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

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

Supervisor

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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 gem 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.

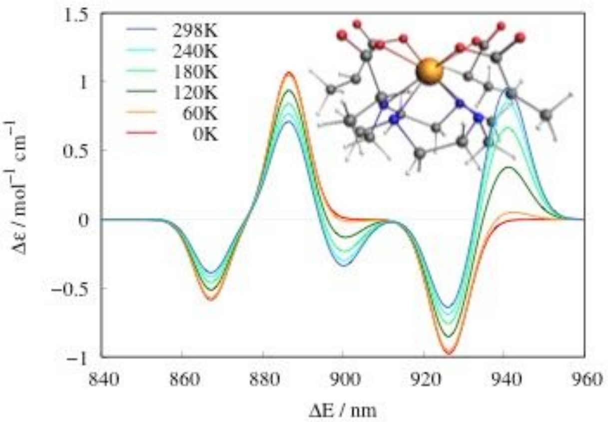


Figure: Calculated CD spectrum of the YbDOTMA complex [5] as a function of T.

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]

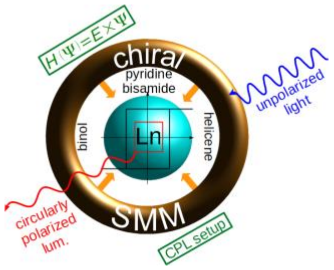
The aim of this PhD project will be to validate this computational protocol by testing its robustness on a large panel of lanthanide complexes characterized by our experimental partners. Additionally, the accuracy of the method will be further tested by comparison with other approaches recently developed 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-founded 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 Boris Le Guennic by e-mail, with a CV and a motivation letter, including clear description of previous Master internship(s).

References:
[1] M. Górecki, L. Carpita, L. Arrico, F. Zinna, L. Di Bari *Dalton Trans.* **2018**, *47*, 7166.
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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.
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[7] B. Helmich-Paris *J. Chem. Phys.* **2019**, *150*, 174121.

Computational design of novel 2D perovskite materials for energy applications: Electronic structure and Interfaces from first-principles

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

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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 within the framework of the 'Chaire de Recherche – Rennes Metropole'.

Owing to both the rapidly increasing global demand for energy and the dramatic environmental impact of fossil fuels, the development of efficient strategies for discovering novel materials for energy generation has become a top scientific priority. Within the proposed PhD project we want to pursue two distinct research directions. At first the candidate will investigate the discovery and design of novel energy materials. To do so, the project targets to look at the structural, electronic and optical properties of the two-dimensional (2D) counterparts (i.e. Ruddlesden-Popper and Dion-Jacobson phases) of the lead-free halide double perovskites that have been recently discovered: $Cs_2InAgCl_6$, $Cs_2BiAgCl_6$, $Cs_2BiAgBr_6$, $Cs_2SbAgCl_6$, $Cs_2SbAgBr_6$, Ba_2IAgO_6. In particular, the candidate will assess their stability and characterize their opto-electronic properties by means of first-principles, but also will feedback with the supervisors' established experimental partners to attempt synthesis, and subsequent characterization.

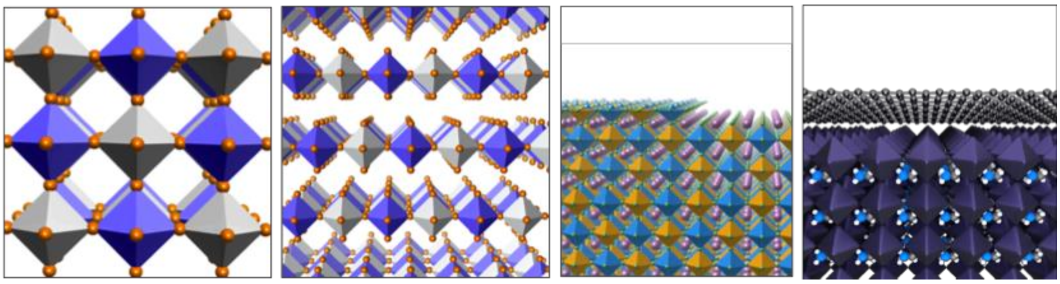

Figure: Prototype models of structures that will be investigated within the proposed PhD thesis. (From left to right) Double perovskite, layered double perovskite, surface of double perovskite, interface between 2D monolayer and prototype perovskite.

At a second stage, the candidate will move on to investigate the surface and interfacial properties of the most promising materials investigated in the first part. The interfaces that will be probed are first in combination with prototype bulk compounds like Ag, Au, TiO_2, ZnO, SnO_2, and Si, and following the same methodology, the interfaces with prototype 2D materials (e.g. graphene, MoS_2, $MoSe_2$, InSe, Black-p, etc.) will be explored. The properties of interest are the surface stability, the absolute band energy levels, and the energy level alignment when interfaces with other compounds of interest. Moreover, we will aim to uncover possible charge-transfer and electrical dipole formations at the most important interfaces for opto-electronic application.

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 “Chaire de Recherche Rennes Metropole” project coordinated by George Volonakis. The position is fully funded for three years starting from October 2020. A Master’s degree in Physics, Chemistry, Materials Science or closely related field is required. A strong background in any of the following subject is desired: solid-state physics, quantum-chemistry, materials modelling approaches, and atomistic simulations. The successful candidate should be highly motivated, with excellent communication skills and the ability to work in close collaboration with other theoreticians and experimentalists.

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 research experience, including any Master internship(s).

References:

[1] G. Volonakis et al., J. Phys. Chem. Lett. 7, 1254 (2016).
[2] G. Volonakis et al., J. Phys. Chem. Lett., 8, 772 (2017).
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[4] L. Pedesseau et al., ACS Nano 10, 9776 (2016).
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Magnetic and Multiferroic properties of mixed-anion cuprates tuned by chemical and physical pressures

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

Supervisor

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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).

Magnetoelectric (ME) multiferroics (MF), which combine electric and magnetic dipole orders, are multifunctional materials with a high potential in new technologies. It can be used to reduce computer memory energy consumption, to improve magnetic field sensors or in spintronic applications.[1,2] Two classes have been defined based on the mechanism promoting the spontaneous polar order.[1,2] **Type I ME-MF**, known as proper ferroelectrics, are based on displacive mechanism (lone-pair, geometric and charge ordering), while **type II ME-MF**, also named spin-driven ferroelectrics (SDF), are improper ferroelectrics in the sense that the polar state is driven by a magnetic transition. Unfortunately, **too few ME crystals are known to date**, and even less could lead to industrial applications. Indeed, they usually give a small response (electric polarization, P_S) and need low functioning temperature to exhibit the desired ME-MF properties. Two main routes to overcome these problems have been considered in the past: (1) the elaboration of composite materials and (2) the search of new crystals exhibiting improved ME-MF properties.

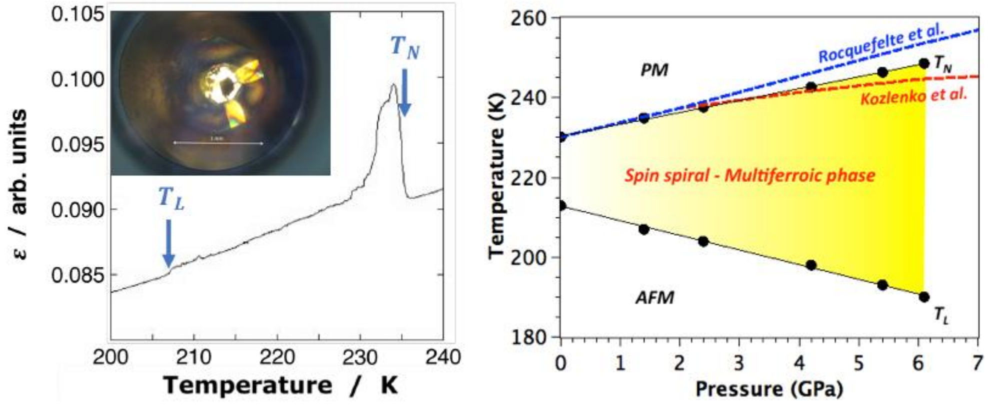

Figure. Left: Dielectric constant (capacitance) measurement on a single crystal of CuO under a pressure of 1.4 GPa. At T_N a large jump of the signal occurs. At T_L a much smaller but still clearly visible anomaly is seen. The inset shows the sample of CuO pressurized in the diamond anvil cell for dielectric constant measurements seen through the diamonds. Right: Schematic representation of our recent measurements of T_N and T_L (black dots) under high-pressure.

We aim at the investigation of a series of compounds (known to be ME-MF or not) having the following specifications: (1) large magnetic exchange couplings in order to reach high temperature functioning and (2) magnetic frustrations to have a strong ME-MF coupling mechanism based on exchange-striction and thus large ferroelectric polarization (P_S). Cuprates are ideal candidates for these two reasons and interestingly exhibit both types I and II ME-MFs.[3-6] **The present project combines advanced experimental techniques** (X-ray, neutron and Raman techniques under pressure, magnetometry, dielectric measurements…) and **state-of-the-art calculations** (density functional theory (DFT), multireference wavefunction (WFT) calculations and Monte-Carlo (MC) simulations).

The present PhD thesis is part of an ANR project named HTHPCM which **combines advanced experimental techniques** (X-ray, neutron and Raman techniques under pressure, magnetometry, dielectric measurements…) and **state-of-the-art calculations** (density functional theory (DFT), multireference wavefunction (WFT) calculations and Monte-Carlo (MC) simulations). The main **goal of this project** is the search of high-temperature and high-polarization cuprate multiferroics (HTHPCM), i.e. (1) with a **large ME-MF coupling** and thus large P_S, (2) **operating at room-temperature** (RT), and (3) showing an **electric-field magnetization reversal**. Our focus is cuprate MFs.

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

The PhD will be in charge of the DFT calculations to generate all structural models under chemical and physical pressure. He will also estimate the elastic and vibrational properties (phonon calculations) and estimate the electric polarization. In addition, he will do two or three stays of 2 months in the PHELIQS laboratory) to respectively, (1) participate to the elaboration of single crystals, and to do the complete structural characterization, (2) learn how to setup high-pressure experiments and (3) to participate eventually to a high-pressure experimental campaign. ***The selected student will have a solid experience in solid state science and DFT calculations.*** *Refs 7-10 illustrate the theoretical strategy we will use during the PhD.*

Application

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

References:

1. Why are there so few magnetic ferroelectrics? Hill, N. A., J. Phys. Chem. B 104, 6694 (2000)
2. Revival of the magnetoelectric effect. Fiebig, M., J. Phys. D 38, R123 (2005)
3. Multiferroic and magnetoelectric materials. Eerenstein, W. et al., Nature 442, 759 (2006)
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5. Application of magnetoelectrics. Scott, J. F. J. Mater. Chem. 22, 4567 (2012)
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Quantum chemical inspection and magnetic measurements of divalent and trivalent organolanthanide Single Molecule Magnets

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

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

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Complexes containing lanthanide ions are of great interest in molecular magnetism. They can give rise to Single Molecule Magnets (SMMs) with slow magnetic relaxation, uniaxial magnetic anisotropy and high-energy barrier to the reversal of the magnetic moment.[1] These features originate from the subtle interplay between the spin-orbit coupling and the crystal field interaction created by the ligands surrounding the lanthanide ion. In the recent years, organometallic complexes based on trivalent lanthanide ions reached liquid nitrogen operable temperature opening new application perspective in the field.[2]

In this frame, wavefunction-based quantum chemical calculations (SA-CASSCF/PT2/SI-SO) are among the most appropriate tools to get a reliable insight into the electronic structure of these compounds. In the last 10 years, in strong collaboration with experimentalists, we actively participated to the popularity development of this quantum chemical approach.[3] However, whereas the magnetic properties of trivalent lanthanide coordination complexes are usually well reproduced and rationalized, this is less the case when divalent lanthanide ions or peculiar ligands are concerned.[4] One of the aims of this PhD thesis is thus to extend the current ab initio protocol playing with other quantum chemical methodologies such as RASSCF, NEVPT2, DMRG… to reach a quantitative description of the electronic properties of organolanthanide systems (Figure).

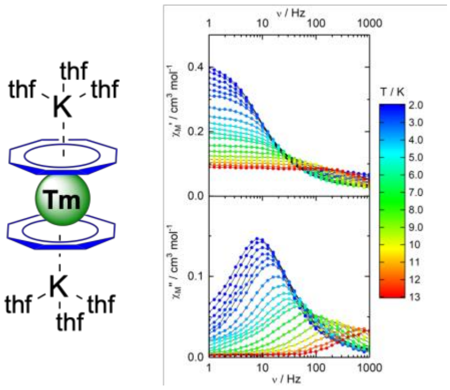

Figure: Example of targeted organolanthanide systems that will be investigated

Due to the extreme sensibility of the targeted complexes, the second challenge of this PhD will concern their proper magnetic investigations based on magnetometry (SQUID, PPMS).[3,5] In more details, the static and dynamic magnetization needs to be carried out in inert atmosphere and in controlling the thermal stability of the materials. The complete magnetic characterization will then be confronted with the results of the quantum chemical calculations.

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-founded PhD is part of the **RelaxMax ANR Project** coordinated by G. Nocton (Ecole Polytechnique, Palaiseau). This project aims at synthesizing and fully characterizing new divalent and trivalent organolanthanide complexes presenting slow magnetic relaxation. 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:

[1] D. N. Woodruff, R. E. P. Winpenny, R. A. Layfield *Chem. Rev.* **2013**, *113*, 5110.
[2] a) C. A. P. Goodwin, F. Ortu, D. Reta, N. F. Chilton, D. P. Mills *Nature* **2017**, *548*, 439. b) F.-S. Guo, B. M. Day, Y.-C. Chen, M.-L. Tong, A. Mansikkamäki, R. A. Layfield *Angew. Chem. Int. Ed.* **2017**, *56*, 11445. c) F.-S. Guo, B. M. Day, Y.-C. Chen, M.-L. Tong, A. Mansikkamäki, R. A. Layfield *Science* **2018**, 362, 1400.
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Daiguebonne, O. Guillou, F. Gendron, B. Le Guennic, T. Guizouarn, R. Sessoli, M. Mannini, K. Bernot *Ang. Chem. Int. Ed.* **2020**, *59*, 780.
[4] a) M. Xémard, A. Jaoul, M. Cordier, F. Molton, O. Cador, B. Le Guennic, C. Duboc, O. Maury, C. Clavaguéra, G. Nocton *Angew. Chem. Int. Ed.* **2017**, *56*, 4266. b) M. Xémard, M. Cordier, F. Molton, C. Duboc, B. Le Guennic, O. Maury, O. Cador, G. Nocton *Inorg. Chem.* **2019**, *58*, 2872.
[5] a) F. Pointillart, K. Bernot, S. Golhen, B. Le Guennic, T. Guizouarn, L. Ouahab, O. Cador *Angew. Chem. Int. Ed.* **2015**, *54*, 1504. b) F. Allouche, G. Lapadula, G. Siddiqi, W. W. Lukens, O. Maury, B. Le Guennic, F. Pointillart, J. Dreiser, V. Mougel, O. Cador, C. Copéret *ACS Cent. Sci.* **2017**, *3*, 244

Unraveling white light emission and non-linear optical responses of chromophores using quantum chemistry

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

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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 Ministry of Higher Education, Research and Innovation.

Predicting and modeling the optical responses of chromophores such as those of interest for the next generation of white-light emitters or two-photon probes remains a challenge. If achievable at a low computational cost, it would save natural, human and financial resources. This thesis work proposes to tackle the problem by *combining state-of-the-art Time Dependent Density-Functional Theory (TD-DFT) calculations on newly designed synthetic targets with the development of a cost-effective protocol based on "Density Functional Tight-Binding" (DFTB).*

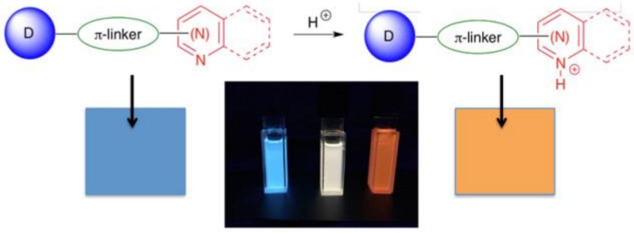

Figure: Change of color upon protonation to obtain white-light emission

On one hand, the project will be carried out in the context of long-term collaborations between experimentalists from our institute and abroad who develop organic molecules targeted for specific spectroscopic applications. Currently, we are actively seeking for novel classes of white organic light emitting diodes (WOLEDs). A new strategy consists in integrating a single emitting specie with two forms of complementary colors. White light emitting materials could be achieved based on an equilibrium between neutral and protonated forms (Figure) [1,2]. The next step is to increase the external quantum efficiency through triplet harvesting by thermally activated delayed fluorescence (TADF) [3]. Besides, we are also involved in the design of drug delivery systems demonstrating high uncaging efficiencies upon two-photon (TP) excitation using near-infrared light [4-6]. Both these developments require a fine tailoring of the chemical structure of the molecules, based upon a rationalization of the electronic structure and optical features with theoretical studies. *To this end, the PhD student will elaborate a state-of-the-art theoretical spectroscopy methodology, based on TD-DFT methods, able to predict qualitatively and quantitatively, the behavior of series of targeted molecules*.

On the other hand, such studies can involve considerable computational resources that may appear as the limiting factor at some point. In order to perform an efficient molecular design and allow considering ever more complex situations (larger compounds, explicit description of the environment), *the PhD candidate will also be in charge of developing a computational protocol based on the "Density Functional Tight-Binding" (DFTB) model*. Especially, the TD-DFTB formalism [7] would routinely permit a rapid description of the excited state properties for systems encompassing hundreds of atoms. This methodological work will be supported by another ongoing collaboration with the CMS group at the Bremen University. This will include assessment of the DFTB method' accuracy and its adaption to the properties of interest, starting with linear optical properties up to non-linear 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

The PhD candidate should possess a general background in quantum chemistry. Prior experience with DFT/TD-DFT methods and/or theoretical spectroscopy is a plus. The work will be conducted with regular discussions and meetings with experimentalists and good command in English will be appreciated. Scientific curiosity and general knowledge in physical chemistry are 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).

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