

LIGHTinPARIS		Marie Skłodowska-Curie Actions Second call for COFUND PhD fellowships
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Doctoral School	EDOM (Waves and Matter)	
Selection Domain	EDOM (Waves and Matter)	
Supervision		
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PHD THESIS PROJECT		
LUMINeSCe - Light-induced Ultrafast dynamics in Metalloporphyrins: investigating Ionic and Neutral Species with Coincidence detection and X-ray probes		
Summary / Abstract		
This project aims to investigate the ultrafast photophysics of metalloporphyrins and metallophthalocyanines in the gas phase through femtosecond pump (UV/Vis)–probe (XUV/X-ray) spectroscopy on both neutral and ionic species. The goal is to unravel the mechanisms underlying their roles in photosynthesis and their function as photosensitizers. The approach combines the complementary expertise of the ISMO and DESY groups: ISMO recently developed a kHz-repetition laser-desorption setup for neutral molecular beams coupled to a coincidence electron–ion spectrometer, while the DESY group has extensive experience in gas-phase spectroscopy of biomolecular ions by interfacing electrospray-ionisation (ESI) tandem mass-spectrometers to advanced light sources. In particular, the element-specific probing with XUV/X-ray light will enable tracking site-resolved ultrafast dynamics. By bridging neutral and ionic molecular species, the project connects model systems to biologically relevant molecules. Principal 3i dimension: international Keywords • Extreme light, optics at the limits (ultrahigh intensity, relativistic optics, ultrashort pulses, X-UV optics, and sources) • Photophysics; Photochemistry and charge transfer • Atomic, molecular and plasma physics • Ultrafast XUV/X-ray spectroscopy • Gas-phase biomolecules		

LUMINeSCe - Light-induced Ultrafast dynamics in Metalloporphyrins: investigating Ionic and Neutral Species with Coincidence detection and X-ray probes

Key Objectives

1) Identify and characterize ultrafast relaxation pathways (metal–ligand charge transfer, intersystem crossing) in selected metalloporphyrins/phthalocyanines with different metal centers. 2) Compare neutral and ionic species to determine how the oxidation state of the metals affects charge dynamics and light absorption properties. 3) Extend to high-mass biomolecular ions using ESI, enabling benchmark gas-phase spectroscopy of larger, biologically relevant molecules (e.g., metalloproteins). 4) Perform preliminary static electronic structure characterization at synchrotron facilities (e.g., SOLEIL, PETRA III) and complementary time-resolved UV–Vis/IR studies using femtosecond lasers at ISMO. 5) Achieve site-specific insight with XUV/X-ray probes (HHG/XFEL), possibly integrating coincidence detection to correlate electronic dynamics with fragmentation pathways.

Project

Context and state-of-the-art of Scientific Research project

Metalloporphyrins and phthalocyanines are central to natural and artificial light-driven processes. They lie at the heart of photosynthesis [1], oxygen transport [2], photocatalysis [3], and photodynamic therapy [4]. Their photophysics originates from the interaction between the delocalised π -system of the macrocycle and the d orbitals of the metal centre. Upon photoexcitation, the interplay between metal–ligand charge transfer (MLCT), intersystem crossing (ISC), and internal conversion governs their efficiency as light harvesters and charge-transfer units [5]. Resolving these processes on their intrinsic timescales is essential for understanding photoinduced reactivity in both biological and artificial systems. Most previous studies were performed in condensed phases [6] or matrices [7], where environmental effects blur the intrinsic electronic and nuclear dynamics. Gas-phase spectroscopy, by contrast, provides direct access to these fundamental processes but remains experimentally demanding for large macrocycles. Generating intact neutral and ionic species in vacuum requires advanced preparation. Recent technological progress has made this frontier accessible. kHz laser-desorption molecular-beam setups compatible with state-of-the-art femtosecond light sources, now allow intact neutral macrocycles to be introduced into vacuum and probed via coincidence detection [8], while electrospray ionisation (ESI) combined with tandem mass spectrometers enables controlled preparation of ionic species for interrogation by XUV or X-ray radiation at synchrotrons and XFELs [9]. Along with high-order harmonic generation (HHG) sources, they open new possibilities for site-specific, time-resolved spectroscopy in the gas phase. These recent advances open the way to studies of neutral and ionic members of the same molecular family under equivalent isolated conditions. The oxidation state of the metal centre profoundly affects the photoactivity, yet this influence has never been explored with ultrafast, element-specific probes. Gas-phase studies of free-base phthalocyanine (H_2Pc) [10], iron phthalocyanine ($FePc$) [11], and isolated metalloporphyrin cations [12–13] demonstrate the expertise within the two groups. The LUMINeSCe project overcomes the gap between related ionic and neutral species by combining ISMO’s expertise in femtosecond UV/Vis–XUV spectroscopy and coincidence detection on neutral molecules with the DESY group’s experience in ESI-based ion-beam preparation and gas-phase X-ray spectroscopy of biomolecular ions. This synergy enables the first direct comparison of ultrafast relaxation in neutral and ionic metalloporphyrins and phthalocyanines. Using site-resolved XUV/X-ray probes to trace charge and spin flow at specific metal centres.

Description

Impact

The LUMINeSCe project will deliver a fundamental understanding of ultrafast photoinduced charge and spin dynamics in metalloporphyrins and phthalocyanines, two key classes of metal–organic chromophores central to energy conversion and biological light-harvesting. By combining time-resolved spectroscopy of both neutral and ionic species, the project bridges molecular physics and chemical reactivity in complex biomolecular systems. This knowledge will provide benchmark insights into the intrinsic electronic relaxation mechanisms that underpin the function of photosensitizers, photocatalysts, and metalloproteins. Beyond the specific molecular systems, the results will advance experimental strategies for ultrafast, site-specific investigations of complex molecules in the gas phase, directly relevant to future research at large-scale facilities (XFELs, synchrotrons) and to the broader field of photophysics and photochemistry.

Relevance for the Sciences of Light

LUMINeSCe lies at the intersection of ultrafast laser science, spectroscopy, and molecular physics. It exploits femtosecond UV/Vis–XUV pump–probe techniques to observe transient charge migration and spin-state evolution with element and site selectivity. The project contributes directly to the science of light by developing and applying new ways to use light pulses — from table-top high-harmonic generation (HHG) to large-scale X-ray free-electron lasers (XFELs) — to trigger and probe fundamental photophysical events. The ultrafast pump-probe measurements will provide a time-resolved picture of light–matter interactions in complex coordination compounds.

Methodology

The project combines advanced experimental techniques for neutral and ionic species, developed respectively at ISMO and DESY. At ISMO, the PhD student will employ a kHz femtosecond laser system coupled to a newly developed laser-desorption molecular-beam source and a coincidence electron–ion spectrometer, enabling time-resolved UV/Vis–XUV pump–probe measurements on neutral metalloporphyrins and phthalocyanines. These experiments will identify primary relaxation pathways (MLCT, ISC, internal conversion) and their timescales. At DESY, the student will work with an electrospray-ionisation (ESI) tandem mass spectrometer interfaced with synchrotron beamline, enabling soft X-ray spectroscopy of selected ionic species. Static and time-resolved X-ray absorption and emission experiments will be performed to probe metal-centred dynamics and oxidation-state effects. Electronic-structure calculations (DFT, CASSCF, RAS-CI) will complement the measurements, aiding the interpretation of charge-transfer and spin-crossover mechanisms.

Expected Results

- Identification of ultrafast relaxation pathways (metal–ligand charge transfer, intersystem crossing, internal conversion) in selected metalloporphyrins and phthalocyanines with different metal centres.
- Direct comparison between neutral and ionic species, revealing the influence of oxidation state and metal identity on charge and spin dynamics.
- Benchmark data for the photoinduced dynamics of large coordination molecules in the gas phase, relevant for biomolecular and catalytic systems.
- Demonstration of element-specific probing using XUV/X-ray radiation with femtosecond temporal resolution.
- Implementation of coincidence detection to correlate electronic relaxation with fragmentation, providing a multidimensional view of ultrafast molecular dynamics.
- Dissemination and impact: results will be published in molecular physics and chemical physics or general scientific journals, and presented at conferences.

Timelines

Here is a tentative timeline, but can be readapted with the PhD student. Year 1: Training at ISMO in ultrafast laser spectroscopy and coincidence detection. Commissioning of the laser-desorption setup with metalloporphyrins; first time-resolved measurements on neutral species. Participation in beamtimes at SOLEIL or DESY for static X-ray measurements. Year 2: Research stay at DESY to learn ESI-based ion-beam preparation and gas-phase soft X-ray spectroscopy. Comparative static and time-resolved studies on ionic species at PETRA III or XFEL facilities. Year 3: Integration of neutral and ionic results, focusing on oxidation-state effects and spin crossover. Advanced analysis combining coincidence data and X-ray spectroscopy. Preparation of publications and PhD thesis. Throughout the project: regular joint ISMO–DESY meetings will ensure coordination, data analysis exchange, and student mentoring. The fellow will gain dual expertise in ultrafast laser science and X-ray molecular spectroscopy.

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Facilities and quality of research environment available for the researcher

The LUMINeSCe project will be carried out within two highly complementary and well-equipped research environments: ISMO (Université Paris-Saclay, France) and S. Bari's group at DESY (Hamburg, Germany), both internationally recognized for their expertise in molecular spectroscopy and ultrafast photophysics.

At ISMO, the fellow will work in a dedicated laboratory equipped with a coincidence electron-ion spectrometer coupled to a laser-desorption source, enabling the preparation and detection of neutral molecular beams. Several laser systems are available to test and optimize desorption and detection conditions, as well as to characterize the performance of the spectrometer and cooling setup. In addition, the fellow will have access to the laboratory's femtosecond laser facility (3 kHz), which allows UV/Vis and IR (250–800 nm) pump–probe experiments, ideal for studying ultrafast relaxation dynamics in neutral species. These facilities provide a complete experimental environment for developing and performing time-resolved studies up to the femtosecond regime.

ISMO also benefits from proximity to major French synchrotron and laser infrastructures, such as SOLEIL and ATTOLAB, where the team has strong on-going collaborations. These external resources provide access to complementary techniques, including static and time-resolved X-ray spectroscopy, essential for linking laboratory-scale results to large-scale experiments.

At DESY, the fellow will join a laboratory with extensive experience in gas-phase spectroscopy of biomolecular ions, operating an advanced electrospray-ionisation (ESI) tandem mass spectrometer designed for coupling to laser, synchrotron and XFEL sources. The group has also access to UV helium lamp to perform valence ionisation and a tunable UV/Vis laser for static spectroscopy, both coupled to their instrument. DESY has the PETRA III synchrotron and the FELs FLASH I and FLASH II onsite as well as the European XFEL in close proximity, enabling experiments by beamtime applications and established collaborations.. Together, these facilities offer a unique combination of table-top femtosecond spectroscopy and large-scale X-ray instrumentation, providing the fellow with a complete experimental platform to investigate ultrafast molecular dynamics across multiple energy and time scales, in both neutral and ionic species.

3i Dimension - international

Description and expected outcomes

The LUMINeSCe project represents an opportunity to establish a new international collaboration between ISMO (Université Paris-Saclay, France) and DESY (Hamburg, Germany). Although this partnership is recent, it builds on complementary scientific expertise and shared research interests in ultrafast XUV/X-ray spectroscopy of complex molecular systems.

The PhD project will serve as the foundation for this collaboration, bringing together ISMO's experience in table-top femtosecond spectroscopy of neutral molecules and DESY's expertise in gas-phase X-ray spectroscopy of ionic species using ESI tandem mass spectrometers. The fellow will complete in total 12-months research stays at DESY, gaining hands-on training in advanced instrumentation, and participation to beamtimes at international large-scale facilities (PETRA III, European XFEL), as to their heavy data treatment. Regular joint meetings, coordinated beamtime proposals, and co-supervision will help formalize this emerging partnership into a long-term collaboration between the two laboratories. The fellow will thus play a key role in building this new international link, gaining first-hand experience in cross-institutional research while contributing to the development of an enduring Franco-German network in ultrafast molecular spectroscopy.

Approximate timeline of internships / external stays corresponding to the 3i dimension

- **Year 1 (October 2026 – September 2027)**

2 x 2 months stays to provide hands-on experience with DESY's electrospray-ionisation (ESI) tandem mass spectrometer perform preliminary measurements in the lab.

- **Year 2 (October 2027 – September 2028)**

3 x 2 months stays to prepare and participate to static and time-resolved beamtimes at DESY

- **Year 3 (October 2028 – September 2029)**

1 x 2 month stay to interact more easily with the DESY team in order to 1) complete data treatment and interpretation if needed and 2) be helped in the writing on the DESY's related part of the thesis manuscript.

Profile of PhD fellow

PhD studies and research work require curiosity, creativity, rigour, teamwork, and organisational skills. A minimum B2 level of English is mandatory. The below criteria are specific to the thesis project.

pre-requisite	The PhD fellow should have a strong background in chemical physics, atomic or molecular physics, non-linear optics or femtosecond lasers.
pre-requisite	Previous experience with experimental work possibly including one or more of the following: vacuum techniques, lasers, optics, electronics, time-of-flight spectrometers, electrons spectrometers, vaporization techniques, working at large radiation centers.
pre-requisite	A first experimental approach in the domains of light matter interaction or photophysics/photochemistry would be appreciated.
advantageous	Previous work using large-scale radiation facilities would also be appreciated.
advantageous	Academic background on quantum mechanics would be a plus. The same goes for experience in data treatment

Ethics issues in the project as per Horizon Europe Ethics Self-assessment

Section 1. Human embryonic stem cells (hESCs) and human embryos (hEs)			No
Section 2. Humans	No	Section 3. Human cells and tissues	No
Section 4. Personal data	No	Section 5. Animals	No
Section 6. Third Countries	No	Section 7. Environment, health and safety	Yes
Section 8. Artificial Intelligence	No	Section 9. Other ethics issues	No
Section 10. Crosscutting issue: potential misuse of results			No

7. Environment, health and safety

All French labs are required to have health and safety procedures in place, which takes into account the use of high-energy light sources such as lasers of class 3 and above, and the use of hazardous / toxic chemical and biological products. The institution and the laboratory comply with the highest safety requirements, and PhD fellows have mandatory health and safety training, with additional training if required.