

COMMUNICATION

Excited-state Intramolecular Proton Transfer of HDI and HBF: Excited-state Hydrogen-bonding Dynamics and Electronic Structures

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Abstract: Employing Density Functional Theory (DFT) and Time-dependent Density Functional Theory (TDDFT) methods, the theoretical study on two ESIPT molecules, HDI and HHF, was performed. The optimized structures and infra spectra (IR) results show that, upon photoexcitation, the intramolecular hydrogen bond of HDI is weakened while that of HHF is strengthened. These results further imply that the strengthening of the intramolecular hydrogen bond is not the indispensable condition for the occurrence of ESIPT. Meanwhile, by the results of frontier molecular orbitals, the observed differences of the electron density redistribution between HDI and HHF in K* show us why HDI only shows the forward ESIPT while HHF undergoes the ESIPT equilibrium. Finally, the energy curves of HDI and HHF reveal the preferred forward ESIPT for HDI and the easily occurred backward ESIPT for HHF, further supporting the results of frontier molecular orbitals.

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Excited-state Intramolecular Proton Transfer (ESIPT), a common phenomenon in nature, is

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of great significance in the fields of the biosensors, lighting materials, enzyme catalysis and so forth [1-4]. A large number of works employing both the theoretical and experimental methods have been performed to investigate its physical and chemical properties [5-10]. It is well known that most of the ESIPT reactions involve the proton transfer through the intramolecular hydrogen bond in the excited state, giving rise to a structural change from Enol form (E^* form) to Keto form (K^* form). Due to the dramatic structural alternation, the ESIPT molecule in K form usually possesses a totally diverse photochemical property with respect to the original species (E form). In this way, the ESIPT dyes usually present a large Stokes shift, which is considered as the remarkable merit of the ESIPT molecule [11-12].

Intramolecular hydrogen bond plays an important role in ESIPT process. The dynamics of the intramolecular hydrogen bond in the excited state is always regarded as the key of the ESIPT [13-17]. Considerable works have demonstrated that the strengthening of the intramolecular hydrogen bond can facilitate the occurrence of ESIPT [17]. However, whether the strengthening of the intramolecular hydrogen bond is the necessary condition for ESIPT is not yet completely confirmed. In recent years, Zhao and Han put forward for the first time that IR spectra can provide a clear-cut signature of excited-state hydrogen-bonding dynamics which can help us understand the relationship between the intramolecular hydrogen-bonding dynamics and ESIPT reaction [13-14]. In detail, hydrogen-bonding dynamics can be monitored by the blueshift or redshift of the vibrational frequencies of the stretching vibrations involved in the hydrogen bond. The strengthening of the hydrogen bond can induce the redshift of the vibrational frequencies of hydrogen-bond-involved stretching vibrations, while the weakening of the hydrogen bond gives rise to the blueshift.

These days, the field of luminescent materials, especially the white lighting materials, has witnessed a great improvement [18-21]. A lot of molecules have been designed and synthesized, aiming to produce the more advanced materials. As it well known that the white lighting material is unusual because the natural luminophore cannot give the emission covering a wide range of the visible spectra [18]. In this case, the researchers all over the world made a great effort to develop the ESIPT molecule as the white lighting materials. In 2010, Chou and co-workers synthesized three ESIPT dyes, that is, 7-hydroxy-2,3-dihydro-1H-inden-1-one (HDI shown in **Figure 1**), 1-hydroxy-9H-fluoren-9-one (HHF shown in **Figure 1**) and 1-hydroxy-11H-benzo[b]fluoren-11-one (HHBF), respectively [18,22]. HHF and HHBF are the chemical modification of HDI. According to Chou's experimental results, HDI undergoes an ultrafast rate of forward ESIPT, giving rise to a unique K^* emission, whereas the excited-state equilibrium is established for both HHF and HHBF. Our previous theoretical works have shown the mechanism of the excited-state equilibrium for HHBF [23]. The electron density swing is demonstrated to be the basic reason for the excited-state