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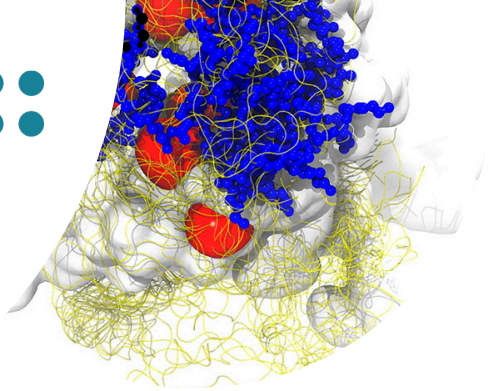

Scientific Newsletter

SPRING 2021

A direct way to transform CO_2 into methane with renewable electricity

Methane, the main component of natural gas, is one of the major energy sources in our economy. To meet the objectives of the Paris Agreement, its extraction from fossil deposits will nevertheless have to be stopped by 2050. Hence the idea of producing this fuel directly from recycled CO_2 and renewable energies, and thus develop a circular carbon economy. But how can such a virtuous cycle be achieved?

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CBM
Chemistry and Biology of Metals Laboratory
Carole Duboc
Département de chimie moléculaire
Université Grenoble Alpes

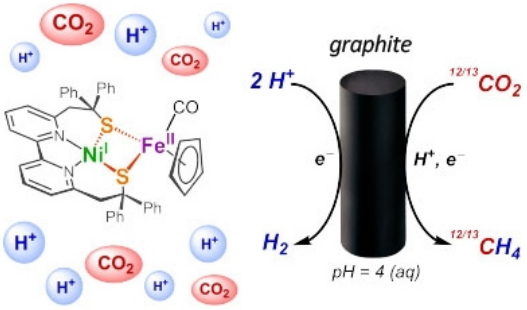
Turning CO_2 into methane using renewable electricity is a promising alternative to biogas production. This challenge was taken up by teams of researchers from the IRIG, the Department of Molecular Chemistry at the University of Grenoble Alpes, and the Indian association for the cultivation of science in Kolkata (India), who have just described a nickel-iron-based catalyst capable of carrying out this reaction. Directly inspired by the active site of enzymes, the catalysts of the living world, this unique compound has a selectivity comparable to the best metal-based materials described so far.

Electrochemistry can provide the solution. The CO_2 molecule, long considered as waste, can be transformed into many products at the electrode surface depending on the number of protons and electrons brought to it. The most common and simplest reactions involve only two electrons and two protons to form, for example, synthesis gas or formic acid. It is also possible to produce methane from CO_2, but the reaction to obtain it directly is more complex, involving eight electrons and eight protons. Efficient catalyst for this multi-electronic process thus remains to be identified.

These teams just achieved it by using a complex based on nickel and iron, directly inspired by active sites of metalloenzymes involving these same metals in CO_2 metabolism. This complex has proven to be very efficient in catalytically converting CO_2 into methane. The selectivity of this molecular complex is unique for this complex reaction, even compared to the best catalytic materials described so far.
To further improve the selectivity of methane production, the researchers are now trying to understand the mechanism at the origin of this chemical transformation.

REFERENCE

Ahmed ME, Adam S, Saha D, Fize J, Artero V, Dey A and Duboc C. Repurposing a bio-inspired NiFe hydrogenase model for CO_2 reduction with selective production of methane as the unique C-based product. *ACS Energy Letter*, 2020



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Optimizing oil production by microalgae by taking inspiration from a Drosophila enzyme

In order to improve oil production by microalgae for applications such as biofuel development, the choice of species is crucial. While some microalgae are well known and can be used to target genes, the study of other microalgae starts with a blank page. This is the case of the Heterokont group, a little-known branch of evolution in which we can find oleaginous microalgae that are very interesting because they can be grown industrially, such as *Microchloropsis gaditana*. It is this microalgae that has been selected by researchers and engineers of the Irig within the framework of a partnership with TotalEnergies, a partnership initiated in 2014.

Contact: Éric Maréchal
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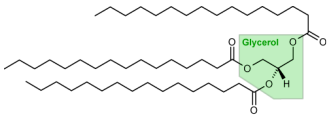
When the choice of microalgae species is made, the rational approach to increase oil production requires the selection of gene targets, increasing or decreasing their expression and/or function. As for the oil to be produced, it corresponds to a highly hydrophobic triacylglycerol (TAG) molecule. Inside the cell, TAG is sequestered in a spherical structure called an "oil droplet"; it is in equilibrium with other cellular glycerolipids, such as those found in biological membranes that contain only two fatty acids.



A triacylglycerol (TAG) molecule consists of a glycerol skeleton on which three fatty acids are esterified. Example of tripalmitoylglycerol. The general formula of TGA is:

CH2-COO-R1
|
CH-COO-R2
|
CH2-COO-R3

While studying *M. gaditana*, the researchers noted that there was an enzyme called "***ACS Bubblegum***", an ***Acyl-CoA Synthetase*** (ACS) type never before described in photosynthetic organisms. By genomic editing using molecular scissors (TALEN method), it was not possible to completely abolish this gene in *M. gaditana*, highlighting its vital role. However, several very fine modifications of the gene coding ACSBG have altered its function. In these mutants, a study of all membrane glycerolipids and TAG was performed on the LIPANG lipidomics platform of the IRIG's Cell & Plant Physiology Laboratory. This study made it possible to characterize the precise role of ACSBG. This enzyme prepares fatty acids for their esterification on certain membrane lipids. Mutations introduced in the gene cause structural modifications that directly influence its activity (*Figure*). These alterations in the synthesis of membrane lipids are then compensated by a reorientation of the fatty acids, which are found in excess, towards TAGs, resulting in a gain in oil productivity.

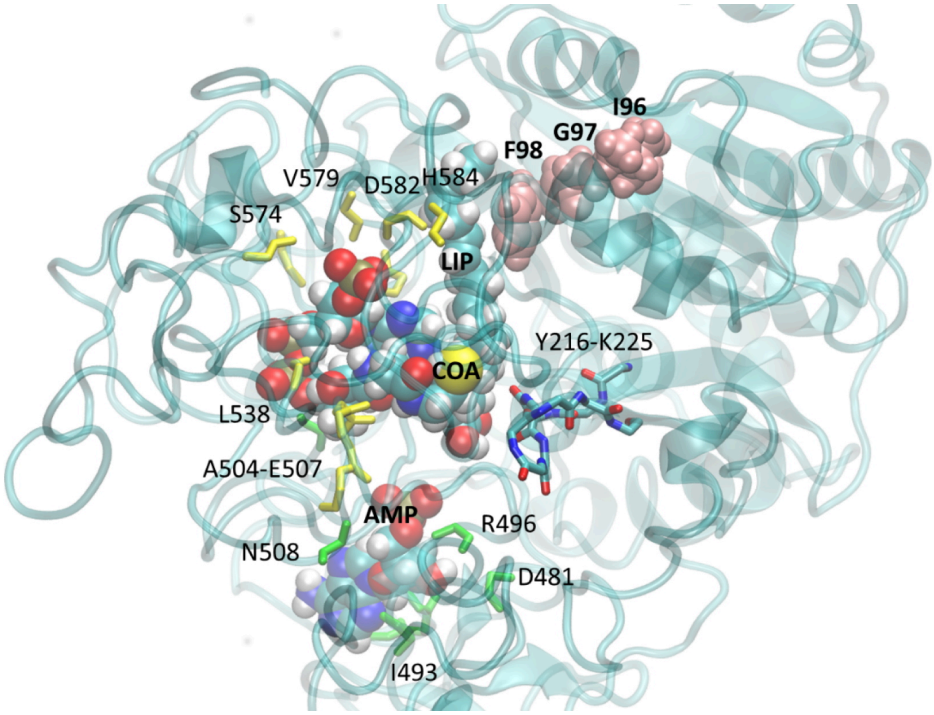
The ACS known as "***ACS Bubblegum***" (or ACSBG), takes its name from the effect of the corresponding mutation in the Drosophila fly, characterized by the appearance of bubble-like structures in the first optic ganglion, as well as a strong lipid imbalance.

It is possible to act on the enzymes that direct fatty acids to membrane lipids or TAGs. Fatty acids cannot be esterified directly because the ***esterification*** reaction requires energy. They must first be coupled to a chemical group, for example Co-enzyme A (CoA), through a bond that "stores" the energy required for subsequent esterification. Fatty acids are thus "prepared", or energetically activated, by association with CoA by enzymes called ***Acyl-CoA Synthetases*** (ACS).

This work was conducted in collaboration between the Lipid, the Photosynthesis, the Signal and the Flo_RE teams at LPCV and TotalEnergies. Serge Crouzy from the Chemistry and Biology of Metals laboratory of the Irig carried out the structural modeling of the enzyme. This work was the subject of a patent.

REFERENCE

Billey E, Magneschi L, Leterme S, Bedhomme M, Andres-Robin A, Poulet L, Michaud M, Finazzi G, Dumas R, Crouzy S, Laueffer F, Fourage L, Rébeillé F, Amato A, Collin S, Jouhet J and Maréchal E. Characterization of the Bubblegum acyl-CoA synthetase of *Microchloropsis gaditana*. *Plant Physiology*, 2021



3D model of *M. gaditana*'s ACSBG protein, associated with its substrates, Coenzyme-A (CoA), Adenosine Monophosphate (AMP) and a fatty acid (LIP). The point mutations introduced by genetic editing using TALEN are found at the level of the amino acids "IGF" (in pink). These mutations modify the conformation of the protein at the catalytic site (identified by the numbered amino acids), and cause a decrease in enzymatic activity leading to a complete reorientation of fatty acid flows in the cell.

Kidney cancer: Two targets for one therapy

Kidney cancers are well known for their resistance to radio/chemo-therapeutic treatments as well as to targeted therapies against extensive neo-vascularization. This formation of new functional blood vessels (angiogenesis), is often the cause of resistance to treatment as it provides the irrigation and nutrient supply necessary for tumor growth. Many cancers originate from the aberrant activation of intracellular signaling pathways in which protein kinases play essential roles. Therefore, the search for new drugs targeting these enzymes may be a privileged approach within the framework of targeted therapies, aiming at disrupting the activity of some of these dysregulated enzymes.

Contact: Odile Filhol-Cochet
Biosanté
Biology and Biotechnology for Health Laboratory

IRIG researchers intend to identify new candidate targets for the treatment of metastatic clear cell renal cell carcinoma (mccRCC), the eighth most common cancer in the world and representing 4% of all cancers. Based on the principle of ***synthetic lethality***, they evaluated the effects of more than 8,000 protein kinase inhibitor combinations on the viability of a cell line representative of metastatic renal cancer using a ***chemogenomic screening***. The screening performed at IRIG in the Center for the screening for bio-active molecules, allowed the selection of one of these combinations targeting two protein kinases involved in cell survival and DNA repair mechanisms: protein kinases CK2 and ATM. For several years, IRIG researchers have shown that protein kinase CK2 is involved in multiple biological events such as cell plasticity, response to stress and cell proliferation. In addition, they have unambiguously demonstrated that this enzyme is dysregulated in many cancers (kidney, prostate, breast, choliocarcinoma...) fostering the development of an innovative approach to inhibit CK2 using small chemical molecules. The ATM protein kinase which is activated following DNA double-strand breaks is a key player in the DNA repair machinery.

In their study, the researchers found that simultaneous inhibition of the CK2 and ATM kinases by small chemical molecules in renal tumor cells and in patient tumor samples induces synthetic lethality. Importantly, this dual inhibition spares normal cells. Mechanistic studies carried out on renal carcinoma cells cultured as spheroids (3D culture) revealed that this double inhibition causes an excessive production of intracellular free radicals leading to massive cell death by apoptosis.

These results highlight the interest of a therapy combining the simultaneous inhibition of protein kinases CK2 and ATM to treat resistant/aggressive forms of kidney cancer.

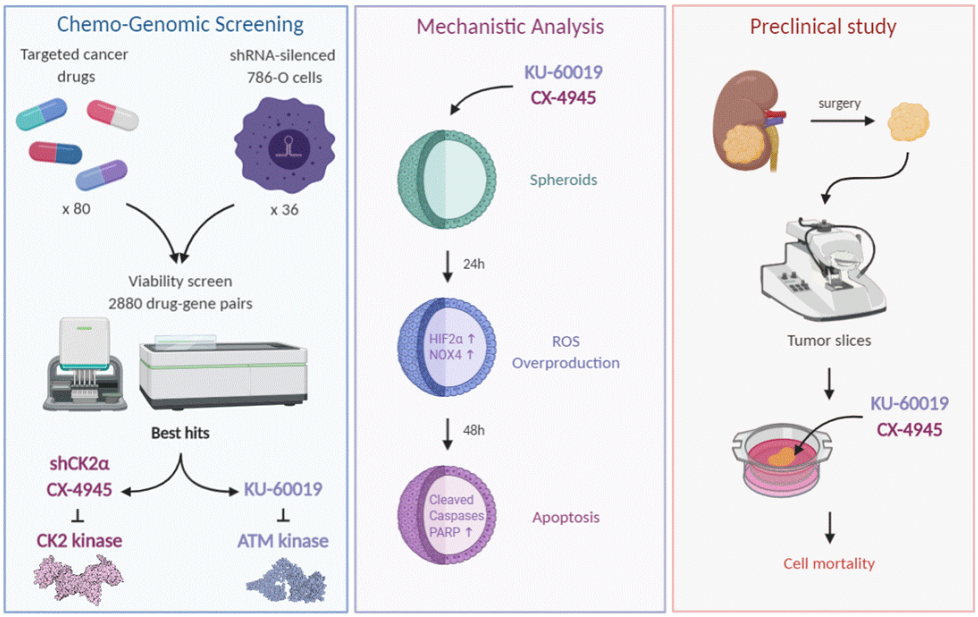
Synthetic lethality: cell death resulting from the deficiency of two or more genes/proteins.

Chemogenomic screening aims to identify among chemical molecules and/or interfering RNAs that target proteins whose inactivation induces an interesting cell phenotype.

REFERENCE

Giacosa S, Pillet C, Séraudie I, Guyon L, Wallez Y, Roelants C, Battail C, Evrard B, Chalmel F, Barette C, Soleilhac E, Fauvarque MO, Franquet Q, Sarrazin C, Peilleron N, Fiard G, Long JA, Descotes JL, Cochet C and Filhol O. Cooperative blockade of CK2 and ATM kinases drives apoptosis in VHL-Deficient Renal Carcinoma Cells through ROS overproduction. *Cancers (Basel)*, 2021

Patent PCT/EP2016/072458: A synthetic lethal drug combination for treating renal cell carcinoma. Filhol O, Cochet C, Giacosa S, Pillet C, Barette C, Soleilhac E.



A. Chemogenomic screening: 80 small chemical molecules targeting protein kinases, tested on 36 786-O renal cancer cell lines, each expressing a shRNA to decrease the expression of a particular gene identified an inhibitor-shRNA couple (KU-60019-shCK2α) that is particularly effective in affecting cell viability. This couple targets the ATM and CK2 protein kinases, respectively. Then, shRNA directed against CK2α was replaced by a chemical molecule, CX-4945, which specifically inhibits this enzyme.
B. Analysis of the mechanism of action of the combination (KU-60019 and CX-4945) using spheroids (3-dimensional cell culture) shows that these inhibitory molecules induce, *via* HIF-2α and NOX4 proteins, an overproduction of reactive oxygen species (ROS) leading to massive cell death.
C. Tested on human kidney tumor samples (COMBOREIN preclinical study), this combination of inhibitors shows its effectiveness in inducing cancer cell death.

Promiscuity without excess for the couple "client-chaperonne".

Chaperones are essential proteins whose role is to help the folding of other proteins as well as the transfer of poorly soluble proteins to the intracellular location where they fulfill their functions. Chaperones thus help proteins in their maturation by preventing the formation of aggregates primarily by binding the hydrophobic, aggregation-prone parts of their "cargo", using hydrophobic patches on the chaperone surface. These hydrophobic interactions lead to a promiscuous "chaperone-client" complex. At the same time, this interaction must not be too strong to allow the two proteins to separate, especially when the complex reaches its final destination. In addition, chaperones must maintain a balance between promiscuity, which allows them to transport a wide variety of proteins, and specificity, which helps organize the final location of their "clients". Our knowledge of how interactions enable this balance between promiscuity and client specificity is limited.

The mitochondrion is an organelle surrounded by a two membranes (*i.e.* two phospholipid bilayers). The human mitochondrial proteome is estimated to contain more than a thousand proteins, 99% of which must be imported inside the mitochondria, *i.e.* in one of the mitochondrial membranes, in the intermembrane space, in the matrix or in very specific locations. The molecular mechanisms of this import are still poorly understood and involve chaperones.

A study by IRIG researchers has made it possible to decipher the specific mechanism of the chaperone system present in the intermembrane space of the mitochondria. Their study highlighted how TIM8-13 and TIM9-10, two homologous chaperones but with different functions, interact with two different membrane proteins of the inner mitochondrial membrane, namely Tim23 and mitochondrial-carrier proteins, which allow the mitochondrial matrix to exchange molecules with its surrounding. By combining NMR, small angle X-ray scattering (SAXS), analytical ultracentrifugation and molecular dynamics simulation techniques with other biophysical/biochemical approaches, the researchers were able to study the structures of the TIM8-13 and TIM9-10 chaperones in complex with different membrane proteins. They revealed that the delicate balance between promiscuity and specificity that these chaperones must satisfy is the result of a combination of a multitude of hydrophobic and hydrophilic interactions towards different client proteins.

REFERENCE

Sučec I, Wang Y, Dakhlaoui O, Weinhaupl K, Jores T, Costa D, Hessel A, Brennich M, Rapaport D, Lindorff-Larsen K, Bersch B and Schanda P. Structural basis of client specificity in mitochondrial membrane-protein chaperones. *Science Advances*, 2020

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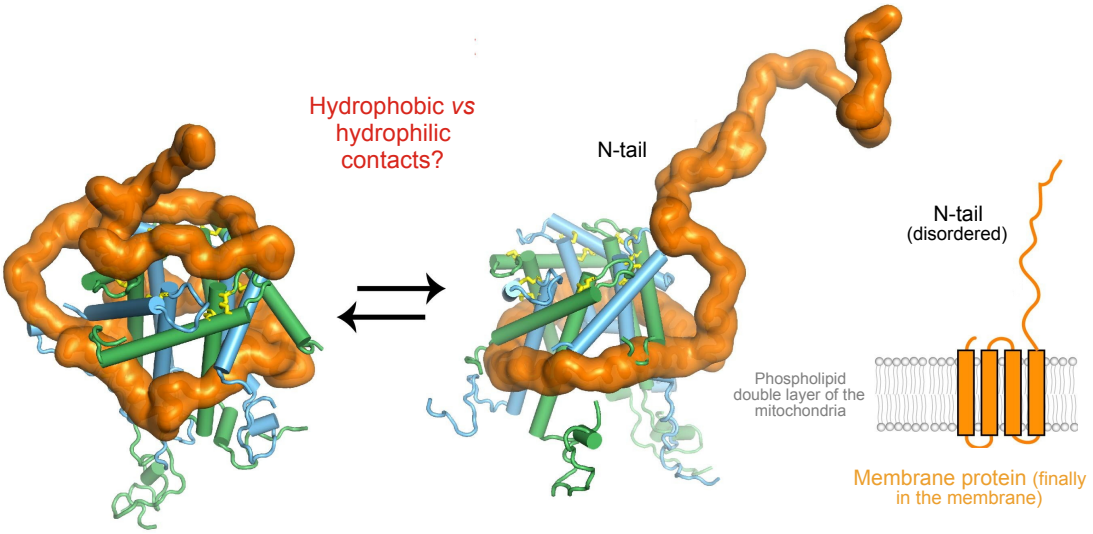


The TIM chaperone (green/blue) carries a membrane protein (orange) to its final destination in the inner membrane of the mitochondria. The hydrophobic interactions between the chaperone cavity (bottom) and the hydrophilic interactions with the more polar part of the membrane protein ("N-tail") establish a highly dynamic complex, which is exchanged between multiple states. This flexibility also allows the membrane protein to be released for insertion into the membrane.

Cryo-CMOS for quantum research

Applications of quantum phenomena require low-temperature functioning in order to preserve the essential properties of quantum states. Integrating classical electronics at the same temperature as the quantum device is a challenge in order to control and detect quantum states with greater speed and efficiency while limiting the wiring towards the instrumentation at room temperature. How to develop dedicated cryogenic electronics based on the known technology of CMOS (*Complementary Metal Oxide Semiconductor*) components and compatible with silicon quantum bits?

Contact: Louis Jansen
Pheliqs
Quantum Photonics, Electronics and Engineering

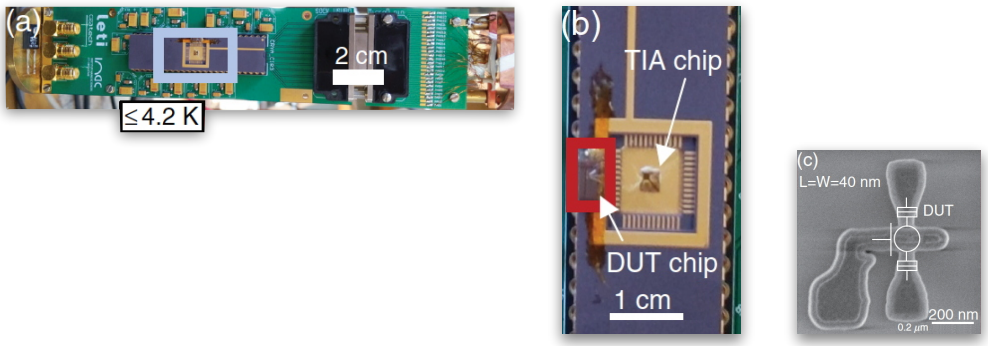
Researchers from IRIG and Leti have prototyped hybrid circuits combining silicon quantum-dot devices with a conventional trans-impedance amplifier (TIA). The TIA is particularly well suited for measuring the current across a semiconductor quantum-dot system (in the pico-ampere range). These nanometer-sized quantum dots have quantized electronic states with an energy spectrum that can be detected as a function of a gate voltage by measuring a current corresponding to single electron transport through the quantum structure.
Trans-impedance amplifiers integrated with current measuring devices are designed and fabricated with the commercial 28 nm fully depleted silicon-on-insulator (FDSOI) CMOS technology at STMicroelectronics. The chip of the nano-device to be measured was placed side by side with the TIA chip or both quantum and conventional systems were realized on the same chip (*Figure*). The circuit with the TIA operates at 10 mK with only 1 µW of power consumption, which avoids the heating of the cryostat. It has a linear response up to ±40 nA with a bandwidth of 2.6 kHz. The assembly has a circuit footprint of only 0.1mm x 0.1mm. These technical data are very promising for quantum applications at the lowest temperatures. In a more complete version, the chip integrates other analog and digital functions (multiplexer, buffer, signal amplifier, oscillator, level shifter) to make current measurements under excitation in the GHz range.

Following this proof of concept in the realization of a cryogenic TIA, further improvements will focus on increasing the bandwidth of the amplifier for even faster current sensing schemes.

Loïc Le Guevel is a PhD student supervised by Gaël Pillonnet (CEA-Leti) and Louis Jansen (IRIG's Pheliqs laboratory). He is a member of the Grenoble Silicium Quantique research group headed by Maud Vinet.

REFERENCE

Le Guevel L, Billiot G, Cardoso Paz B, Tagliaferri MLV, De Franceschi S, Maurand R, Cassé M, Zurita M, Sanquer M, Vinet M, Jehl X, Jansen AGM and Pillonnet G. Low-power transimpedance amplifier for cryogenic integration with quantum devices. *Applied Physics Review*, 2020



Realization of the TIA with the device to be measured.
a. Circuit board with the connectors,
b. Chip carrier with the TIA; (DUT=quantum dot chip),
c. SEM image of the FDSOI device with source and drain contacts and quantum dot formed under the gate (circle).

Towards DNA-functionalized, biocompatible and environment-friendly quantum dots

Fluorescent emitters are of great interest for biomedical applications. With appropriate functionalization, they can be used to detect or label biomolecules in order to follow *in vivo* their evolution in complex biological environments (cells, organisms). Among the large variety of luminescent probes, semiconductor quantum dots (QDs) have the advantages of being stable and much more resistant to optical (or laser) excitation than organic fluorophores. Besides, depending on their sizes and chemical compositions, they are able to emit light over a broad spectral range, from visible to infrared. QDs have thus an important advantage for multicolor and long duration imaging. Emission in the near infrared is particularly interesting because the absorption and scattering of light by the biological environment are strongly reduced. But, are these QDs biocompatible?

The classical QDs emitting in the near infrared range present often cytotoxicity caused by the presence of metals such as cadmium or lead. This is why great efforts are currently made for the development of biocompatible QDs, without the use of toxic heavy metals. Among the environment-friendly QDs, those based on silver and indium, $AgInS_2$, are particularly promising thanks to their high photoluminescence quantum yield (***PLQY***); PLQYs up to 66% have been reported in the literature. To make them compatible with biomedical applications, it is necessary to make appropriate functionalization on the surface of these QDs, while limiting the decrease of the photoluminescence quantum yield related to such a modification.

The complementary expertise of three teams at IRIG (*see box*) has made it possible to develop a new method for the synthesis of $AgInS_2$ QDs. Such QDs were then covered with a ZnS shell and functionalized by single-strand DNAs (*Figure*), while preserving their high luminescence (final PLQY of 42% with infrared emission at 650-750 nm). In practice, the colloidal synthesis was carried out in aqueous medium allowing to obtain directly water-soluble QDs. The single-strand DNAs were incorporated during the growth of the ZnS shell around the $AgInS_2$ QD, forming QD-DNA complexes. The success of DNA anchoring on QDs was demonstrated by several techniques (UV-visible spectroscopy, gel electrophoresis, dynamic light scattering, and zeta potential). Furthermore, surface plasmon resonance imaging (SPRi) on a DNA chip (composed of complementary DNA spots and negative control DNA spots deposited on a gold film), has shown that the QD-DNAs are exclusively bound onto the spots of complementary DNA *via* hybridization (*Figure*). This further demonstrates the success and the stability of the QD-DNA coupling and the preservation of the biological activity of the anchored DNA.

The non-toxicity, long-term stability and biocompatibility of these QD-DNAs open important perspectives. In addition to potential applications as fluorescent probes for live cell imaging or as building blocks for nanosensors, they can also be coupled to other functional blocks in which DNA serves as smart linker: FRET nanoprobes involving energy transfer between fluorescent molecules or plasmonic nano-antennas for bio-imaging and biodetection.

$AgInS_2$: silver indium sulfide, ternary compound I-III-VI of chalcopyrite type.

PLQY: *PhotoLuminescence Quantum Yield* is the ratio of the number of photons emitted to the number of photons absorbed.

REFERENCE

Delices A, Moodelly D, Hurot C, Hou Y, Ling WL, Saint-Pierre C, Gasparutto D, Nogues G, Reiss P and Kheng K. Aqueous synthesis of DNA-functionalized near-infrared $AgInS_2$/ZnS core/shell quantum dots. *ACS Applied Materials & Interfaces*, 2020

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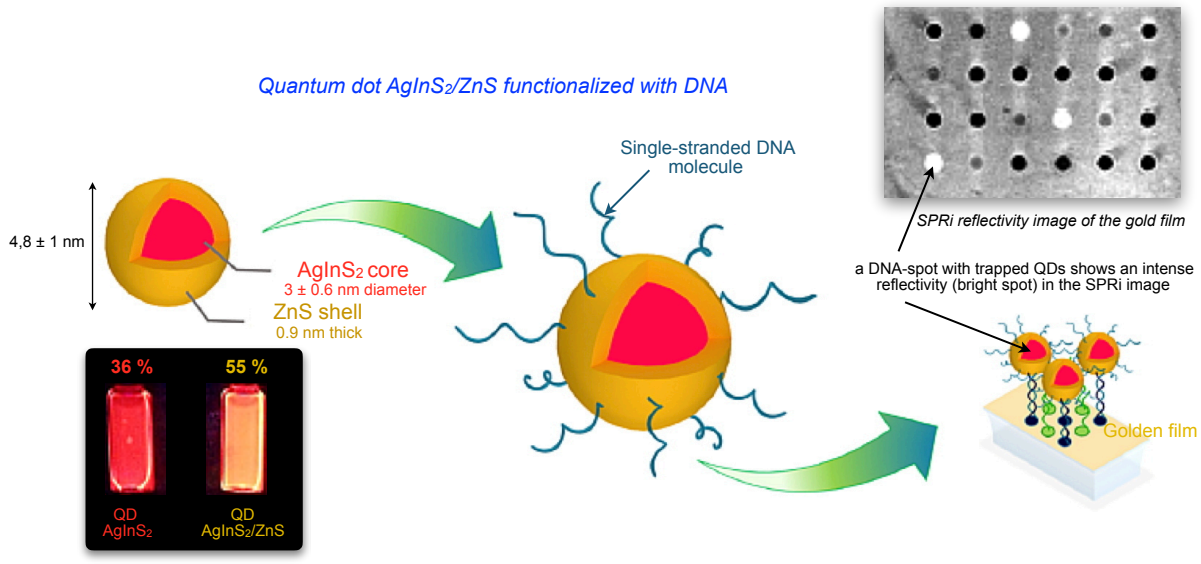
D. Gasparutto, Y. Hou-Broutin & P. Reiss
SyMMES
Molecular Systems and nanoMaterials for Energy and Health laboratory

This landmark result was achieved in the DRF-Impulse funded HybriDimer project (2018-2020), which recruited Annette Delices as a postdoc. The project aims to design, realize and characterize mixed nano-architectures composed of a semiconductor nanocrystal (Quantum Dot or QD) connected to a gold nano-rod (GNR, Gold NanoRod) by DNA strands. This hybrid structure allows to control the light emission properties of the QD (diameter ~ 5 nm) by plasmonic coupling, by adjusting the length of the DNA strands.
This project brings together a large multidisciplinary consortium within IRIG: specialists in condensed matter physics and nanostructures for electromagnetic simulations and optics (NPSC team of the Pheliqs laboratory), colloidal synthesis of QDs (STEP team of the Symmes laboratory), surface chemistry for regio-selective functionalization of GNRs (CREAB team of the Symmes laboratory), biochemistry for DNA synthesis and purification (CREAB), nanocharacterization of biological and biohybrid structures (IBS and MEM laboratory).
The project continues with the thesis of Nicolas Daveau (2020-2023) funded jointly by the labex ARCANE and LANEF.



Quantum dot $AgInS_2$/ZnS functionalized with DNA.
QDs consisting of an $AgInS_2$ core (PLQY = 36%) and a ZnS shell (PLQY = 55%) are functionalized with single-stranded DNA molecules (final PLQY of 42%). SPRi showed that the DNA-QDs are selectively bound onto the spots functionalized with their complementary DNA strands *via* hybridization, giving an intense reflectivity signal.

Exploration of elementary particles: One step beyond, one step more stable

The Great National Heavy Ion Accelerator (GANIL) in Caen is one of the largest international research laboratories studying the physics of the nucleus, the atom and condensed matter. It consists mainly of (i) an injector source of charged particles, (ii) elements that produce a magnetic field to focus the trajectory of the particles, and (iii) elements that produce an electric field to accelerate the particles. As the slightest fluctuation of the electric field causes losses of particles, it is essential to control the temperature and pressure in the acceleration part very precisely in order to obtain the most stable electric field possible.

Contact: Patrick Bonnay
DSBT
Low Temperature Systems Department
Pierre-Emmanuel Bernaudin
Institut de recherche sur les lois fondamentales de l'Univers

Commissioning of LINAC, the new superconducting linear accelerator (*Picture*), continues apace at GANIL, in SPIRAL 2 (2nd generation On-line Radioactive Ion Production System). In LINAC, a beam acceleration is provided by 26 cavities that generate a radiofrequency electric field to increase proton energy. These cavities are cooled to 4.5 K in baths of liquid helium in order to use the superconducting properties of their material and considerably minimize thermal dissipation caused by the interaction of the particles with the intense electric field.

Since these cavities are very sensitive to helium pressure variations, IRIG researchers have developed a numerical model of the cryogenic system to ensure helium pressure stabilization using an intelligent LQ (*Linear Quadratic*) type regulator. This type of regulator provides better performance than a conventional PID (*Proportional*, *Integral*, *Derivative*) regulator. The modeling used for this regulation is based on programming tools specifically developed by the IRIG researchers over the last ten years, under the title Simcryogenics. These tools allow to obtain a simplified model to regulate the pressure of the cavity and the level of the helium bath. Modeling also provides a better understanding of physical phenomena and thus allows better control and detection of possible anomalies.

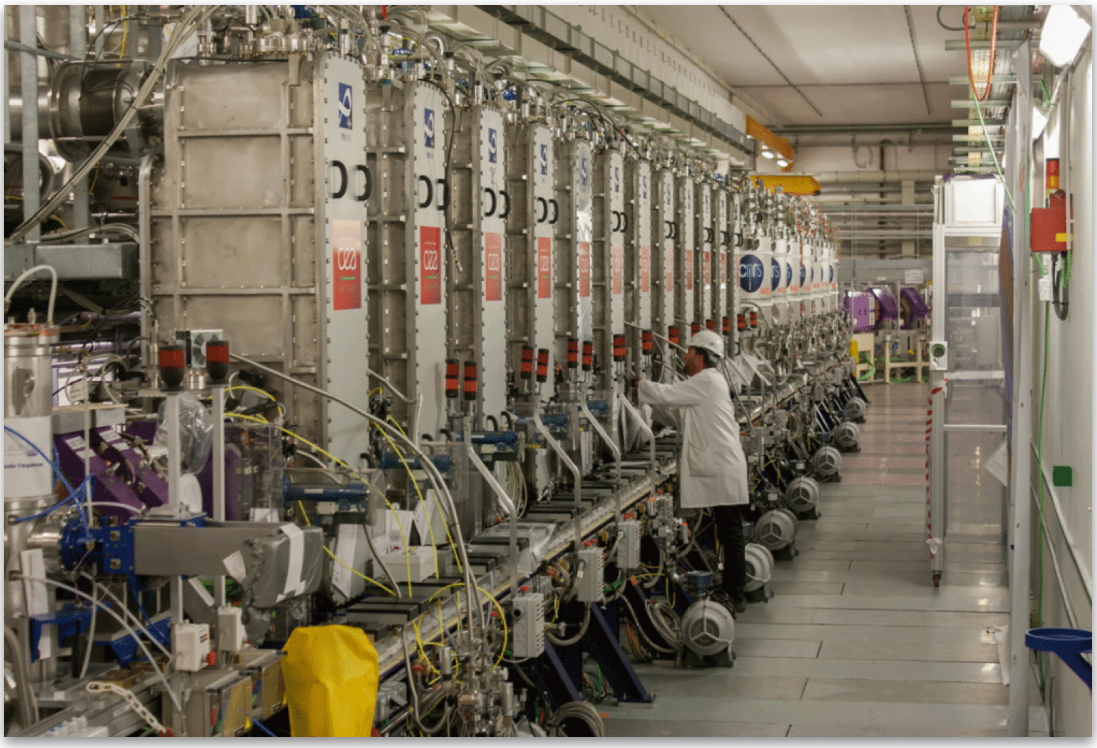
Optimization work continues with the GANIL in order to improve the modeling and obtain an even more efficient regulation. This multidisciplinary collaboration is making a significant contribution to the final power increase of 200kW for the new LINAC.

This result is the outcome of a collaboration between DSBT and IRFU/GANIL.

The *Grand accélérateur national d'ions lourds*, or GANIL, (Great National Heavy Ion Accelerator) is an Economic Interest Grouping (GIE) created by two research organisms associated in equal parts for its construction and operation: the CEA and the CNRS. The CEA staff is affiliated with the IRFU/GANIL department.
IRFU: *Institut de recherche sur les lois fondamentales de l'Univers* (Institute for Research on the Fundamental Laws of the Universe).

REFERENCE

Bonne F, Varin S, Vassal A, Bonnay P, Hoa C, Millet F and Poncet JM. Simcryogenics: A library to simulate and optimize cryoplant and cryodistribution dynamics. *IOP Conference Series: Materials Science and Engineering*, 2020



View of the linear accelerator of SPIRAL2 showing the different cryomodules, of which twelve were designed by CEA, and seven by CNRS.
© P.Stroppa CEA

Cellulose nanofibrils: Wood as a vector for green chemistry

Cellulose nanofibrils (CNF) obtained from wood are a biosourced and renewable material that is of interest in recent applications, for example fibers and composites for concrete, the automotive industry or packaging materials. In addition, the large specific surface area of CNFs (50-150 m^2/mg), their non-toxicity and their high mechanical stability also make them relevant as nano-chemistry platforms, especially for innovative applications in the fields of energy or health. In the health field, for example, nanofibrils are being considered as "smart" drug delivery systems with controlled release. However, the success of this approach depends heavily on the ability to understand in detail the surface chemistry involved in grafting the active molecule.

Contact: Gaël De Paëpe
MEM
Modeling and Exploration of Materials

IRIG researchers, in collaboration with the Centre Technique du Papier (CTP) and three other Grenoble laboratories (LGP2, DPM and CERMAV), have succeeded in studying in detail the surface of CNFs functionalized by a therapeutic molecule. The results were obtained thanks to an original characterization technique developed at IRIG: high-resolution solid-state NMR coupled with dynamic nuclear polarization (DNP). This technique increases the sensitivity of conventional solid-state NMR by several orders of magnitude. Thus, while this study focused on CNF with a low grafting rate, DNP has allowed us to obtain important information on their surface chemistry during the different transformation steps, from the starting material to its functionalization.

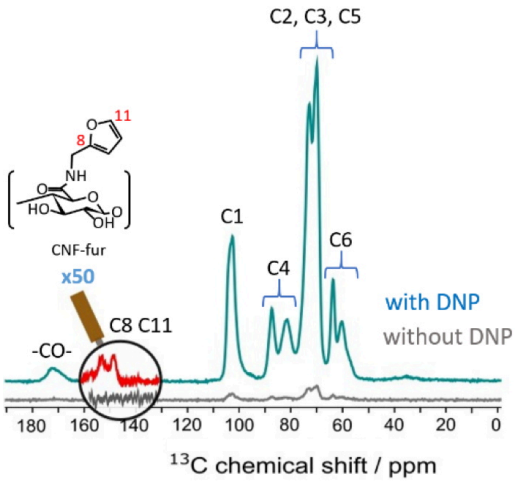
Regarding the starting material, the researchers were able to detect unambiguously fragments of the chemical compound ***TEMPO*** used for the pre-oxidation of CNF. They were also able to detect the presence of depolymerized cellulosic units. After grafting on the surface of the CNFs, the data obtained by DNP reveal the persistence of the presence of residual coupling agents used for the functionalization reaction (amidation), even after several washings. Moreover, the measurements allow estimating the amount of active molecules present on the surface, while differentiating adsorption from covalent grafting. This remarkable information could be obtained without using isotopic labelling, which was out of reach for conventional characterization techniques.

These initial results pave the way for using the information provided by DNP for the development of efficient and reproducible surface chemistry of cellulose nanofibrils.

TEMPO: (2,2,6,6-Tetramethyl-piperidin-1-yl)oxy.

REFERENCE

Kumar A, Durand H, Zeno E, Balsollier C, Watbled B, Sillard C, Fort S, Baussanne I, Belgacem N, Lee D, Hediger S, Demeunynck M, Bras J and De Paëpe G. The surface chemistry of a nanocellulose drug carrier unravelled by MAS-DNP. *Chemical Science*, 2020



^{13}C multi-CP5 NMR spectra of CNF-t, shown with peak deconvolution of C6, C4, C1.
Spectra with (Blue) and without (Grey) the application of microwave irradiation suitable for DNP enhancement on CNF.
The inset shows x50 magnified view of the 115–165 ppm region for CNF-fur.

Twist the spin

Devices based on the use of electron spin are gaining importance in microelectronics. Indeed, this spin is complementary and distinct from the charge and can therefore be used as an information carrier. In a ferromagnetic material, characterized by a fixed magnetization, the electrons carrying the current have their spin aligned with it. What happens when electrons with a spin not aligned with the magnetization are introduced into this material? This is the question that researchers at IRIG have asked themselves.

Contact: Laurent Vila
Spintec
Spintronics and Component Technology

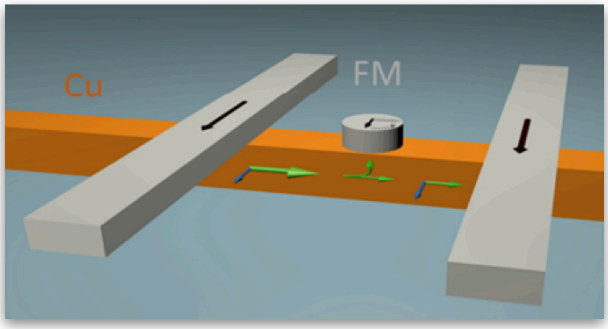
In a ferromagnetic material characterized locally by a magnetization directed in a certain direction in space, the electrons carrying the current have their spin oriented in the same or opposite direction to the magnetization, those of the same direction being the majority. At equilibrium, the ratio between the two spin groups is fixed. But this equilibrium can be broken to create an imbalance in this spin population. With the help of special structures, it is for example possible to introduce electrons of spin opposite to the magnetization of the material. The minority spins are then in excess. It is also possible to rotate the spin of the electrons perpendicular to the magnetization of the material, without changing it. There will then necessarily be a return to equilibrium, and the spins in the perpendicular direction or in excess will be absorbed.
The question that the IRIG researchers asked themselves was the following: are these two types of imbalance identical in terms of their return to equilibrium? In other words, does the direction of the magnetization play a role in the absorption of the electron spin?

Measuring this effect is easier to imagine than to do. Physicists have many techniques to measure this return to equilibrium, but they are difficult to implement at the local scale. Often, parasitic effects complicate the interpretation.

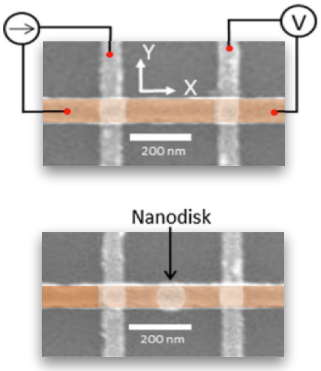
Based on their expertise in electron beam lithography and their knowledge of ferromagnetic materials, the Irig researchers created a measuring device to evaluate this absorption (*Figure*). They were then able to show that the absorption was stronger when the spin of the "non-equilibrium" electrons is perpendicular to the magnetization of the material. This observation allowed to access fundamental parameters of the spin transport, experimentally not well known.

REFERENCE

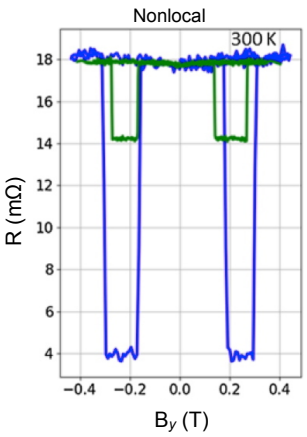
Cosset-Chéneau M, Vila L, Zahnd G, Gusakova D, Pham VT, Grèzes C, Waintal X, Marty A, Jaffrès H and Attané JP. Measurement of the spin absorption anisotropy in lateral spin valves. *Physical Review Letters*, 2021



Scheme of the device. The small disk above the orange wire is used to absorb the spins generated by the grey transverse wires representing ferromagnetic materials.



Photographs of the device with and without absorbing nanodisk.



Signal measured with (green) and without (blue) nanodisk.

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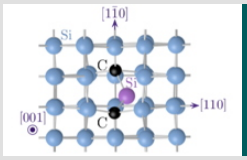

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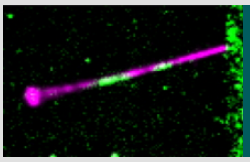

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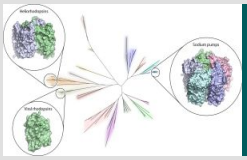

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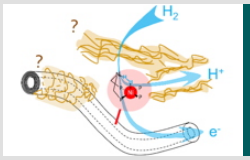

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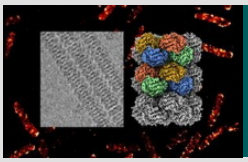

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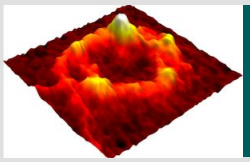

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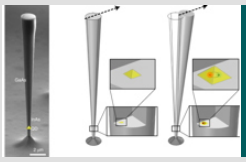

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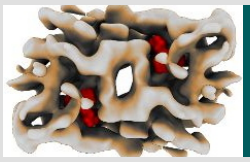

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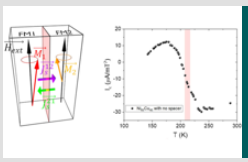

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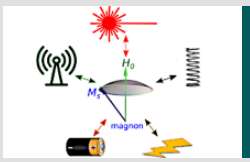

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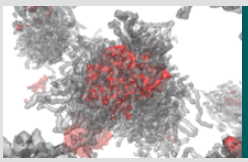

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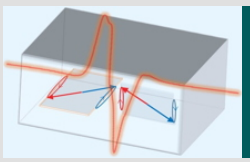

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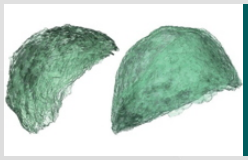

Let there be green!

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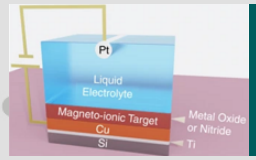

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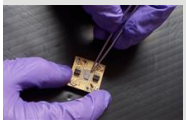

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