• Teaching an old dog new tricks: How to make a rhodopsin emissive

Many organisms use retinal proteins, to capture or sense light, since light is a useful energy source or because it helps for orientation or regulating photo-synthesis. All vertebrates use rhodopsin in their eye's cones and rods, since their light absorption triggers the complex biochemical processes and modulation of transmembrane potentials leading to vision.

All retinal proteins rely on a protonated form of retinal (PSBR) as the light-absorbing chromophore. The electrostatic and steric interactions of PSBR with the protein environment are key for the different colors of rhodopsins, but also for the speed and efficiency of the primary photochemical event, the photo-isomerisation. This reaction switches the protein from the "off" to an "on" state, wherein it fulfils its specific function.

The paper published by the teams of M. Olivucci (U Siena & Bowling Green, USIAS fellow 2016) and S. Haacke (IPCMS), within

the ANR-DFG project Femto-ASR, shows how the photo-isomerisation reaction can be fastened or slowed down, when proteins are mutated at some specific points. Slowing down the non-radiative isomerisation process, prolongs the excited state lifetime and thus increases the fluorescence quantum yield. For Anabaena Sensory Rhodopsin, a particular retinal protein, the authors achieved an increase by almost an order of magnitude. Nevertheless, the quantum yield remains < 1%.

The real value of this paper relies in the identification of a new mechanism that rules the shape of the excited state potential energy surfaces (PES) of the PSBR. The PES is in fact the result of the mixing of two excited states of opposite symmetry (Ag and Bu) and electronic character (charge transfer vs. di-radical). Their mixing is enhanced when both states are degenerate. Such a resonance can be induced by the dielectric properties of amino acids flanking the PSBR (polar vs hydrophobic).



When, as a consequence of Ag/ Bu mixing, PSBR's charge transfer character is reduced, the otherwise reaction-driving electrostatic interactions are minimised and an activation barrier appears in the excited states. This prolongs the excited state lifetime, as observed for a specific double mutant of ASR.

The paper opens new perspectives for rationally predicting point mutations that could render rhodopsins fluorescent, with a potentially large impact for optogenetics.

M. del Carmen Marín, D. Agathangelou, Y. Orozco-Gonzalez, A. Valentini, Y. Kato, R. Abe-Yoshizumi, H. Kandori, A. Choi, K.-H. Jung, S. Haacke, and M. Olivucci, J. Am. Chem. Soc., 141, 262 (2019). DOI: 10.1021/jacs.8b09311

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 Figure caption: Mutating the amino acids W76 and Y179 of Anabaena Sensory Rhodopsin (left) increases its fluorescence quantum yield by almost one order of magnitude, due to an increased mixing of the ¹Bu and ²Ag excited state, inducing a potential barrier along the isomerisation reaction coordinate (right).

AWARDS

• Our colleague Bodhan KUNDYS is one of the seven laureates of the 2019 prize "Espoirs de l'Université de Strasbourg" which recognizes the quality of the work and scientific achievements of young researchers within the University of Strasbourg.

• The 2019 Young Researcher Prize from the Division of Chemistry of Coordination rewarded Mattéo MAURO, Associate Professor at the University of Strasbourg, and researcher at the IPCMS.

• The SUPERBRANCHE project led by Delphine Felder-Flesch won the Grand Prize of the jury at the iLab National Innovation Competition. SuperBranche is a start-up working in the field of nanomaterials for health, and more specifically for diagnostic imaging and image-guided therapy in oncology. The prize was awarded to Delphine on July 4th by Ms Frédérique Vidal, Minister of Higher Education, Research and Innovation.

• The SFµ (French Society of Microscopies) awarded the Grand Prix «Raimond Castaing» 2019 to Ovidiu ERSEN, Professor at the University of Strasbourg and researcher at the IPCMS for his outstanding contribution to the development of electron microscopy tomography. The "Raimond Castaing" Grand Prix rewards well-known scientists conducting their research in France and having made a remarkable contribution to microscopy in the broad sense (TEM, SEM, OM, STM, AFM, APT ...).

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Summary

Electron pulses reveal fast kinetics in nanocrystals p. 2

Defect-Driven Magnetization Configuration of Isolated Linear Assemblies of Iron **Oxide Nanoparticles** p.2

Simple, mild and straightforward reaction to generate nitrile and dihydrogen from primary amines p.3

A novel building block for nanomaterials based photodetectors in high doping regime p. 3

Teaching an old dog new tricks: How to make a rhodopsin emissive p. 4

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Editorial

On February 1st, 2019, CNRS organized the first convention of laboratory directors in Paris. I attended this important event together with about 1000 of my colleagues. On this occasion, the French Prime Minister, Mr Edouard Philippe, and the Minister of Higher Education, Research and Innovation, Ms Frédérique Vidal, launched the idea of a new framework for research in our country. A new law was expected to be presented by the end of this year. To this end, a vast discussion took place at every level of our institutions. The IPCMS took part in the discussion by relaying propositions stemming from everyday life in a lab that could improve the organization and efficiency of our French model. All ideas and proposals were analysed, and several reports were produced by the CNRS, the INSERM, different Universities, scientific and professional Societies, as well as the French Parliament. These reports constitute a good basis for the future law, announced for February 2020 by the French President Mr Emmanuel Macron at the occasion of the CNRS 80th birthday on November 26th 2019. We are eager to see the proposed framework and hope that the ambition of this act will not be significantly dampened by political and financial constraints.

The awareness that the politicians have demonstrated about science can be met with enthusiasm. The same enthusiasm pushes us for conducting research projects in new directions. We present in this issue a few examples that benefit from the association of colleagues with complementary experimental and theoretical skills. A seminal result concerns single-shot ultrafast electron microscopy that was employed to scrutinize the nickel oxide reduction reaction mechanisms. It is shown also that ultrafast spectroscopy is an efficient tool for probing and eventually controlling the photo-isomerization of proteins participating in many biological processes. Observation of a defect-driven magnetization configuration in nanoparticle assemblies was made possible thanks to a multi-disciplinary approach. As for materials, ionic glasses, that were introduced in optoelectronic devices, seem to be very promising electronic components. Finally, improving the processes to produce commercial functional bricks, is the purpose of colleagues who proposed a new efficient way to product nitrile moieties through a simple, mild and straightforward chemical reaction. In addition, during the last months, we celebrated the recognition awarded to young colleagues for their promising research, as well as the launching of one startup and one new research - industry partnership. The recognition and dynamism of our scientific activity, in a way, support the model of a laboratory "à la française". I hope you enjoy reading this new issue of IPCMS News and I wish you in advance a very fruitful and happy 2020.

The IPCMS is involved in CARMEN, a new research laboratory devoted to the CARME characterization of materials for new energies. This lab associates the CNRS, the "Centre de Résonance Magnétique Nucléaire à très haut champ" from ENS-Lyon, the IFP Energies nouvelles, the "Laboratoire de physicochimie des électrolytes et nanosystèmes interfaciaux" of Sorbonne University and the IPCMS.

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Pierre Rabu, Director

New joint laboratory





IPCMS*News*

• Electron pulses reveal fast kinetics in nanocrystals

Fast chemical reactions in nanocrystals are difficult to investigate. At high temperatures, it may take micro- or only nanoseconds until a reaction front has entirely traversed a nanometer-size crystal. Nevertheless, understanding reaction kinetics in nanocrystals is highly important, e.g., in catalysis where the kinetics of oxidation or reduction of nanoparticles is essential for optimizing the catalytic action. What is needed is an analytical tool with combined high spatial and high temporal resolution.

A novel approach of analytical electron microscopy, able to probe the structure and elemental composition of nanomaterials during physicochemical transformations with nanometer spatial and nano-



second time resolution, was developed at the IPCMS. This new ultrafast transmission electron microscope (UTEM) has been designed within an EQUIPEX project. In a pump-probe approach, physical or chemical transformations are induced by a laser pulse and studied after an adjustable delay with a nanosecond electron pulse. The main experimental challenge is the irreversible nature of most reactions so that the whole experiment has to be done within one single pump-probe cycle. It was shown, for the first time, that electron energy-loss spectroscopy (EELS) in the single-shot operation mode is feasible. Combined imaging, diffraction and EELS studies turned out to be possible so that a comprehensive picture of the reaction kinetics in nanocrystals can be obtained.

This technique was applied in a study of the fast reduction of nickel oxide nanocrystals at high temperature. Unprecedented insight into the dynamics of the reaction in nanoparticles was gained. The kinetics, in particular the reaction order and rate constant as well as the presence of liquid nickel as a short-lived transition state, allows the detailed understanding of the reaction mechanisms. With this new technique of fast analysis, the reaction kinetics in small solid systems can now be studied in detail.

S. K Sinha, A. Khammari, M. Picher, F. Roulland, N. Viart, T. LaGrange, and F. Banhart, *Nature Comm.* **2019**, 10, 3648. DOI : 10.1038/s41467-019-11669-w

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The ultrafast transmission electron microscope (UTEM) at the IPCMS (left) and a schematics showing the laser-induced fast reduction of an oxide nanocrystal with a time series of electron energy-loss spectra (right).

• Defect-Driven Magnetization Configuration of Isolated Linear Assemblies of Iron Oxide Nanoparticles



The magnetization state of one-dimensional magnetic nanoparticle (NP) chains plays a key role for a wide range of applications ranging from diagnosis and therapy in medicine to actuators, sensors and quantum recording media. The interplay between the exact particle orientation and the magnetic anisotropy is in turn crucial for controlling the overall magnetization state with high precision. Here, we report on a three-dimensional description of the

magnetic structure of one-NP-wide chains. In this aim, we combined two complementary experimental techniques, magnetic force microscopy (MFM) and electronic holography (EH) which are sensitive to out-of-plane and in-plane magnetization components, respectively. To obtain further insight, we employed micromagnetic simulations which confirmed the results obtained with MFM and EH. The findings are at variance with the known results on unidirectional nanoparticle assemblies, and show that magnetization is rarely strictly collinear to the chain axis. The magnetic structure of one-NP-wide chains can be interpreted as head-to-head magnetic domain structures with off-axis magnetization components, which is very sensitive to morphological defects in the chain structure such as minute size variation of NPs, tiny misalignment of NPs and/or crystal orientation with respect to easy magnetization axis. Our findings are highly decisive for the development of future devices

based on NP chains for application fields such as magneto-resistive sensors and biomedicine. Indeed, tuning the arrangement of NPs with only small defects open possibilities toward manipulating the magnetic behavior of such chains.

This work is an original and efficient contribution resulting from the combination of high level skills detained by IPCMS, more specifically, nanoparticle design (B. P. Pichon), near field probe microscopy (M. V. Rastei), electronic holography (V. Pierron-Bohnès), advanced TEM (C. Bouillet) and micromagnetism (R. Hertel).

M. V. Rastei, V. Pierron-Bohnes, D. Toulemon, C. Bouillet, A. Kákay, R. Hertel, E. Tetsi, S. Bégin-Colin, and B. P. Pichon, *Adv. Funct. Mater.* **2019**, 1903927. DOI : 10.1002/adfm.201903927

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• Simple, mild and straightforward reaction to generate nitrile and dihydrogen from primary amines

Nitrile function is like an «embryonic cell» for a synthetic chemist because it gives birth to many other functional groups. Additionally, nitriles are found in many useful compounds, drugs or natural products. However, classic synthetic procedures to install a nitrile function involve the use of stoichiometric, toxic reagents or harsh reaction conditions and are most often poorly compatible with other functional groups or generate waste products. An alternative and elegant strategy uses transition metals for the homogenous catalytic dehydrogenation of amines to nitriles with dihydrogen H₂ gas as the sole side product. Obtaining two equivalents of H₂ from a single C-N bond makes the acceptorless dehydrogenation of primary amine to nitriles an interesting strategy for Liquid Organic Hydrogen Carriers elaboration (LOHCs). Up to date, there is only one single 'well defined' catalyst known to conduct this reaction in absence of stochiometric additives such as bases or dioxygen.



• A novel building block for nanomaterials based photodetectors in high doping regime

Controlling the charge carrier density is pivotal in nanoelectronic devices and quantum materials. It allows for tailoring Schottky or p-n junction band bending, triggering electronic phase transition, achieving higher electronic mobility and fine tuning of carrier recombination mechanisms. To date, two main approaches have been engineered using either dielectric (SiO₂, Al₂O₃...) or electrolyte (ion gel, polymer electrolyte...). Dielectric gating allows fast bias sweeping over a broad range of temperatures but requires a large operating bias, and result in carrier density limited to the 10¹² cm⁻² range. Electrolytes enable larger carrier concentration thanks to large capacitances, lead to the significant reduction of operating bias but are limited to slow and guasi-room-temperature operation, and prohibit direct top access as the nanomaterials is buried under the electrolyte.

In a collaborating work lead by the IPCMS, researchers demonstrated a novel technology of phototransistor using solid lonic Glasses as gating medium. The lonic Glass gate allows achieving very high doping levels exceeding those of dielec-

trics, while preserving operability at lower temperature and direct top access not accessible with electrolyte, combining advantage of both techniques. The researchers demonstrate that lonic Glass is optimal technology to build infra-red 2D materials-based phototransistor. They unveil the unique property of this method to control the nature of the carrier recombination processes while annihilating the traps' contribution. This remarkable property results in a photoresponse that can be modulated electrostatically by more than two orders of magnitude, while at the same time increasing the gain bandwidth product. The devices demonstrate I_{ON}/I_{OFF} ratio exceeding five decades and photoresponse 100 time faster than state of the art MoSe₂ devices.

These results demonstrate the use of lonic Glass technology is a game changer to explore novel photoconduction processes and alternative architectures of devices in integrated circuits, photodetectors We have recently developed a straightforward access to nitrile from amine by employing a commercially available ruthenium precursor with no need of additional ligand and with no oxidant, base or additives. In the presence of this catalyst, the reaction is highly selective, starting with various alkylamine derivatives (short, branched or long carbon chains). For instance, benzyl amine derivatives demonstrated good activity and selectivity.

T. Achard, J. Egly, M. Sigrist, A. Maisse-François and S. Bellemin-Laponnaz, *Chem. Eur. J.* **2019**, 25, 13271-13274. DOI : 10.1002/chem.201902557.

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 Selective formation of nitrile without hydrogen acceptor additive and under oxidant free condition.



Left : Schematic of the lonic glass/2D $MoSe_2$ photodetector. Right : Photocurrent at 100 Hz for different incident power in electron doping regime.

and photovoltaic cells. The approach is generic, and can be easily extended to any photoconducting nanomaterials, including 2D material, organic thin film and hybrid materials.

U.N. Noumbé, C. Gréboval, C. Livache, T. Brule, B. Doudin, A. Ouerghi, E. Lhuillier and J.-F. Dayen, *Adv. Funct. Mater.*, **2019**, 29, 33, 1902723. DOI : 10.1002/adfm.201902723

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