



# IPCMS

International Newsletter

# News

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## Editorial

The IPCMS was officially founded at the end of 1987, taking advantage of the synergies between physicists and chemists in Strasbourg, and highlighting the strategic importance of materials for innovative technologies. Such interdisciplinary approach was extremely original in the French scientific landscape at that time, as it exhibited a very interdisciplinary organization of science. The 30<sup>th</sup> anniversary of the laboratory was celebrated on April 4<sup>th</sup>-6<sup>th</sup> 2018, in the presence of all previous directors and the representatives of local and national institutions. Scientific presentations by present and former members of IPCMS, as well as by colleagues of partner laboratories, were organized during a 3 day meeting. This workshop gave a valuable insight on the evolution of the IPCMS and its present and future scientific activity.

Less than one month after this exciting scientific event, life recalled us it is made of joy or sadness. Two of our most renowned colleagues, Eric Beaurepaire and Jean-Yves Bigot passed away within a few days apart. They personified a success story in interdisciplinary research based on state of the art physics.

The initial spirit of the research in physics and chemistry of materials at the IPCMS is still alive and striving. Research topics and instrumental innovation evolved significantly during these three decades, fostering the relation to new scientific and societal concerns, with a marked interest in domains at the interfaces, particularly towards biology or quantum technologies. We provide in this issue some recent examples of activities developed by young researchers, for which the complementary competences of our physics and chemistry knowhows are a strong asset.

Pierre Rabu, *Director*



From left to right : Jean-Claude Bernier, Bernard Carrière, François Gautier, Marc Drillon, Pierre Rabu, Stefan Haacke.



Université	
de Strasbourg	

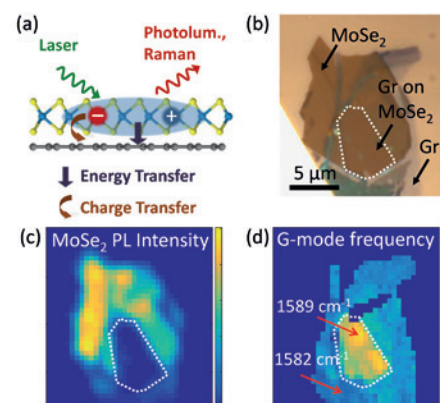
## ♦ Charge versus Energy transfer in 2D semiconductor/graphene junctions

Physicists from IPCMS (UMR7504, Université de Strasbourg and CNRS) have disentangled the contributions from interlayer charge and energy transfer from atomically thin semiconductors to graphene.

Research into two-dimensional materials is one of the hottest topics in physics and material science. These thin, flexible structures exhibit many unique material, optical, and electrical properties that make them well suited to applications as diverse as photodetectors, solar cells, light-emitting screens, and biosensors. Taking this a step further, innovative devices could be built by tightly stacking atomically thin layers to create designer materials. These structures, known as van der Waals heterostructures (vdWHs), can exchange charge carriers and energy across the interfaces between layers on short timescales following optical excitation. These competing processes govern the optoelectronic response of vdWHs but remain poorly understood. Here, we experimentally study a model vdWH to better understand these interlayer charge and energy transfers.

Specifically, we investigate a metal-semiconductor junction made of a graphene monolayer transferred onto a transition metal dichalcogenide (TMD, here molybdenum diselenide) monolayer. By measuring light emission from the TMD, we demonstrate that interlayer coupling to graphene drastically reduces the photoluminescence yield and exciton lifetime. Additionally, using Raman spectroscopy, we finely probe the frequency and linewidth of the optical phonon modes in the monolayers. These parameters are highly sensitive to the charge carrier density and show a net photo-induced electron transfer from TMD to graphene. Remarkably, exciton dynamics in a TMD-graphene vdWH is largely independent of the existence of a net charge transfer.

This key result strongly suggests that picosecond interlayer energy transfer from TMD to graphene dominates the photoreponse of these heterostructures. Highly efficient energy transfer now has to be carefully considered when designing devices based on 2D materials. ■



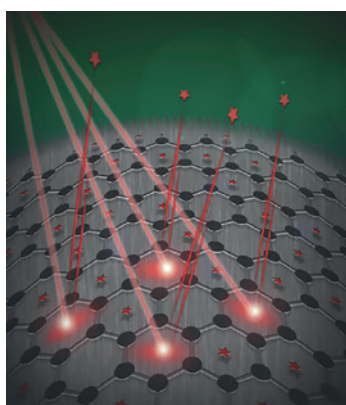
▲ Illustration of photoinduced charge and energy transfer from a monolayer of transition metal dichalcogenide (here MoSe<sub>2</sub>) to graphene (Gr), (b) Optical image of a MoSe<sub>2</sub>/graphene (Gr) heterostructure. The map of the Gr Raman G-mode frequency, (c) and of the MoSe<sub>2</sub> photoluminescence intensity, (d) reveals clear signatures of interlayer coupling on the heterostructure (dashed contour in b-d).

G. Froehlicher, E. Lorchat, S. Berciaud  
Physical Review X 8, 011007 (2018)  
doi: 10.1103/PhysRevX.8.011007  
Preprint at: <https://arxiv.org/abs/1703.05396>

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## ♦ A carbon-based mesoporous silica nanomaterial for the delivery of drugs under near-infrared light

The design of nano-objects for nanomedicine able to combine in one formulation imaging and therapy modalities is today a great challenge in the field of materials for health. Such engineered nanomaterials called “theranostics” (therapy and diagnostics) are anticipated as relevant tools for the development of a personalized treatment, especially in the case of anticancer treatments.



Recently, in coll. with ICPEES (Dr D. Bégin) and INSERM U1109 (Dr S. Harlepp) we developed an original type of nanocomposites made of carbon-based materials (carbon nanotubes or graphene) and coated with a porous silica shell to ensure a high level payload of an anti-tumoral drug,

doxorubicin (DOX). The carbon materials are highly attractive materials for multi-therapy to ensure phototherapy (i.e., conversion of near infra-red (NIR) light into local heat) and drug delivery that can be remotely triggered by NIR light irradiation. Such C-based materials are also expected in the future for various medical imaging such

as fluorescence, photoacoustic, or Raman imaging.

In this work, a first step was the processing of carbon nanotubes and graphene sheets into smaller pieces to reduce their size distribution more suitable for biological applications. Then, we showed that the mesoporous silica shell can be grown at the carbon surface with a thickness that can

be finely tuned by the sol-gel parameters (e.g., amount of precursor, sol-gel time). The drug loading was achieved in such porous reservoirs and we show that modifying the surface with a polysiloxane layer (aminopropyltriethoxysilane) led to a very high payload of drugs (even higher than the mass of the nanocomposites). Different stimuli were thus assessed to trigger the drug release and results shown that a mild acidic pH (pH=4) or a heating induced by application of NIR-light on these activable nanocomposites allowed to release on a controlled and pulsatile way the encapsulated drugs in aqueous solution. ■

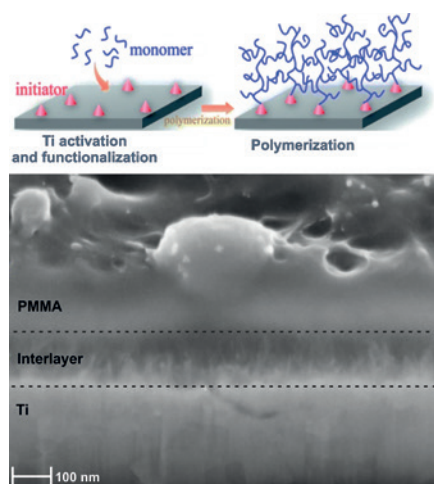
C. Wells, O. Vollin-Bringel, V. Fiegel, S. Harlepp, B. V. der Schueren, S. Bégin-Colin, D. Bégin, D. Mertz  
Adv. Funct. Mater. 2018, 28 (17), 1706996.  
DOI : 10.1002/adfm.201706996

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## ♦ Biocompatible hybrid-layered structures for designing craniofacial prostheses

In the area of complex craniofacial prostheses design, monomaterials present many drawbacks, such as the inappropriate mechanical properties when compared to the bone. The discrepancy existing between the mechanical properties of the implant and the bone that has to be replaced represents the most limiting factor for a successful implant repair. To solve this problem, researchers from the IPCMS propose the use of biocompatible titanium (Ti) /poly methyl methacrylate (PMMA)/titanium sandwich structures.



Their strategy is to design PMMA/Ti interfaces free of epoxy resins which are often used as adhesive agents in sandwich sheets and are known to be not biocompatible. The goal of this work is to employ surface-confined polymer layers as adhesives for a strong bond between the polymer and the Ti which ensures the final shaping of the sandwich without delamination. This original methodology of Ti surface functionalization allows the design of hybrid organic-inorganic interfaces having both a covalent and an interlocking nature. It allows the growth of thick (from hundreds of nanometres to a few microns), stable and biocompatible polymer layers. The polymer is covalently attached to titanium flat surfaces using an alkali-activation of the substrates coupled with a surface initiated atom transfer radical polymerization of the monomer. The development of such hybrid-layered structures consisting of PMMA and Ti with mechanical properties closer to those of target tissues can be used as a means to control stress shielding in implants.

◀ PMMA-coated Ti surfaces are obtained by activation of Ti with NaOH, grafting of the Bromoisobutyrate-undecyl-1-phosphonic acid initiator, and growth of the PMMA by surface-initiated atom transfer radical polymerization. The scanning electron microscopy image shows a cross section of the as obtained PMMA-coated Ti.

The results recently reported by the scientists of the IPCMS in *ACS Appl. Mater. Interfaces* are part of a wider research work conducted in collaboration with Clausthal University of Technology and Sapienza University of Rome. This research is expected to open new insights of paramount interest in the field of polymer science and engineering which can be applied to many industrial sectors, such as electronic, automotive and biomedicine. ■

M. Reggente, P. Masson, C. Dollinger, H. Palkowski, S. Zafeiratos, L. Jacomine, D. Passeri, M. Rossi, N-E. Vrana, G. Pourroy and A. Carrado, *ACS Appl. Mater. Interfaces*, **2018**, 10, 5967–5977.  
DOI:10.1021/acsami.7b17008

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## OBITUARY: ERIC BEAUREPAIRE (1959-2018), JEAN -YVES BIGOT (1956 – 2018)

At the end of April and the beginning of May, two of our most renowned colleagues E. Beaurepaire and J.-Y. Bigot, passed away within only a few days apart.



Eric Beaurepaire

They were both researchers of the Institute of Physics and Chemistry of Materials of Strasbourg (IPCMS) who had joined the CNRS in 1984. Eric was initially hired at the Laboratory of Magnetism and Electronic Structures of Solids and Jean-Yves at the Laboratory of Spectroscopy and Optics of Condensed Matter. These two laboratories would a few years later constitute the seed of two research departments of what is now the IPCMS.

Both were outstanding researchers, truly passionate about science and curious about new issues, beyond their own field of expertise. Eric was particularly interested in the magnetism of nanostructures and in organic or molecular spintronics. Jean-Yves has developed special expertise in the field of light-matter interaction, using femtosecond laser sources to explore ultrafast processes. It is quite natural that these two passionate researchers joined their efforts to produce the pioneering work on "femtomagnetism". Both had an international stature that greatly contributed to the reputation of our laboratory. We are grateful to them.

Recognized researchers, outstanding experimentalists, teachers, Eric and Jean-Yves were also laboratory scientific leaders. They were managers and mentors for us by their scientific aura, their knowledge of the laboratory, and their involvement in the scientific animation of our institute and its environment.

Our emotion was intense and our feelings difficult to express at a time when we lost these two eminent colleagues and friends. Celebration days will take place in the autumn to honor the memory of Eric and Jean-Yves.



Jean-Yves Bigot

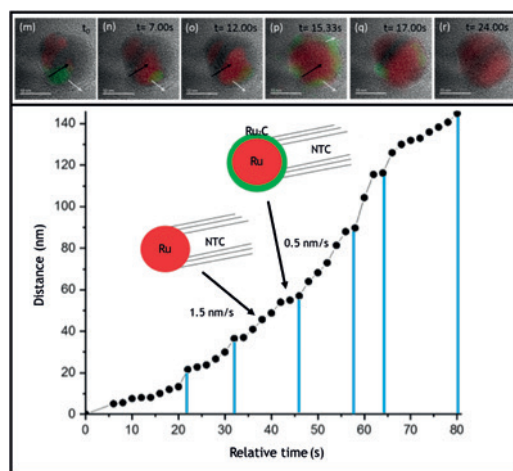
## ♦ In situ observation of an oscillatory growth of carbon nanotubes

The availability of environmental cells is opening a bright new field of electron microscopy studies in the nanoworld. In this work we studied the growth of carbon nanotubes resulting from the reduction of CO by H<sub>2</sub> (CO/H<sub>2</sub>=2) catalysed by ruthenium nanoparticles, one to ten nanometres in size, under an atmospheric gas pressure at 500° C. High resolution images were recorded every 0.33 seconds in order to analyse the dynamics of the nanotubes growth as well as the morphological changes of the Ru nanoparticles. A crystallographic analysis demonstrates that during the operando process, the ruthenium particles strongly react with carbon forming a shell of ruthenium carbide (see the time series on the figure). This is the first observation of this chemical specie at atmospheric pressure that was previously only observed at 5 GPa. At 1 atm. ruthenium carbide is unstable: the addition of carbon in the outer part of the nanoparticles softens the binding energy and we measured that as soon as it decreases down to 41 meV, carbon is released outside contributing to the formation of the carbon nanotubes walls. In this experiment the ruthenium particles do play a dual role: i) they act as a catalyst favouring the reduction of

CO by H<sub>2</sub>, ii) they act also as a transient carbon reservoir for the growing of nanotubes. As a result of the production of an outer shell made of unstable ruthenium carbide, an oscillatory relaxation process takes place that governs the growth of the carbon nanotube. The lower part of the figure reports on the distance covered by a nanoparticle versus time. This graph clearly exhibits two speed regimes occurring alternatively: a slow one at 0.5 nm/s at the time of the filling up of the carbide reservoir and a fast one at 1.5 nm/s when the carbon atoms are released, speeding up the growing rate of the pushing nano-tube. The core-shell formation occurs through a transformation from a cubic crystal to a rounded particle via a truncated octahedral crystal. ■

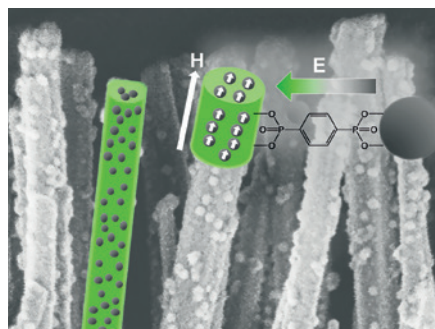
Nanoscale, **2018**, 10, 14957  
M. Bahri, K. Dembélé, C. Sassoye, D. P. Debecker, S. Moldovan, A.S. Gay, Ch. Hirlimann, C. Sanchez et O. Ersen

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▲ (m-r) TEM time series of a Ru nanoparticle observed in operando mode when submitted to a CO/H<sub>2</sub>=2 gas flow at a pressure of 1 atm. and a temperature of 500° C. The red colour exhibits the crystalline Ru part of the particle while the green one shows the presence of Ru<sub>2</sub>C, ruthenium carbide, that forms a shell at t= 15 s. Bottom graph shows the distance covered by a nano particle versus time. One can clearly observe the two speed regimes that result from the relaxation oscillatory growth of the carbon nano tube.

## ♦ Synergistic photo optical and magnetic properties of hybrid nanocomposite consisting in a zinc oxide nanorod array decorated with iron oxide nanoparticles



Multifunctional nanocomposite materials recently emerged as a powerful concept because they offer to combine physical properties of different inorganic materials. Besides the simple combination of physical properties, the real challenge is to provide high control on the structure of nanocomposites (spatial arrangement of the two entities, interface or separating distance, etc.). In this case, synergy between the two entities may be favoured

in order to dramatically enhance the physical properties. We reported on a multifunctional hybrid nanocomposite material consisting of a zinc oxide (ZnO) nanorod array decorated with iron oxide (Fe<sub>3</sub>-δO<sub>4</sub>) nanoparticles. Our approach consists in self-assembly of metal oxides mediated by 1,4-phenylenebis(phosphonic acid) (PBA) through specific chemical interactions. Mild conditions (room temperature) allow the preservation of crystal structure of both Fe<sub>3</sub>-δO<sub>4</sub> nanoparticles and ZnO nanorod arrays. The structure of such hybrid nanocomposites were investigated by means of a large panel of characterisation techniques SEM, TEM, FTIR and XPS. The assembly mechanism was studied by varying several experimental parameters, such as the concentration of ligand solution and nanoparticle suspension as well as the reaction time. Finally, we show for the first time that the ZnO/PBA/Fe<sub>3</sub>-δO<sub>4</sub> nanocomposite displays enhanced magnetic

and optical properties as a result of dual synergy. The ZnO nanorod array acts as a very efficient anisotropic scaffold which favours unidirectional dipolar interactions and enhances in-axis collective magnetic properties of Fe<sub>3</sub>-δO<sub>4</sub> nanoparticles (10-fold increase of coercive field in comparison to the same magnetic nanoparticles in the powder state). ZnO nanorods also benefit from Fe<sub>3</sub>-δO<sub>4</sub> nanoparticles by enhancing their optical properties in the visible range (2-fold increase of photoluminescence (PL) intensity with respect to bare ZnO nanorods) which we propose to result from photon energy transfer. ■

B. Azeredo, A. Carton, C. Leuvre, C. Kiefer, D. Ihwakrim, S. Zafairatos, M. Gallart, P. Giliot, B. P. Pichon  
Journal of Materials Chemistry C, **2018**, 6, 10502-12.

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## ♦ Simultaneous reorientation and alignment of small $\pi$ -conjugated molecules using room-temperature mechanical rubbing

Organic semiconductor thin films have been intensively investigated during the last decades due to their potential for various electronic applications including organic light-emitting diodes (OLEDs), organic solar cells, and organic field effect transistors (OFETs). In these organic electronic devices, a precise control of the molecular in-plane orientation can play a key role for performances and requires specific alignment techniques, such as mechanical rubbing of a predeposited polyimide or poly(tetrafluoroethylene) layer.

It recently turned out that semiconducting polymer films can be directly aligned by rubbing without use of prealignment layer and in that context; it was extremely relevant to examine the suitability of this technique to small molecules or short oligomers. We thereby rubbed solution-processed polycrystalline thin films of a reference ambipolar material, consisting of a quinoiald quaterthiophene with alkyl side-chains.

Alignment was effectively obtained, with high absorption dichroic ratios and anisotropy of charge carrier mobilities as high as 130, and even further anisotropy increase after subsequent solvent vapor annealing. Unexpectedly, X-ray diffraction and atomic force microscopy measurements revealed that the rubbing does not only lead to an excellent 1D orientation of the QQT(CN)<sub>4</sub> molecules over large areas but also modifies the orientation of the crystals relative to surface, moving molecules from an edge-on to a face-on configuration. We have found the reasons for such an orientation switchover in the plastic characteristics of the QQT(CN)<sub>4</sub> layer and in the role of the flexible side-chains in the molecular packing. The nearly complete conversion from edge-on to face-on orientation by mechanical treatment in polycrystalline small-molecule-based thin films opens perspectives in terms of fundamental research and practical applications of the rubbing technique in organic optoelectronics. ■

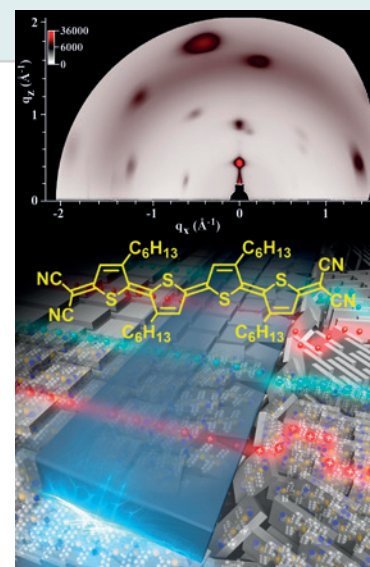
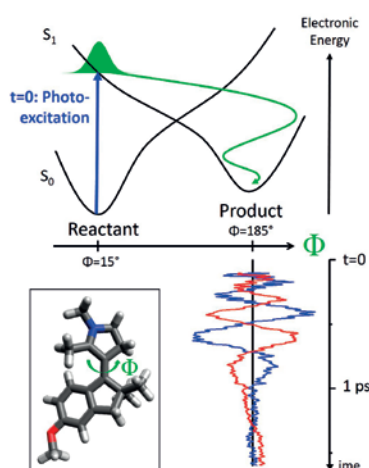


Illustration of the molecular crystal reorientation and 1D-alignment by the rubbing process, as evidenced by XRD analysis.

J.-C. Ribierre, T. Tanaka, L. Zhao, Y. Yokota, S. Matsumoto, D. Hashizume, K. Takaishi, T. Muto, B. Heinrich, S. Méry, F. Mathevet, T. Matsushima, M. Uchiyama, C. Adachi, T. Aoyama  
Adv. Funct. Mater. **2018**, 28, 1707038  
DOI: 10.1002/adfm.201707038

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## ♦ Understanding the excellent quantum yield of some chemical photoreactions



Vibrationally coherent photoisomerization. The molecule in insert converts light energy (absorbed photon) into mechanical energy (torsion  $\Phi$ ), according to a vibrationally coherent photo isomerization (top): a coherent nuclear motion drives the molecule from the excited state  $S_1$  to the ground state  $S_0$  (photoproduct), as revealed by an oscillating transient absorption signal (bottom right) with a period of 0.4 ps and corresponding to the torsion motion  $\Phi$  of the photoproduct.

The process of vision in vertebrates is triggered by the *cis*-to-*trans* photoisomerization of retinal (a form of vitamin A) in the rhodopsin protein (Rho). After photo-excitation, the retinal decays to the electronic ground state by a rotation around a C=C double bond. This triggers the protein's biological activity. The probability to form the *trans* rather than its initial *cis* state - that is the quantum yield (QY) of the photoreaction - is the result of a concerted motion of the nuclei. In the condensed phase the interaction with the environment leads to the rapid (1ps) randomization of the relative phase of the nuclei motions. This is called "vibrational decoherence". Rho is the only example of a photoisomerization occurring faster than the randomization of the motions that critically control the QY. As a result, the photoisomerization QY of retinal in Rho is remarkably high (67%), and higher than that of any synthetic molecular device using C=C double isomerization for opto-mechanical energy conversion (see the 2016 Nobel Prize).

We demonstrated that a similar - i.e. vibrationally coherent - photoisomerization can

be reproduced in a small molecule in solution, synthesized at the University of Siena. Using very short laser pulses (<10 fs) it is possible to trigger the photoreaction synchronously in an ensemble of molecules in solution and to follow the spectroscopic signatures of their coherent vibrational motion along the course of the photoreaction. The central result is that a small initial twist ( $\sim 15$  degrees) of the isomerizing C=C double bond, induced by a minor chemical change in the compound, is necessary to accelerate the rotation and to observe this vibrationally coherent photoreaction. This opens up a new field of investigations consisting of optimizing the chemical structure of synthetic molecular systems to generate this type of vibrational coherence and, if possible, exploit it to control the photoreactivity, as Rho does with the retinal. ■

M. Gueye, M. Manathunga, D. Agathangelou, Y. Orozco, M. Paolino, S. Fusi, S. Haacke, M. Olivucci, J. Léonard « Engineering the vibrational coherence of vision into a synthetic molecular device ». Nature Communications **9**, 313.  
<https://doi.org/10.1038/s41467-017-02668-w>.

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## ♦ Spin-state switching and amphiphile-like self-assembling in a sublimed film of an Iron(II) complex

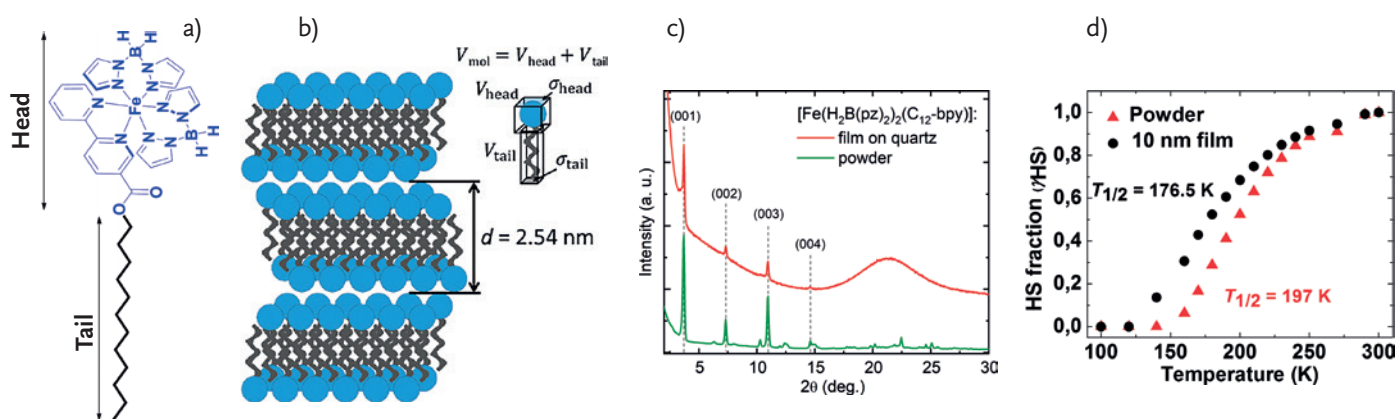
Spin-crossover (SCO) complexes capable of undergoing reversible low-spin (LS) to high-spin (HS) switching need to be implemented as surface-bound thin films to harness their electronic/spintronics application potential. Fabrication of thin SCO complex films by sublimation however often results in the drastic alteration of the spin-state switching characteristics relative to the bulk behaviour, as a consequence of the modified intermolecular interactions around the surface-bound switching entity. An ideal solution to tackle this issue is to **Direct the Molecules to Organize** (DMO) the same way in thin film state as in bulk. To do this, we invoked a

molecular self-assembling strategy that mimics amphiphilic systems through the design of a vacuum sublimable charge neutral Fe<sup>II</sup> complex bearing an alkyl chain: [Fe(H<sub>2</sub>B(pz)<sub>2</sub>)<sub>2</sub>(C<sub>12</sub>-bpy)], with pz = pyrazole, bpy = 2,2'-bipyridine, C<sub>12</sub>-bpy = dodecyl[2,2'-bipyridine]-5-carboxylate. The antagonistic iron complex "head" and alkyl chain "tail" then naturally drives the self-assembly toward their spatial separation into layers. And indeed, the bulk-powder and 10 nm thin film forms showed comparable spin-state switching characteristics, owing to their similar lamellar structure. The realized "proof of concept" molecular-engineering oriented approach, to pro-

gramme on-surface switching characteristics of vacuum sublimable SCO complexes by the control of the nanostructure morphology, is encouraging towards the fabrication of SCO based device architectures. ■

K. Senthil Kumar, M. Studniarek, B. Heinrich, J. Arabski, G. Schmerber, M. Bowen, S. Boukari, E. Beaurepaire, J. Dreiser, M. Ruben  
Adv.Mater. **2018**, 30, 1705416  
DOI: 10.1002/adma.201705416

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## AWARD

### 2018 prize « Espoirs de l'Université de Strasbourg »

This prize rewards the quality of the work and background of young researchers of the University of Strasbourg. This year, ten laureates, three men and seven women were selected for the originality of their work and the dynamism in the implementation of their promising research.

Our colleague, **Emilie DELAHAYE-LEROI** is one of the laureates (on the photo : 3rd from the right in the back row).



## IPCMS News

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