Solvent effect on the excited-state intramolecular double proton transfer of 1,3-bis(2-pyridylimino)-4,7-dihydroxyisoindole

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Abstract

Density functional theory (DFT) and time-dependent density functional theory (TDDFT) are used to study the solvatochromic effect and the excited-state intramolecular double proton transfer (ESIDPT) of 1,3-Bis(2-pyridylimino)-4,7-dihydroxyisoindole (BPI-OH) in different kinds of solvents. The hydrogen bonding parameters and IR spectra reveal that in the excited state, the strength of excited hydrogen bond increase with the decrease of solvent polarity. Furthermore, the reduction density gradient (RDG) analysis confirms the corresponding conclusion. Frontier molecular orbitals (FMOs) are analyzed, illuminating that the smaller the polarity of solvent, the smaller the energy gap between the HOMO and LUMO. The structures of BPI-OH (N) (normal), BPI-OH (T₁) (single), and BPI-OH (T₂) (double) were optimized. Previous reports found the double protons in BPI-OH molecule are transferred step-by-step process BPI-OH(N)→BPI-OH(T₁)→BPI-OH(T₂) in the ground state (S₀) and the first excited singlet state (S₁). Here, the potential energy curves of O₁–H₂ and O₄–H₅ in the S₀ and S₁ states were scanned in four kinds of solvents, respectively. It was found that in S₁ state, BPI-OH(N)→BPI-OH(T₁) was more prone to proton transfer than BPI-OH(T₁)→BPI-OH(T₂). In addition, by comparing the reaction energy barriers of the four kinds of solvents, it can be found that ESIPT is difficult to occur with the increase of solvent polarity. Meanwhile, it was also studied that MeOH as an explicit solvent was more likely to promote the ESIPT process than other implicit solvents.

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Graphic abstract

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1 Introduction

Hydrogen bond is a common secondary bond in nature [1, 2]. It is found that the presence of hydrogen bond will have an important impact on the properties of compounds (boiling point, melting point, surface tension) [3, 4]. Hydrogen bond interaction exists and is often used to explore the mechanism of the ESPT process [5, 6]. However, the dynamic characteristics of the hydrogen bond system in the S_1 state are more complicated than that of S_0 state [7]. In general, hydrogen bonds are also important in many biochemical reactions [8]. Recently, the hydrogen bond enhancement theory in the excited state was proposed by Zhao and Han et al. [9–11]. In particular, when the system has multiple hydrogen bonds, the excited state multidimensional proton transfer is more complicated. Therefore, it is important to study the different mechanisms of hydrogen bond interaction in the S_1 state.

An important photochemical process, the ESIPT, exists in a four-level photocycle [12, 13]. In general, the strengthening of hydrogen bond is caused by the change of the acid–base properties of the group under the action of electron density

during the photoexcitation process [14]. The premier ESIPT species was first reported by Weller et al. [15]. Since then, ESIPT has shown a variety of potential applications in many biological, chemical, physical and other fields, such as laser dyes [16], white light emitting materials [17], molecular switches [18, 19], fluorescence sensors [20–25] and so on [26, 27]. Moreover, the ESIPT fluorophore is characterized by its ultra-fast time scale [28, 29] and large Stokes displacement [30]. In addition, ESIPT is sensitive to the polarity of solvent and types of solvent [31]. According to this conclusion, the ESIPT and fluorescent mechanisms have been studied by many groups [11, 32, 33].

In recent years, some derivatives of BPI have been found to have potential applications in laser dyes, high-energy radiation detectors, light stabilizers and so on. Based on 1,3-bis(imino)isoindole diol motif, a new class of ESIPT dyes have been synthesized [34]. The BPI-OH molecule, which contains two intramolecular hydrogen bonds, can occur large Stokes displacement by ESIPT reaction. In the experiment, the electronic spectra of BPI-OH molecules were measured and were compared with the

Fig. 1 Views of BPI-OH (normal BPI-OH), BPI-OH (T_1) (single-proton transfer of BPI-OH) and BPI-OH (T_2) (double-proton transfer of BPI-OH). Atom labels involved in two intramolecular hydrogen bonds are marked on BPI-OH structure. Red: O atom; Blue: C atom; Gray: H atom; Orange: N atom

derivatives [34]. In the previous study, the reaction mechanism is the step-by-step proton transfer BPI-OH(N)→BPI-OH(T_1)→BPI-OH(T_2) [35]. It is further proved that BPI-OH(N)→BPI-OH(T_1) is more prone to proton transfer than BPI-OH(T_1)→BPI-OH(T_2). It is worth noting that such structures are sensitive to the surrounding environment. In this paper, the ESIPT mechanism of BPI-OH molecule in dimethyl sulfoxide (DMSO), methanol (MeOH), dichloromethane (DCM) and toluene (TOL) will be studied using DFT and TDDFT. To explore the effect of the different kinds of solvents, the geometric parameters, RDG function have been applied. In addition, the FMOs [36], electro-static potentials and the charge distribution are determined by the Mulliken's charge. The potential energy curves (PECs) is constructed to describe the proton transfer processes. Moreover, to further explore the competition of intramolecular and intermolecular H-bonding, MeOH as an explicit solvent to study the influence of solvent types on ESIPT process.

2 Computational details

All the calculations were used Gaussian 16 program suite [37]. All the computational studies were based on the PCM and the solvation model with integral equation form variables (IEF) [38, 39]. Four kinds of solvents were selected and solvent dielectric constants (ϵ) of dimethyl sulfoxide (DMSO), dichloromethane (DCM), methanol (MeOH), and toluene (TOL) is 46.8, 32.7, 8.9 and 2.4, respectively. The geometries of BPI-OH (N), BPI-OH (T_1) and BPI-OH (T_2)

are optimized using B3LYP [40, 41] and TZVP basis set [42, 43]. There was no virtual frequency. The PECs in the S_0 and S_1 states were constructed by fixing the O_1-H_2 and O_4-H_5 distance to further explore the ESIDPT process in four kinds of solvents. We also used Multiwfn software to analyze Mulliken's charge distribution [44, 45].

3 Results and discussion

3.1 Optimized geometric structures, IR vibrational spectra and RDG isosurfaces

The configurations of BPI-OH, BPI-OH (T_1) and BPI-OH (T_2) (shown in Fig. 1) are obtained. The significant parameters involved $O_1-H_2\cdots N_3$ and $O_4-H_5\cdots N_6$ are listed in Table 1. The geometric structure of BPI-OH is symmetrical, the bond length and angle of $O_1-H_2\cdots N_3$ is the same as the corresponding parameters of $O_4-H_5\cdots N_6$. In the S_0 state, the bond length of O_1-H_2 in four kinds of solvent (DMSO, MeOH, DCM and TOL) is 0.9814, 0.9814, 0.9813 and 0.9808 Å, respectively. In the S_1 state, the bond length of O_1-H_2 is 0.9972, 0.9972, 0.9975 and 0.9977 Å, respectively. Thus, from S_0 to S_1 state, the bond of O_1-H_2 is weakened, and the hydrogen bond lengths of H_2-N_3 in DMSO, MeOH, DCM and TOL solvents are shortened from 2.0592, 2.0592, 2.0590 and 2.0598 Å, to 1.9529, 1.9524, 1.9486 and 1.9425 Å, respectively. After photoexcitation, the bond angle of $O_1-H_2\cdots N_3$ are increased from 143.7°, 143.7°, 143.8° and 143.8° in the S_0 state to

Table 1 Calculated primary bond lengths (Å) and angles (°) of BPI-OH normal structures in the DMSO, MeOH, DCM, TOL solvents

	DMSO		MeOH		DCM		TOL	
	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
O_1-H_2	0.9814	0.9972	0.9814	0.9972	0.9813	0.9975	0.9808	0.9977
H_2-N_3	2.0592	1.9529	2.0592	1.9524	2.0590	1.9486	2.0598	1.9425
$\delta(O_1-H_2-N_3)$	143.7703	147.2060	143.7748	147.2255	143.7995	147.3705	143.8052	147.6378
O_4-H_5	0.9814	0.9972	0.9814	0.9972	0.9813	0.9975	0.9808	0.9977
H_5-N_6	2.0592	1.9529	2.0592	1.9524	2.0590	1.9486	2.0598	1.9425
$\delta(O_4-H_5-N_6)$	143.7859	147.2059	143.7912	147.2254	143.8248	147.3705	143.8074	147.6363

Fig. 2 Calculated stretching vibrational frequencies of the O₁-H₂ bond on the S₀ and S₁ states in four kinds of solvents (Short dash: S₀; Solid: S₁)

147.2°, 147.2°, 147.4° and 147.6° in the S₁ state in four kinds of solvents. The changes of the geometric structure parameters instruct that the excited-state hydrogen bonding is enhanced, which provides the driving force for the ESIPT reaction. Moreover, with the increase of solvent polarity (from TOL to DMSO), the bond length of O₁-H₂ is decreased and the H₂⋯N₃ is increased, which illustrate that the excited-state hydrogen bonding enhancing mechanism with the decrease of solvent dielectric constant.

Infrared vibration frequency is an important index for analyzing the strength of hydrogen bond [46]. Figure 2 shows the infrared vibration frequency of O₁-H₂ of BPI-OH molecule in the four kinds of solvents. In DMSO, MeOH, DCM, TOL, the frequency of O₁-H₂ is 3481.28, 3481.58, 3484.45, 3495.11 cm⁻¹ in the S₀ state and is 3186.91, 3186.22, 3180.89, 3176.42 cm⁻¹ in the S₁ state, respectively. The red shift of 294.37, 295.36, 303.56 and 318.69 cm⁻¹ is exhibited in the S₁ state, illustrating the strengthened of hydrogen bond in S₁ state. Therefore, when the red shift is increased and the excited-state hydrogen bonding is enhanced, the ESIPT is favored with the decrease of solvent dielectric constant.

RDG analysis is a visualized method of weak interaction. Herein, the hydrogen bonds are further analyzed through RDG scatter plots and isosurfaces. As shown in Fig. 3, the hydrogen bond strengthened in TOL (−0.0312) is more obvious than that in DMSO (−0.0305). Thus, as the decrease of dielectric constant, the excited-state hydrogen bonding is strengthened.

3.2 Electronic spectra, frontier molecular orbitals (FMOs) analysis and Mulliken's charge distribution

The electronic spectra of BPI-OH are computed in four kinds of solvents. As shown in Fig. 4, the obtained absorption data in DMSO, MeOH, DCM and TOL are 433, 429, 430 and 441 nm, which are agreement with the experimental data (400–430 nm). Theoretical fluorescence data of the BPI-OH (N) is 511, 515, 515 and 500 nm from DMSO to TOL, respectively, which is close to the emission wavelength of the experiment (540–575 nm). In the T₁ form, the emissions results are 636, 645, 646 and 636 nm in DMSO, MeOH, DCM and TOL. In the T₂ form, the corresponding results are 658, 670, 672 and 627 nm. To explore the configuration of double proton transfer, the fluorescence peaks of T₁ and T₂ are calculated. During ESIPT process, there are double emission fluorescence, accompanied by a large Stokes shift value in DMSO (125 nm), MeOH (130 nm), DCM (131 nm) and TOL (136 nm), respectively. As the dielectric constant decreases, the Stokes shift increases. After photoexcitation, the transition and redistribution of electrons could occur [47]. The MOs of BPI-OH molecules in DMSO, MeOH, DCM and TOL solvents are shown in Fig. 5. The calculated wavelengths, corresponding oscillator strength (*f*) are listed in Table S1. The first comprehensive TDDFT study (in DCM) on BPI-OH was reported by Chai et al. [48]. However, the vertical excitation energy calculated by us in DCM solution (2.87 eV) is closer to the experimental value (2.88 eV) than that calculated by Chai et al. (2.96 eV). Herein, the HOMO and the LUMO, lead to the distinct $\pi \rightarrow \pi^*$ feature of S₀→S₁ transition. The chemical activity can be expressed by the energy gap between HOMO and LUMO. The low kinetic stability and high chemical activity are indicated by small energy gaps [49, 50]. The energy gap is 2.888, 2.885, 2.882 and 2.858 eV, respectively, in DMSO, MeOH, DCM and TOL. Thus, the solvent polarity has effect on the electron transition and energy gap. In addition, the electron density of the BPI-OH molecules in four kinds of solvents are also changed, and the electron density on O₁ decreases, while that on N₃ increases, which facilitates the transfer of proton H₂ from O₁ to N₃. In fact, the trend and process of ESDPT can be explained by subtle changes in electron density.

Meanwhile, *S* represents the space separation of holes and electrons, and *D* represents the length of charge transfer, and these values were listed in Table S2. The Δr indexes are 1.969, 1.977, 1.989, and 2.037 Å in DMSO, MeOH, DCM and TOL solvents, respectively. The *S* values are 0.672, 0.672, 0.671 and 0.669 from DMSO to TOL. The *D* values are 1.970, 1.976, 1.989 and 2.037 Å from DMSO to TOL (as shown in Fig. S1). It is obvious that the charge transfer length increases with the decrease of solvent

H-bond Van der Waals Repulsion
 -0.05 ← 0.05
 $\rho > 0$ $\rho > 0$
 $\lambda_2 < 0$ $\lambda_2 \approx 0$ $\lambda_2 > 0$
 Sign (λ_2) ρ Sign (λ_2) ρ
 decrease add

(a) ● DMSO

(b) ● MeOH

(c) ● DCM

(d) ● TOL

Fig. 4 Calculated absorption (abs) and fluorescence (flu) wavelength of BPI-OH in different kinds of solvents; **a** DMSO; **b** MeOH; **c** DCM; **d** TOL; N: normal form; T₁ and T₂: tautomer form

Fig. 5 Calculated frontier molecular orbitals (HOMO and LUMO) of BPI-OH on the S₁ state and its transition energy

polarity. As listed in Table 2, in DMSO, the Mulliken's charge of O₁ is decreased from −0.298 to −0.288 and N₃ is increased from −0.221 to −0.230, which indicates the

Table 2 Calculated Mulliken's charge distribution of molecule BPI-OH in S₀ and S₁ states

	Mulliken's charge (TZVP)				Mulliken's charge (aug-cc-pvtz)			
	O ₁		N ₃		O ₁		N ₃	
	S ₀	S ₁	S ₀	S ₁	S ₀	S ₁	S ₀	S ₁
DMSO	−0.298	−0.288	−0.221	−0.230	−0.097	−0.830	−0.525	−0.364
MeOH	−0.297	−0.288	−0.221	−0.230	−0.096	−0.830	−0.525	−0.364
DCM	−0.294	−0.286	−0.221	−0.231	−0.093	−0.828	−0.525	−0.365
TOL	−0.285	−0.279	−0.221	−0.231	−0.084	−0.821	−0.525	−0.365

electronegativity of N₃ increased and that of O₁ decreased. Thus, the ESIPT reaction is affected by charge density. Since Mulliken's charges are very sensitive to the choice of basis set, to eliminate this effect, Aug-cc-pVTZ basis set is used. The charge of O₁ atom changes from −0.097 to −0.830 during the S₀ to S₁ states in DMSO solvent. The reduced electronegativity of O atom indicates that the attraction of the donor to H atom is reduced during photoexcitation process, which promotes the occurrence of H proton transfer. Therefore, the same conclusions can be obtained.

3.3 Potential energy curves of the proton transfer reactions

In previous reports, it was found that the double protons in BPI-OH molecules follow a step-by-step transfer mechanism. Potential energy curves are constructed in four kinds of solvents with a function of O₁–H₂ bond length

Fig. 6 Potential energy curves of S_0 and S_1 states of BPI-OH as a function O_1-H_2 bond length in different kinds of solvents; **a** DMSO; **b** MeOH; **c** DCM; **d** TOL

Fig. 7 Potential energy curves of S_0 and S_1 states of BPI-OH (T_1) as a function O_4-H_5 bond length in different kinds of solvents; **a** DMSO; **b** MeOH; **c** DCM; **d** TOL

Fig. 8 Proton transfer processes of the BPI-OH molecule in four kinds of solvents in S_0 and S_1 states

and O_4-H_5 bond length at B3LYP/TZVP level, as depicted in Figs. 6 and 7. As shown in Fig. 6, potential reaction energy ($BPI-OH(N) \rightarrow BPI-OH(T_1)$) in the S_0 state in DMSO, MeOH, DCM and TOL is 11.56, 10.89, 10.71 and 10.69 kcal mol⁻¹, respectively. It can be seen that the potential barrier for proton transfer in S_0 state is high, which is not conducive to proton transfer reaction. In the S_1 state, the energies of T_1 structure are lower than that of N structures in four kinds of solvents, which suggests that the thermodynamic feasibility of ESIPT process. In the S_1 state, the ESIPT energy barriers in DMSO, MeOH, DCM and TOL are 4.41, 4.03, 3.96, 3.96 kcal mol⁻¹, respectively. The potential barriers of reverse ESIPT reactions in DMSO, MeOH, DCM and TOL is 10.34, 12.39, 13.11 and 13.19 kcal mol⁻¹, respectively. Thus, it is difficult to occur the reverse proton transfer. The increase of the dielectric constant of the solvent will lead to the weakening of hydrogen bond strength and ESIPT reaction is difficult to proceed. Thus, among the four solvents, TOL is more suitable for proton transfer reaction.

As shown in Fig. 7, for $BPI-OH(T_1) \rightarrow BPI-OH(T_2)$, the energies T_2 structure are lower than that enol structure (T_1) in four kinds of solvents in the S_1 state. The ESIPT energy barriers in DMSO, MeOH, DCM and TOL are 8.42, 7.88, 7.69, 7.67 kcal mol⁻¹, respectively. It is not difficult to see that the proton transfer process of the second step is inhibited to some extent with the increase of solvent polarity. The results are similar to those reported by Chai et al. [48] using DCM as a solvent. This further confirms the accuracy of our other studies. For the second step, the solvent TOL is more favorable for the reaction. In addition, in the two-step proton transfer reactions, the relative energy barrier of the influence

Table 3 Calculated bond lengths (Å) and angles (°) of BPI-OH–MeOH (N), BPI-OH–MeOH (T_1), and BPI-OH–MeOH (T_2) in the S_0 state and the S_1 state, respectively

	BPI-OH–MeOH (N)		BPI-OH–MeOH (T_1)		BPI-OH–MeOH (T_2)	
	S_0	S_1	S_0	S_1	S_0	S_1
O_1-H_2	0.9848	1.0033	2.1285	2.6798	2.2581	2.5283
H_2-N_3	2.0255	1.9073	1.0217	1.0325	1.0158	1.0266
O_5-H_4	0.9688	0.9661	0.9792	0.9861	0.9759	0.9820
H_4-O_1	1.9888	2.1007	1.7817	1.6720	1.8048	1.7047
$\delta(O_1-H_2-N_3)$	144.1	147.9	133.3	118.5	129.1	119.6
$\delta(O_5-H_4-O_1)$	159.7	152.7	169.1	164.7	169.1	161.1
O_6-H_7	0.9847	1.0030	0.9827	0.9986	2.2523	2.5250
H_7-N_8	2.0278	1.9105	2.0706	1.8643	1.0159	1.0266
$O_{10}-H_9$	0.9689	0.9662	0.9684	0.9682	0.9760	0.9821
H_9-O_6	1.9827	2.1039	2.0045	2.0065	1.8012	1.7052
$\delta(O_6-H_7-N_8)$	144.1	147.9	142.9	148.1	129.3	119.5
$\delta(O_{10}-H_9-O_6)$	160.3	152.6	161.7	156.7	168.3	160.9

Fig. 9 Frontier molecular orbitals (HOMO and LUMO) of BPI-OH-MeOH (N)

of the solvent is 0.45 and 0.75 kcal/mol, respectively, which indicates that the solvent TOL has a greater influence on the second step proton transfer. In the S_1 state, for the two-step proton transfer reaction, the reaction barrier of the second proton transfer is higher than that of the first proton transfer. In the BPI-OH system, the ESIPT can be happened to form BPI-OH (T_1) or BPI-OH (T_2) in S_1 state through proton transfer path (BPI-OH (N) $\rightarrow$ BPI-OH (T_1) $\rightarrow$ BPI-OH (T_2)). In addition, BPI-OH (T_1) and BPI-OH (T_2) return to the S_0 state by a radiative transition. The relative high energy barrier prevents BPI-OH (T_1) and BPI-OH (T_2) molecules from undergoing a reverse proton transfer. Meanwhile, we also show the intramolecular proton processes of the whole molecule in the S_0 and S_1 states (Fig. 8).

3.4 BPI-OH-MeOH complex

Then, the effect of explicit solvent (methanol) on the excited state properties of BPI-OH compound are investigated, and

we optimized the N, T_1 and T_2 forms of BPI-OH-MeOH (shown in Fig. S2). In view of previous reports, methanol molecules were also considered at the donor site in this study [51, 52]. The significant parameters of the BPI-OH-MeOH-N, BPI-OH-MeOH- T_1 and BPI-OH-MeOH- T_2 are listed in Table 3. For example, the O_1 - H_2 bond length change from 0.9848 Å in the S_0 state to 1.0033 Å in the S_1 state (increasing 0.0185 Å) and the H_2 - N_3 bond length change from 2.0255 Å in the S_0 state to 1.9073 Å in the S_1 state (decreasing 0.1182 Å) for BPI-OH-MeOH (N). Meanwhile, the O_5 - H_4 bond length change from 0.9688 Å in the S_0 state to 0.9611 Å in the S_1 state (decreasing 0.0077 Å) and the H_4 - O_1 bond length change from 1.9888 Å in the S_0 state to 2.1007 Å in the S_1 state (increasing 0.1119 Å). The changes of the geometric structure parameters instruct that the hydrogen bond is enhanced and the change values of bond length and angle of compound BPI-OH in explicit solvents is more obvious than that in implicit solvents, in the S_1 state. That is because compound BPI-OH is subjected to more hydrogen bonding forces in explicit solvent (methanol).

The absorption and emission spectra of BPI-OH-MeOH complex are computed (shown in Fig. S3), which are in good agreement with the spectra provided in the experiment [34]. Meanwhile, the FMOs of BPI-OH-MeOH (N) are shown in Fig. 9. The calculated wavelengths, corresponding oscillator strength (f) are listed in Table S3. Herein, the HOMO and LUMO, lead to the distinct $\pi \rightarrow \pi^*$ feature of $S_0 \rightarrow S_1$ transition. The energy gap is 2.466 eV, which is lower than that of other implicit solvents, indicating higher stability of the BPI-OH-MeOH complex in the explicit solvent.

PECs were constructed to gain the effects of explicit solvent on ESIPT (shown in Fig. 10). The reaction barrier for BPI-OH-MeOH (N) $\rightarrow$ BPI-OH-MeOH (T_1) is 0.91 kcal/mol in the S_1 state. Then, the energy barrier of proton transfer reaction from BPI-OH-MeOH (T_1) to BPI-OH-MeOH (T_2) in the S_1 state is 1.23 kcal/mol. Importantly, the complex is more likely to undergo the ESIPT process in explicit solvents than in implicit solvents, because it is subjected to more intermolecular hydrogen bonding in explicit solvents.

Fig. 10 Potential energy curves of the S_0 and S_1 states for BPI-OH-MeOH complex along with the O_1 - H_2 and the O_6 - H_7 bond lengths. (a) BPI-OH-MeOH (N) $\rightarrow$ BPI-OH-MeOH (T_1); (b) BPI-OH-MeOH (T_1) $\rightarrow$ BPI-OH-MeOH (T_2)

Fig. 11 **a** RDG scatter plot of the S_0 state for BPI-OH–MeOH; **b** RDG partial magnification scatter plot and isosurface in MeOH solvent; **c** RDG scatter plot of the S_1 state for BPI-OH–MeOH; **d** RDG partial magnification scatter plot and isosurface in MeOH solvent

To verify our conjecture, we have performed RDG analysis on the explicit solvent of the BPI-OH–MeOH complex.

The hydrogen bonds of BPI-OH–MeOH forms (-0.0402) in the S_0 state are significantly stronger than that in implicit solvents (DMSO: -0.0305 ; MeOH: -0.0305 ; DCM: -0.0308 ; TOL: -0.0312), especially in the S_1 state (BPI-OH–MeOH form is -0.0467) (shown in Fig. 11b, d). Thus, the type of solvent has a more significant effect on hydrogen bond, which also confirms our above conjecture that BPI-OH–MeOH complex is subjected to intermolecular hydrogen bond interactions in the explicit solvent.

4 Conclusion

In conclusion, from the theoretical perspective, we studied the impacts of the solvent polarity and solvent type on the ESIDPT for the BPI-OH molecule. In four kinds of solvents, the hydrogen bonding parameters, RDG analysis and IR spectra of the BPI-OH have been calculated, which illustrate that the strengthening of excited-state H-bonding. The excited-state hydrogen bonding strengthened follows the trend: DMSO < MeOH < DCM < TOL. Meanwhile, according to FMOs and PECs in the S_1 state, as the polarity solvent decrease, ESIPT reaction is favorable to occur. Moreover, in explicit (methanol) solvent, the ESIPT process of BPI-OH–MeOH complex is carried out very little energy potential barrier, which is easier to occur than that

in implicit solvent. In addition, isomers BPI-OH (T_1) and BPI-OH (T_2) can be got through a step-by-step process BPI-OH(N) $\rightarrow$ BPI-OH(T_1) $\rightarrow$ BPI-OH(T_2), which reveals a step-wise ESDPT process.

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Declarations

Conflict of interest There is no conflict of interest.

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