PhD 2022-2024

MODELLING EMISSION OF BIOINSPIRED FLUORESCENT COMPOUNDS

DESCRIPTION: **PhD position in theoretical chemistry: 3 years from Oct. 2022.**
Financed by the ANR – BiBiFlu Project.

LOCATION: Team **ModES**: *Modélisation Et Spectroscopie*
Lab: CEISAM, UMR CNRS 6230, Nantes Université
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GENERAL CONTEXT

Although there are many photoluminescent compounds in nature, natural dyes are often very weakly emissive, except when heavy chemical modifications are performed. In other words, natural fluorophores are not competitive to date as compared to the synthetic ones. The BIBIFLU project, financed by the French ANR, aims to circumvent this problem, by **transforming, through well-designed substitutions, evaluated *in silico*, natural fluorophores** (carbolines, phenantridines, emodins, etc.) **into emitters displaying photophysical features that are competitive with the best synthetic dyes of fossil origin**. To this end, one needs not only to accurately predict the fluorescence wavelengths, but also to obtain reliable estimates of the related emission quantum yields.

RESEARCH PROGRAM

Given the expertise of the group, we trust that the accurate calculations of the position and shape of the emission bands, through determination of vibronic couplings, will not be a major issue. **For estimating the fluorescence yield, two approaches will be used by the PhD student: dynamical and static.** For both approaches, several chemically-realistic substitution patterns (various donating and accepting groups at selected positions) will be tested so as to guide the experimental efforts towards the *brightest* structures. A feedback loop with the experimental team and the measurements will be used so as to assess the quality of the theoretical predictions.

For the former approach, the PhD student will explicitly **simulate the non-radiative relaxation of a molecule after photon-absorption from an electronic excited state back to the ground state**, without any *a priori* assumption on the process. Indeed, these dynamics simulations do not require precise knowledge of the relaxation mechanism, meaning that all relaxation pathways are explored, non-radiative relaxations being included based on the calculation of non-adiabatic couplings between quasi-degenerate electronic states. The underlying methods used will be a semi-classical surface hopping algorithm relying on a multi-reference (CASSCF, CASPT2) electronic structure description. This approach will be used to explore the potential energy surface of unknown fluorophores as well as to provide benchmark values for the static calculations on compact dyes.

For the latter approach, he/she will use the **Fermi Golden rule so as to recover estimates of both the radiative and internal conversion rates** (k_r and k_{ic}) from *ab initio* calculations of the vibronic couplings, and hence to estimate the emission quantum yield if all other non-radiative processes are negligible, which is the case for the most effective fluorophores. In practice both k_r and k_{ic} will be estimated using the thermal correlation vibration function (TCVF) formalism using the results of TD-DFT or EOM-CC calculations. Depending on the dyes, the PhD student will have to account for other deactivation pathways, e.g., accessible conical intersections, inter-system crossing, proton transfer… so as to build a model encompassing all active radiative and non-radiative pathways relevant to predict the emission yield for each relevant families of fluorophores studied by the collaborators.

PROFILE OF THE CANDIDATE

The candidate should have a Master degree in chemistry, chemistry-physics, theoretical chemistry or physics, or equivalent obtained in 2021 or in 2022 and must have a solid training in physical and theoretical chemistry. Experience in *ab initio* molecular calculations as well as programming skills (e.g., Python...) are assets. Frequent exchanges with the experimental team of Gilles Ulrich (CNRS, Strasbourg) are expected. Applicants must send a CV and a cover letter to the contacts given above.