



► across ordered  $H_2Pc$  with a barrier of 0,148 eV. The conductance exhibits the signature of resonant tunneling across the energy levels of the molecules. Below 130 K, transport is activated with a barrier of  $5,8 \cdot 10^{-4}$  eV and exhibits at low temperature a zero-bias conductance anomaly.

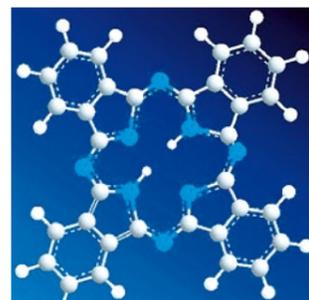
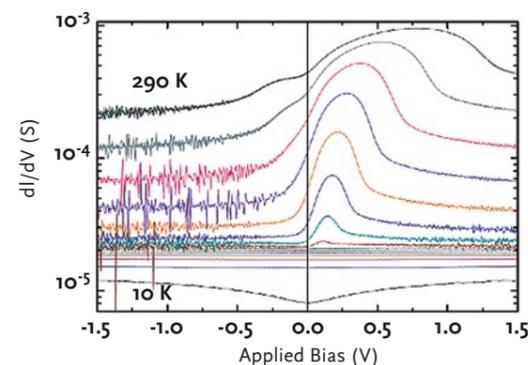
Underscoring the absence of magnetoresistance, our bias- and temperature-dependent measurements reveal the overarching role of defects/trap levels that are present within the structurally ordered phthalocyanine spacer on the junction's electrical and spin transport response.

These results invite greater scrutiny on the structural quality of organic spacer layers in junctions. In a future step, it will be crucial to achieve an all-epitaxial organic junction with ferromagnetic electrodes in order to explicitly promote the convergence between experiment and theory in the dynamic and expanding field of organic/molecular spintronics. ■

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S. Boukari, A. Ghaddar, Y. Henry, J. Arabski, V. Da Costa, M. Bowen, J. Le Moigne, E. Beaurepaire.  
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$Co(40\text{ nm})/H_2Pc(100\text{ nm})/Permalloy(20\text{ nm})$ : Conductance as a function of applied bias for several temperatures in 20 K steps. On the right, phthalocyanine molecule  $H_2Pc$ .

## IPCMS News

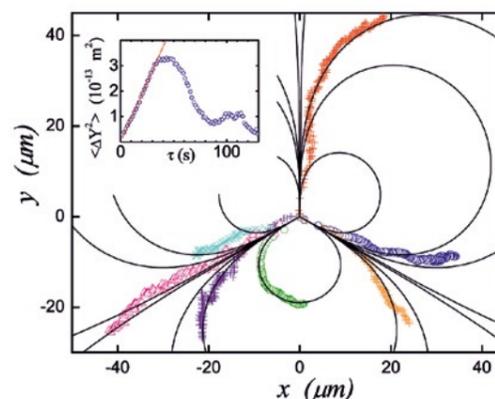
### ◆ Colloidal interaction in the nematic phase

We studied the attraction that disclination lines produce on colloidal particles dispersed in a liquid crystal nematic phase. The disclination lines, or defect lines, are places where the orientation of the molecules in the nematic phase cannot be defined. They produce a distortion around them that interferes with the distortion generated by the particle. Therefore, the consecutive distortion change produces a variation in the overall elastic energy that corresponds to the interaction of the particle with the line. At large distance, the distortions are small, and the elastic energy may simply be written as a quadratic form, similar to the electrostatic energy. Both problems should therefore be analogous to each other.

In order to test this prediction, we have measured the velocity of small glass particles ( $\sim 1\ \mu\text{m}$ ) that are dispersed in a nematic phase close to a disclination line. We then

deduced the attraction force that the line exerts onto them from the hydrodynamic drag expression. It is of the order 1 picoNewton, and decreases as the square inverse of their distance to the defect, as in electrostatics. However, we observe that the trajectory, after averaging the Brownian fluctuations, are not rectilinear, and that consequently the force field around a defect line is not radial (see figure). In fact, this unusual property results from the non-radial symmetry of the defect line itself. In that sense, the electrostatic analogy is not complete.

Ultimately, the particle reaches the disclination line and sticks onto it. Other particles are attracted too and similarly stick on the disclination line until, after a while, they build up a kind of necklace at the microscopic scale. ■



Agreement between the model of non-radial trajectories and the experiment. The inset shows the analysis of the Brownian motion around the average trajectory, which yields the particle radius.

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### Summary

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### Editorial

The present issue of *IPCMS News* reports some recent developments carried out in our institute in the field of soft condensed matter and in the domain of simulation and physical studies of nanomaterials. The first reported room temperature nematic  $C_{60}$ -based material opens the way to multifunctional materials that can take advantage of an easy orientation of active chromophores to be particularly efficient, for example in the design of photovoltaic materials. An experimental study of the nematic force in the interaction of a colloidal particle with 1D system has been performed; it is shown that this defect attracts the beads along nonradial tracks in a self-assembling process. On the other hand, DFT calculations have demonstrated that highly Si-doped  $C_{60-m}Si_m$  heterofullerenes are thermally stable as long as Si atoms neighbors of C atoms in segregated regions are predominant over inner Si atoms. For the first time, 3D-electron microscopy technique has allowed to visualize the filling of carbon nanotubes by Pd nanoparticles; it is demonstrated that it can be extremely useful to get more insight on the morphology and location of metal nanoparticles within a porous material. Finally, transport measurements on a ferromagnetic hybrid metallic/organic semiconductor junction reveal the fundamental role of defects and/or trap levels, present in the structurally ordered phthalocyanine layer, on the junction's electrical and spin transport response.

In view of strengthening the partnerships of IPCMS with foreign institutions, a visit of several scientists of IPCMS has been organized in June 2007 at Bangalore in the framework of the 4<sup>th</sup> Meeting of the Indian-French Laboratory for Solid State Chemistry. Following the close interactions existing between both countries for many years, Indian and French partners will propose the creation of an Associated International Laboratory on the same themes, involving the Indian Institute of Science of Bangalore (*IISc*), the Indian Institute of Technology in Bombay (*IIT*), the Indian Institute of Technology in Madras (*IIT*), the Institut de Chimie de la Matière Condensée de Bordeaux (*ICMCB*), the Laboratoire de Cristallographie et Science des Matériaux de Caen (*CRISMAT*) and the Institut de Physique et Chimie des Matériaux de Strasbourg (*IPCMS*).

Marc Drillon  
Director

## ◆ 3D electron microscopy study of metal nanoparticles inside carbon nanotubes

During the past few years, several attempts have been focused on the introduction of foreign elements inside the carbon nanotubes with a hope of generating new composite materials with atypical properties. The filling is based on the low surface tension of the aqueous solution containing the metal salt with respect to carbon nanotube, and capillarity forces which aspirate the liquid into the nanotube channel. The most popular technique for the study of elements trapped inside nanotubes is the transmission electron microscopy (TEM) which delivers a first insight of the particle size and morphology provided by 2D projections of the solid structure. Nevertheless, the real location and morphology of the deposited foreign elements are not fully established due to the 2D char-

acter of traditional TEM images that are in fact projections of a 3D solid structure. In this framework, the location of palladium nanoparticles on and inside the multi-walled carbon nanotubes channel is presented for the first time using electron tomography (3D TEM). This technique consists in the volume reconstruction of an object from one or several series of its projections recorded by electron microscopy and is able to yield information of volumetric character on complex objects. In our case, it allows one to obtain precisely the position of the nanoparticles with respect to the nanotube and to calculate the efficiency of the filling process: a filling efficiency of about 50% can be achieved with tube having an inner diameter of ca. 30 nm whereas it became almost



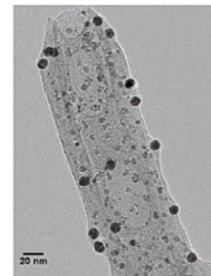
nil when the inner diameter of the tube was decreased from 30 to 15 nm. 3D-TEM analysis also allows one to confirm that after acidic treatment both surfaces of the nanotube were similar in nature, leading to a high dispersion of the Pd particles with narrow size distribution. Moreover, from the analysis of the reconstructed volume, the morphology of this complex sample was also precisely deduced: excepting the nanoparticles and the nanotube, a residual phase coming from the liquid solution is trapped inside the nanotube channel and on the outer surface. ■

This work is a part of an exemplary collaboration between IPCMS and LMSPC (Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse). The data acquisition was carried out at the IGBMC of Strasbourg.

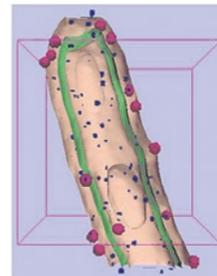
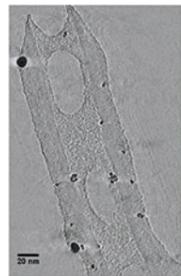
Ovidiu Ersen, Jacques Werckmann, Matthieu Houle, Marc-Jacques Ledoux, and Cuong Pham-Huu. Nano Letters 7 (2007) 1898-1907.

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(Left) Typical 2D-TEM image (one of the projections of the object).



(Middle) Longitudinal section through the reconstructed volume.



(Right) View of the 3D reconstruction model: in red, gold particles; blue, palladium particles; green, carbon nanotube.

## ◆ Doping fullerenes with silicon : identification of a dynamical threshold

The main purpose of doping fullerenes is the enhancement of their chemical reactivity, this condition being especially met in substitutional doping, where the original cage structure is altered mostly in the vicinity of the dopant atom. In early mass spectroscopy experiments Si was selected as a viable candidate to ensure minimal electronic and structural perturbation of the cage. This is due to its vicinity to carbon in the periodic table, Si and C having the same number of valence electrons. The question arises on the largest number of Si replacing C in  $C_{60}$  without altering irreversibly its peculiar cage structure. We have addressed this issue in the framework of first-principles molecular dynamics. This approach allows for the self-consistent



$$C_{40}Si_{20} : \rho = 0.07 e / (a.u.)^3$$

One example of Si-doped heterofullerene:  $C_{40}Si_{20}$ , shown with the electronic valence density, predominantly distributed on the C atoms. Pockets of electronic density are visible in between the Si atoms (in black).

evolution of the temporal trajectories, the electronic structure adjusting adiabatically to changes in the atomic configurations. As a first step, stable isomers for various Si contents have been found by structural optimization at  $T=0K$ .  $C_{(60-n)}Si_n$  systems are characterized by the separation of C and Si in two distinct networks. These arrangements are largely favored over a set of disjointed Si and C regions.

Molecular dynamics performed at various temperatures in the range  $1000 K < T < 4000 K$  for  $C_{36}Si_{24}$  and  $C_{30}Si_{30}$  reveals that the seed of thermal instability has to be localized in the innermost Si region, since those atoms are the first to depart from their equilibrium positions when the temperature is increased. The

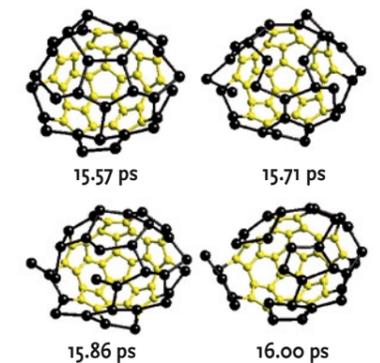
origin of this instability can be understood by observing the charge distribution within the cage. Highly coulombic Si-C bonds, stemming from the larger electronegativity of C, stabilize the Si atoms at the frontier with C atoms. This interaction compensates the unfavorable  $sp^2$  environment of the Si atoms involved. Such counteracting effect does not occur inside the Si regions where charges essentially vanish.

Therefore, the effect of temperature is to induce strong repulsive interactions among pairs of Si, by causing the fragmentation of the cage. Based on this rationale, we assert that  $C_{40}Si_{20}$ , in which the number

of Si atoms at the frontier with C equals the number of inner Si atoms, is the best candidate for the upper limit of structural stability in  $C_{(60-n)}Si_n$  systems. This works opens new perspectives toward the synthesis of doped fullerene materials by highlighting the dynamical nature of their lack of stability for a large doping content. ■

M. Matsubara, J. Kortus, J.-C. Parlebas, C. Massobrio. Phys. Rev. Lett. 96, 155502 (2006).

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Dynamical evolution of  $C_{30}Si_{30}$  during the first stages of fragmentation at  $T=3000K$ .

## ◆ First Room Temperature Nematic [60]Fullerene supermolecule

Over the last decade, [60]fullerene has attracted considerable attention in materials science. Notably, several efforts have been aimed at producing liquid-crystalline  $C_{60}$ -based materials for added value in the form of increased processability, film formation, and control over self-assembly. As [60]fullerene can be considered as a versatile hard building block for dendritic systems due to its tunable core valency (1 to 6) and regioselective polyaddition, we were interested to look further at its use as a template to build multicomponent supermolecules. Applying the "orthogonal transposition" described by B. Krautler and the Diederich's method of "tether directed remote functionalization" for specific multifunctionalized [60]fullerenes, it would be possible to regioselectively prepare new three dimensionally structured molecules and thus new structural

motifs impossible to obtain starting from other multivalent cores such as silsesquioxanes or gold nanoparticles.

The work described is a first step towards our attempts to reach and to control ordered arrays containing [60]fullerene. Hexaaddition on the carbonated polyhedron has allowed the preparation, in high yield, of an enantiotropic, room tempera-

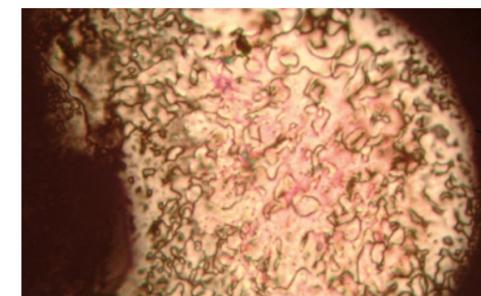
ture nematic material, despite the absence of mesomorphism of the malonate side-group promoters.

On subsequent heating-cooling cycles, a stable and reproducible behavior took place with the reversible sequence Glass (G) 13 Nematic (N) 60 Isotropic (I).

The highly symmetric [60]fullerene accordingly represents a particularly versatile scaffold for the regioselective covalent assembly of a variety of regular three dimensionally structured molecules, some of which may enlarge the existing repertoire of programmed molecular components for the construction of useful ordered materials. ■

H. Mamlouk, B. Heinrich, C. Bourgogne, B. Donnio, D. Guillon, D. Felder-Flesch, J. Mater. Chem. 2007, 17, 2199-2207

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Threaded optical texture of the nematic phase.

## ◆ Electrical transport across structurally ordered phthalocyanine

Interest in the electrical transport properties across molecules is increasing within the paradigm of molecular electronics, and has recently led to the demonstration that the electron spin may be manipulated in molecular devices. The transport properties of these molecular systems are different from their inorganic counterpart because the electronic structure of the

molecules can change significantly upon applying a bias voltage. Furthermore, the molecular conformation can be temperature-dependent. This raises the question of the impact on electrical and spin transport of the structural properties of the organic spacer, from the molecule to thin films. This question is especially relevant in the context of compelling yet not fully under-

stood results such as the observation of spin-polarized transport across an amorphous organic spacer as reported recently. In such cases, the observation of magnetoresistance, which can reach large values despite sparse sample preparation precautions and large junction areas, suggests that hidden parameters may be at play. We performed transport measurements ►►