

PhD Thesis in theoretical chemistry 2018-2021

TOWARDS TRIPLY AND QUADRUPLY EMISSIVE DYES

DESCRIPTION : PhD position in theoretical chemistry for 3 years starting Sept 1st 2018.
Funding obtained.

LOCATION: Team: **ModES: Modelling & Spectroscopy**
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CONTEXT

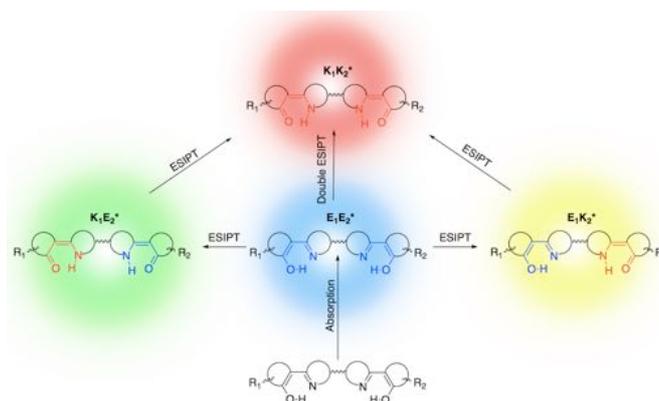
This PhD is part of the **Fluo-34** project that aims to design organic molecules presenting very broad fluorescence spectra. To this end, the key idea is to combine two different molecular units displaying ESIPT (Excited-State Intramolecular Proton Transfer) into a single molecule. In ESIPT dyes, the most-stable tautomeric forms are different in the ground-state (*enol*) and in the excited-state (*keto*). By choosing dual ESIPT emitters (fluorescence from both *enol* and *keto*) instead of "pure" ESIPT emitters (*keto* emission only) as components, it will be possible to obtain three or four clearly distinguishable emission bands. This, in turn, will pave the way towards the production of a purer and brighter white light from a single organic molecule than the one obtained with compounds reported to date. In that framework, theoretical tools that allow driving the synthesis towards the most valuable targets are extremely useful, and **Fluo-34** will take advantage both density-based and wavefunction-based *ab initio* approaches.

RESEARCH PROGRAM

The proposed PhD deals with the theoretical exploration of potential energy surfaces of electronically excited-states of ESIPT dyes, with the aim of identifying the most adequate substituent patterns leading to multiple emission bands. The molecular backbones considered at the beginning of the thesis will be a selection of the most efficient systems (large quantum yields) described in the literature.

Two different molecular designs will be tested: either two ESIPT centres will be coupled through an unconjugated bridge or through a π -conjugated linker. The first approach is probably simpler, but two main limitations have to be lifted anyway: a) the energy transfer between the two components should be limited to avoid non-radiative de-excitation; and b) the position of the two *keto* bands has to be significantly different. In the second approach, emerging properties could be obtained and even a symmetric design, could yield three different fluorescence bands.

From the theoretical point of view, the **Fluo-34** project will rely on first-principle approaches, namely Time-Dependent Density Functional Theory and second-order approaches, e.g., CC2, to characterize the excited-states proton transfer and to predict the position of the fluorescence maxima. A specific focus will be set on the environmental modelling. Indeed, for the compounds in solution, the PhD student will use a methodology designed to simultaneously account simultaneously for both linear-response and state-specific solvation effects, which is crucial to describe on an equal footing both *enol* and *keto* tautomers. The best candidate in solution will be synthesized and also modelled in a polymer matrix. To tackle this large scale molecular dynamics simulations using empirical potentials with appropriate inter-molecular terms will be used. This will allow realistic exploration of the structural effects of semi-crystalline polymer matrix on the local molecular structure of the dye.



The PhD will be performed in Nantes under the joint supervision of D. Jacquemin (CEISAM laboratory) and C. Ewels (IMN Laboratory). The work will be carried out in close collaboration with the experimental group of G. Ulrich (Strasbourg) to define the best target compounds.

PROFILE OF THE CANDIDATE

The candidate should have a 2017 or 2018 Master in chemical physics, physical chemistry, theoretical chemistry, theoretical physics or equivalent. A background in DFT, as well as an experience with recognized computational codes are assets. The candidate should be motivated, show initiative and an ability to work both independently and in a group. Good communication skills are, of course, welcome. The interested candidate should contact D. Jacquemin Denis.Jacquemin@univ-nantes.fr

REFERENCES

1. K. Benelhadj, W. Muzuzu, J. Massue, P. Retailleau, A. Charaf-Eddin, A. D. Laurent, D. Jacquemin, G. Ulrich and R. Ziessel, *Chem. Eur. J.* **20** (2014) 12843.
2. M. Raoui, J. Massue, C. Azarias, D. D. Jacquemin and G. Ulrich, *Chem. Commun.* **52** (2016) 9216.
3. C. Azarias, S. Budzak, A. D. Laurent, G. Ulrich and D. Jacquemin, *Chem. Sci.* **7** (2016) 3763.
4. E. Heyer, K. Benelhadj, S. Budzak, D. Jacquemin, J. Massue, G. Ulrich and R. Ziessel, *Chem. Eur. J.* **20** (2017) 7324