

Explaining Anomalous *Thermally Activated Delayed Fluorescence* (TADF) Response for a Phenothiazine Derivative through a TD-DFT Approach

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Abstract: Thermally activated delayed Fluorescence (TADF) mechanism can occur by a complicated and fascinating route involving the triplet manifold. Here, we report a computational approach based on *Time Dependent Density Functional Theory* (TD-DFT) to shed light on the anomalous response of a phenothiazine derivative exhibiting efficient TADF only upon aggregation. The strong red-shifted peak in the photoluminescence spectrum of the molecule dispersed in a non-polar solvent (i.e. cyclohexane) is explained in terms of aggregation of monomers and dimer formation.

Molecular fluorescence is conventionally interpreted as a two-step process. An initial absorption induces an electronic transition to a singlet excited state of the quantum system, which then decays radiatively into the electronic ground state, with a certain quantum efficiency. In 2012, Adachi and co-workers [1] introduced the term TADF to indicate the phenomenon for which the singlet state can be populated-back by electrons coming from the nearest triplet state, according to what is called a reverse intersystem crossing (rISC) process. In order to achieve good TADF performance, an emitter must ensure a small enough triplet-singlet energy gap (less than 0.1 eV), [2] which allows to maximize the opportunity of harvesting triplet state by thermally activating the rISC process, i.e. high RISC rate in conjunction with minimum phosphorescence (k_P) and non-radiative (k_{ISC}) decay. Moreover, a high *Photo Luminescence Quantum Yield* is ensured through a larger transition dipole moment between the singlet excited state and the ground state. The reduction of the singlet-triplet gap it has been shown to be achieved by charge transfer states that minimizes the exchange energy.

In this work, we investigated the TADF performance of a phenothiazine derivative consisting of a strong donor (phenothiazine) and an acceptor (fluorenone) in the quasi-equatorial conformation [3], see Fig. 1(a).

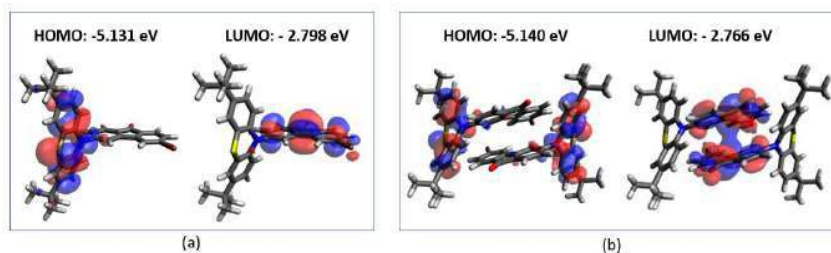


Fig. 1 (a) HOMO and LUMO orbitals of the phenothiazine derivative in the quasi-equatorial conformation. (b) HOMO and LUMO orbitals of the phenothiazine derivative excimer in the quasi-equatorial conformation relaxed in the dimer ground state.

All simulations were performed by using the ORCA 5.0 package. The geometry of the ground state was optimized in the gas phase by employing the B3LYP functionals and a TZVP basis set, with the def2/*J* auxiliary basis set for the RIJCOSX approximation to the Coulomb integrals [4]. Electronic and optical properties were analyzed for the monomer in the cyclohexane solvent, allowing identification of the first singlet (S_1) and triplet (T_3) charge transfer states. Coherently with experiments, revealing the appearance of a two-peak structure for the photoluminescence spectrum of the molecule in cyclohexane, we found out different TADF properties for the analyzed molecule in the monomer and excimer arrangements.

We performed several DFT simulations to select the most stable dimer conformation (relative orientation and distance between monomers), see Fig. 1(b), and compared its behavior to the monomer. A promising change in the relative position of the electronic states of interest for TADF and a red-shift of the emission peak, this being coherent with the appearance of an extra peak in the experimental PL spectrum (about 1 eV red-shift with respect to the monomer). The hypothesis of the formation of a dimer electronic state would, thus, explain the dependence of the TADF performance for such kind of phenothiazine derivative on the molecule concentration and aggregation conditions. This study could open new perspective toward an on-demand control and activation of the TADF phenomenon in molecules of interest for optoelectronics and nanomedicine applications.

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