

A joint experimental and computational study on the influence of packing on organic compounds luminescence in the condensed phase.

Une étude conjointe expérimentale et théorique sur l'influence de l'arrangement moléculaire sur les propriétés de luminescence de composés organiques en phase condensée

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Project Description:

The dynamics of molecules at their electronic excited states results from the interplay of a diversity of radiative and nonradiative kinetic processes. In this framework, the physical state of the molecule, i.e. solution or solid state, plays a particularly determining role. While progresses in the molecular engineering of luminescent compounds in solution has not ceased since the middle of the 19th century, the design of solid-state fluorophores has experienced a breakthrough in the early 2000s, with the concept of Aggregation-Induced Emission (AIE) popularized by B.Z. Tang and the burst of new technologies based on solid-state fluorescence. Such compounds and materials are the keystone of a variety of applications, as luminescent contrast agents for biomedical purposes (diagnostic, theranostic...), solid state luminophore for organic lasing, or mechanochromic materials for the measurements of mechanical constraints or counterfeiting applications, among many others.¹

Among the so called AIEgens, tetraphenylethylene (TPE) stands out for its tremendous AIE properties which are preserved even in highly substituted derivatives. Nevertheless, in such substituted highly derivatives, control of the stereochemistry of the central double bond is a parameter of paramount importance: indeed, large structural differences may exist between the 3D structure of the molecule in their (Z) and (E) configurations.

In a recent series of paper, we have demonstrated that these differences may translate into the crystal packing parameters of the molecules at their solid state, with dramatic influence on the luminescence efficiency and thus on its performances for the target applications.²⁻³ Such a control is not intrinsically achievable through classical synthetic methodologies affording TPE derivatives, and requires lengthy and tedious procedures.

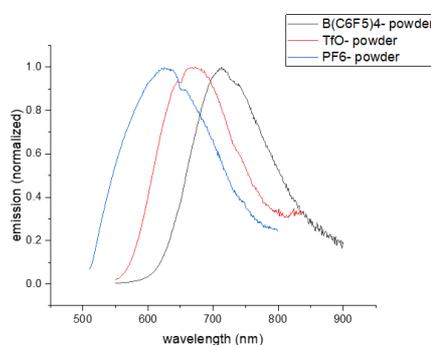
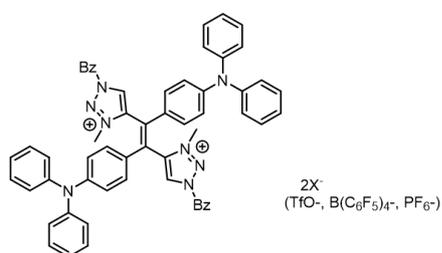


Figure 1. Example of molecular structure already synthesized and associated solid state emission spectra, with different counterions

Preliminary studies showed that these molecules display, upon nanoprecipitation, very favorable spectroscopic properties: they combine large luminescence quantum efficiency with

We have recently proposed a novel synthetic approach to closely related analogues of TPE (*ie* built around tetrasubstituted central ethylene bond), in which differences in the electronic parameters of the substituent ensures selective access to a thermodynamically favored (Z) isomer.

emission wavelengths that can be tuned over a large range of wavelengths with small structural variations. In particular, cationic derivatives of these molecules were found to display intense solid state emission in the far-red and near infra-red, with emission maxima that were found to depend on the nature of the counter-ion, suggesting that the latter has a determining importance on the molecular packing (Figure 1).

Wishing to further explore this class of molecules and to gain insight into the quantum mechanics processes that govern their photophysical properties, most critically at their solid state, we are looking for a motivated and talented young candidate to initiate a thesis project on this new family of molecules (or related compounds).

The candidate will be involved in the synthesis and full spectroscopic and photophysical studies of the synthesized molecules, with a specific emphasis on the solid-state luminescence properties. He will aim at obtaining crystal structures of these compounds, in order to shed light on their packing parameters. Using state-of-the-art computational chemistry methodologies based on TD-DFT, he/she will investigate *in silico* the spectroscopic properties of these molecules. In particular, a major breakthrough of this project will be to develop a robust methodology to perform this investigation in condensed phase. Finally, based on these theoretical data, he/she will participate in the rational conception of new molecular targets with improved solid state emission properties.

Profile of the candidate:

Laureate of a M2 in physical-chemistry or molecular chemistry, the candidate should be proficient in spectroscopy, and ideally have an experience in computational chemistry. He/she should have a taste for experimental chemistry and have a previous lab experience involving the synthesis of molecules. He/she should be eager to participate to an inherently multi-faceted project, involving synthesis, spectroscopy and computational chemistry.

Laboratory environment

Located on the campus of the ENS de Lyon, in Gerland's district, the laboratory of chemistry, UMR 5182 is a world recognized research institute with a strong expertise in molecules, supramolecules and materials. It benefits of a highly interdisciplinary environment, and hosts chemists, physicists and biochemists (ca 40 permanent researchers) who collaborate in the framework of ambitious projects at the interface of these disciplines. It is equipped by state-of-the-art spectroscopy equipment, including three spectrofluorimeter (ranging from the UV to the Short-Wave-Infrared), and a laser platform giving access to nonlinear and transient spectroscopies. In term of computational resources, the laboratory benefits from the local computational center containing more than 15 000 CPUs.

Related references

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2. Rouillon, J.; Monnereau, C.; Andraud, C., Reevaluating the Solution Photophysics of Tetraphenylethylene at the Origin of their Aggregation-Induced Emission Properties. *Chem. Eur. J.* **2021**, *27* (30), 8003-8007.
3. Rouillon, J.; Blahut, J.; Jean, M.; Albalat, M.; Vanthuyne, N.; Lesage, A.; Ali, L. M. A.; Hadj-Kaddour, K.; Onofre, M.; Gary-Bobo, M.; Micouin, G.; Banyasz, A.; Le Bahers, T.; Andraud, C.; Monnereau, C., Two-Photon Absorbing AIEgens: Influence of Stereoconfiguration on Their Crystallinity and Spectroscopic Properties and Applications in Bioimaging. *ACS Appl. Mater. Interfaces* **2020**, *12* (49), 55157-55168.