

## Ab initio calculations of circular dichroism (CD) and circularly polarized luminescence (CPL) parameters in lanthanide complexes

3-year PhD position  
(Oct. 2020 – Sept. 2023)

### Supervisors

Dr. Boris Le Guennic

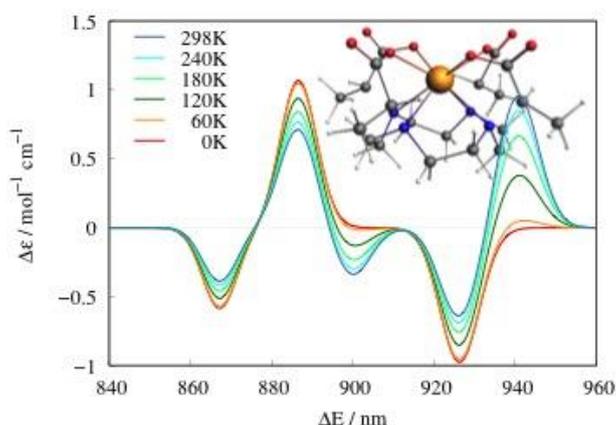
Phone: +33 (0)2 23 23 35 21

[boris.leguennic@univ-rennes1.fr](mailto:boris.leguennic@univ-rennes1.fr), [Webpage](#)

Institute of Chemical Sciences of Rennes, CNRS - University of Rennes 1 (France)

A full-time PhD position is available in the department of [Inorganic Theoretical Chemistry](#) (CTI) at the [Institute of Chemical Sciences of Rennes](#) (ISCR, University of Rennes 1) for a talented and ambitious student. The position is fully funded by the French Research National Agency (ANR).

There is a growing interest in the use of circular dichroism (CD) and circularly polarized luminescence (CPL) for the characterization of electronic structures in lanthanide-based complexes.[1] CPL measures the differential spontaneous emission of right-circularly vs. left-circularly polarized light by chiral molecular systems and can be viewed as the emission analogue of CD.[2] To date, CPL has been used mainly to investigate configurational and conformational changes in chemical and biological edifices because it combines the sensitivity of luminescence measurements and the specificity of the signal for the chiral environment. However, one may expect CPL to be soon of great interest in light-emitting or storage devices.[3] The experimentally observed quantity is known as the dissymmetry factor  $g_{em} = 2(I_L - I_R)/(I_L + I_R)$ , where  $I_L$  and  $I_R$  stand for the intensity of the left- and right-circularly polarized emissions, respectively. Whereas CPL has been measured thoroughly in chiral organic molecules with, most often, small circular polarization, i.e.  $g_{em} < 0.01$ , chiral lanthanide complexes have shown to exhibit much higher  $g_{em}$  values. Usually, enantiopure Eu(III) and Tb(III) complexes – the most emissive Ln(III) ions – present transitions with  $g_{em}$  values between 0.1 and 0.5.[4] This originates from intraconfigurational Laporte-forbidden  $f-f$  transitions. It is thus necessary to lean on other processes than a direct excitation of the weak  $f-f$  absorption bands to efficiently populate the Ln excited states. The sensitization can be achieved efficiently by an indirect energy/electron transfer from an organic ligand that acts as an antenna.



**Figure:** Calculated CD spectrum of the YbDOTMA complex [5] as a function of T.

Experimentally, the interpretation of the CD and CPL spectra of such systems is far to be straightforward, principally because of their rather complex electronic structures arising from the partially filled  $4f$  shell. These systems are also very challenging for quantum chemistry due to (i) the presence of degenerate electronic states with multi-configurational character and (ii) the importance of the spin-orbit coupling in the calculations of the spin-forbidden transitions. We recently developed a new approach for the calculation of such properties (Figure) that combines complete and restricted active space self-consistent field wavefunction methods with the spin-orbit coupling treated via state interaction, which usually leads to reasonable agreement with the experimental data.[6]

The aim of this PhD project will be to validate this computational protocol by testing its robustness on a large panel of lanthanide complexes characterized by our experimental partners. Additionally, the accuracy of the method will be further tested by comparison with other approaches recently developed in other groups,[7] and continuously developed to replace for instance CASSCF/RASSCF wavefunctions by Density Matrix Renormalization Group (DMRG) ones.

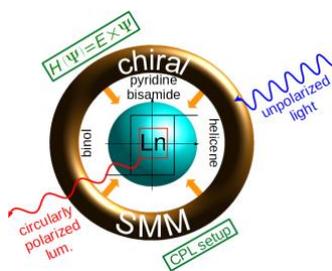
### The CTI team

The PhD student will work in the [Inorganic Theoretical Chemistry \(CTI\) team](#), in the [Institute of Chemical Sciences of Rennes](#). The CTI team gathers several theoreticians (14 permanent staff members, 15 students) with complementary skills in theoretical chemistry but also physics, working with a broad set of quantum chemical tools, ranging from high precision *ab initio* wavefunction-based calculations to fast semi-empirical methods. The studied systems in CTI are diverse, including isolated species, bulk materials and surfaces, mainly of high experimental and societal interest. This has led to fruitful joint collaborations with experimentalists from ISCR as well as major national and international groups. The team is also strongly involved in the collective effort made by the French community of theoretical chemists at the national level, in the quest of bridging the gap between state-of-the-art quantum tools and real life applications. The CTI team thus provides a stimulating scientific environment, also offering regular team meetings, invited seminars as well as visitors internationally recognized. Local and national computing means are available for the purposes of the scientific projects.



### Profile of the candidate

This 3-year fully-funded PhD is part of the **SMMCPL ANR Project** coordinated by B. Le Guennic. This project aims at investigating both experimentally and theoretically the synergy between Single-Molecule Magnet (SMM) behavior and Circularly Polarized Luminescence (CPL) in chiral lanthanide-based mononuclear complexes. This PhD project thus requires a motivated student with a good background in quantum chemistry and physical chemistry. The work will be conducted with regular discussions and meetings with the experimentalists of the project. Scientific curiosity and general knowledge in chemistry are then also expected.



### Application

The PhD project will start in October 2020. Applications are already open and candidates shall contact both supervisors by e-mail, with a CV and a motivation letter, including clear description of previous Master internship(s).

**References:**

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- [4] J. L. Lunkley, D. Shirotani, Y. Yamanari, S. Kaizaki, G. Muller *J. Am. Chem. Soc.* **2008**, 130, 13814.
- [5] L. Di Bari, G. Pintacuda, P. Salvadori *J. Am. Chem. Soc.* **2000**, 122, 5557.
- [6] F. Gendron, B. Moore II, O. Cador, F. Pointillart, J. Autschbach, B. Le Guennic *J. Chem. Theory Comput.* **2019**, 15, 4140.
- [7] B. Helmich-Paris *J. Chem. Phys.* **2019**, 150, 174121.