-stimuli devices. Researchers at IPCMS, in collaboration with CEA Paris, the Helmholtz Zentrum Berlin Sheffield University and Freiberg Institute for Experimental Physics found a new method to write magnetic properties optically via the photo-ferro-

elastic coupling. Light can polarize electrically the multiferroic BiFeO₃ due to its photovoltaic property.

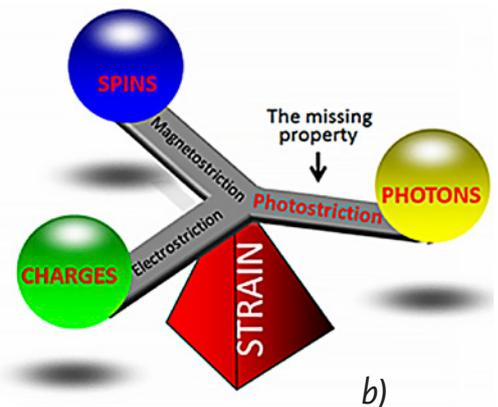
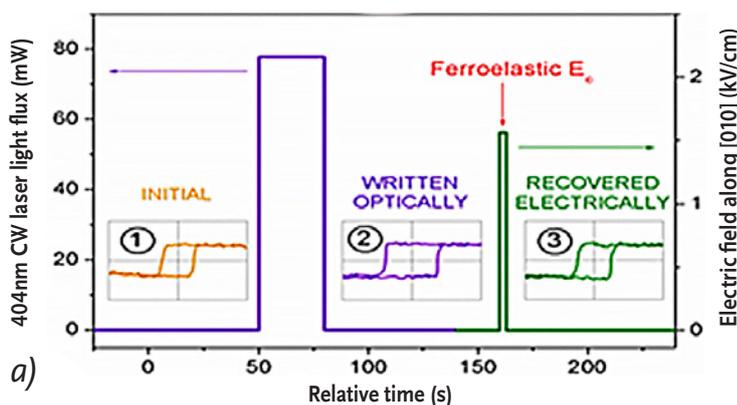
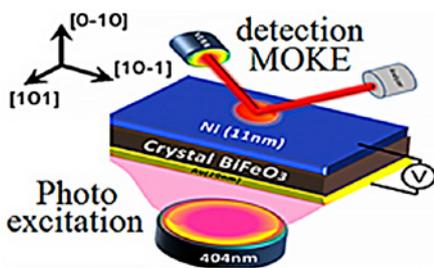
This leads to the possibility to create multiple remanent polarization states by using different illumination times. Thanks to piezoelectricity these light induced polarization states of the ferroelectric are connected with its deformation. The latter can be used to stress a superposed ferromagnetic Ni film in order to modify its magnetic anisotropy. As a proof-of-principle of this concept related to intertwined ferroic properties, a 75 % change in coercivity in the Ni film is achieved via optical and non-volatile control (Figure 1a). Ferroelasticity makes possible to reverse this indirect photoferromagnetic effect by static or *ac* electric depolarization of the substrate. Hence,

the strain dependent changes in magnetic properties are written optically, and erased electrically.

Light-mediated straintronics can therefore be an alternative way for multi-functionality between spins, electrons and electric charges where the photostriction was a missing property (Figure 1b). ■

V. Iurchuk, D. Schick, J. Bran, D. Colson, A. Forget, D. Halley, A. Koc, M. Reinhardt, C. Kwamen, N.A. Morley, M. Bargheer, M. Viret, R. Gumenuik, G. Schmerber, B. Doudin and B. Kundys, Phys. Rev. Lett., **2016**, 117, 107403.

Contact:
kundys@ipcms.unistra.fr



Opto-electric manipulations with magnetic properties (a) and photostrictive-approach to multifunctionality (b).

◆ Towards liquid optoelectronics

The last few decades have witnessed the prosperous development of organic materials for optoelectronics. Motivated by the perspective of ultimate flexible and stretchable devices, solvent-free liquid optoelectronics has recently emerged as a new research field. Alongside the quest for extreme softness, non-volatile liquid optoelectronic materials present several advantages over conventional solid-state ones, i) solvent-free processing, ii) intrinsic resilience and self-healing ability iii) good interface contact with porous and nanostructured materials and iv) possibility to compensate for the degradation (via microfluidic technology), by supplying the device with fresh liquid.

In this line, we have reported a powerful procedure to confer large aromatic species with a liquid state at room tempera-

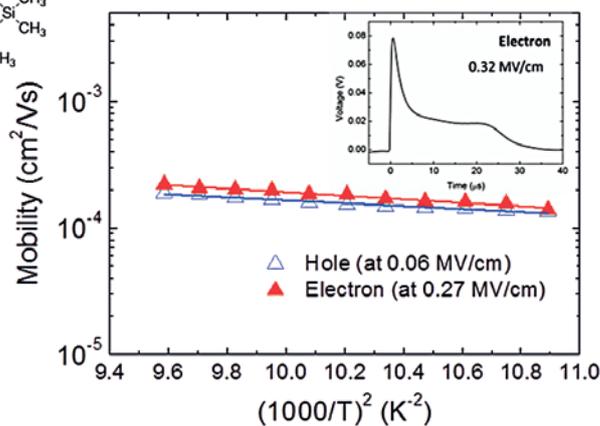
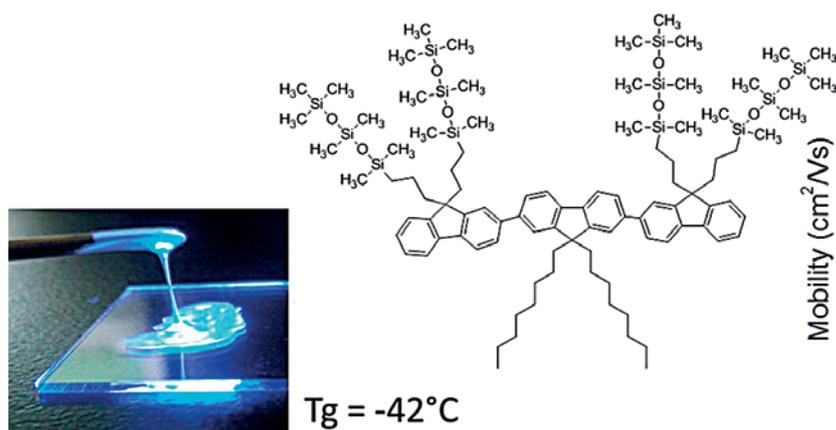
ture, through a convenient siloxane chain functionalization. The first results obtained in a series of oligofluorene led to solvent-free liquid compounds that exhibit both remarkable charge transport properties and strong fluorescence.

The materials were found to exhibit ambipolar charge transport properties (hole- and electron-transport) with mobilities of about 10^{-4} cm²/Vs, i.e. a value comparable to the one of the best solid-state amorphous glasses used in various optoelectronic applications (photovoltaics, OLEDs...). In parallel, thanks to an extremely low threshold amplified stimulated emission ($< 2 \mu\text{J cm}^{-2}$) and high quantum yield (PLQY $> 80\%$), these materials successfully led to the first demonstration of a distributed feedback (DFB) laser in a monolithic liquid semiconductor.

Overall, these results demonstrate that solvent-free liquid organic semiconductors functionalized by siloxane segments can compete in terms of photophysical and charge transport properties with organic glassy semiconductors, thus paving the way for the development of liquid optoelectronic devices. ■

J.-C. Ribierre, L. Zhao, M. Inoue, P.-O. Schwartz, J.-H. Kim, K. Yoshida, A.S.D. Sandanayaka, H. Nakanotani, L. Mager, S. Méry & C. Adachi, *Chem. Commun.*, **2016**, 52, 3103-3106.

Contact: stephane.mery@ipcms.unistra.fr



Photograph (at ambient and under UV light) of the strongly luminescent fluorene derivative functionalized with short siloxane chains, showing nonvolatile and stable liquid state at room-temperature. Graph (right) showing the temperature dependence of the ambipolar charge transport mobility, with typical recorded ToF signal in the insert.

IPCMS News

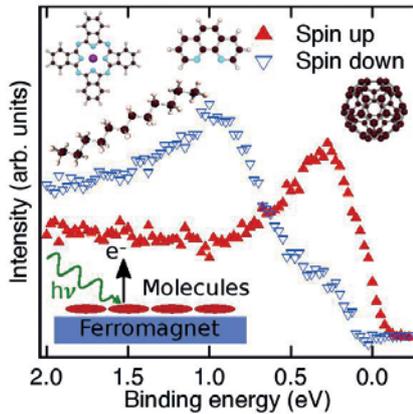
◆ High Spin Polarization at Ferromagnetic Metal–Organic Interfaces

Organic spintronics aims to transmit information across molecular layers using the electron's spin degree of freedom. One anticipates the development of new hybrid multi-functional devices based upon organic and magnetic materials. One of the building blocks of these devices is the interface between a ferromagnetic

metal and the molecules of an organic semiconductor. Such interfaces are endowed with hybridized electronic states that can be highly spin-polarized at electron energies close to the Fermi level, so as to promote a high spin polarization of current flowing across them. In the past, one has therefore strived to spectroscopically

witness such states. However, only recently we presented evidence of a highly polarized metal-organic (MO) interface at room temperature consisting of phthalocyanine (Pc) molecules on ferromagnetic Co and of amorphous carbon on Co. In reaction to this, one immediate question raised was whether this property is confined to flat and

conjugated carbon-based systems, such as Pc molecules or amorphous carbon, or whether these results are indicative of a broader pattern.



Spin-resolved photoemission spectra as a function of the binding energy induced by depositing one monolayer of Pc on Co, and non-planar C₆₀ on Fe.

The goal of our study was to show how general the phenomenon of highly spin-polarized states at ferromagnetic MO interfaces is. The figure shows the spin-resolved photoemission spectra as a function of the binding energy induced by depositing one monolayer of Pc on Co. Close to the Fermi level the intensity is dominated by a spin-up structure, while the spin-down channel, on the other hand, exhibits a gap. Similar situations are found with another ferromagnetic substrate, namely Fe, and with other organic molecules such as the conjugated molecule phenanthroline, the non-planar molecule C₆₀, and the non-conjugated alkane pentacontane.

We could thus show that quite disparate ferromagnetic MO interfaces behave similarly with respect to the interfacial electronic structure. In particular, the presence of highly spin-polarized interface states is not limited only to conjugated organic systems, *i.e.* to systems with π -electrons. We thus

bring both good and bad news for the community. Our work is good news because the presence of highly spin-polarized interface states appears to constitute a generic property of organic molecules deposited onto a ferromagnetic surface. On the other hand, it is very often claimed that substituting one molecule with another is an intriguing pathway to tailoring the spin properties of the ferromagnetic MO interface. However, our results on rather different interface systems show that the latter are probably not as different as expected. ■

F. Djeghloul *et al.*, "High Spin Polarization at Ferromagnetic Metal–Organic Interfaces: A Generic Property", *J. Phys. Chem. Lett.*, **2016**, 7, 2310–2315.

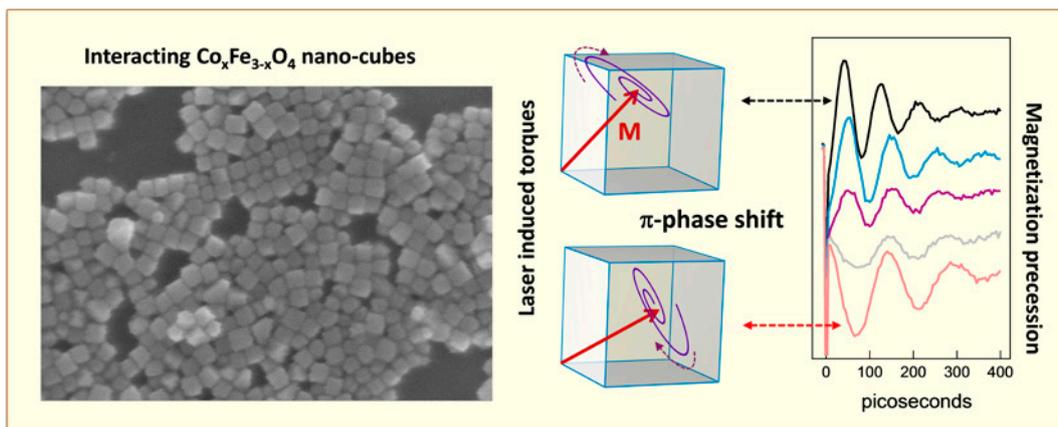
Contact:
Wolfgang.Weber@ipcms.unistra.fr

◆ Dynamical torque in Co_xFe_{3-x}O₄ nanocube thin films characterized by femtosecond magneto-optics: a π -shift control of the magnetization precession

The impulsive perturbation of the magnetization with laser pulses leads, in certain conditions, to a motion of precession which can be observed and analyzed directly in the time domain. Such impulsive method is particularly well suited to extract valuable information on the intrinsic parameters of confined magnetic nanostructures. In addition, one can follow the dynamics of the magnetization vector in the time domain and to directly

relate it to the torque as described in Landau-Lifshitz equation. However, the torque itself can be a dynamical quantity via the time dependent anisotropies of the system. A challenging problem then is to disentangle the relative importance of various sources of anisotropies in the dynamical torque, such as the dipolar field, the crystal structure or the shape of the particular interacting magnetic nanostructures.

Using interacting cobalt ferrite crystalline cubic nanoparticles, assembled in monolayers, we have recently shown how the frequency and phase of the magnetization precession can be controlled by femtosecond laser pulses. More precisely, the phase of the precession Φ_{prec} displays a π -shift for a particular angle Θ_H of an external static magnetic field \mathbf{H} . The π -shift results from the interplay between the



Monolayer of cobalt ferrite nanocubes and laser induced torque responsible for the π -phase shift of the magnetization precession.

time dependent magneto-crystalline and shape anisotropies. The value of Θ_H can be controlled with the concentration of Co which modifies the magneto-crystalline anisotropy of the nanocubes. It also depends on the laser intensity or on the degree of organization of the nanocubes which can be varied during their assembling in the presence of a magnetic field.

The experimental observations are well described by modeling the magnetiza-

tion dynamics using the Landau-Lifshitz-Gilbert equation taking into account the time dependent electron, spin and lattice temperatures, as well as the temperature dependent anisotropies.

Our approach allows studying the various types of anisotropies present in interacting nanostructures, and how they dynamically modify the torque which drives the precession of the magnetization. ■

M. Vomir, R. Turnbull, I. Birced, P. Parreira, D. A. MacLaren, S. L. Lee, P. Andre, and J.-Y. Bigot, "Dynamical torque in $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ nanocube thin films characterized by femtosecond magneto-optics: a π -shift control of the magnetization precession", *Nano Lett.*, **2016**, 16, 5291.

Contact:
Jean-Yves.Bigot@ipcms.unistra.fr

IPCMS News

AWARDS AND DISTINCTIONS

Several members of our lab have received prestigious distinctions this year :

- **Ms. Véronique Pierron-Bohnes**, research director (CNRS-IPCMS) has been honoured as "**Chevalier de la Légion d'Honneur**" (civil promotion January 2016)

She has joined the CNRS in 1982 and works on the coupling between structural and magnetic properties, as well as on the effect of nanostructuration in transition metal bimetallics, as alloys, multilayers and nanoparticles. She supervised 11 PhD students and 25 master trainees. She has published 93 publications in peer-reviewed journals, 4 book chapters, and 61 publications in peer-reviewed conference proceedings. She has established long-term collaborations with numerous teams, in France, but also in Mexico, the United States, Germany, Japan, Poland, Austria, Thailand and Algeria. In addition to her research work, her involvement in national research committees and in outreach activities was honoured by this distinction. In the framework of the SNCS scientific researcher union, she was elected and participated for 9 years to the National Committee for Scientific Research (CoNRS) in the committee dealing with 'Condensed matter physics: structures and electronic properties'. Moreover, she has different functions within the French Physics Society (SFP): first Treasurer then President of the Alsace group, member of the Scientific Council of the 'Condensed Matter' Division, member of the executive committee and then of the national Board of Directors, in charge of the commission "Women and Physics". She was interested in spreading science through the SFP, but also "Femmes & Sciences" and AMUSS organizations. Finally, with the "ConnaiSciences" association, she works to improve the integration of the campus in the Cronenbourg district, in particular by supporting the 'Disciples' association to help pupils in their homework on science subjects, both as voluntary and by finding other scientific volunteers.



From left to right: Michel Spiro, Claudine Hermann, Véronique Pierron-Bohnes, Marie-Claire Cadeville, René Voltz



- **The SFP (French Physical Society) has awarded the prize Ricard 2016 to Jean-Yves Bigot**, director of research at IPCMS. He is recognized for his work in the field of femtosecond spectroscopy.

Jean-Yves Bigot has conducted pioneering work in the field of femtosecond laser spectroscopy by opening a new research area with many ramifications to spin electronics, physics of the interaction between light and the magnetic field. ■■■

■■■ Areas of application encompass information storage, magnetic modulators, spatial and temporal control of nanoscale objects, transport and collection of charges in the light receiving devices. As of today, Jean-Yves Bigot and his team go further and develop numerous research projects at the scale of the attosecond (10⁻¹⁸ second) to observe the movements of electrons in atoms, study quantum wave functions or excited states of metal systems.

• CNRS Bronze medal winner for 2016 : Stéphane Berciaud

Stéphane Berciaud is an expert of graphene properties. His doctorate carried out between 2003 and 2006 at the University Bordeaux 1 focused on the optical absorption of individual nano-objects (in particular metallic nanoparticles, but also semiconductor nanocrystals and carbon nanotubes) by developing a photothermal spectroscopy technique.



During a postdoctoral stay at the Columbia University he became interested in graphene, while continuing research on carbon nanotubes. In 2010 he entered the University of Strasbourg and joined IPCMS. Inspired by the unique physico-chemical properties of graphene, his research is centered on optical, optoelectronic and optomechanical properties of quasi-two-dimensional systems.

From left to right: Patrice Soullie, regional representative of CNRS, Catherine Florentz, vice-president of "Université de Strasbourg", Stéphane Berciaud, Stefan Haacke, IPCMS director, and Niels Keller, Scientific deputy director of CNRS Institute of Physics

• Two members of IPCMS have been appointed as members of the **"Institut Universitaire de France"**, namely Stéphane Berciaud (also CNRS bronze medalist: see above) and Benoît Pichon. This Institute plays the role of a national agency highlighting and rewarding the achievements of outstanding researchers involved in university teaching.



• **Benoît Pichon's** research work aims at designing new magnetic nanomaterials in order to study their intrinsic and collective properties as function of size, shape, chemical composition and direct environment. The project supported by IUF aims at synthesizing and assembling a new type of nanoparticles which are made of several magnetic phases in order to produce permanent nanomagnets at room temperature. The effect of interactions between nanoparticles on their magnetic properties will be carefully investigated by addressing their assembly onto surfaces.

• 2016 prize "Espoirs de l'Université de Strasbourg" : Martin Bowen

As an IPCMS researcher, Martin specializes in spintronics, which is an electronics that takes into account the electron's spin. This magnetic and quantized property of the electron is intended to store and transmit information. Thanks to the quantum properties of materials within innovative devices, tomorrow's electronics will one day be capable of simultaneously treating all the possibilities of a data arborescence. Another vector for tomorrow's electronics, which also utilizes spintronics, is to treat data as would bio-inspired computing, by adapting the memory to the received stimuli, rather than in the deterministic mode of today's computers. These research axes generally pertain to the domain of multifunctional electronics, for which Martin operates and develops a high-performance measurement bench.



IPCMS News

- **Publisher:** Stefan Haacke - **Coordination:** Béatrice Masson
- **Redaction committee:** Emilie Delahaye, Salia Cherifi, Carlo Massobrio, Béatrice Masson
- To subscribe, contact beatrice.masson@ipcms.unistra.fr

I.P.C.M.S

23 rue du Loess - B.P. 43
F - 67034 Strasbourg cedex 2, France
Tél: +33 (0)3 88 10 71 41
Fax: +33 (0)3 88 10 72 50