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PAPER

ESIPT or not ESIPT ? Revisiting recent results on 2,1,3-benzothiadiazole under the TD-DFT light[†]

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Recently, the spectroscopic signatures of amino-substituted benzothiadiazoles were investigated by a complementary experimental and theoretical work [Neto *et al.*, *RSC Adv.*, 2012, 2, 1524–1532]. It was concluded that these molecules were exhibiting excited-state intramolecular proton transfer. In this communication, we revisit these results using a state-of-the-art Time-Dependent Density Functional Theory approach which provides a complete explanation to the spectroscopic observations.

Lately, there has been a growing interest to design dyes undergoing an excited-state intramolecular proton transfer (ESIPT).[1–9] In these chromophores, the most stable isomer differs in the electronic ground and excited states.[5,10–15] Therefore, a proton involved in a strong hydrogen bond shifts from one atomic center to another upon photon absorption, implying large geometric reorganizations at the excited state, and, consequently, large Stokes shifts.[7,16–23] However, this phenomenon, that implies a subtle balance of relative acidites of the atoms participating in the hydrogen bond, is extremely fast, making its definitive determination by sole experimental means a far from trivial challenge. For this reason, computational tools have been widely used to investigate ESIPT and to complement the experimental data.[17–19,23,24]

Recently, one of us synthesized and characterized two novel 2,1,3-benzothiadiazole (BTD) derivatives, one of them is shown in Scheme 1.[25,26] Several characteristics hinted for ESIPT: i) a nearly perfect planar ground-state structure with an hydrogen bond (H···N of 2.39 Å) between the two nitrogen atoms is found, a fact confirmed by calculations that indicate a stable (no imaginary frequency) C_s ground-state; ii) a large Stokes shift (e.g., λ_{max}^{abs} at 422 nm and λ_{max}^{emi} at 547 nm in dichloromethane, implying a Stokes shift of 5415 cm^{-1}); iii) electronic transitions with an intramolecular charge-transfer (CT) nature; iv) significant changes of the optical spectra upon pH variations; and iv) theoretical calculations indicating a possible ESIPT.[25] Quite interestingly, we notice that, contrary to the majority of "conventional" ESIPT system, the proton transfer would create here a zwitterionic species, **III** (see Scheme 1), that have only been rarely described.[12] In the present communication, we reexamine with state-of-the-art theoretical tools these outcomes, which allows us to bring forward an explanation of the observed data without the need of invoking ESIPT. The selected method is described in details in the ESI and had been recently applied to successfully rationalize the complex optical signatures of ESIPT dyes possessing a dual enol-keto fluorescence signature.[23] Here we fully characterize BTD derivatives that constitute increasingly popular electronic acceptor in organic electronics.[27] In particular, ESIPT was invoked to rationalize the behavior of a fluoride ion sensor bearing a very similar benzoselenadiazole core.[9]

In Ref. 25, the selected computational procedure provided a more stable **III** over **II**, by ca. 1.0 kcal.mol^{-1} on the energy scale, which hints for ESIPT. This result relies on a gas phase B3LYP single point calculation performed on an optimal CIS geometry, and this scheme can be improved. On the one hand, CIS is an uncorrelated method which is not ideal for fused aromatics, and, on the other hand, it is well known that B3LYP is not suited for transitions with a strong CT character: it tends to yield both too small transition energies and spurious (i.e. unphysical low-energy) excited-states.[28–30] This is the exact outcome here: the B3LYP//CIS λ_{max}^{emi} of **III** is 1773 nm with an associated oscillator strength of 0.03 a.u., which is clearly not in the line of experiment. Indeed, in toluene, the least polar solvent used, and the most comparable to gas phase calculations- the fluorescence maxima takes place at 536 nm and the associated quantum yield is far from trifling. We have therefore turned towards a more robust approach, less prone to yield inconsistent transition energies and including both vibrational and solvent effects (see the ESI).

scheme 1 Representation of molecule **I** with its intramolecular H-bonds (left) and of the postulated mechanism of Ref. 25 (right).

With the LR-PCM/M06-2X/6-31+G(d) scheme, the relative Gibbs energies (G) of **I**, **II**, **III** and **IV** are 0.0, +64.8, +65.9 and +36.9 kcal.mol^{-1}, respectively (in dichloromethane). In the ground state, **IV** is therefore completely unaccessible and only **I** exists, as expected. In the excited-state, a similar situation pertains as the putative ESIPT product, **III** is less stable than the canonical form **II**. However, this difference remains rather small (ca. 1 kcal.mol^{-1}) and additional checks are welcome. For this reason, we have first redone the calculations with CAM-B3LYP and ωB97X, two range-separated hybrids especially designed for providing a balanced description of CT states. Each provided again a more stable **II** by 1.42 kcal.mol^{-1} (CAM-B3LYP) and 2.89 kcal.mol^{-1} (ωB97X) compared to **III**. These results indicates that while ESIPT cannot be fully ruled out on the sole energetic basis, it is probable that ESIPT does not dominate in the excited-state. Let us now turn towards the spectroscopic properties to obtain a more clear-cut answer.

On the basis of the optimized ground and excited state structures, we have therefore determined both λ_{max}^{abs} and λ_{max}^{emi} using the cLR-PCM/M06-2X/6-311++G(2df,2p) scheme (see the ESI). λ_{max}^{abs} of **I** is 390 nm whereas λ_{max}^{emi} of **II** and **III** are 516 nm and 1616 nm, respectively. But for a slight underestimation of the experimental wavelengths, typical of M06-2X,[31] one notices that the calculations very nicely reproduce the experimental data for the canonical structure (**I** and **II**), whereas the predicted λ_{max}^{emi} for the ESIPT species is completely off. Note that CAM-B3LYP λ_{max}^{emi} is 2102 nm, so that the M06-2X emission wavelength is not so large due to the lack of long-range corrections. The computed M06-2X Stokes shift between **I** and **II**, 6261 cm^{-1}, is in the line of the exper-

imental value (5415 cm^{-1}). The measured large Stokes shift is therefore symptomatic of a strong geometric relaxation in the BTD core, rather than of a proton transfer. The structures of **I** and **II** have therefore been analyzed as well as the importance of CT (Figure 1). Obviously, the geometrical changes on the pyridine and amine sides following photon absorption are rather minimal. In the same time, the six-member ring of the benzothiadiazole looses its quinoidic character and the N-S bonds significantly elongates in the excited state. This is consistent with the density difference plot that indicates a minor participation of the pyridine ring, and confirms the strong accepting character of the heteroatoms of the BTD. Indeed, the nitrogen and sulfur atoms of the five-membered ring gain electron densities upon transition to the excited-state. Note that the hydrogen bond shortens by 0.09 Å when going from the ground to the excited state, but this is not sufficient to induce ESIPT. The computed CT distance is 2.74 Å (see ESI for details), which is a large value for a rather small molecule. For the records, let us also note that both the unsubstituted BTD core and its di-bromo derivative, that have no acidic proton allowing ESIPT, develop experimental Stokes shift of 6011 and 8354 cm^{-1}, respectively in ethyl acetate.[32] This further supports that the observed Stokes shift for **I**↔ **II** is not related to ESIPT.

Fig. 1 Bottom: LR-PCM/M06-2X/6-31+G(d) ground (left) and excited (right) structures (distances in Å, double bonds omitted for clarity). Top: density difference plot between the two states upon absorption (left) and CT vector obtained (see ESI). In the former density plot, the blue (red) zones indicate decrease (increase) of electronic density upon absorption.

To further characterize this system, we have determined the pK_a and pK_a^* using a Born-Haber Cycle (BHC) scheme (see the ESI). In the ground-state, the computed pK_a for the protonation of the pyridine is 4.4, and this nicely fits experiment, as the absorption spectra undergoes strong variations between

pH of 4 and 5.[25] For the records, we tried protonation on both the BTD core and the amine and they led to much less stable optimal structures than their protonated pyridine counterpart, with differences of +11.5 and +15.5 kcal.mol^{-1} on the free energy scale. Therefore, at low pH, the pyridine is protonated, which induces a twist of the structure, the two rings being no more coplanar (42° for the ground-state in water). For this cation, ESIPT can also be discarded as the protonated **III** is less stable than its **II** counterpart by 11.5 kcal.mol^{-1} on the Gibbs free energy scale [LR-PCM/M06-2X/6-31+G(d) level, as above. The computed λ_{max}^{abs} and λ_{max}^{emi} for the protonated compound in water are 335 and 439 nm that can be compared to 389 nm and 532 nm for the neutral structure in the same solvent. The fact that both absorption and emission wavelengths are significantly blue-shifted upon protonation is in the line of experiment (e.g., in water the λ_{max}^{abs} goes from ca. 418 to ca. 369 nm upon protonation, i.e. a 49 nm hypsochromic shift similar to the theoretical prediction of 54 nm).[25] The pK_a corresponding to the deprotonation of the secondary amine is calculated to be 18.3, meaning that the anionic form should not be significantly present in the ground-state under experimental conditions. This is consistent with a single absorption band of nearly constant wavelength in the 5–13 pH range experimentally.[25] However, at large pH, two emission bands are observed at ca. 481 nm and 565 nm in water, the intensity of the latter increasing with the pH value.[25] We have computed the pK_a^* of the excited-state for the deprotonation of the amine and obtained a 7.6 value. In other words, the amine becomes much more acidic after photon absorption, which is consistent with a significant density depletion of this group (mostly in blue in Figure. 1). The computed λ_{max}^{emi} for the neutral and anionic form in water are 532 and 628 nm, respectively, which are both red-shifted compared to the experimental data but with a difference comparable to the measurements.[33] It is therefore reasonable to state that, though the anionic form is not significantly present in the ground-state (absorption), the strong decrease of the pK_a after excitation allows the formation of a fraction of anion at the excited-state (with the help of an external base), and hence, fluorescence from the anion could be observed in addition to emission from the neutral molecule (two emission bands).

In summary, we have shown that excited-state intramolecular proton transfer is unlikely to take place in the amino-substituted BTD considered. The large Stokes shift being explained by the nature of BTD core where the charge-transfer electronic transition is localized. The presence of two maxima at large pH is explained by the photo acidic character of the dye, implying a intermolecular proton transfer to an external base at high pH. This work is a confirmation of the usefulness of advanced theories in the simulation of ESIPT.

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33 The somehow large differences between experiment and theory could certainly be partly ascribed to the lack of solvent-solute hydrogen bonds in our model.

Graphical Abstract

No ESIPT

STOP

H

N

S

N

N

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N

H

...but CT