

IPCMS

International Newsletter

News

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Editorial

Ten months ago (IPCMS News No. 23), I focused my editorial on the government's project for a new law defining the framework for the French research for the future. We (the scientific community) were at that time enthusiast about awareness of politicians concerning science, yet fearing some political or financial constraints at the end. Actually, discussions took place, forums were organized to gather all ideas from the scientific community to feed up the text law with appropriate proposals. Nevertheless, the text discussed and about to be approved by the parliament gives rise to many criticisms, and does not seem consistent with our high expectations of a kind of New Deal for research in France. We will see if what the politicians, i.e. our representatives, decide today is efficient or not tomorrow.

Another, and quite bigger challenge is to live with the disease of the year, I mean the Covid-19. The pandemic is severely disrupting our research activities since several months. In March, we experienced a complete lockdown of the labs for 3 months, followed by a gradual re-opening with uncertainties about the continuation of our financial supports, the extension of PhD and postdoctoral grants, and with extensive use of remote work. After the summer, University re-opened completely, all people were back in the lab and we enjoyed so much to meet again colleagues and students. Unfortunately, a second wave is propagating, leading to remote work again. Hopefully, we learned from the first crisis. We adapt our lab organisation in a way that the scientific and teaching activities are still running on in the best possible conditions.

In this context, we report hereafter a selection of recent results obtained by physicists and chemists of IPCMS. Beyond the purely academic issues, these articles also unravel the esthetical touch exhibited by our researchers when approaching puzzling questions. Thus, you will read on phantom but safe walls for fluidics, polar vortex states investigated through ferroelectric hysteresis simulation, a Janus-type bridge in a new complex emitting red light, molecular flashes in prototypical components "turning the dream of molecular optoelectronics into closer reality", the understanding of color tuning of the oxyluciferin fluorescence, and a chemical game in the realm of luminescent d-block metallomesogens. Science is beautiful!

I wish you a pleasant reading and good health.

Pierre Rabu, *Director*

AWARDS

The Prize «Espoirs de l'Université de Strasbourg» recognizes the quality of the work and scientific achievements of young researchers within the University of Strasbourg. The 2020 edition rewarded two of our colleagues: Damien Mertz (researcher) and Guillaume Weick (academic). Congratulations to both of them!

◆ Phantom Fluidics

Imagine a liquid channel without solid walls that can circulate inside other liquids on a microscopic scale. Microfluidics is a rapidly growing technology involving the miniaturisation of fluid circuits to better control the flow of fluids. However, due to the small size of the channels, sometimes tens of microns, they can be easily blocked, their walls fouled, and require large pressures to induce a flow. Many teams have tried to engineer the surfaces to reduce these problems, but the approach here was to do away with solid channel walls altogether.

Using a magnetic field, with zero in the centre but strong on the boundaries, produced by four magnets, a ferrofluid – iron oxide nanoparticles suspended in an oil – is attracted towards regions of strong magnetic field. This allows the stable formation of a channel of a second, immiscible liquid called an ‘antitube’ in weak field areas. Antitube diameters as small as 14 μm can be achieved, and modelling predicts sub- μm antitubes are possible. As there is no solid wall, the flow resistance is significantly less than in a solid-walled channel, even for viscous liquids like honey or glycerol, with extraordinarily slip lengths $> 1\text{ mm}$ reported.

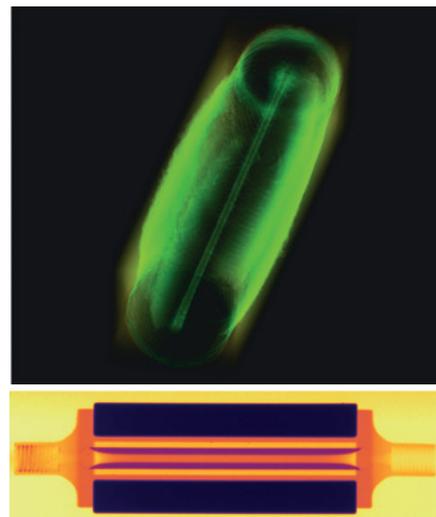
Moreover, the magnetic field can be modified in real-time, the additional magnets act as valves stopping the flow. A changing field enables contactless, magnetostaltic pumping, important for handling delicate material like blood which suffers cellular degradation when it is put under stress. Magnetostaltic pumping showed a clear decrease in red blood cell rupture compared to a peristaltic pump. More practical and less dangerous for health, this system could be used in heart surgery as a peristaltic pump, or in dialysis. The invention has been patented, under the aegis of the SATT Conectus, leading to the creation of a startup, Qfluidics, to commercialise this technology.

The long term goal is to take nanomagnetism and spin electronic technologies, currently used for information storage, to open up a new world of frictionless fluidic circuits at the nanoscale. ■

Liquid flow and control without solid walls.

P. Dunne, T. Adachi, P. Dunne, T. Adachi, A. A. Dev, A. Sorrenti, L. Giacchetti, A. Bonnin, C. Bourdon, P. H. Mangin, J. M. D. Coey, B. Doudin, T. M. Hermans, *Nature* **581**, 7806 (2020). DOI: 10.1038/s41586-020-2254-4

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▲ Top: X-ray tomography of an 80 μm antitube of water encapsulated in a magnetically stabilised ferrofluid, and bottom: X-ray contrast image showing the magnets (black), ferrofluid (purple) and the 3D printed housing shown (orange).

◆ Controlling Polar Vortex States in Core-Shell Ferroelectric Nanoparticles

Ferroelectric nanoparticles have recently attracted much interest, both as model systems for fundamental studies of the polarization and because of their potential for applications in storage and logical devices. Compared to nanoscale ferromagnets, whose magnetic properties have been studied intensively over several decades, relatively little is known about configurations of the polarization unfolding in ferroelectric nanoparticles.

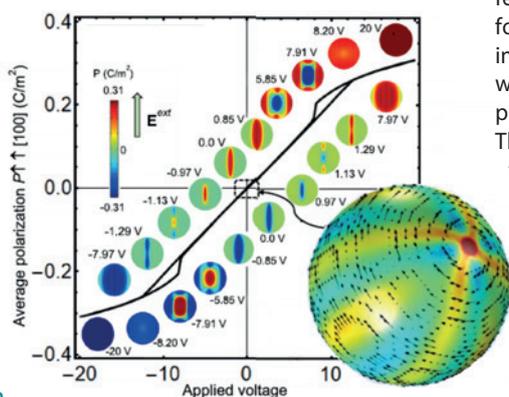
In a recent theoretical study conducted by scientists from the IPCMS, the Ukraine, the Czech Republic, and the United States, the possibility to generate and manipulate vortex-type polarization states in ferroelectric core-shell nanoparticles has been investigated. By using finite-element simulations based on the Landau-Ginzburg-Devonshire theory, unforeseen resemblances were evidenced on the nanoscale between magnetic states in ferromagnets and polar states in ferroelectrics. The uncanny similarities found in ferroelectric nanoparticles also include the formation of Bloch points, which are exotic configurations that were previously only known from micromagnetics. The study primarily focusses on the formation of vortex states in ferroelectric nanospheres, showing that the vortices are stable at zero field, and that their orientation can be controlled with an electrical

field. Surprisingly, the polarization vortices can contain a stable central “kernel”, *i.e.*, an elongated, nanoscale domain similar to the core of a ferromagnetic vortex. The vortex kernel is shown to effectively act as a “handle” for external fields, through which the ferroelectric vortex states can be manipulated.

It is argued that the observed multiplicity of possible ferroelectric vortex states could open a path for applications of core-shell nanoparticles as multi-bit memory units. Furthermore, the article speculates on how the classical properties of the vortex axis could be used to imitate a qubit-type behavior in arrays of interacting nanoparticles. ■

A. N. Morozovska, E. A. Eliseev, R. Hertel, Y. M. Fomichov, V. Tulaidan, V. Yu. Reshetnyak, D. R. Evans, *Acta Materialia*, **200**, 256 (2020) DOI: 10.1016/j.actamat.2020.09.003

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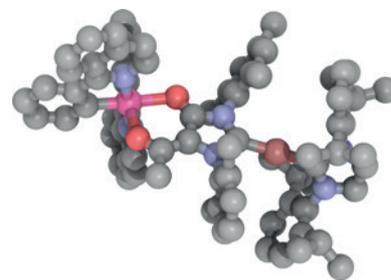
◀ Simulated hysteresis of a spherical, ferroelectric core-shell nanoparticle. The vortex state at remanence contains an axial “kernel” where the polarization points along the vortex axis.

◆ Twisting the knob of the radiative rate constant in bimetallic complexes

Ir^{III} complexes have proven to be leading emitters with real-market applications as efficient organic light-emitting diodes. To date, fine modulation of optical properties has been mainly achieved by proper molecular design and control of the geometry and isomerization linkage of the coordinated ligands, which selectively operate onto both, the topology of the potential energy surfaces and the electron density reorganization. Surprisingly, major efforts have been devoted to investigating monometallic species; whereas, bi- and multi-metallic counterparts have been largely overlooked. Despite, the presence of a second heavy metal in close proximity could provide manifold advantages, such as *i*) increased structural rigidity, which renders less accessible nonradiative channels, and *ii*) larger values for the radiative rate constant, k_r , due to either enhanced

spin-orbit coupling (SOC) or decrease of the energy gap between the states that mix via SOC. Therefore, judicious design of multi-metallic species might afford compounds with outstanding optical properties. Nonetheless, compounds that efficiently emit into the red are still challenging due to the energy gap law.

In this framework, we have recently reported on a novel class of cationic heterobimetallic $\text{Ir}^{\text{III}}/\text{M}^{\text{I}}$ complexes, where $\text{M}^{\text{I}} = \text{Cu}^{\text{I}}$ and Au^{I} . The two metal atoms are connected by a hybrid Janus-type bridge that combines both, a chelating acetylacetonato-like and a monodentate N-heterocyclic carbene sites, coordinated onto an Ir^{III} and a M^{I} center, respectively. These systems efficiently emit into the red region and display enhanced photophysical properties when compared



to mononuclear benchmark congeners. This finding is ascribed to the increased singlet metal-to-ligand charge transfer ($^1\text{MLCT}$) character of the emitting state due to the smaller energy gap between the triplet ligand-centered and $^1\text{MLCT}$ manifolds, which mix via SOC. Remarkably, an overall two-fold increase of k_r and photoluminescence quantum yield is achieved, rendering these compounds amongst the most efficient cationic red-emissive Ir^{III} complexes to date. ■

A. Bonfiglio, L. Pallova, V. César, C. Gourlaouen, S. Bellemin-Laponnaz, C. Daniel, F. Polo, M. Mauro, *Chem. Eur. J.*, **26**, 11751-11766 (2020) (HOT paper and inside cover). DOI : 10.1002/chem.202002767

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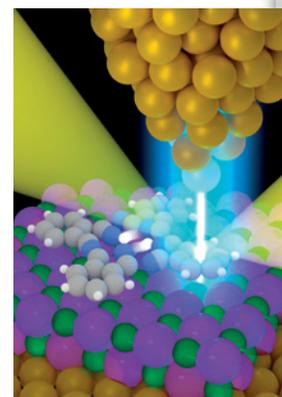
Atomic-scale activation of molecular flashes

Molecules are perceived as the ultimate compound for future electronic and optoelectronic devices of extremely low dimension. In such a molecular circuit, each molecule can hold specific functionalities such as carrying electronic current, emitting photons, or switching on and off a signal. By developing an ultra-resolved nanoscopy technique, we have discovered and fluctuating light bursts in a conventional molecule and trace the origin of these fluctuations to the fast motion of a pair of hydrogen atoms forth and back within the molecular switch.

Single-molecule devices have attracted a tremendous interest fuelled by the objective of transforming a fundamental research topic into a new and powerful technology. Due to their intrinsic quantum nature, molecules open up functionalities that go beyond today's electronics. Among these perspectives, the concept of single molecule optoelectronics, which consists in combining optical and electronic properties within a sin-

gle molecule, is only emerging. In a wish list of molecular optoelectronics, it is envisioned that light could be used to convey information at high frequency between well-separated molecular components of a nano-scale circuit. Now, we have implemented a nanoscopic technique that allows distinguishing the exact origin of light flashes inside a prototypical molecular optoelectronic component with atomic-scale precision. Together with theoretician colleagues from the Center for Materials Physics (CSIC-UPV/EHU) in San Sebastian, we could associate the successive flashes to the switching of hydrogen atoms between two positions of the molecule, occurring about 1000 times per second, in a mechanism known as tautomerization. This result provides new information on this reaction, and shows that a molecule may be used as an intermittent emitter, or molecular nanostrobe, potentially controllable, and relevant for optical communications at the nano-scale.

Light bursts from a switching molecule under the tip of an STM. ▶



The next step will be to find a method to manipulate the "on" and "off" state of this molecular strobe to use it as a controllable molecular-scale light emitting switch, thus turning the dream of molecular optoelectronics into a closer reality. This work is published in *Nature Nanotechnology*. ■

B. Doppagne, T. Neuman, R. Soria-Martinez, L. E. Parra López, H. Bulou, M. Romeo, S. Berciaud, F. Scheurer, J. Aizpurua, G. Schull, *Nat. Nanotechnol.* **15**, 207 (2020)

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◆ Oxyluciferin fluorescence color tuning

Oxyluciferin is the chromophore responsible for bioluminescence, a natural phenomenon used by many living organisms to convert chemical energy into light. Light emission results from the enzymatic oxidation of luciferin by the luciferase protein, producing oxy-

luciferin in its first excited state. This enzymatic reaction, powered by ATP, is widely used as a luminescent probe for bioassays or bioimaging, because it emits fluorescence without any light excitation *i.e.*, on a completely dark background.

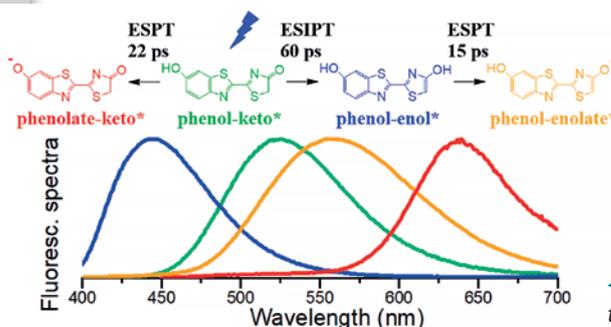
Natural bioluminescence is observed to vary from green to red. Although such a variety of emission wavelengths would be of practical use for biotechnological applications, the "color-tuning" mechanism remains to be understood. The main difficulty resides in the

high complexity of the environment-sensitive photochemistry of oxyluciferin which may exist under six different chemical forms (having different emission wavelengths) depending on pH in solution or on specific hydrogen bonds with luciferase.

Our goal was to unravel the conversion kinetics between different chemical forms occur-

ring in the excited state of oxyluciferin, in particular proton transfers and keto-enol conversion, best investigated in solution at pH=5. Time-resolved spectroscopy of several synthetic derivatives mimicking different chemical forms of oxyluciferin allowed us to reveal the complete scheme of the photochemical reactions involving all chemical forms in water solution.

adapting the same strategy and incorporating the synthetic compounds in the natural binding pocket of luciferase, in order to unravel the photoluminescence mechanism of the oxyluciferin-luciferase complex. ■



Although these results do not directly apply to the photoreactivity inside the luciferase binding pocket, they demonstrate the key role of the pH (hence, H-bonds) for controlling the bioluminescence spectrum via the tuning of excited-state reaction kinetics. As a next step, we work at

◀ Emission spectra and conversion kinetics of the four forms of oxyluciferin involved in the emission spectrum observed in water.

P. Gosset, G. Taupier, O. Crégut, J. Brazard, Y. Mély, K.-D. Dorkenoo, J. Léonard, P. Didier, *J. Phys. Chem. Lett.* **11**, (9), 3653–3659 (2020). DOI : 10.1021/acs.jpcclett.0c00839

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♦ Playing with Pt^{II} and Zn^{II} coordination to obtain luminescent metallomesogens

Luminescent d-block metallomesogens exhibit strong polarized light emission and are investigated for practical applications such as backlighting in displays, stimuli-responsive material in sensors, security inks... However, prior to their implementation in applications, the luminescence properties in the mesophase must be improved and controlled. Achievement of this goal requires efficient molecular design strategies allowing to render any d-metal complex mesomorphous and to control self-assembly and transition temperatures.

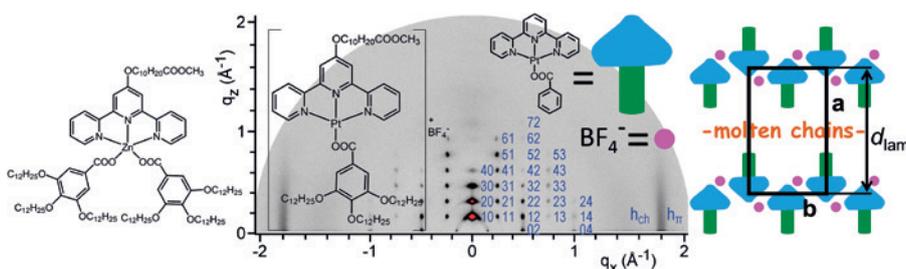
In this context, we introduced lipophilic gallate units as monodentate ligands of Pt^{II} and Zn^{II} terpyridine complexes, in the hope that the antagonistic nature of

peripheral alkyl chains would be sufficient to prevent crystallization and induce mesomorphism. Strategy was successful since both complexes were found to be mesomorphous at room temperature and up to 255°C and 105°C, respectively. In compliance with molecular engineering rules, mesophases were lamellar in presence of a single gallate unit and columnar with two units. Specifically, while the Zn^{II} complex led to a classical hexagonal columnar structure made of wires of piled complexes surrounded by a molten chain continuum, the Pt^{II} complex formed an original mesophase of *p2mg* symmetry with layers of intermingled stacked complexes, ions and gallate extenders that alternate with molten chain layers (figure).

The metallomesogens showed luminescence in both solution and mesophases, which validates our approach. However, emission wavelength, quantum yield and lifetime were modified by the presence of the gallate units as well as by the supramolecular interactions in the mesophase. This complexifies the quest of performing luminescent metallomesogens and emphasizes the need of new molecular design rules. Additionally, we found great sensitivity of the metal center with respect to its molecular environment that will be further exploited for chemical sensor applications. Research is going on! ■

A. A. Andelescu, B. Heinrich, M. A. Spirache, E. Voirin, M. La Deda, G. Di Maio, E. I. Szerb, B. Donnio, O. Costisor, *Chem. Eur. J.* **26**, 4850–4860 (2020)
DOI : 10.1002/chem.202000124

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◀ Formula of Zn^{II} complex; formula, GIWAXS pattern (PLS-II synchrotron line 9A - South Korea) and molecular organization of Pt^{II} complex

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