

## ♦ Self constructing organic interconnects. A new paradigm for supramolecular electronics.

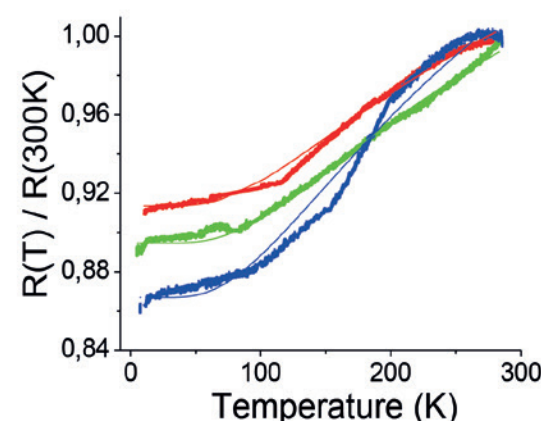
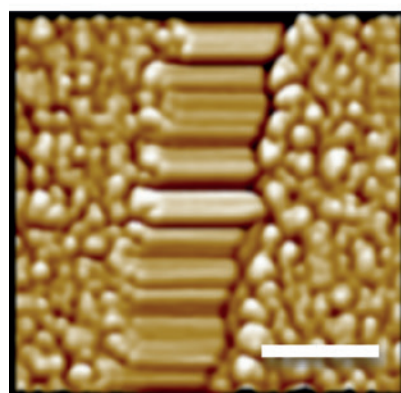
*Nature Chemistry*, 4, 485-490 (2012)

Organic conductors are becoming ubiquitous in nowadays electronics, with the advent of original technical solutions for entertainment and mobile electronics. However, metallic organic conductors remain very seldom, and creating fully organic organic circuitry remains a severe technical bottleneck. The most attractive existing candidates are based on carbon allotropes, more specifically carbon nanotubes or graphene. However, mastering their properties, and in particular their interface with standard metal-based interconnects, remains a far reaching goal.

Researchers at IPCMS and ICS laboratories developed an original approach to implement organic elements in a circuitry, showing unique metallic properties of organic conductors made of nanowires, which "self-assemble" when triggered by a flash of light. In previous work published in 2010 (1), N. Giuseppone and his colleagues observed that chemically modified "triarylaminates", exposed to light are partly transformed into more reactive radicals that trigger self-assembly in solution, resulting in miniature fibers. These wires, around 100 nanometers long and 10 nm in diameter, are made up of a "supramolecular" assembly of several thousand molecules. In collaboration with B. Doudin's team, the researchers then investigated how to self-assemble between metallic electrodes.

For this purpose, they used robust metallic interconnects separated by a tuned distance of 100 nm, designed in the clean-room facilities of IPCMS STnano (2). Their first important finding was that, when triggered by a flash of light, the fibers self-assemble solely between the electrodes. The second surprising result was that these structures, which are as light and flexible as plastics, turn out to be capable of transporting extraordinary current densities, above  $2 \cdot 10^6$  Amperes per square centimeter ( $A \cdot cm^{-2}$ ), approaching those of copper wires. In addition, they have very low interface resistance with metals: 10,000 times below that of the best organic polymers (3).

When investigating how the electrical resistance behaves when lowering the temperature, they found a systematic decrease of the value when cooling down, a typical signature of a metal. This milestone discovery opens new possibilities in the field of supramolecular electronics, where the weak bond between molecules make self-repair and adaptability of the structures possible. The multiple possible variations of the molecules side chains allows the chemist to tune the properties, opening, for example, the possibility to create longer and more robust fibers. These results also illustrate how metallic interconnects can be grown at desired controlled locations, which is an old dream for scientist working with carbon nanotubes and supramolecular nanowires. ■



◀ Left: AFM picture (courtesy M. Maaloum, ICS) of the self-assembled wires (horizontal bars) sandwiched between two Au electrodes. Scale bar is 100 nm long.

Right: relative change of resistance as a function of temperature for three different samples.

### References:

1. The Hierarchical Self-Assembly of Charge Nanocarriers: A Highly Cooperative Process Promoted by Visible Light, E. Moulin, F. Niess, M. Maaloum, E. Buhler, I. Nyrkova, N. Giuseppone, *Angew. Chem. Int. Ed.* **49**, 6974-6978 (2010)
2. Nanotrench for nano and micro particle electrical interconnects, J.-F. Dayen, V. Faramarzi, M. Pauly, N. T. Kemp, M. Barbero, B. P. Pichon, H. Majjad, S. Begin-Colin and B. Doudin, *Nanotechnology*, **21**, 335303 (2010)
3. Light triggered self-construction of supramolecular organic nanowires as metallic interconnects, V. Faramarzi, F. Niess, E. Moulin, M. Maaloum, J.-F. Dayen, J.-B. Beaufrand, S. Zanettini, B. Doudin, N. Giuseppone, *Nature Chemistry* **4**, 485-490 (2012)
4. Conduction électrique par des assemblages supramoléculaires de triarylaminés, N. Giuseppone, B. Doudin, V. Faramarzi, J.-F. Dayen, E. Moulin, F. Niess, brevet F10 58954
5. Electrical conduction through supramolecular assemblies of triarylaminés, N. Giuseppone, B. Doudin, V. Faramarzi, J.-F. Dayen, E. Moulin, F. Niess, Provisional US US61/418645

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## Summary

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## Editorial

On January 1st, 2013 IPCMS has got a new board of directors, with the nomination of Stefan Haacke (director) and Carlo Massobrio (deputy director). The former head of IPCMS, Marc Drillon, looks back on a remarkably successful 10-years mandate, during which he has shaped the Institute by contributing to the creation of high-performance technology platforms, the promotion of new interdisciplinary research axes across the Institute's departments, and the establishment of IPCMS as a nationally and internationally renowned center for Nanomaterial Science. The recent success at the national excellence initiatives "Investissements d'avenir" crowned his sustained effort and visionary actions, and those of his former deputy directors C. Hirlimann, D. Guillon, Y. Galerne and J.-Y. Bigot.

In the new directory duo Carlo Massobrio is an expert of atomic-scale ab-initio computational methods in the area of material science. Stefan Haacke has a research record on ultrafast phenomena in biomolecules as well as organic and inorganic nanostructures, and was the former head of the department for Ultrafast Optics and Nanophotonics at IPCMS. Stefan and Carlo, in close connection with the five heads of the IPCMS departments (E. Beaurepaire, J.-L. Gallani, P. Gilliot, G. Pourroy, W. Weber) will build on former actions with the aim of sustainably enabling innovation and scientific breakthroughs at IPCMS.

The present issue of IPCMS News gathers six research highlights recently published. Low-temperature STM experiments performed across a single Co atom exhibit a systematic dependence of the Abrikosov-Suhl-Kondo resonance linewidth as a function of the conductance of the junction, providing new insights of these quantum effects in the limit of ballistic conductance. High resolution analytical electron tomography of nitrogen doped multi-wall CNTs has shown the formation of intra-wall arches and interesting modifications of the nanotube morphology close to the arch end points, pointing to a N concentration-dependent growth method of the arches. Along similar lines, a new milestone in supramolecular electronics has been reached by connecting metallic contacts to self-assembled organic wires with very low interface resistance. Those wires reproducibly display metal-like current densities and temperature dependencies of conductivity. Equally remarkable results were obtained for nano-contacts with thin sheets made of zwitterionic molecules, opening new perspectives for the control of charge and possibly spin injection into organic nanomaterials. Regarding magnetic nanomaterials, a combined investigation of the ultrafast laser-induced response and the chemical topology of core shell Co-Pt nanoparticles exhibit in detail how their magnetic properties change from superpara- to ferromagnetic upon high temperature annealing. Last but not least, new insights into the microscopic origins of anisotropic magnetoresistance across a domain wall were obtained in a combined experimental and theoretical study that shed new light on the so far overestimated role of spin-orbit interactions.

Stefan Haacke, Director

### IPCMS News

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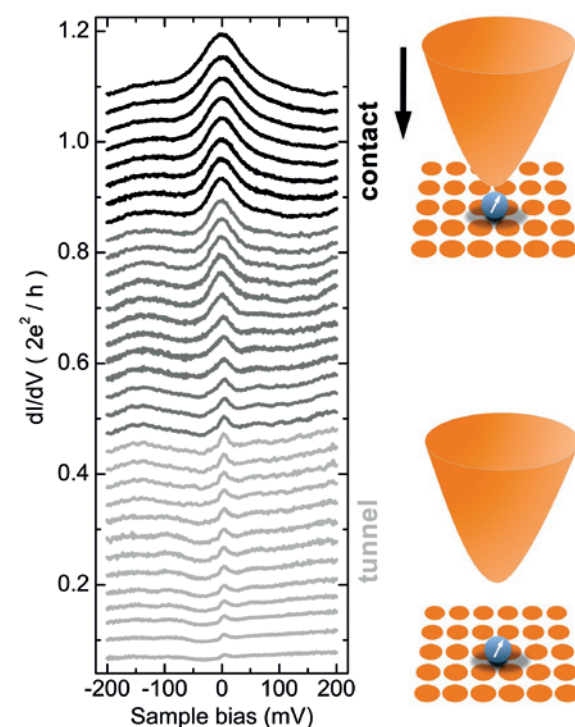
## ◆ Conductance-driven change of the Kondo effect in a single cobalt atom

The Kondo effect offers the unique opportunity of studying electron correlations in a single object, which are of importance to the emerging field of spintronics where partially filled d or f shells play a central role. This many-body effect arises due to spin-flip processes involving a localized spin carried by an impurity and the electronic spins of the host metal. The Kondo effect has been successfully evidenced through a zero-bias anomaly, also known as the Abrikosov-Suhl-Kondo (ASK) resonance, in the conductance of lithographically defined quantum dots, carbon nanotubes, or single molecules coupled to metallic electrodes. A fine-tuning of the impurity-electrode hybridization could provide an interesting way to test the impact of structural changes on Kondo correlations. It was recognized quite early—for example, by exerting a hydrostatic pressure on the host crystal—that the Kondo effect is in fact exponentially sensitive to these changes. To date, however, the lack of control over this hybridization has resulted in a strongly device-dependent effect.

Surprisingly, the ASK resonance was shown in previous studies of this kind to be little affected by structural changes induced by the tip-atom contact. Motivated by this apparent discrepancy, we revisit in this study the tip contact with a Co atom on Cu(100). We show that atomic relaxations produced by the tip displacement continuously affect both the ASK resonance and the conductance prior to and after tip contact. A reproducible exponential variation of the ASK line width with the conductance is evidenced and explained through an Anderson-based model. Our findings demonstrate that the Kondo effect of single atoms adsorbed on a metal surface may be tuned via the ballistic conductance of the junction. ■

D.-J. Choi, M. V. Rastei, P. Simon, L. Limot, *Phys. Rev. Lett.* **108**, 266803 (2012)

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▲ Sketch of the experimental setup showing a copper-coated tip moving into contact with a Co atom on Cu(100). The set of  $dI/dV$  spectra shows the evolution of the Kondo effect from the tunneling regime to the contact regime. Each spectrum is acquired by freezing the geometry of the junction at a given conductance.

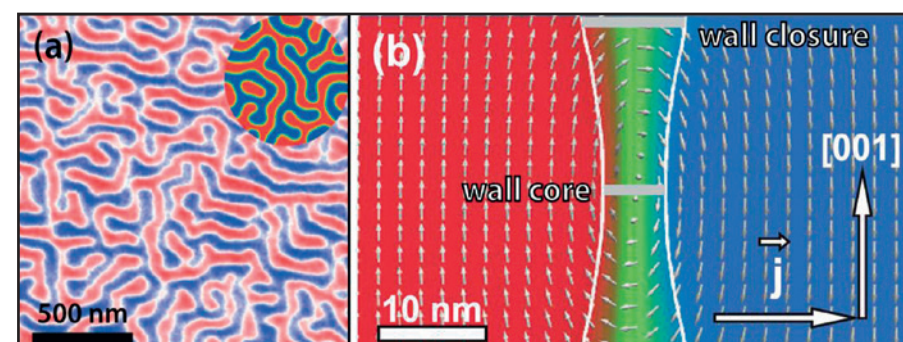
## ◆ Understanding domain wall resistivity

Modern nanospintronic technology attempts to exploit domain walls for information storage and processing. A domain wall is

a transition region in a ferromagnet where the magnetization changes its direction, typically by  $180^\circ$ . Such domain walls can

be manipulated and detected by means of electric currents. The detection is usually based on the long-known anisotropic magnetoresistance effect (AMR), which experiences a renaissance in the wake of these developments.

The AMR was discovered by Lord Kelvin who found that an electric current running through a ferromagnet experiences a change in resistivity depending on the angle enclosed between the current flow direction and the orientation of the magnetization. This can be regarded as the foundation of modern spin- and magnetoelectronics. Intense research on the interaction between electric currents and ferromagnets has eventually led to the Nobel-Prize-winning discovery of the giant magnetoresistance effect.



▲ X-ray magnetic circular dichroism photoelectron emission microscopy image of the domains in a  $L1_0$ -ordered FePd film of 30 nm thickness (a). The circle in the upper right displays the simulated domain structure on the surface (a). The domain wall profile changes along the film thickness, as evidenced by cross-sections calculated with micromagnetic simulations (b).

While spintronics and magnetoelectronics made spectacular scientific progress in the past years, a solid basis for the AMR effect and its microscopic origins still represents a challenge for theory. Moreover, when the AMR effect is applied to domain walls, it is important to consider that their profile is more complex than often suggested in textbooks.

First-principles calculations have been employed to quantify the electron transport through a domain wall, but they

require the precise domain wall profile as input parameter. This information was provided by three-dimensional finite-element micromagnetic simulations which reproduce in great detail the magnetic domain structures observed in experiments. The experiments directly connect to the micromagnetic simulation studies, ensuring that the computed magnetic structure corresponds to the real one. Hence, by combining ab initio electron theory, micromagnetic simulation studies, experimental AMR measurements and high-resolution

magnetic imaging techniques, the domain wall resistance could be analyzed precisely. The study shows that the spin-orbit interaction only plays a minor role, and that the smallest transition region dominates the overall resistance of a domain wall. ■

K. M. Seemann et al., *Phys. Rev. Lett.* **108**, 077201 (2012)

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## ◆ Analytical electron tomography of nitrogen doped carbon nanotubes

We illustrate here the application of the energy filtered transmission electron microscopy (EFTEM) in the tomographic mode to determine the precise 3D distribution of nitrogen within nitrogen-doped carbon nanotubes (N-CNTs). Several tilt series of energy-filtered images were acquired on the K ionization edges of carbon and nitrogen on a multiwalled NCNT containing a high amount of nitrogen. Two tilt series of carbon and nitrogen 2D maps were then calculated from the corresponding energy-filtered images by using a proper extraction procedure of the chemical signals. The use of iterative reconstruction algorithms provided two spatially correlated C and N elemental-selective volumes, which were then simultaneously analyzed using the shape-sensitive reconstruction deduced from Zero-Loss record-

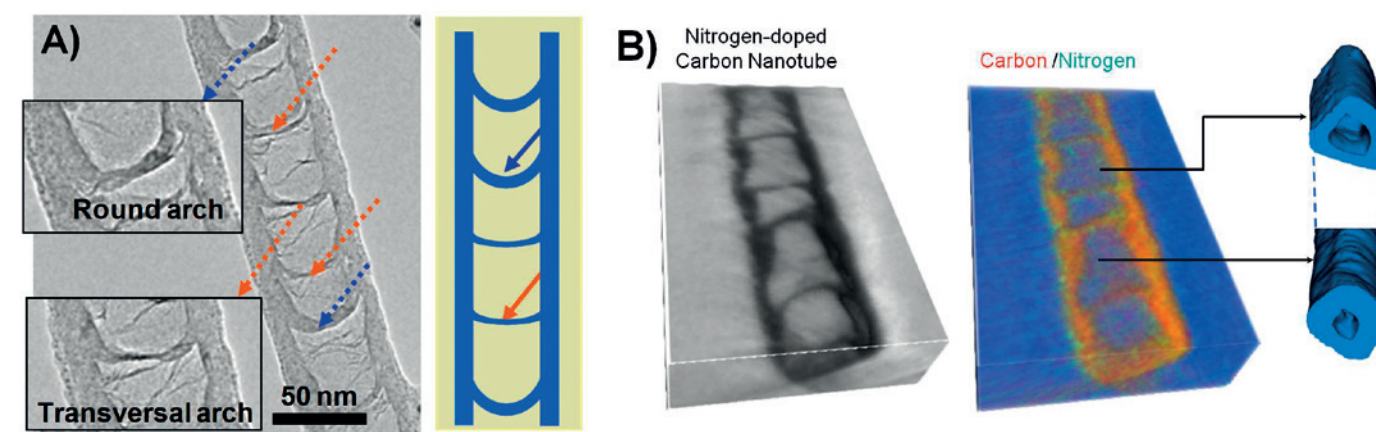
ings. Crucial information was obtained by analyzing the 3D chemical maps showing that, among the two kinds of arches present in these nanotubes (transversal or rounded ones), the transversal arches do contain more nitrogen than the round ones. In addition, a detailed analysis of the shape-sensitive volume allowed the observation of an unexpected change in the morphology of the NCNT along the tube axis: close to the round arches (with less N), the tube is roughly cylindrical, whereas near the transversal ones (with more N), its shape changes to the one of a prism. The new analytical tomography technique presented here is very powerful in the field of material science because it combines the ability of the classical electron tomography to solve 3D structures and the chemical selectivity of the EFTEM imaging, allowing

thus to resolve the spatial distribution of the various constituents of the material of interest at the nanoscale. ■

3D Analysis of the Morphology and Spatial Distribution of Nitrogen in Nitrogen-Doped Carbon Nanotubes by Energy-Filtered Transmission Electron Microscopy Tomography

Ileana Florea, Ovidiu Ersen, Raul Arenal, Dris Ihiawakrim, Cédric Messaoudi, Kambiz Chizari, Izabela Janowska and Cuong Pham-Huu, *J. Am. Chem. Soc.* **134**, 9672–9680 (2012).

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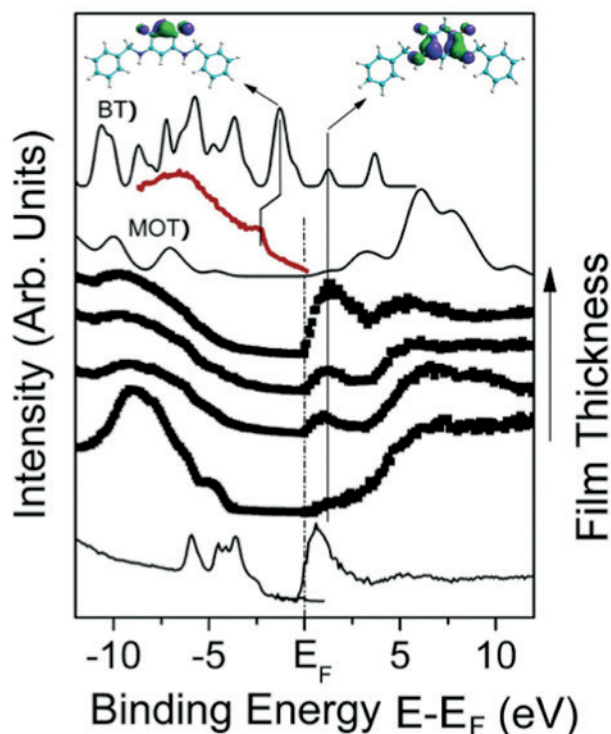


▲ Morphology and spatial distribution of nitrogen in N-doped carbon nanotubes. A) 2D microstructure of highly nitrogen doped CNTs. B) 3D chemical representation obtained using EFTEM tomography and showing a direct correlation between the shape of the tube in cross-section and the local nitrogen content.

## ♦ Engineering the organic-metal interface electronic properties using zwitterionic molecules

Electronic properties at the metal-organic interface are a key issue in organic electronics. The large density of carriers in a crystalline metallic conductor does not match easily to the scarce unbound charges and the disordered character of organic adlayers. Electrical properties in molecules rely on the position of the highest occupied (HOMO) and lowest unoccupied (LUMO) energy levels, which also characterize, while broadened, organic layers. In organic semiconductor devices, the alignment of the metal electrode Fermi level with the HOMO (LUMO) determines how easy it is to inject holes (electrons) in the semiconductor. However, molecular levels are generally shifted when the molecules are brought into contact with a conducting substrate, and simple explanations based on vacuum levels alignment fail. The fundamental reason is that the energy level alignment is dependent on the interfacial electronic structure and on interfacial dipole layer, possibly complicated by charge exchange and chemisorption of the molecular films. Significant interface resistance becomes an important bottleneck to device efficiency, and explains in particular why miniaturization of organic electronics devices remains a challenge. This is especially critical for spintronics devices, where one would like to inject and collect spins over significant distances, requiring lowering of the interface resistance.

A possible method to tune the energy level of the charges injection is to rely on dipolar molecules, known to screen and shift efficiently the interface dipoles. However, the charge injection remains limited by the intrinsic dielectric properties of the typical 'long' non-conjugated molecules used. In his search for efficient spin injectors, the team of B. Doudin started collaboration with the team of P. Braunstein (Institut de Chimie, Strasbourg). They developed a unique class of molecule, which are zwitterionic molecules of the p-benzoquinoneminoimine. Although electrically neutral



◀ Density of states (DOS) of ultra-thin films of zwitterions, measured with a combination of photoemission and inverse photoemission spectroscopies. The bottom curve is the reference Au substrate, while Fermi level is indicated by the dashed vertical line. The films exhibit a shoulder in their DOS, indicative of possible good conduction. Their DOS cannot be explained through a simple broadening of free molecule levels (MOT), and need calculations based on band structure hypothesis (BT).

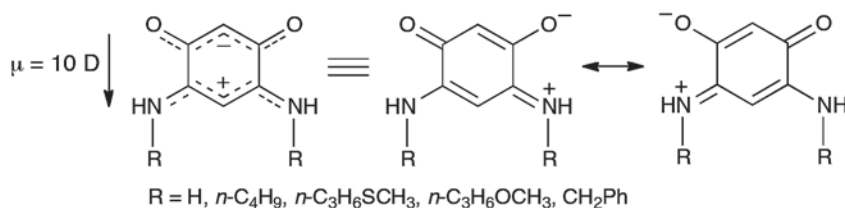
as a whole, these quinoneminoimines carry positive and negative charges on opposite parts of the molecule that are electronically isolated but chemically connected through carbon-carbon single bonds. The overall  $12\pi$  electrons are thus partitioned into two  $6\pi$ -electrons sub-units: the positive charge is delocalized between the nitrogen functions over four bonds involving  $6\pi$ -electrons, while the negative charge is likewise spread between the oxygen atoms (Scheme 1). The resulting large electric dipole of typically 10 D is formed across the planar six-membered ring structure of the benzoquinoneminoimine "core". They are therefore a unique class of 'short' molecules with a large electric dipole.

In a collaborative effort involving scientists at ICS (team of G. Decher) and University of Nebraska-Lincoln, USA (team of P. Dowben), a combination of surface analysis

techniques was used to characterize thin films of quinonoid zwitterions on metallic surfaces. They found that ultra-thin films (1-2 nm) without pinholes self-assemble, and exhibit unique electronic properties. These films are made of molecules 'standing-up', with some cases of crystalline ordering showing dense  $\pi$ - $\pi$  stacking. Their surface electronic properties show a remarkably good screening of the interface dipole, and charges-transparent interfacial properties. Initial test of electrical device properties indicate that the films improve the charge injection, with possible n-type semiconductor of high mobility. A patent has been successfully granted. ■

L. Routaboul, P. Braunstein, J. Xiao, Z. Zhang, G. Dalmas, V. DaCosta, C. Felix, O. Kizilkaya, P. A Dowben and B. Doudin, *Molecular Films of p-benzoquinoneminoimine Zwitterionic Compounds*, J. Amer. Chem. Soc. **134**, 8494-8506 (2012)

Utilisation de molécules à caractère zwitterionique pour la formation d'une couche de transport de trous ou d'électrons, B. Doudin, P. Braunstein, L. Routaboul, G. Dalmas, P. Dowben, Z. Zhang, patent F 03428



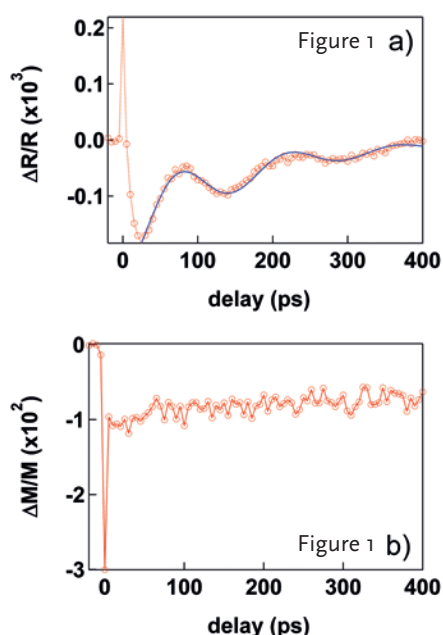
▲ Scheme 1: The resonance form of the quinonoid zwitterion molecules.

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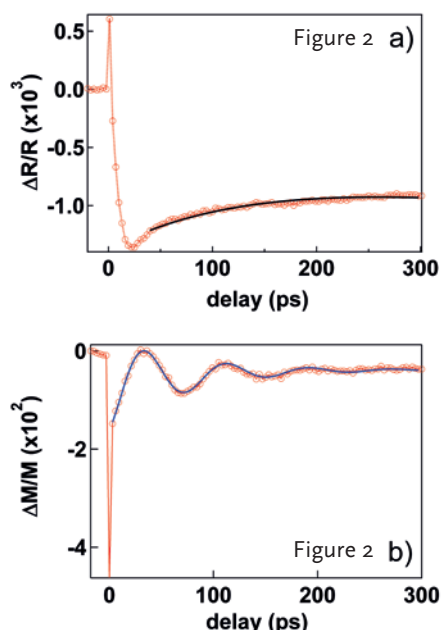
# ◆ Magnetic Properties of Annealed Core-Shell Co-Pt Nanoparticles

Close packed core-shell magnetic nanoparticles, made through soft chemistry, are interesting for applications in magneto-optics, data storage or nano-electronics. One way for obtaining high densities of such nanoparticles is to let them self-assemble and realize supra-crystals or simply to compress the nanoparticles into pellets. In this work, we have studied the effect of thermal annealing on the optical and magnetic properties of the nanoparticles.



We started from Co-Pt core-shell nanoparticles assembled into pellets (cobalt core has average diameter 5 nm and platinum shell has average thickness 1.5 nm). These nanoparticles are superparamagnetic at room temperature with a blocking temperature  $T_B = 66$  K. A mild laser annealing, obtained by local heating of the surface of the nanoparticles, reorganizes them into a supra-crystalline phase without modifying individually the nanoparticles. As a consequence, the time resolved reflectivity of the sample, measured by ultrafast pump-probe spectroscopy, displays oscillations with a 145-ps period as shown in Figure 1a). These oscillations are due to the collective mode of the supra-crystalline ordering (the nanoparticles vibrate coherently). In contrast, the magnetization dynamics, measured by ultrafast magneto-optical Kerr effect, displays a monotonous behavior as seen in Figure 1b). Three main temporal behaviors are present, corresponding to the laser induced demagnetization, a partial re-magnetization when the spins

and lattice reach the same temperature, and the long lasting heat diffusion into the environment.



The situation is very different when a higher temperature annealing is performed in an oven up to 650 K. In that case the nanoparticles become ferromagnetic with a new blocking temperature  $T_{B, \text{anneal}} = 347$  K. Consequently, the dynamical reflectivity of the pellet sample is monotonous as seen in Figure 2a) because the supra-crystalline order has disappeared due to a heat induced disorder. In that case, the magnetization dynamics presents damped oscillations (Fig. 2b) due to the motion of

precession of the magnetic vector, characteristic of ferromagnetic nanoparticles which behave as nano-gyroscopes.

A detailed electron microscopy study performed before, during and after the annealing allowed us to show that these dynamical behaviors are due to the diffusion of the platinum shell into the cobalt core, so that CoPt nanoparticles with a larger anisotropy (and coercive field) are formed upon annealing. Figure 3 displays the electron microscope imaging, with an in situ temperature variation and a chemical analysis: 3a) HAADF images of the pellet with thermal treatment up to 700 K and 3b) Intensity profiles of an individual particle extracted from the HAADF images along the arrow in a). Clearly, the morphology of a core-shell like nanoparticle (300 K) evolves progressively with the increasing temperature, such that at 700 K the core-shell structure becomes a homogenous one with CoPt and CoPt<sub>3</sub> crystalline structure.

These studies show the importance of controlling the structural and dimensions of core-shell nanoparticles to optimize their magnetic and optical properties in view of their applications to optoelectronics and spin-photonics. ■

J.-Y. Bigot, H. Kesserwan, V. Halté, O. Ersen, M. Simona Moldovan, *Magnetic properties of annealed core-shell CoPt nanoparticles*, *Nano Letters*, **12**, 1189-1197, 2012

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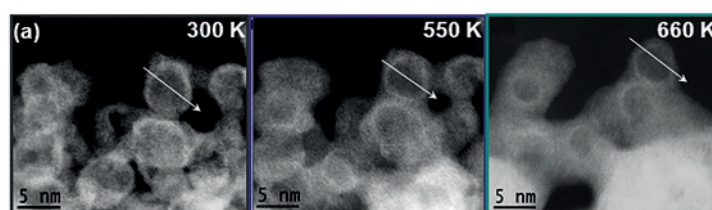


Figure 3

