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Photo-induced proton transfer in fluorene- and carbazole-based compounds as red- and orange-light-emitting molecules: A TD-DFT study

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ABSTRACT

In this explore, intramolecular photo-induced proton transfers in fluorene- and carbazole-based compounds of 5H-indeno[1,2-b]pyridin-9-ol (**IPO**) and 5H-pyrido[3,2-b]indol-9-ol (**PIO**) are investigated using TD-DFT method at PBE0/6-311++G(2d,2p) level of theory. The potential energy surfaces were calculated for ground and excited states. In contrast to the ground state, photoexcitation from S_0 state to S_1 one induces the operation of the excited-state intramolecular proton transfer process. The calculated fluorescence emission wavelength for both molecules is >600 nm. Both compounds exhibit unusually high Stokes shifts fluorescence. The structural parameters, H-bonding energy, absorption and emission bands, vertical excitation and emission energies, oscillator strength, fluorescence rate constant, dipole moment, atomic charges and electron density at critical points were calculated. Molecular orbital analysis shows that vertical $S_0 \rightarrow S_1$ transition in the studied molecules corresponds effectively to the excitation from HOMO (π) to LUMO (π^*). The potential of these molecules as emissive materials in designing and generation of new displays and light sources are predicted based on their high Stokes shifts (374 and 291 nm).

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1. Introduction

In recent years, there has been a raising attention in excited-state intramolecular proton transfer (ESIPT) reactions [1–12] because of their wide applications to such systems as UV-light polymer stabilizers, laser dyes, molecular switches, fluorescence sensors, and particularly in biological systems [13–21]. For instance, it is well accepted that the fluorescence ability of the green fluorescent proteins is controlled by the several-proton transfer after photoexcitation [22].

The ESIPT is important in determining the spectroscopic properties of organic molecules, which usually produce a large Stoke shift. The ultrafast rate of ESIPT, together with a large Stokes shift between absorption and tautomer emission, provides a broad spectral window to fill in other complementary emission color free from energy transfer and reabsorption [23]. It is well known that fluorescent dyes with longer wavelength and large Stokes shift are favorable for fluorescence imaging in cells for the following reasons: (1) photons with longer wavelength tend to reduce environmentally-induced light scattering, be less susceptible to the experiment noise from endogenous chromophores, and usually

cause less light-induced organelle damage [24,25]; (2) the large Stokes shift can highly improve the sensitivity of fluorescence microscopy wherein emission photons can be detected against the background from excitation photons [26]. Yang et al. [27] reported synthesis of type [a] and [b] benzoxanthenes that can display three emission maxima of approximately equal intensities, in the blue, green, and red spectral regions, respectively. Hansen et al. [28] reported a class of ESIPT fluorescent dyes involving the 1,3-bis(imino)isoindolediol motif (**BPI**), having an emission in red region (about 600 nm), high quantum yields (up to 45%) and a Stokes shift (>165 nm). Recently, Chen et al. [25] have investigated a new **BPI** dye, 1,3-bis(bispyridin-2ylimino)isoindolin-4-ol, with an emission in bright red region and a 218 nm Stokes shift.

Extensive investigations have exposed that conjugated organic nanomaterials show a wide variety of interesting electrical, optical, photoelectric, and magnetic properties in the solid states [29–31]. The fluorene and carbazole molecules are composed of a biphenyl unit bridged with a methylene and NH unit at the 9 position, respectively. Many possible applications of fluorene and its heteroanalogues, namely, carbazole, dibenzofuran, and dibenzothiophene, making use of their photochemical features have been described in recent times. The useful electronic properties of these materials make them promising candidates for use in such diverse technologies as organic light-emitting diodes, thin-film transistors,

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chemical sensors, photovoltaics, photorefractives, holography, electronic data storage, and electroluminescent devices [32–39]. The nanofibrils fabricated from the carbazole exhibit strong blue fluorescence upon excitation under UV light. Zang et al. have used these nanofibrils for expedient detection of nitroatomatic and highly volatile nitroaliphatic explosives [40]. Due to superior properties carbazole and fluorine functional groups are particularly important for molecular design of novel organic multifunctional compounds [41–45].

To choose or design the suitable fluorescent compounds for a variety of applications, it is needed to understand their photophysical properties of them. It is, however, time-consuming and cost-intensive to study the physical properties of all interesting fluorescent compounds. Thus, study of the photophysical properties of fluorene- and carbazole-based compounds by computational methods can be an efficient and needed approach. The fluorene- and carbazole-based materials of 5H-indeno[1,2-b]pyridin-9-ol (**IPO**) and 5H-pyrido[3,2-b]indol-9-ol (**PIO**) are not experimentally reported. These compounds present many interesting photophysical and hydrogen-bonding donor–acceptor properties.

Computational quantum chemical study on relevant model systems is a promising way to reveal the mechanism of the proton transfer through the ESIPT process. Several computational papers published in recent years [46–58] have allowed a remarkable advance toward a full understanding of the photoisomerization process, providing the ground for interpreting the quickly growing the experimental results [59–61]. In recent years, we have studied proton transfer reactions in different systems [62–64]. Recently, we have investigated excited state intramolecular proton transfer (ESIPT) in naphthalene-fused analog of **HBO**, 2-(2′-Hydroxynaphthyl)benzoxazole) and 2-(2′-hydroxyphenyl) benzazole family (HBO, HBI and HBT) [65,66]. In the present work, we investigate the intramolecular photo-induced proton transfer in 5H-indeno[1,2-b]pyridin-9-ol (**IPO**) as a fluorene derivative and 5H-pyrido[3,2-b]indol-9-ol (PIO) as a carbazole derivative. Although many studies on ESIPT process in a series of molecules have been published, to the best of our knowledge no investigations of the ESIPT process in **IPO** and **PIO** have been presented. In addition, H-bonding interaction along the proton transfer between enol– and keto–froms of the **IPO** and **PIO** are characterized by quantum theory of atoms in molecules (QTAIM) [67–69] analyses. The ESIPT in 10-hydroxybenzo[h]quinoline (10-HBQ), with a structure similar to **IPO**, has been explored theoretically and experimentally [70,71]. The first band of the absorption spectrum of 10-HBQ in cyclohexane at around 380 nm was assigned to the $S_1 \leftarrow S_0$ ($\pi\pi^*$) transition. Besides, the $S_1 \rightarrow S_0$ emission energy of 10-HBQ is obtained to be 1.98 eV (626.2 nm) [69].

2. Computational details

The stationary points on the S_0 and S_1 potential energy surfaces of **IPO** and **PIO** were optimized using DFT methods (PBE0 for S_0) and (PBE0-TD for S_1) [72] in conjunction with the 6-311++G(2d,2p) basis set. DFT methods are used as a reliable standard tool for the theoretical treatment of electronic structure and spectroscopic properties of various types of compounds [73]. Despite the absence of adjustable parameters, PBE0 (TD-PBE0) has already provided excitation spectra in very good agreement with the available experimental results [60,74–78,53,79]. Vibration frequency calculations were performed at the same level to validate that the optimized structures were the energy-minima or transition states. The presence of minima can be confirmed by the absence of imaginary modes and transition states by a single imaginary mode. The calculations were carried out using the GAMESS [55] and GAUSSIAN 03 program packages [57]. Bulk solvent

effects on the vertical excitation parameters have been taken into account by means of the polarizable continuum model (PCM) [80] using the integral equation formalism variant (IEFPCM) [81–83] and UFF force field (Radii = UFF). In this model, the molecule is embedded in a cavity surrounded by an infinite dielectric, with the dielectric constant of the solvent.

The Bader theory was also applied to find critical points and to characterize them. Topological properties of bond critical points (BCPs) were calculated at the PBE0/6-311++G(2d,2p) level of theory by using the AIM2000 program package [84].

3. Results and discussions

The stationary points of the **IPO** (X = CH_2) and **PIO** (X = NH) are explored at S_0 and S_1 states. The different configurations of **IPO** and **PIO** are given in Fig. 1. The structure of transition states between enol and keto forms at S_0 and S_1 states are given in Fig. 4. Both enol (E) and keto (K) forms of the two compounds are planar with C_s symmetry. In the ground S_0 state, enol and keto forms **IPO** and **PIO** are denoted as S_0-E and S_0-K, respectively. In the S_1 state, two E and K forms are symbolized as S_1-E (FC), S_1 (E) and S_1-K, respectively.

Fig. 2 illustrates the energy diagram of phototautomerization in the **IPO** and **PIO**. The PT reaction at the S_1 state for **PIO** is different with the **IPO**. The PT in the **PIO** begins from the Franck–Condon point S_1-E (FC), with the geometry of the S_0-E state; it reaches to the S_1-E state with the structural rearrangement. From S_1-E state, the molecule can undergoes a tautomerization via ESIPT to the excited state S_1-K or emits a photon and returns to the S_0-E state. From the S_1-K, molecule emits a photon and falls to the ground state S_0-K with the energy difference corresponding to the fluorescence spectrum. Finally, S_0-K in ground state is converted to the S_0-E. The molecule **IPO** is not stable in the S_1 (E) form and thus we could not find the stationary point of its S_1-E form by using PBE0 functional. The S_1-E (FC) structure of **IPO** is directly converted to its keto form S_1-K through ESIPT. The molecule at the S_1-K emits a photon and falls to the ground state S_0-K with the energy difference corresponding to the fluorescence spectrum.

Since **IPO** is not a true minimum at PBE0/6-311++G(2d,2p) level in the gas phase, we decided to explore and check the S_1-E stationary point of **IPO** using the M06-2X functional. Laurent et al. [85] have shown that the hybrid meta exchange–correlation functional M06-2X can well predicts stationary points of S_1 states of **HBI** derivatives. Although PBE0 functional does not predict S_1-E form of **IPO** as a true minimum, M06-2X functional gives the S_1-E stationary point as a local minimum on the potential energy surface of **IPO** so that that it can be converted to S_1-K form through a transition state S_1-E (TS).

3.1. Structural parameters, H-bonding energy and potential energy curves at S_0 state

The selected optimized structural parameters involved in PT reactions are summarized in Table 1. The value of H-Bond angle in E form of **IPO** and **PIO** at the S_0 state is 145.7° and 144.0°, respectively. The O–H bond length in the **IPO** and **PIO** is 0.974 and 0.970 Å and the N···HO distance is 2.040 and 2.196 Å, respectively. Thus, it is predicted that the strength of H-bonding interaction decreases on going from **IPO** to **PIO**.

Proton transfer in the E to K conversion causes the structural changes in the **IPO** and **PIO** at S_0 state. We have examined how the structural parameters are affected by the proton transfer by performing optimization of structures on the potential energy surfaces. Fig. S1 in the Supplementary Data shows the variations of d(N–H), d(O–H), d(O···N) and O–H···N angle versus RC along the