

REGULAR ARTICLE

A DFT/TDDFT investigation on the ESIPT mechanism of a novel sensor BIP

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Abstract: In the present work, (E)-2-(((1H-benzo[d]imidazol-2-yl)-imino)methyl)-5-(dimethylamino)-phenol (BIP), as one kind of the novel and few studied sensors containing both NH and OH binding sites, has been selected to investigate the excited state dynamic properties based on the time-dependent density functional theory (TDDFT) method. Our calculated absorption and fluorescence spectra based on the TDDFT method are in agreement with the experimental results. Two kinds of structures of BIP chromophore (BIP-enol and BIP-keto) are found in the first excited (S_1) state, which should be resulted from the excited state proton transfer reaction. The phenomenon of hydrogen-bond strengthening has been found in the S_1 state, which was based on comparing staple bond lengths and bond angles involved in hydrogen bond between the S_0 state and the S_1 state. In addition, the calculated infrared spectra at the O-H stretching vibrational region and calculated hydrogen bond energy also declare the phenomenon of hydrogen bond strengthening. The frontier molecular orbitals (MOs) analysis and Natural bond orbital (NBO) manifest the intramolecular charge transfer of BIP chromophore, which reveals the tendency of proton transfer. The potential energy surfaces of the S_0 and S_1 states are constructed to explain the mechanism of the proton transfer in excited state in detail.

AMS subject classifications: 65D18, 78M50, 74E40

Keywords: Hydrogen bond; ESIPT; Frontier molecular orbitals; Electronic spectra; Potential

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energy curves.

1. Introduction

As one of the most important weak interactions, hydrogen bond (no matter whether it is inter- or intra- molecular hydrogen bond) is omnipresent in nature, based on which life-cycle can be sustained in the world [1-5]. Hydrogen bond plays important roles in organometallic molecules, crystal packing of many organic, nucleic acids, stabilization of the secondary structure of biomolecules like proteins, and so forth [1-5]. Peculiarly, in biological systems, the dual effect has been found: on one hand, hydrogen bond can be used to establish supramolecular architectures in the form of a conjointly strong directional interaction, which are unescapable for the construction of fundamental building blocks of life [6]. On the other hand, it acts as an active site for the occurrence of a vista of interactions based on its dynamic features [6]. Its significance is conspicuous in various real life examples and a thorough investigation of hydrogen bond interactions will be vital to delve into the critical evaluation of many phenomenon coming up not only in the crystal state, but also in solutions and living organisms [7-9]. Zhao and Han have determined that intermolecular hydrogen bond between solute and solvent molecules should be significantly strengthened in the corresponding electronic excited states after photo-excitation theoretically [10-18], since then, many investigations of mechanism involved in excited state hydrogen bond need to be revisited in physics, chemistry and biology.

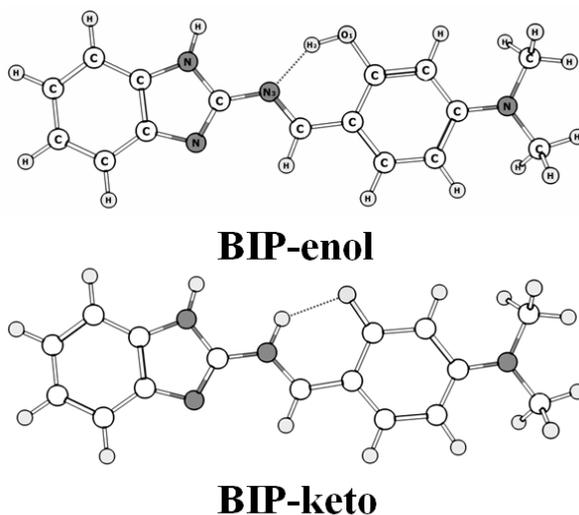


Figure 1: Views of optimized structures for BIP-enol and BIP-keto based on B3LYP/TZVP theoretical level. (BIP-enol: normal BIP structure; BIP-keto: proton transfer BIP structure).

Up to now, many different sensing mechanisms, such as intramolecular charge transfer (ICT), photo-induced electron transfer (PET), fluorescence resonance energy transfer (FRET), and excited state proton transfer (ESPT) and so forth [19-38], are relevant with hydrogen bond. Particularly, the excited state inter- and intra- molecular proton transfer (ESIPT) reactions have been drawing great attention due to their unique photo-physical and photo-chemical properties. Many novel optoelectronic applications, such as fluorescence sensors, laser dyes and LEDs, UV filters, molecular switches and so forth [39-49], are facilitated based on ESIPT reactions. Naturally, the attention focused on this phenomenon is both cognitive and applied, through which it crops up as a demanding subject of research even today.

As one kind of the few reported sensors containing both NH and OH binding sites, the novel sensor (E)-2-(((1H-benzo[d]imidazol-2-yl)-imino)methyl)-5- (dimethylamino)phenol (BIP) was synthesized and reported recently [50]. Bearing both the NH and OH subunits, this novel fluorescence sensor BIP displayed a highly selective and sensitive recognition property for fluoride [50]. Even though this sensor has weak fluorescence, it was reported that the anion-binding adduct of BIP is expected to be highly fluorescent based on ESPT channel experimentally [51, 52], however, the mechanism of BIP in excited state is very limited. In effect, only experimental spectroscopic techniques, such as steady-state absorption spectroscopy, fluorescence spectroscopy and the time resolved fluorescence spectroscopy, just provide the indirect information about photo-physical and photo-chemical properties [10-38]. Up to now, the theoretical investigations about the BIP are very scarce in addition to the experiments. In fact, the theoretical investigations can be adopted to strengthen comprehension on aspects of mechanisms effectively. In the present work, therefore, a quantum chemical computational study has been adopted to investigate the proton transfer mechanism based on the DFT and the TDDFT method in both S_0 and the S_1 states, respectively. The structures of BIP-enol (normal form), BIP-keto (the form after proton transfer) and BIP-open (the non-hydrogen bonded form) have been calculated carefully. Herein, the BIP-open form is that the hydrogen bond -OH group is rotated 180° apart from the hydrogen bonded configuration to generate the non-hydrogen bonded open form. The configurations of S_0 state and S_1 state are optimized, and further vertical excitation energies, IR vibration spectra, the frontier molecular orbitals and homologous S_0 and S_1 states potential energy curves are calculated and analyzed to provide the direct information of the ESIPT process.

2. Computational Details

In the present work, all the calculations of relevant electronic structures were accomplished based on the Gaussian 09 program suite [53]. The geometric optimizations of BIP-enol, BIP-open and BIP-enol were performed using DFT in the S_0 state and using TDDFT in the S_1 state. Especially, the TDDFT method has become a very useful tool to theoretically investigate

the hydrogen bond interaction that occurs in the excited-state of hydrogen-bonded systems [19-38]. In addition, Becke's three-parameter hybrid exchange functional with Lee–Yang–Parr gradient-corrected correlation (B3LYP functional) was selected in both the DFT and TDDFT methods [54-57]. The triple- ζ valence quality with one set of polarization functions (TZVP) [57] was chosen as the basis set throughout, which is an appropriate basis set for the system. No constraints for symmetry, bonds, angles or dihedral angles were applied in the geometric optimization calculations. In order to evaluate the solvent effects, compared with experimental result, acetonitrile (ACN) was selected as the solvent through our calculations based on the polarizable continuum model (PCM) using the integral equation formalism variant (IEFPCM). All the local minima were confirmed by the absence of an imaginary mode in the vibrational analysis calculations. The S_0 and S_1 potential energy surfaces have been scanned by constrained optimizations and frequency analyses to obtain the thermodynamic corrections in their corresponding electronic states, and keeping the O_1-H_2 bond length fixed at a series of values. The potential energy surfaces are constructed beginning from the optimized structure with keeping the O_1-H_2 bond lengths fixed from 0.995 to 2.445 Å.

Fine quadrature grids 4 were also employed. Harmonic vibrational frequencies in both the ground-state and excited-state were determined using diagonalization of the Hessian [58]. The excited-state Hessian was obtained by numerical differentiation of the analytical gradients using central differences and default displacements of 0.02 Bohr [59]. The infrared intensities were determined using the gradients of the dipole moment.

3. Results and discussion

3.1 Geometric structures

The optimized structures of the BIP-enol and BIP-keto of S_0 and S_1 states were obtained based on the B3LYP function with the TZVP basis set and a subsequent vibrational frequency analysis to ensure the validity of the stationary points (shown in **Figure 1**). Considering the consistent with previous experiment [50], ACN has been selected as the reaction solvent in the IEFPCM model. All of the important bond lengths (Å) and bond angles ($^\circ$) involved in hydrogen bond for BIP-enol, BIP-keto and BIP-open forms have been listed in **Table 1**. After comparison, one should be noted that almost little configuration changes can be found among enol and keto as well as open forms except for the bond lengths and angles involved in hydrogen bond. The bond length of O_1-H_2 of the BIP-open form was calculated to be 0.966 Å, which does not change at all when excited to the S_1 state. It can be concluded that photoexcitation does not play any part in O_1-H_2 bond for BIP-open form. However, it changed to be 0.995 Å for BIP-enol form in the S_0 state, which clearly indicates the formation of

hydrogen bond $O_1-H_2\cdots N_3$ in the S_0 state. In addition, it should be noted that the elongation of the O_1-H_2 bond from 0.995 Å in the S_0 state to 0.998 Å in the S_1 state, and the shorting of $H_2\cdots N_3$ bond from 1.731 Å to 1.704 Å with the concomitant enlargement of $O_1-H_2\cdots O_3$ angle from 148.2° to 149.2° following the photoexcitation. Based on these calculated results, the intramolecular hydrogen bond $O_1-H_2\cdots N_3$ is strengthened in the S_1 state [10-18]. In addition, in view of the BIP-keto form, the length of O_1-H_2 ($O_1\cdots H_2$) changes from 1.902 Å in the S_1 state to 1.745 Å in the S_0 state. While the H_2-N_3 changes from 1.022 Å in the S_1 state to 1.037 Å in the S_0 state and the enlargement of $O_1\cdots H_2-N_3$ from 134.2° to 137.6° . It demonstrates that the intramolecular hydrogen bond $O_1\cdots H_2-N_3$ is more stable in the S_0 state than the S_1 state. In other words, BIP-keto* form is likely to undergo the radiative transition to the S_0 state forming the stable BIP-keto structure.

Table 1 Calculated primary bond lengths (Å) and angles ($^\circ$) of BIP-enol, BIP-open and BIP-keto forms in the S_0 and S_1 states.

	BIP-enol		BIP-open		BIP-keto	
	S_0	S_1	S_0	S_1	S_0	S_1
O_1-H_2	0.995	0.998	0.966	0.966	1.745	1.902
H_2-N_3	1.731	1.704	---	---	1.037	1.022
$\delta(O_1-H_2-N_3)$	148.2°	149.2°	---	---	137.6°	134.2°

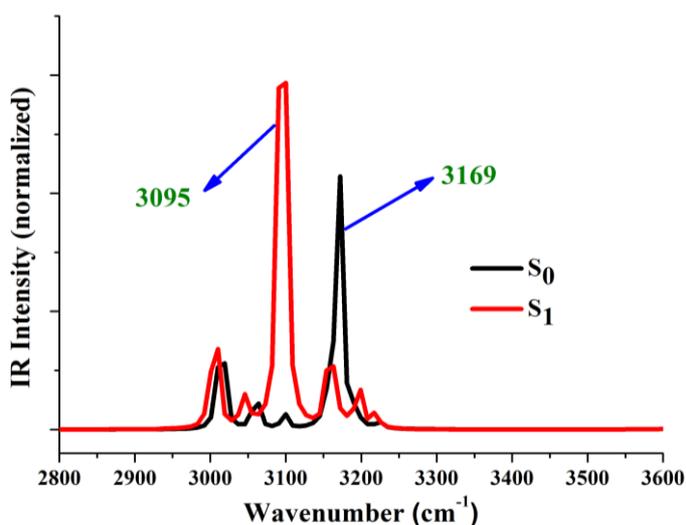


Figure 2: The calculated IR spectra of BIP-enol and BIP-enol* structures in ACN at the spectral region of O-H stretching band.

Furthermore, the hydrogen bond strengthening or weakening could also be revealed based on monitoring the spectral shifts of vibrational modes involved in the formation of hydrogen bonds [10-18, 38-46]. The vibrational spectra of BIP-enol chromophore in the conjunct vibrational regions of the O₁-H₂ stretching modes have been shown in **Figure 2**. It should be noted that the calculated O₁-H₂ stretching vibrational frequency is located at 3169 cm⁻¹ in the S₀ state, whereas it is located at 3095 cm⁻¹ in the S₁ state. The 74 cm⁻¹ red-shift of O₁-H₂ stretching frequency demonstrates intramolecular hydrogen bond O₁-H₂...O₃ was strengthened in the S₁ state. In addition, the strong and intuitional evidence, the energy of hydrogen bond, has also been provided based on the method that the energy of BIP-enol form minus the energy of BIP-open form [60]. In other words, a representative plot of variation of energy as a function of the twist angle leads to the formation of the nonhydrogen-bonded open form from hydrogen-bonded enol and keto forms. Our calculated results demonstrates that the hydrogen bond energy is 7.52 kcal/mol in the S₀ state and 10.85 kcal/mol in the S₁ state, which further indicates the intramolecular hydrogen bond is strengthened. Therefore, the conclusion of strengthened hydrogen bond in the S₁ state may be a tendency of the ESIPT process.

3.2 Electronic spectra and Frontier Molecular Orbitals

Based on the TDDFT/B3LYP/TZVP calculated level, the corresponding absorption and fluorescence spectra of BIP structures have been calculated carefully. Although the steady-state spectral characters of BIP chromophore have been reported in the experiment [50], the investigations of the proton transfer mechanism are very limited theoretically. The theoretical results show that calculated absorption peak of BIP-enol is located at 401 nm (listed in **Table 2**), which is in consistent with 410 in the experiment [50]. The first excited state of BIP-enol chromophore has been fully optimized based on the ground state optimized geometric conformations as the initial conformations with the TDDFT method. In effect, the first excited state has two structures. The one is BIP-enol*, and the other is BIP-keto*. The fluorescent result of BIP-enol* reveals a normal emission maximum in ACN (434 nm), which is also in consistent with the experimental result [50]. All these agreements with previous experiment demonstrate that the method we adopted could reasonably shed light on the excited-stated properties of BIP chromophore in ACN solvent. In fact, the phenomenon of ESIPT is percussion of the substantial adjustment of electronic charge density distribution on the heavy atoms induced by photoexcitation. The detailed investigation of the charge distribution over the atoms involved in intra- or inter- molecular hydrogen bond can be used as a reasonable evidence to explore the proton transfer reaction based on the Mulliken's charge distribution analysis method. The one should be noted that the decrease of negative charge distribution about O₁ atom of the O₁-H₂ moiety is from -0.439 in the S₀ state to -0.385 in

the S_1 state together with the increase on the N_3 atom from -0.292 to -0.354 based on the B3LYP/TZVP theoretical level. In addition, the NBO analysis method has also been used to study the charge distribution. The analogous results that the decrease of O_1 atom negative charge distribution from -0.595 to -0.551 and increase of N_3 atom negative charge distribution from -0.559 to -0.602 have also been concluded. Therefore, the ESIPT process can be predicted based on the above discussion.

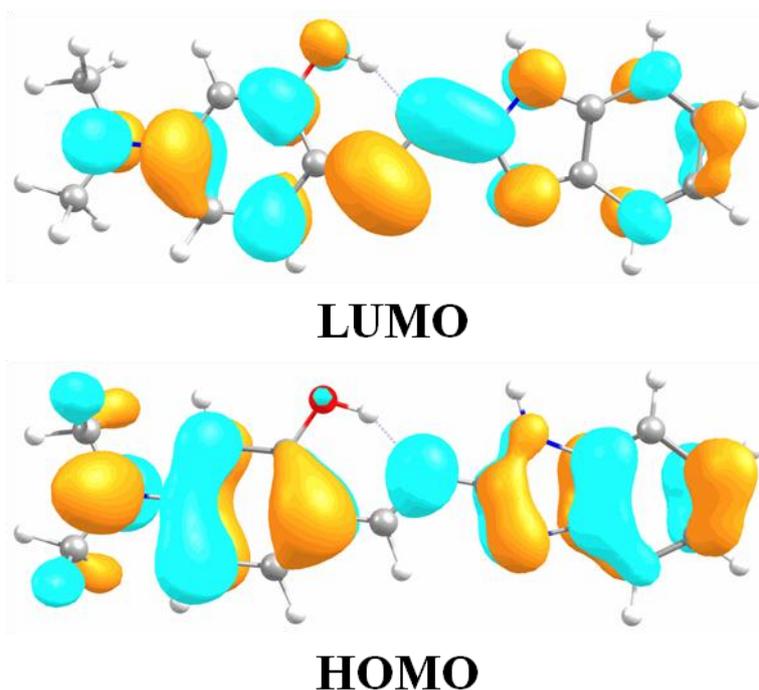


Figure 3: Views of HOMO and LUMO orbitals for BIP-enol structure.

Table 2 Electronic excitation energy (nm), corresponding oscillator strengths and the corresponding compositions of the low-lying singlet excited states for BIP-enol form.

	Transition	λ (nm)	f	Composition	CI (%)
	$S_0 \rightarrow S_1$	401	1.4926	H \rightarrow L	98.41%
BIP-enol	$S_0 \rightarrow S_2$	327	0.0163	H-3 \rightarrow L	32.32%
				H-1 \rightarrow L	49.79%

In addition, since the variation of charge distribution can deepen understanding of excited state dynamic behavior [10-18], therefore, it is necessary to focus on charge

distribution in the process of photoexcitation. The frontier molecular orbitals (MOs) of the BIP-enol in ACN solvent are shown in **Figure 3**. Herein, only the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) are shown, because the S_1 state is mainly associated with these two orbitals (shown in **Table 2**). The π character for the HOMO as well as the π^* character for LUMO can be seen clearly. Therefore, it is determined that the first excited state is due to a distinct $\pi\pi^*$ feature. Furthermore, one should be noticed that the HOMO and LUMO are localized on different moieties of BIP-enol structure, especially, the part involved in the intramolecular hydrogen bond $O_1-H_2\cdots N_3$. To be specific, the electron density of hydroxyl moiety decreases and of N atom increases upon the transition from HOMO to LUMO. That is to say, the first excited state is the intramolecular charge transfer state, and the change of electron density in the hydroxide radical moiety can directly enhance the intramolecular hydrogen bond $O_1-H_2\cdots N_3$ and promote excited state proton transfer. Consequently, excited-state BIP should favor protonation of the -N- group and deprotonation of the hydroxide group. Therefore, the ESIPT process is expected to happen due to the intramolecular charge transfer.

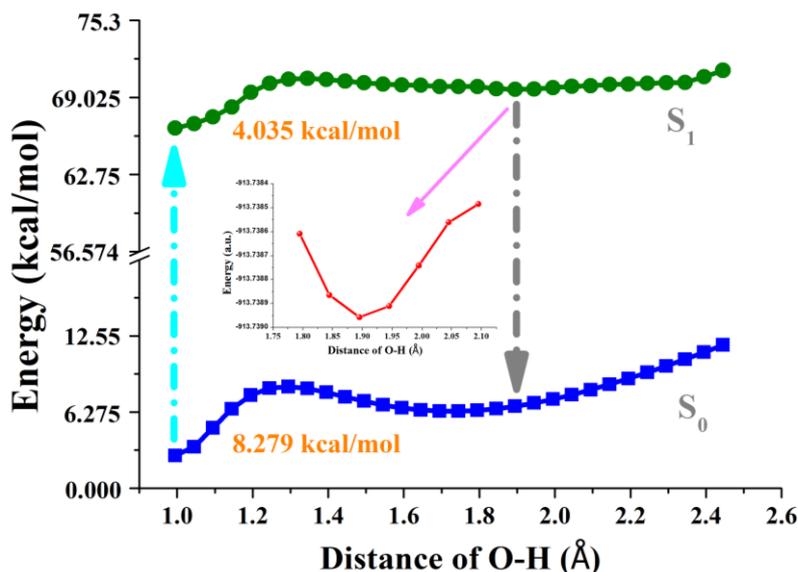


Figure 4: The constructed potential energy curves of both S_0 and S_1 states of BIP as functions of both O_1-H_2 bond length. The inset shows the amplifying part of S_1 -state potential energy curves.

3.3 The potential energy curves and the PT mechanism

Different from previous experiment, in the present work, the specific potential barriers in both S_0 and S_1 states have been provided based on quantum chemical computational study,

which could deepen comprehending the ESIPT mechanism. Even though the TDDFT/B3LYP calculated level may not be expected to be precise sufficiently to decide the correct ordering of the closely spaced excited states, investigations have indicated that this method may be efficient as far as the form of hydrogen-transfer potential energy curves is concerned [10-38]. It can provide qualitative energetic pathways for the ESIPT process of BIP chromophore. Therefore, in the present work, the S_0 state and the S_1 state potential energy surfaces have been scanned, which is based on constrained optimizations in their corresponding electronic states keeping the O_1-H_2 distances fixed from 0.995 to 2.445 Å in steps of 0.05 Å. We have to say that the process of constructing potential energy surfaces is very time-consuming, even though the 0.05 Å may be a little larger selected for the step, it is enough to depict the detailed tendency of proton transfer process in potential energy surfaces (shown in **Figure 4**). It should be noted that the high energy barrier (about 8.279 kcal/mol) in the S_0 state dictates that non-viability for the ground state intramolecular proton transfer process. As can be seen in **Figure 4**, the S_1 -surface reflects remarkable reduction of the potential barrier (about 4.035 kcal/mol) across the proton transfer coordinate following the photoexcitation from the S_0 state. In other words, the proton transfer process should be more likely to occur in the S_1 state than S_0 state. In addition, it can be also found that the potential energy barrier from BIP-keto* form reversing to BIP-enol* is almost neglectful (herein, we do not provide the insignificant value), that is to say, the ESIPT and reverse ESIPT processes can occur in the S_1 state. Even though the fluorescent intensity was not reported in previous experimental work, we can forecast that the fluorescent intensity of BIP-enol* may be higher than BIP-keto* due to the reverse ESIPT process from BIP-keto* to BIP-enol*. Therefore, the ESIPT can be concluded as follow (seen in **Figure 5**): Upon the photoexcitation, the BIP-enol in the S_0 state is excited to become BIP-enol* form in the S_1 state, then, ESIPT process occurs with crossing a lower potential barrier forming the BIP-keto* form in the S_1 state. Subsequently, the BIP-keto* decays to the ground state BIP-keto form through radiating fluorescence, which induces the distinct bathochromic shift in their fluorescence emission spectra as compared with that of BIP-enol* structure. In addition, due to the lower potential energy barrier in the S_1 state, BIP-enol* and BIP-keto* forms could coexist based on ESIPT and reverse ESIPT processes. Therefore, it provides a possible explanation for the fluorescence quenching. In addition, the BIP-keto form can undergo the reverse ground state proton transfer process back to BIP-enol form with the inappreciable potential barrier.

4. Conclusion

In summary, the ESIPT mechanism of BIP chromophore has been investigated based on the calculated geometries, electronic spectra and potential energy curves using DFT and TDDFT methods. The absorption and fluorescence spectra are well represented by the vertical

transition energies calculated based on the optimized geometries of S_0 and S_1 states. A relatively stronger intramolecular hydrogen bond has been testified based on bond lengths, bond angles and corresponding IR vibrational spectra involved in hydrogen bond in the S_1 state. The further calculations of hydrogen bond energy also prove this point. In order to discuss the condition of charge distribution and charge transfer qualitatively, the homologous frontier MOs were also analyzed. The increased electron density of N_3 atom of BIP-enol can enhance the intramolecular hydrogen bond, which promotes the proton transfer effectively. Based on the viewpoint of valence bond theory, the interplay between lone pair of N_3 atom and O_1-H_2 σ^* orbital is mainly conscientious for ESIPT process. The charge analysis using NBO and Mulliken population have been done in both S_0 and S_1 states. The constructed potential energy surfaces demonstrate that the ESIPT process can happen due to the relative lower potential barrier. After proton movement on the S_1 state, BIP-keto* decays to the S_0 state through fluorescence, which is quenched due to the ESIPT process.

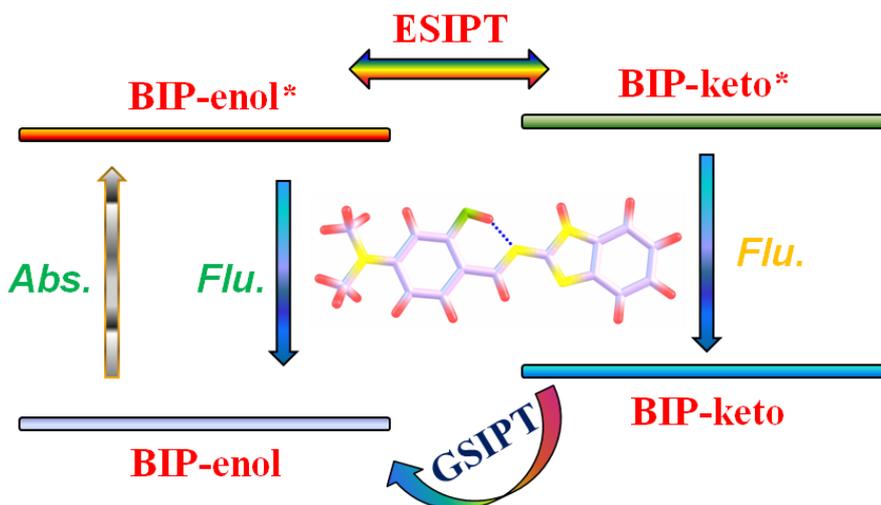


Figure 5: The schematic diagram of dynamic process for BIP sensor in both S_0 and S_1 states.

Acknowledgements

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