Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 183 (2017) 123–130

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

A quantum-chemical insight into the tunable fluorescence color and distinct photoisomerization mechanisms between a novel ESIPT fluorophore and its protonated form

Huijuan Yuan, Songyan Feng, Keke Wen, Qiuling Zhu, Beibei An, Xugeng Guo *, Jinglai Zhang *

Institute of Environmental and Analytical Sciences, College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, People's Republic of China

ARTICLE INFO

Article history:
Received 13 February 2017
Received in revised form 8 April 2017
Accepted 16 April 2017
Available online 19 April 2017

Keywords:
ESIPT
TD-DFT
Photoisomerization
Fluorescence color
Potential energy surface

ABSTRACT

Enol-keto proton tautomerization and cis-trans isomerization reactions of a novel excited-state intramolecular proton transfer (ESIPT) fluorophore of **BTImP** and its protonated form (**BTImP**$^+$) were explored using density functional theory/time-dependent density functional theory (DFT/TD-DFT) computational methods with a B3LYP hybrid functional and the 6-31 + G(d,p) basis set. In addition, the absorption and fluorescence spectra were calculated at the TD-B3LYP/6-31 + G(d,p) level of theory. Our results reveal that both **BTImP** and **BTImP**$^+$ can undergo an ultrafast ESIPT reaction, giving rise to the single fluorescence emission with different fluorescence colors, which are nicely consistent with the experimental findings. Calculations also show that following the ultrafast ESIPT, **BTImP** and **BTImP**$^+$ can experience the distinctly different cis-trans isomerization processes. The intersystem crossing between the first excited singlet S_1 state and triplet T_1 state is found to play an important role in the photoisomerization process of **BTImP**$^+$. In addition, the energy barrier of the trans-keto → cis-keto isomerization in the ground state of **BTImP**$^+$ is calculated to be 10.49 kcal mol^{-1}, which implies that there may exist a long-lived trans-keto species in the ground state for **BTImP**$^+$.

1. Introduction

This work was motivated by the report of a switchable fluorescence color based upon the switching of the excited-state intramolecular proton transfer (ESIPT) sites by means of acidic stimuli and the desire to theoretically shed light on the underlying mechanisms [1]. It is well-known that an ESIPT molecule possesses both proton-donating and proton-accepting groups, thereby forming a five-, six- or even seven-membered-ring intramolecular hydrogen bond (H-bond) [2–9]. Upon UV light irradiation, such a pre-existing H-bond can be activated in a so-called Franck-Condon excited state and a proton can be migrated from a proton donator group (*e.g.*, hydroxyl group) to an acceptor of the proton (*e.g.*, the pyrrole or imidazole ring nitrogen), giving rise to a photo-induced proton tautomerization from the excited-state enol (E*) to keto (K*) forms. Following the ESIPT process, the molecule can often emit strong fluorescence. In the case in which the energy barrier for the ESIPT reaction is low enough or even zero (that is, the ESIPT process is barrierless), ESIPT can take place with an extremely ultrafast rate so that the steady-state fluorescence spectra only exhibit a single emission band arising from K* [10–12]. In numerous cases, however, a high energy barrier for the proton transfer process is clearly involved, and hence both E* and K* emissions can contribute to the experimental fluorescence spectra, that is, so-called dual fluorescence emission [13–16]. After K* → K fluorescence emission, the transient K species can return back to the more stable E conformer *via* a reverse ground-state hydrogen transfer (RGSHT) reaction in a facile tautomerization. Thus, a four-level photocycle reaction (E → E* → K* → K → E) is eventually achieved. It has been generally accepted that the ultrafast behaviors of ESIPT accompanied by a large Stokes shift provide enormous opportunities for the applications of such chromophores in a variety of fields, for example, when the fluorescence quantum yield of the K* emission is large, these properties may be used for making the laser dyes [17], fluorescence sensors [18,19], and so forth; while when the K* fluorescence quantum yield is small, it can be useful for designing the ESIPT photostabilizers [20,21].

Owing to such important applications, organic dyes undergoing ESIPT continue to receive wide attention from the experimental and theoretical aspects [1,22–34]. Recently, Sakai et al. reported the synthesis and comprehensive optical properties of a novel ESIPT fluorophore bearing the imidazole (Im) and benzothiazole (BT) moieties, 2-(1,3-benzothiazol-2-yl)-4-methoxy-6-(1,4,5-triphenyl-1H-imidazol-2-yl)phenol (**BTImP**) [1]. They observed that the fluorescence color of **BTImP** was tunable from green to orange on the basis of the switching of intramolecular hydrogen-bonding sites by acid/base stimuli. What is more, such a phenomenon could be achieved in a **BTImP**-doped

---

* Corresponding authors.
E-mail addresses: xgguo@henu.edu.cn (X. Guo), zhangjinglai@henu.edu.cn (J. Zhang).

http://dx.doi.org/10.1016/j.saa.2017.04.025
1386-1425/© 2017 Elsevier B.V. All rights reserved.

Nafion film by writing a letter on it with acidic or basic water as ink, which provides a new possibility for applications such as rewritable data recording using water as ink [1].

To our best knowledge, the report about the fluorochromism of the ESIPT fluorophore derived from switching of the intramolecular H-bond is rather limited, and the nature of the tunable fluorescence color and the mechanism for the photoinduced isomerization reactions are still scarce. Herein, in this work, we employed the density functional theory (DFT) and its time-dependent version (TD-DFT) to systemically investigate the photophysical properties of the novel ESIPT fluorophore of **BTImP** and its protonated form **BTImP**$^+$ (*cf.* Fig. 1). The potential energy surfaces along the ESIPT and possible cis-trans isomerization reactions involving the ground state (S_0), first excited singlet state (S_1) and triplet state (T_1) were described. In addition, their structural and spectral properties were also explored. It was our hope that the present computational study can help to improve our understanding of the intrinsic photophysical properties of ESIPT fluorophores.

2. Computational Details

Geometry optimizations were carried out to determine the minimum energy structures of **BTImP** and **BTImP**$^+$ using DFT method for the S_0 and T_1 electronic states and TD-DFT approach for the S_1 state. In both cases, Becke's three-parameter hybrid exchange functional with Lee-Yang-Parr gradient-corrected correlation (B3LYP density functional) [35–37] was employed, and the 6-31 + G(d,p) basis set [38] was used for all atoms. In addition, the absorption and fluorescence spectra of the two targeted molecules were also explored by the TD-B3LYP/6-31 + G(d,p) calculations under the S_0 and S_1 minimum structures, respectively. To verify the rationality of the present approach, a comparison of the TD-B3LYP and TD-CAM-B3LYP calculated results is presented in Table S1 of the supporting information. Taking into account the fact that the spectroscopic experiments of **BTImP** were conducted in a typical solvent of tetrahydrofuran, the integral equation formalism (IEF) [39,40] version of polarizable continuum model (PCM) [41,42] was considered for both **BTImP** and **BTImP**$^+$ with THF ($\varepsilon = 7.4257$) as solvent throughout the whole theoretical calculations unless otherwise stated. The test calculations on **BTImP**$^+$ indicated that using AcOH ($\varepsilon = 6.2528$) as solvent had a negligible effect on its structural parameters and spectral properties, in comparison with the results in THF solution (see Tables S2 and S3 in the supporting information).

To provide a deep insight into the whole photoisomerization process, the constrained energy profiles (CEPs) of **BTImP** and **BTImP**$^+$ were constructed by performing the point-to-point optimizations with B3LYP for S_0 and T_1 and TD-B3LYP for S_1. For every stationary-point optimization, the reaction coordinate was fixed at a given value, whereas other degrees of freedom were optimized without any constraint. The CEPs of proton transfer reactions were calculated along a series of values of the reaction coordinates defined by the O_1-H_1 distance (*cf.* Fig. 1 for atom numbering). In the case of the subsequent cis-trans isomerization processes, the dihedral angle N_1-C_1-C_2-C_3 for **BTImP** and N_2-C_5-C_4-C_3 for **BTImP**$^+$ were defined as the reaction coordinates by fixing at a given value from 0° to 180°.

All the DFT and TD-DFT calculations were performed with the Gaussian 09 package [43].

3. Results and Discussion

3.1. Conformers of the Ground and Excited States

B3LYP/TD-B3LYP optimized conformers and relative energies of **BTImP** and **BTImP**$^+$ involving both S_0 and S_1 states are depicted in Figs. 2 and 3, respectively, and their key structural parameters are included in Tables S4 and S5 of the supporting information, respectively. In addition, the conformer forms of the T_1 states of **BTImP** and **BTImP**$^+$ optimized at the B3LYP level of theory are provided in Figs. S1 and S2, respectively. For convenience of discussion, we will hereinafter represent by cis-E-S_0 and trans-K-S_1 the cis-enol form in the S_0 ground state and the trans-keto form in the S_1 excited state, respectively, and the meanings of other abbreviations are similar with the two ones.

As shown in Fig. 2, all the cis-conformers exhibit a six-membered ring intramolecular hydrogen bonding structure; however, owing to the rotation of C_1—C_2 bond between the imidazole and phenolic rings, the six-membered unit is broken in the trans-conformers of the neutral **BTImP** molecule. Among the five conformers considered here, the cis-E-S_0 form is a global energy minimum with an O_1-$H_1 \cdots N_1$ intramolecular H-bond distance of 1.630 Å. In the S_1 excited state, the cis-E-S_1 species is calculated to locate 66.35 kcal mol^{-1} above the cis-E-S_0 form (*cf.* Fig. 2). Upon relaxation into the cis-E-S_1 conformer, the strength of the O_1-$H_1 \cdots N_1$ interaction is enhanced with a shorter H-bond distance of 1.519 Å with respect to that of cis-E-S_0. Generally, a stronger intramolecular H-bond interaction in the excited-state enol-conformer will lead to a smaller structure adjustment and a smaller energy barrier in the ESIPT process, thus facilitating the occurrence of ESIPT reaction [31]. On the other hand, the cis-K-S_1 species is computed to lie at 63.07 kcal mol^{-1} above the cis-E-S_0 structure and 3.28 kcal mol^{-1} below the cis-E-S_1 species (*cf.* Fig. 2), which means that the photoinduced proton tautomerization reaction from the cis-E-S_1 to cis-K-S_1 forms of **BTImP** is highly exergonic, also in favor of the occurrence of ESIPT. It is worthy of note that the present B3LYP computation failed to locate the minimum energy structure of cis-K-S_0, since all the optimizations for attempting to locate cis-K-S_0 minimum result directly in its cis-E-S_0 form, which in general suggests that the RGSHT reaction from cis-K-S_0 to cis-E-S_0 forms in **BTImP** will be a barrierless process as can be seen in the calculations of potential energy curves (*vide infra*).

It can be seen from Fig. 3 that when the N_1 site of **BTImP** is protonated to form the **BTImP**$^+$ molecule, the phenolic —OH group can form a strong intramolecular H-bond interaction with the N_2 atom of the benzothiazole moiety in the cis-E-S_0 conformer, and its O_1-$H_1 \cdots N_2$ H-

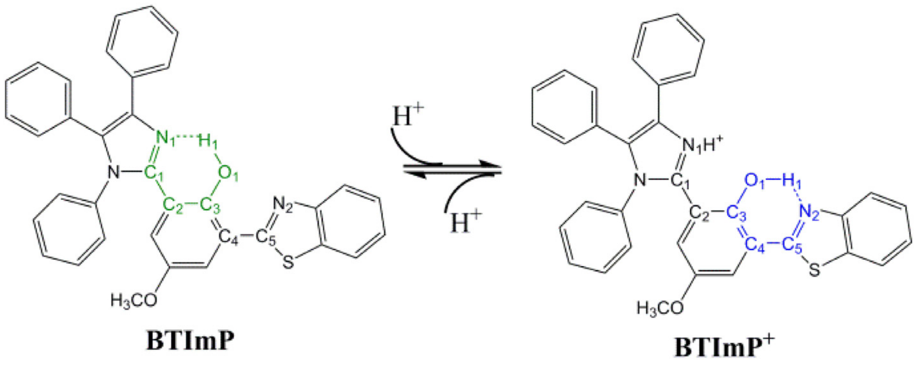

Fig. 1. Structures and partial atom numbering of two targeted molecules.