

Editorial

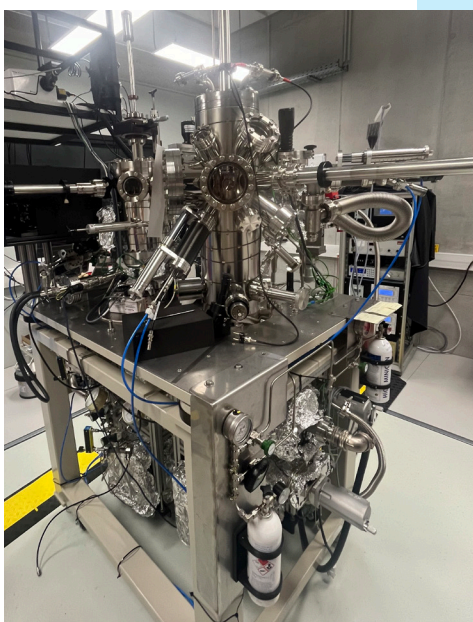
After a long break, IPCMS News is back. In 2024, we have chosen to adopt a digital format, making it easier to circulate. I hope that this new format will satisfy our readers.

2024 was an important year for the IPCMS. Following the positive evaluation of the laboratory by our supervisory bodies, the laboratory began a new 5-year term under the aegis of the CNRS and the University of Strasbourg. Our project is structured around 5 main cross-disciplinary lines of research, to which all the laboratory's physicists, chemists, experimentalists and theoreticians contribute with their own specific expertise: quantum sciences and materials, nanoscience and life, advanced molecular systems, magnetism, and (multi-)functional materials and frugal technologies.

2024 also marked the completion of a number of structuring operations, in particular the installation of our new ultra-low-temperature scanning tunnelling microscopy (STM) platform in an environment that minimizes mechanical, electromagnetic and optical noise, essential for precision measurements at the single-atom scale. This platform enables high-resolution STM microscopy, either for probing the physics of single photon sources, or for magnetic imaging at the atomic scale.



The new STM Platform of IPCMS has been inaugurated on Friday 27th september 2024 in the presence of delegates from the CNRS and the University of Strasbourg as well as representatives of the regional and national authorities who have supported and contributed to the funding of our facilities.
Photos © Thomas Lang



This issue of IPCMS News presents a series of scientific results obtained over the past year, illustrating the multidisciplinary nature of our work, concerning near-infrared (NIR) emissive materials for emitting optoelectronic devices, the confocal detection of highly fluorescent polymeric organic nanoparticles acting as light-harvesting antennas, the mechanistic study of cementitious materials in order to gain energy and reduce their contribution to CO₂ emission, the investigation of Qudits as an alternative to Qubits for quantum calculation, construction of a magnetic image of a surface with atomic-scale spin sensitivity using STM microscopy to improve ultra-dense storage technology, or the design of promising electromagnetic wave absorber composites.

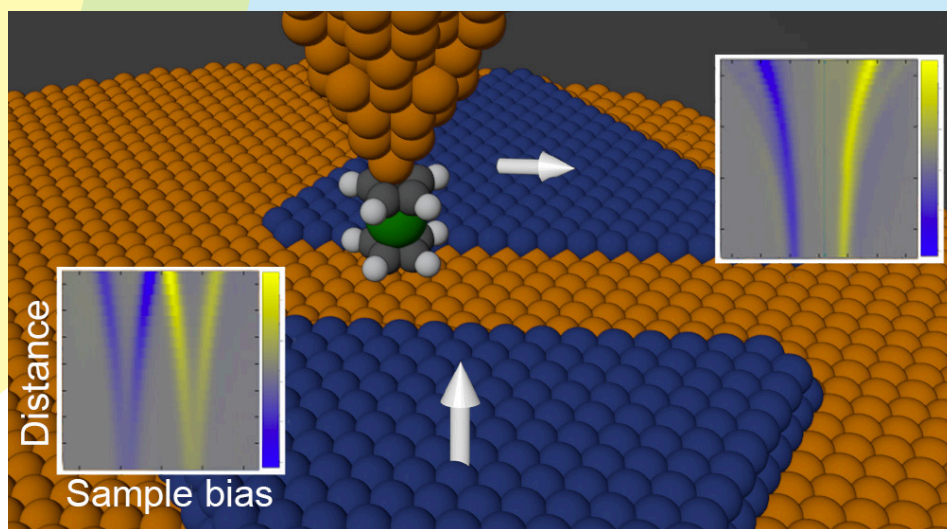
Pierre Rabu, Director

Single-Spin Sensing: A Molecule-on-Tip Approach

Advancements in ultra-dense storage technology have driven the development of spin-sensitive techniques for the precise manipulation and measurement of single spins within magnetic structures. Scanning tunneling microscopy (STM) is uniquely suited for this purpose, offering spin detection and magnetic property imaging. One promising approach involves using a magnetic molecule attached to the STM tip apex as a spin sensor. Although still in its early stages, we successfully demonstrated this method in our recent Science paper using a nickelocene molecule (Nc) with spin $S=1$ [$\text{Ni}(\text{C}_5\text{H}_5)_2$, see Figure]. Atomic-scale spin sensitivity is achieved by monitoring the Nc spin states through spin excitations in the inelastic component of the tunneling current. When the nickelocene-decorated tip is within 100 pm of the magnetic sample, an exchange interaction across the vacuum gap modifies the Nc spin states. A key challenge remains in constructing a magnetic image of the surface by exploiting these changes. To address this challenge we investigated model ferromagnetic cobalt (Co) islands on Cu(111) with varying thicknesses and magnetic properties.

Our imaging technique involved recording the spin excitation spectrum at each coordinate (x,y) , with the molecular tip fixed at a certain height z_0 from the sample surface. Post-processing analysis of the spectral line shape allowed us to extract the exchange interaction and the sample's spin polarization, with knowledge of the sample spin orientation. By associating the exchange interaction and spin polarization with each (x, y) coordinate, we produced spatial maps of these quantities. In our recent publication, we focused specifically on the exchange interaction maps. Remarkably, we observed a strong correlation with spin density

maps calculated using density functional theory (DFT), which describe the "local" magnetization $m(r)$ with $r=(x, y, z_0)$. This imaging technique is compatible with all low-temperature STM systems, including those that operate without an external magnetic field, marking a significant advancement in magnetic imaging and characterization. Future work will explore complex spin textures, such as spin spirals, antiferromagnets, and nano-skyrmion lattices. The simultaneous acquisition of both exchange and spin polarization data holds the promise of providing dual, atomic-scale resolution insights into complex spin textures.



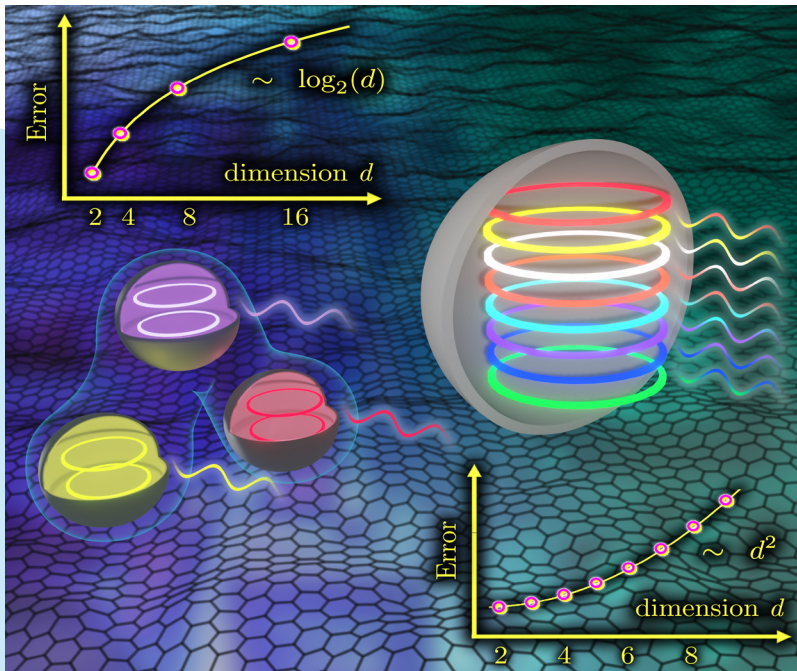
Sketch of the experimental setup. A nickelocene molecule (green: Ni, gray: C, white: H) is attached to the apex of an STM tip and scanned over Co islands grown on Cu(111). The scanned areas are typically a few nanometers wide. The collected data provide information about the sample's spin orientation and allow for the visualization of the tip-sample exchange interaction, as well as the sample's spin polarization within the scanned area. The exchange maps are well reproduced by DFT-calculated spin-density maps.

A. Fetida, O. Bengone, M. Romeo, F. Scheurer, R. Robbs, N. Lorente, L. Limot, ACS Nano, 18, 13829 - 13835 (2024)

Doi : [10.1021/acsnano.4c02470](https://doi.org/10.1021/acsnano.4c02470)

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Exploring the Future of Quantum Computing : Can Qudits Outperform Qubits ?



Quantum computing aims to revolutionize technology by tackling problems too complex for today's computers. Its fundamental units are quantum bits, or qubits, which, unlike classical bits that are either 0 or 1, can exist in any superposition of these states. This allows qubits to explore vast combinations simultaneously through entanglement. However, scaling up qubits is challenging due to difficulties in maintaining their delicate quantum states when interconnected. To address this, scientists are exploring qudits, which can exist in multiple states—three, four, or more—thus carrying more information than a single qubit. This potentially reduces the number of units needed for computations.

The trade-off is that more states increase susceptibility to errors from environmental interactions, a problem known as decoherence.

Our recent study [1] investigated whether qudits can handle errors as effectively as qubits. Using mathematical models and simulations, we compared a qudit and multiple qubits under identical noisy conditions. We found that qudits can compete with qubits in error handling under certain circumstances. The key factor is the operation speed relative to the rate at which errors occur. Specifically, qudit operations must be faster than qubit operations by a factor based on the ratio of the square of their

state number to its logarithm. This requirement is less stringent for qudits with fewer states, making them more practical in the near term. We identified a «critical curve» that defines conditions where qudits can outperform qubits. We also examined current quantum platforms like superconducting circuits, trapped ions, and photonic systems to assess qudit implementation. Some technologies naturally support multiple quantum states and meet our operation speed conditions, making them suitable for qudit-based systems. For instance, nuclear spins in molecular magnets are highly competitive at this stage. Importantly, coupling qudits with advanced error correction techniques could enhance their reliability by mitigating the downsides of having more states.

In conclusion, while qubits have been the primary focus of quantum computing research, qudits offer a promising alternative to overcome current limitations. By embedding more information into each quantum unit and optimizing operation speeds, qudits could enhance quantum computer performance, bringing us closer to realizing the full potential of this transformative technology.

D. Janković, J-G Hartmann, M. Ruben, P-A Hervieux , npj Quantum Inf 10, 59 (2024)

Doi : [10.1038/s41534-024-00829-6](https://doi.org/10.1038/s41534-024-00829-6)

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Microscopic study of the setting dynamics of a cementitious paste

The cement production contributes approximately to 7-8% of global CO₂ emissions, from which 60% result from cement calcination, and the remaining 40% are from the combustion of fossil fuels for energy. Using supplementary cementitious materials such as fly ash, slag, or natural clays to partially replace clinker can significantly reduce these emissions. Among them, metakaolin, which is derived from kaolinite clay, an abundant natural resource, and whose production requires lower energy than clinker production is a promising candidate. Nevertheless, the initial stages of

setting of mixtures of metakaolin and ordinary cement pastes are poorly understood. In particular, during this stage, cement and metakaolin particles flocculate, and when one reaches the isostatic point, the formation of a stable, interconnected particle network occurs, that transitions the paste from a flowable state to an early solid structure, marking the beginning of material strength and rigidity and reducing its workability.

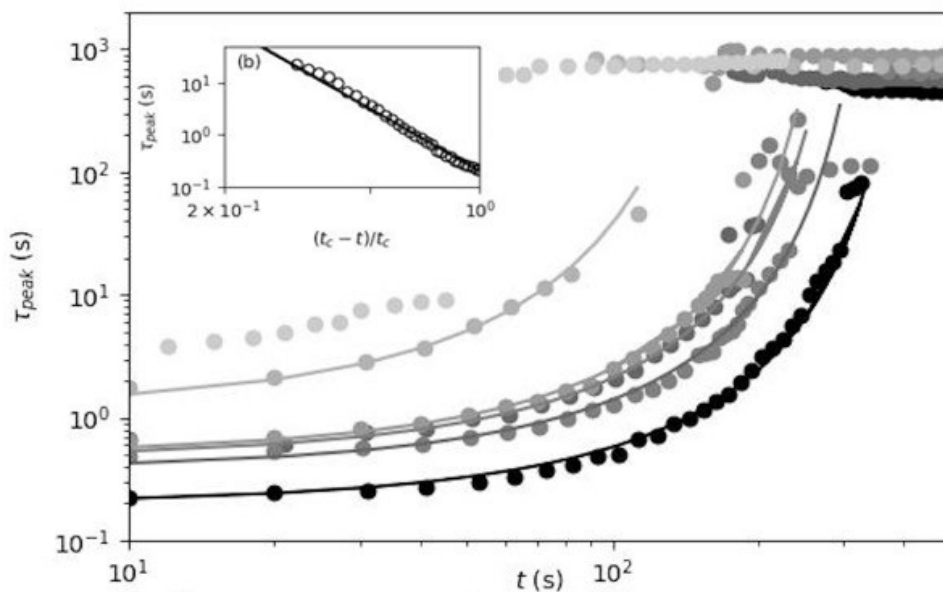
We used a light-scattering device adapted to highly turbid media (Diffusing Wave Spectroscopy) to monitor the flocculation dynamics of a Portland cement/meta-

kaolin paste. We observed that during cement setting, a transition occurs between a liquid system characterized by the existence of a rapid relaxation mode of density fluctuations, and a solid system in which this relaxation mode disappears. The transition between the two regimes is a critical phenomenon for which we have determined the transition exponents, and the substitution of Portland cement by metakaolin accelerates the kinetics of connected network formation. These measures allow to quantify the reduction in workability of cementitious pastes substituted with metakaolin.

O. Ojeda-Farías, D. Lootens and P. Hébraud, *Cement and Concrete Research*, 183, 107573 (2024)

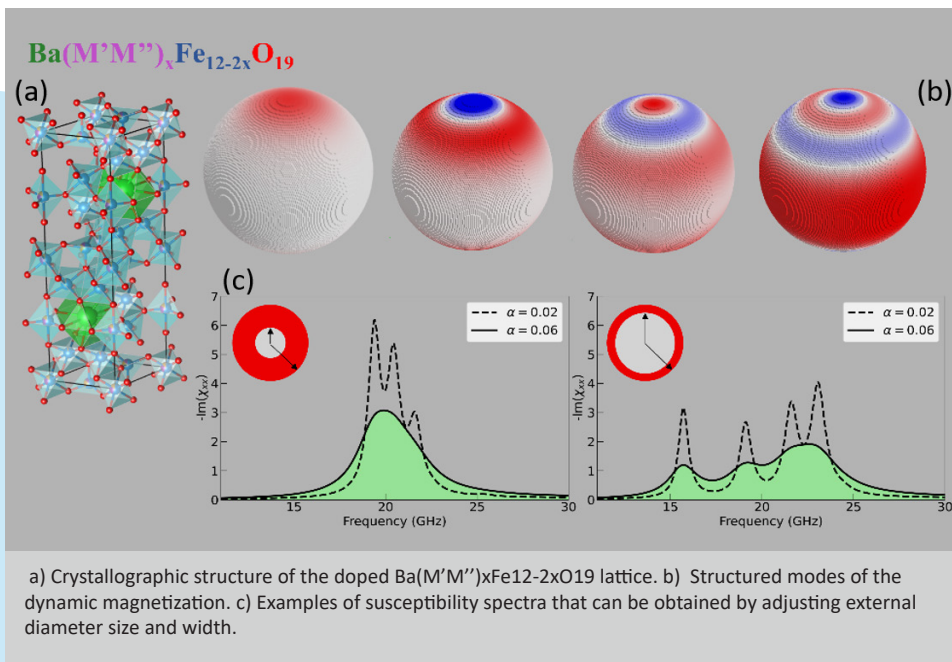
Doi : [10.1016/j.cemconres.2024.107573](https://doi.org/10.1016/j.cemconres.2024.107573)

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Evolution of the characteristic time of the main relaxation mode of a cementitious paste as a function of time, for different substitution ratios of the Portland cement with metakaolin (from dark to light: 0%, 10%, 20%, 30%, 40% and 50% by weight of substitution). The continuous curves are adjustments of the fast relaxation mode with a power law that allow to define the time t_c at which the isostatic transition occurs. Inset: evolution of the decay time of the fast relaxation mode as a function of the distance from the critical time, from which the critical exponent is deduced.

Tuning dynamic susceptibility in barium hexaferrite coreshell nanoparticles



Composites made up of chemically substituted hexagonal ferrites are promising electromagnetic wave absorbers with frequencies operating from 12 to 40 GHz. These are required to possess a strong absorption in a broad frequency band. While the ferromagnetic resonance frequency (FMR) of this family of compounds is known to be correlated to its chemical composition, little attention has been drawn to the effect of the geometrical structuration of each particle alone. Previous studies have shown that removing the core of a ferromagnetic particle could enhance its effective absorption bandwidth by inducing new resonance modes comparable in intensity to the main FMR peak.

This work investigates the zero-field dynamic susceptibility spectra of chemically substituted $BaFe_{12}O_{19}$ hollow spheres supporting single-domain configurations at equilibrium by means of micromagnetic simulations using the MuMax3 tool. Exchange size-dependent resonance eigenmodes, expressed by a spatially structured dynamic magnetic configuration at each eigenfrequency are obtained. Their eigenfrequencies are investigated as a function of the external and internal diameters of the hollow sphere. We show that the number of resonance peaks in the dynamic susceptibility spectra is proportional to the thickness of the spherical shells and it increases when the latter decreases.

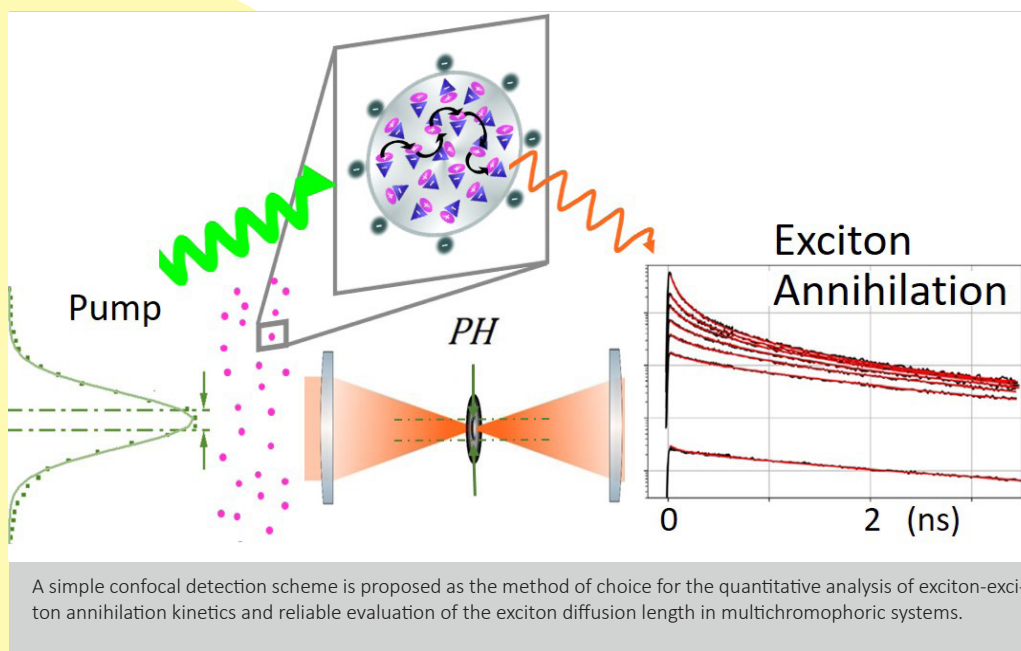
These simulations demonstrate that modulating the shell thickness of $BaFe_{12}O_{19}$ hollow spheres is a useful technique to generate new absorption peaks within the dynamic susceptibility spectra of K-band composites and consequently broaden the frequency absorption band. However, the existence of such exchange modes in $BaFe_{12}O_{19}$ nanoshells has not been proven experimentally yet. The fabrication of these systems is still a challenge, we therefore suggest in our article some synthesis routes that could be effective. In order to account for the effect of the geometrical imperfections that could arise during fabrication, the preservation of these modes in nanoshells that deviate from ideal spherical geometry is also investigated.

The authors acknowledge the joint research laboratory MO-LIERE (Dassault Aviation, IPCMS, IJL) for supporting this work and the High-Performance Computing Center of the University of Strasbourg for providing access to computing resources. Part of the computing resources were funded by the Equipex Equip@Meso project (*Programme Investissements d'Avenir*) and the CPER Alsacalcul/Big Data.

M. J. Vázquez Bernárdez, N. Vukadinovic², D. Stoeffler¹, C. Lefevre¹, ACS Applied Electronic Materials 6, 3274 (2024)
 Doi : [10.1021/acsaelm.4c00096](https://doi.org/10.1021/acsaelm.4c00096)

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Confocal Fluorescence Detection for the Quantitative Monitoring of Exciton Diffusion in Dye-Loaded Nanoparticles



Electronic excitation (or ‘exciton’) transport is the fundamental function of light-harvesting “antennas”, consisting of protein-pigment complexes found in natural photosynthetic systems. Inspired by Nature, our collaborators, Dr. Andrey S. Klymchenko and team (Faculty of Pharmacy, Illkirch, France), designed highly fluorescent, polymeric organic nanoparticles (ONPs) densely loaded with thousands of chromophores. These ONPs feature a “giant antenna effect”: rapid exciton transport across the assembly of chromophores enables efficient energy transfer to a single ‘acceptor’ fluorophore, thus increasing by 3 orders of magnitude the detection threshold of single molecule fluorescence. These ONPs (~40nm in diameter) are therefore very promising for - and applied to - bioimaging and biosensing. They could in principle also act as light-harvesting “antennas” in material science for a similar enhancement of light energy conversion yield or photocatalysis. At IPCMS, we characterized the exciton diffusion length in these ONPs by exploiting exciton-exciton annihilation (EEA): when increasing the light excitation fluence, EEA causes an acceleration of the exciton population decay – hence of the ONP fluorescence decay kinetics – monitored here using a streak camera with a temporal resolution of 10 picoseconds. Such decay kinetics are modelled

by introducing the EEA rate γ , itself linked to the exciton diffusion length.

Monitoring EEA kinetics has long been used to infer exciton diffusion length in organic materials. Still, our first significant finding was to quantify the impact of the intensity profile of the excitation beam, on the overall fluorescence decay kinetics – hence on the retrieved exciton diffusion length. This technical issue is very generally overlooked in similar studies. However, we show both analytically and experimentally, that it can lead to a typical threefold underestimation of γ . To provide an experimental demonstration and overcome this caveat, we built a simple confocal detection scheme (i.e. one pinhole in between two lenses) to monitor fluorescence emission only from the very center of the excitation volume, where the fluence remains nearly uniform. The second major result, is that we could reliably demonstrate an exciton diffusion length as large as 70nm, which is remarkably large for such disordered multichromophoric systems. The innovative combination of experimental techniques and analytical modelling developed during this work sets a new benchmark for monitoring exciton transport in organic nanosystems and materials. Supporting analytical models and simulations, were published as open-source Python software.

A. M. Gharbi, D. S. Biswas, O. Crégut, P. Malý, P. Didier, A. Klymchenko, J. Léonard, *Nanoscale* 16, 11550-63 (2024)
 Doi : [10.1039/D4NR00325J](https://doi.org/10.1039/D4NR00325J)

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From dusk to dawn: deep-red to near-infrared materials for optoelectronic devices

Near-infrared (NIR) emitting optoelectronic devices have great potential for applications in communication, encryption technologies, night-vision display and photodynamic biomedical devices. Nevertheless, their development is currently hampered by the lack of efficient NIR-emissive materials. Indeed, designing and obtaining complexes with a detectable luminescence, when it comes to the NIR region, is intrinsically very challenging due also to the *energy gap law*. In our group, we have recently developed a novel class of cationic binuclear Ir(III) emitters based on a ditopic coordinating scaffold that features the π -deficient thiazolo[5,4-*d*]thiazole and a π -accepting moiety (either pyridine or pyrazine). To highlight the winning dinuclearization strategy, comparison with the parental mononuclear derivatives was made as

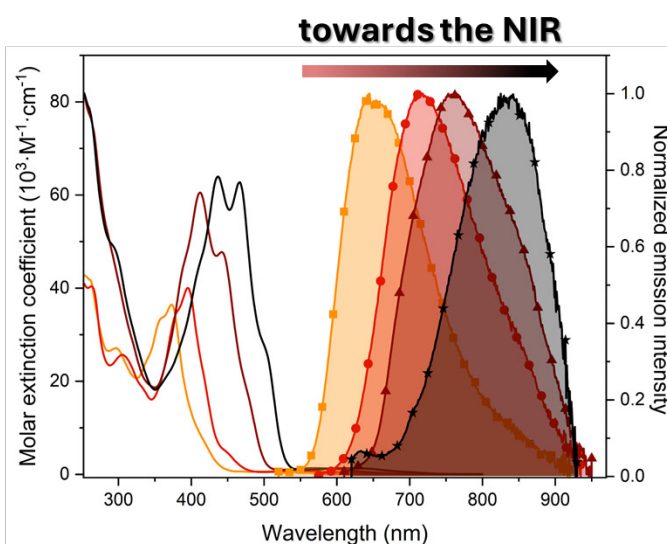
well. Remarkably, the binuclear complexes display NIR photoluminescence in solution with a maximum up to $\lambda_{em} \sim 840$ nm, which represents some rare example of metal complexes emitting in this spectral region. These findings prompted the successful use of these NIR emitters as electroactive materials in light emitting electrochemical cells (LECs). Moreover, the binuclear complexes yielded electroluminescence peaking at λ_{EL} up to 800 nm and device performances that are the highest reported for LECs in this spectral region to date for molecular (i.e. non-excimer) emitters. These findings confirm that the dinuclearization strategy is a promising molecular design approach and it will help to pave the way for achieving efficient NIR emitters for optoelectronic devices.

L. Ballerini, W.-M. Zhang, T. Groizard, C. Gourlaouen, F. Polo, A. Jouaiti, H.-C. Su, and M. Mauro, *J. Mater. Chem. C*, 12, 12769-12783 (2024)
[Doi : 10.1039/d4tc02040e](https://doi.org/10.1039/d4tc02040e)

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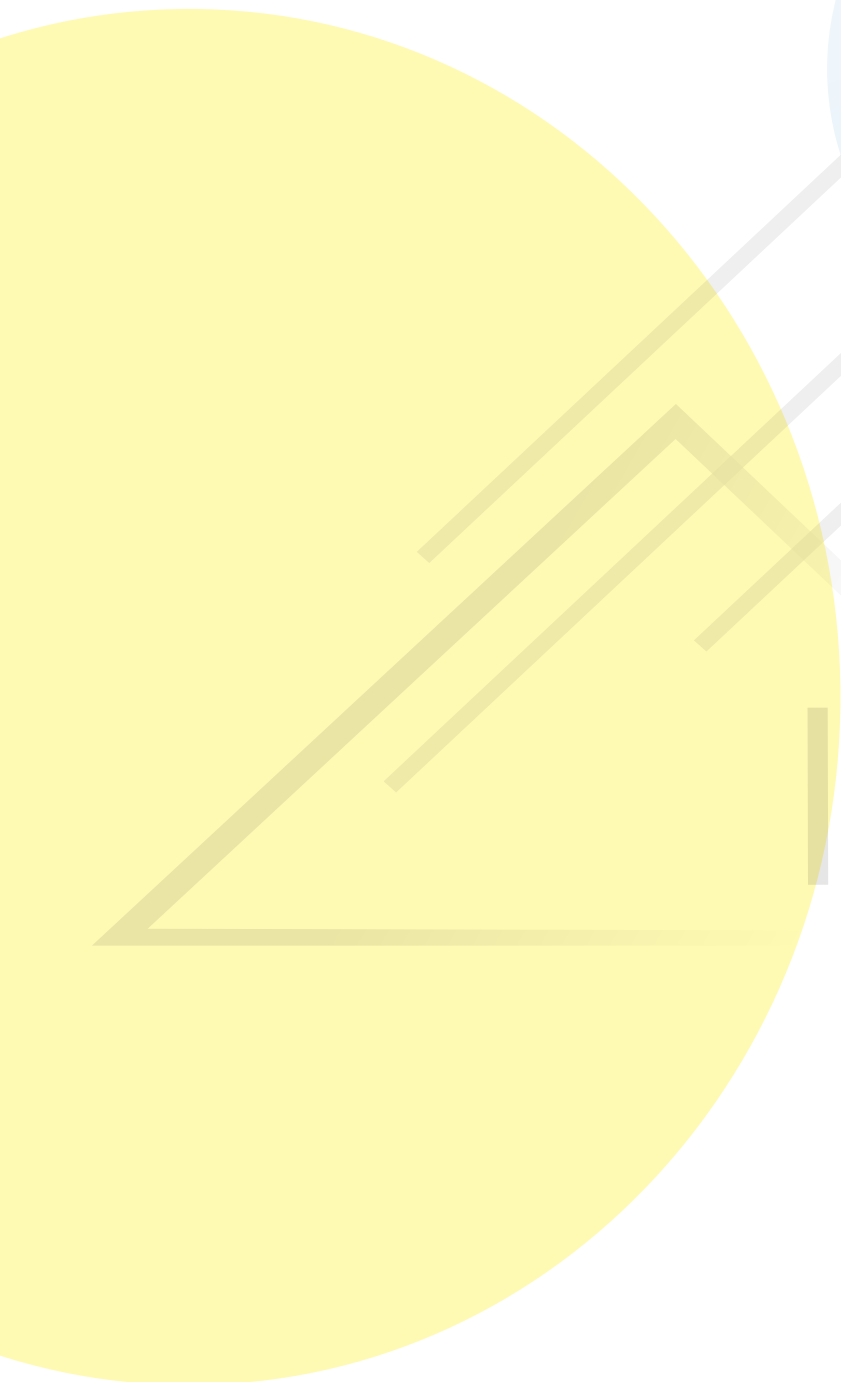
Near-InfraRed Light-Emitting Electrochemical Cells

λ_{em} up to **840 nm**
 λ_{EL} up to **800 nm**



Left: Picture of the electroluminescence of LEC devices operating under an applied electrical bias; Right: optical properties of the investigated compounds displaying the modulation of the luminescence from deep-red to the near infrared region.

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