

		Marie Skłodowska-Curie Actions Second call for COFUND PhD fellowships
Employer	University Paris-Saclay	
Doctoral School	2MIB (Chemical sciences: molecules, materials, instrumentation and bio systems)	
Selection Domain	2MIB (Chemical Sciences)	
Supervision		
Thesis Directors	David KREHER (Primary) and Kais DHBAIBI (co-supervision)	
ORCID	0000-0002-0968-5224 and 0000-0001-7830-6913	
Group / Team (website)	Institut Lavoisier of Versailles (ILV), Team SORG , research axis « functional molecular materials »	
Co-supervisor	Cyrille BARRETEAU	
ORCID	0000-0002-9635-3884	
Group / Team (website)	CEA Paris-Saclay/IRAMIS/SPEC/GMT group - France	
PHD THESIS PROJECT		
CHISOS - CHiral Saddle-shaped Organic Semiconductors		
Summary / Abstract		
Optical rotation, electronic circular dichroism (ECD), and circularly polarized luminescence (CPL) techniques clearly confirm the ability of optically active molecules to modulate the properties of circularly polarized light. This specific interaction between light and chiral matter has generated considerable interest within the scientific community due to its practical applications in various fields and is now considered a cutting-edge technology for 3D display devices. With this in mind, we will explore the synthesis and photophysical and chiroptical properties of enantioenriched chromophores based on combinations of COTPh or COTTh and porphyrin pigments, thereby creating new families of 3D OSCs with improved solubility, stability, and chiroptical activities, thanks to the synergy between the saddle-shaped core and the pigment properties. Principal 3i dimension: Interdisciplinary (2 french labs from two different doctoral schools, i.e. related to chemistry and physics) Second 3i dimension: International (Short stay in Japan at OPERA Lab, Kyushu University, for OLED fabrication and optimization) Keywords • Organic semiconductor • Chirality • Cyclooctatetraphenylene • Chiroptical activities / Multifunctional materials • CP-OLEDs devices		

CHISOS - CHiral Saddle-shaped Organic Semiconductors

Key Objectives

This project deals with the design of multifunctional chiral materials exhibiting marked chiroptical activities (electronic circular dichroism and circularly polarized luminescence) for chiro-optoelectronic applications: it involves theoretical calculations, synthesis and characterization, as well as devices fabrications.

This ambitious project relies on many collaborators, with partners in charge of theoretical modeling on one side (PhD co-Director]), and photophysical measurements on another side (Dr. Peeters, CEA Saclay), both being in Paris-Saclay surroundings, as well as a long-standing Japanese partner to build and characterize the final devices into which our materials will be inserted.

Project

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

Chirality, which refers to right- or left-handedness, has been extensively studied in various fields, but despite its well-recognized role in biological functions, chirality remains underexplored in materials science. An intriguing property of chiral molecules is their ability to interact specifically with left- and right-handed circularly polarized light, either in absorption (Electronic Circular Dichroism, ECD) or emission (Circularly Polarized Luminescence, CPL). The latter phenomenon is now at the forefront of various photonic applications, including 3D displays, anti-counterfeiting systems, and circularly polarized (CP) bioimaging and detection.¹ For a long time, lanthanide complexes have been the preferred class for CPL studies due to their large luminescence dissymmetry factors ($g_{lum} > 1$),² but small chiral organic molecules gained interest as emitters for their tunable photophysical/chiroptical properties, as well as their easier integration into chiro-optoelectronic devices. While these molecules offer higher luminescence quantum yields, their much lower g_{lum} values (10^{-4} - 10^{-2}) limit their use in real-world technological applications.³ Expanding the library of organic chiral emitters and establishing comprehensive structure–property relationships is crucial for designing efficient emitters and advancing this field further.

Description: objectives and scientific impact of CHISOS project

In this work, we will explore the synthesis and photophysical/chiroptical properties of new families of enantioenriched chromophores based on an original combination of Cyclooctatetraphenylene (COTPh)⁴ or Cyclooctatetrathiophene (COTTh)⁵ and porphyrin pigments. This association will give rise to novel 3D organic semiconductors (OSCs) merging multiple desirable properties, including remarkable solubility, good thermal and chemical stability, and significant chiroptical activity, as a result of the synergistic interaction between the saddle-shaped core and the pigment properties (Fig. 1). When the saddle-shaped structure combines with the extensive π -conjugation in a given organic π -conjugated system, it promotes balanced charge mobility and favourable morphology.⁶ Various strategies will be employed to modulate chiroptical properties in both the ground and excited states. These strategies include altering functionalization positions, varying the number of porphyrin units incorporated, and modifying the nature of the metal center in the porphyrin core. CPL activity in the far-red region is anticipated due to the exciton coupling chirality mechanism between the electric dipole-allowed transition moments of the π - π^* transitions in the porphyrin dyes.⁷ Moreover, excellent CPL brightness (BCPL) is expected, owing to the high molar absorptivity of the porphyrin unit.⁸

Bibliography

- [1] J. Crassous, M. J. Fuchter, D. E. Freedman, N. A. Kotov, J. Moon, M.C. Beard, S. Feldmann, Nat. Rev. Mater. 2023, 8, 365.
- [2] Zinna, F, Di Bari, L. Chirality. 2015, 27, 1-13.
- [3] Y. Zhang, S. Yu, B. Han, Y. Zhou, X. Zhang, X. Gao, Z. Tang, Matter, 2022, 5, 837.
- [4] W. S. Rapson, R. G. Shuttleworth, J. N. van Niekerk, J. Chem. Soc. 1943, 326.
- [5] M. Ueda, K. Jorner, Y. M. Sung, T. Mori, Q. Xiao, D. Kim, H. Ottosson, T. Aida, Y. Itoh, Nat Commun., 2017, 8, 346.
- [6] Y. Wang, Y. Zhang, S.Wang, D. Cao, Chem. Eur. J. 2021, 27, 12012.
- [7] N. Berova, L. D. Bari, G. Pescitelli, Chem. Soc. Rev. 2007, 36, 914. c) G. Pescitelli, Chirality. 2022, 34, 333.
- [8] L. Arrico, L. Di Bari, F. Zinna, Chem. Eur. J. 2021, 27, 2920.

Facilities and quality of research environment available for the researcher

ILV is equipped with state-of-the-art facilities (PASTEL and CEFS2 platforms) for advanced research. The group possesses extensive instruments for structural, photophysical, and computational analysis, with dedicated financial, administrative, and technical staff ensuring comprehensive support.

The doctoral student will be co-supervised by Dr. Barreteau (EDOM, CEA/SPEC/GMT group), with Dr. Dhbaibi, recently recruited to ILV as a Lecturer, as their primary supervisor.

The successful candidate will participate in numerous in-house training courses, specifically receiving training in DFT (GMT), in addition to optimizing molecular engineering at ILV. Weekly meetings will be held, in addition to rigorous monitoring of laboratory notebook maintenance, for example. We will ensure his/her smooth integration into our respective teams, supporting them through all the usual stages of research training.

We have worked with Pr. Adachi's team in Japan for more than 7 years, and all my previous PhDs have spent at least 3 months in Kyushu University: thus, our Japanese colleagues know how to welcome and train our students, knowing that they also have dormitories available for them, which means the year planned abroad will be easy to organize.

In addition, the dissemination of scientific results will primarily occur through publications in peer-reviewed journals (Nat. Chem., Angew. Chem. Int. Ed., J. Am. Chem. Soc., Chem. Sci., or more specialized journals such as Adv. Mater). In accordance with the ANR and Horizon 2020's "Open Science" policy, these publications will be made available in the HAL open archive. Furthermore, data published during and after the project will be shared according to the FAIR principle (Findable, Accessible, Interoperable, Reusable).

To sum-up, this multidisciplinary and international scientific environment (IRP) combining modelling, design and synthesis, photophysical and chiroptical characterizations, as well as the study of targeted emissive materials in CP-OLED devices, will fully benefit the doctoral student who would join this consortium, with several months already planned and funded for his/her training in Japan.

3i Dimension – International Interdisciplinary

Description and expected outcomes

The project offers a wide range of perspectives and both an interdisciplinary and international dimension, addressing various aspects: i) bridging experiments and theory: Density functional theory (DFT) will be used by partner 1 to model the electronic structure of various classes of chiral molecules. This approach will enable a fine-characterization of the transition magnetic dipole moments, transition electric dipole moments, and the angle between them. This will help us both to select the most promising targets to be synthesized by project leaders (Fig. 2) and to optimize chiroptical activities via symmetry-based rational design. ii) multi-chiroptical characterization: the chiroptical properties will be examined through ECD, CPL and VCD measurements with the expertise of partner 2:10 this complementary and multifaceted analysis of optical activities will provide a comprehensive understanding of the structure–property relationships in enantioenriched molecules iii) from rational design to real-world applications: the ultimate goal of this project is not only to create a new library of optically active (COTPh) and (COTTh) molecules with unique chiroptical properties but also to deliver meaningful scientific contributions across multiple fields: in particular, we believe they could serve as active materials for emitting dissymmetric CPL in organic light-emitting diodes (CP-OLEDs), which explains the presence in the consortium of partner 3. In addition, if accepted, this innovative project would strengthen the recently-existing collaboration in the framework of the France/Japan CNRS International Research Project (IRP) LUX-ERIT the project leaders belong to. We must emphasize also that the negatively curved architectures of our saddle-shape molecules offer also a promising avenue for high-performance multifunctional chiral materials after modulating their chiroptical properties via supramolecular host-guest interaction with fullerene guest.

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

Year 1:

Synthesis and molecular engineering of new chiral emitters

Design, synthesis, purification and structural characterization of target molecules.

Year 2:

Theoretical calculations (DFT/TD-DFT)

Electronic structure calculations to guide molecular design, optimize chemical structures and rationalize the experimental photophysical/chiroptical properties.

Photophysical and chiroptical characterization

UV–Vis, fluorescence and CPL measurements to establish structure–property relationships of the most promising emitters.

Year 3:

Short research stay in Japan (OPERA Lab, Kyushu University)

CP- OLED device fabrication and optimization using the developed chiral emitters.

Final data analysis, manuscript writing and PhD thesis preparation

Indeed, as described in our methodology already, this collaborative project first requires an important investment of the PhD student in organic synthesis (leader), supported by modeling studies (partner 1), to optimize our chemical designs, develop new chemical routes, and access innovative chiral derivatives belonging to the two families previously described.

During Year 1, the major part of the PhD will be dedicated to the synthesis, purification and full chemical structure characterization of the target molecules.

During Year 2, the project will continue with the optimization of the most promising molecular systems, supported by modeling studies (partner 1). The project will also focus on photophysical and chiroptical studies (partner 2) in order to establish structure–property relationships and identify the best candidates for device integration. During these first two years, the student will mainly stay in the Paris-Saclay environment, between the ILV at Versailles and the two partner labs at CEA Saclay. Geographically, it will be easy to plan regular exchanges and short stays between these different places, allowing efficient interactions between synthesis, modeling, and photophysical characterization.

During Year 3, a research stay (2 months) will be organized in Japan at OPERA Lab, Kyushu University (partner 3), as they possess all the necessary facilities and expertise to fabricate and characterize optoelectronic devices, particularly OLEDs. The objective will be for the student to learn these techniques and consequently fabricate and optimize his/her own OLED devices using the chiral organic materials developed in France. It should also be noticed that the OPERA institute is equipped for chemistry, meaning that the student could resynthesize or slightly modify selected molecular designs if required.

The final period of the PhD will be dedicated to completing the project, final data analysis and manuscript writing.

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	Strong background in organic chemistry and stereochemistry and experience in synthetic molecular design and multistep organic synthesis
pre-requisite	Knowledge of supramolecular chemistry and molecular self-assembly
advantageous	Skills in spectroscopy and chiroptical techniques
advantageous	Experience in materials chemistry and optoelectronic applications
advantageous	Experience in theoretical calculations and computational studies

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.

This exactly the same requirement concerning the Japanese partner, where the PhD candidate will follow specific security formations as well.