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Straightforward Stepwise Excited State Dual Proton Transfer Mechanism for 9-10-HBQ System

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Abstract: A new molecule 9,10-dihydroxybenzo[h] quinoline (i.e. 9-10-HBQ) is focused in the present work about its excited state proton transfer (ESPT) mechanism. Though comparing potential energy barriers, it is found that the ultrafast ESPT process could occur in the S_1 state without potential energy barrier along with hydrogen bond O_3-H_4···N_5 forming 9-10-HBQ-PT1 structure, subsequently, the second proton transfers via another intramolecular hydrogen bonded wire O_1-H_2···N_3 with a low potential energy barrier (about 7.69 kcal/mol) in the S_1 state forming 9-10-HBQ-PT2 configuration. After completing excited state dynamical process, the S_1-state could turn back to S_0 state with occurring reversed ground state proton transfer forming initial 9-10-HBQ structure.

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

Keywords: Proton transfer; frontier molecular orbital analysis; potential energy curves.

Due to its significance in nature, hydrogen bond has drawn great attention on the relevant topics [1-4]. Particularly, excited state hydrogen bond dynamics, elaborating properties involved in hydrogen bond in the excited state, plays important roles in many photophysical and photochemical processes, such as photo-induced electron transfer (PET), intra- or inter-molecular charge transfer (ICT), fluorescence resonance energy transfer (FRET), and so forth [5-8]. As one of the fast and quite complex reactions involved in hydrogen bond, the excited

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state intra- or inter- molecular proton transfer (ESIPT) is considered to be one of the most fundamental and important processes in chemistry, biology and materials [9-14]. Since half a century ago, the ESIPT process was firstly reported by Weller and co-workers in experiment with methylsalicylate [15], it has been a popular research [16-19]. The proton-transfer tautomerization form (normally named keto in the S_0 state and keto* in the S_1 state) has charge redistribution characteristic, which are very fascinating towards the application of laser dyes, UV filters, fluorescence chemosensors, molecular switch, and so on [20-23]. Furthermore, some molecules are highly sensitive to the change in the microenvironments, based on which Sytnik *et al*. reported how the ESIPT chromophores can be used in the study of protein conformations and binding site polarity [24]. Indeed, a lot of spectroscopic techniques were applied to study the ESIPT process in recent years, however, only some indirect information about photochemical and photophysical properties could be provided through experimental investigations, and thus the explanation of ESIPT mechanism still have numerous challenges.

In effect, most of previous reports about ESIPT reactions are single-proton transfer, which occurs along with one intra- or inter- hydrogen bonded wire. Whereas only investigating about this kind of single-proton transfer process in the excited state is not enough, since more and more proton transfer processes in biological systems refer to multiple-proton transfer reactions [25]. Therefore, as a fundamental bridge, more and more inter- or intra- molecular systems containing double or multiple hydrogen bonds have been focused [26, 27]. Recently, as a kind of 10-hydroxybenzo[h]quinoline (10-HBQ) derivative, a

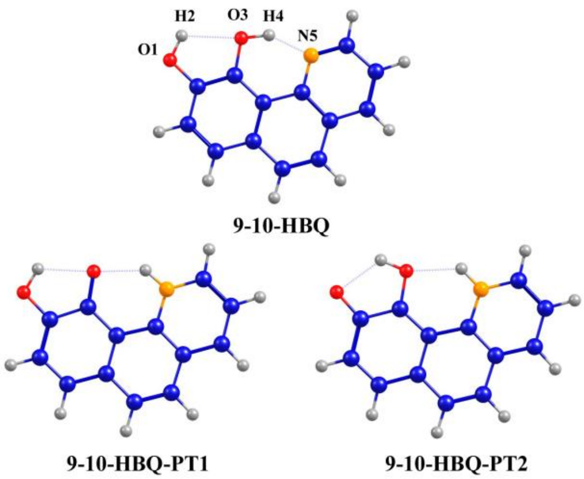

Figure 1: Views of optimized structures for 9-10-HBQ structures (9-10-HBQ-PT1: the single-proton transfer form; 9-10-HBQ-PT2: the double-proton transfer form) based on B3LYP/TZVP theoretical level. (Blue: C atom; Gray: H atom; Yellow: N atom; Red: O atom).

new molecule 9,10-dihydroxybenzo[h]quinoline (9-10-HBQ), containing two intramolecular hydrogen bonds (see **Figure 1**), was synthesized and characterized by UV-Vis spectra [28]. For sake of the interpretation of experimental data, the absorption and emission spectra of 9-10-HBQ and its photo tautomer were simulated using time-dependent DFT (TD-DFT) calculations; however, solvent effect of dichloromethane, which has significant influence on the intramolecular hydrogen bond strength and ESIPT process, was not considered in their calculations. Structurally, 9-10-HBQ is similar to 7-hydroxyquinoline-8-carboxylic acid [26] and 1,8-dihydroxy-2-naphthaldehyde [38], whether 9-10-HBQ can also occur excited state double proton transfer (ESDPT) process? In addition, 10-HBQ is a classical ESIPT molecule and reported in numerous previous works [29-33], whether the 9-10-HBQ owns the similar properties with 10-HBQ is also worth to be discussed.

In this work, all the theoretical calculations presented were accomplished using the DFT and TDDFT methods with Becke's three-parameter hybrid exchange function with the Lee–Yang–Parr gradient-corrected correlation functional (B3LYP) [34-37] as well as the triple-ζ valence quality with one set of polarisation functions (TZVP) [38] basis set by Gaussian 09 programs [39]. Solvent effects (dichloromethane) were included in all calculations based on the Polarizable Continuum Model (PCM) using the integral equation formalism variant (IEF-PCM) [40-42] in our work. All the ground-stated geometries of all the relative structures were optimized without constraint based on DFT methodology, in addition, vibrational frequencies were analyzed at the optimized forms to confirm that all these configurations corresponds to the local minima on the S_0 potential energy curve. All the stationary points along the reaction coordinate were scanned by constraining optimizations and frequency analyses (no imaginary frequency) to obtain the thermodynamic corrections in the corresponding electronic state.

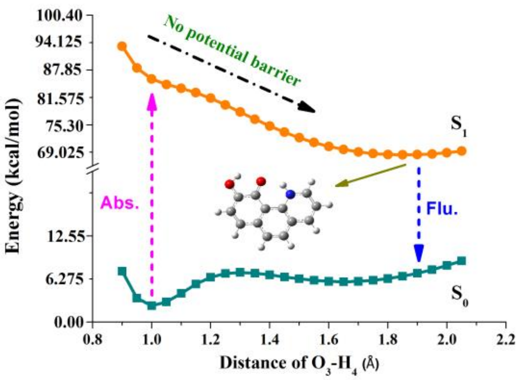

Figure 2: The constructed potential energy curves of both S_0 and S_1 states of 9-10-HBQ as functions of keeping O_3-H_4 bond length fixed from 0.85 to 2.05 Å in steps of 0.05 Å.

Three kinds of stable structures 9-10-HBQ, 9-10-HBQ-PT1 and 9-10-HBQ-PT2 involved in this work have been calculated based on DFT (S_0 state) and TDDFT (S_1 state) methods (see **Figure 1**). It is interesting that the optimized S_1-state 9-10-HBQ structure is identical to the optimization result of 9-10-HBQ-PT1, that is to say, maybe there is not stable 9-10-HBQ configuration in the S_1 state, and the ultrafast ESIPT process occurs without potential energy barrier upon photo excitation. To verify our speculation, we have constructed the potential energy curves of 9-10-HBQ system at S_0 and S_1 states, as shown in **Figure 2**. It is worth mentioning that some previous work has indicated the feasibility of DFT and TDDFT methods to provide qualitative energetic pathways for inter- or intra- molecular proton transfer process [43-45]. From **Figure 2**, it can be clearly found that a no potential barrier process happens in the S_1 state along with the increase of O_3-H_4 bond length from 0.85 to 2.05 Å in steps of 0.05 Å. For the S_0 state, however, it needs to cross a potential energy barrier to finish the proton transfer reaction. Compared to the S_1-state barrierless process, we believe that 9-10-HBQ is more likely to occur ESIPT process.

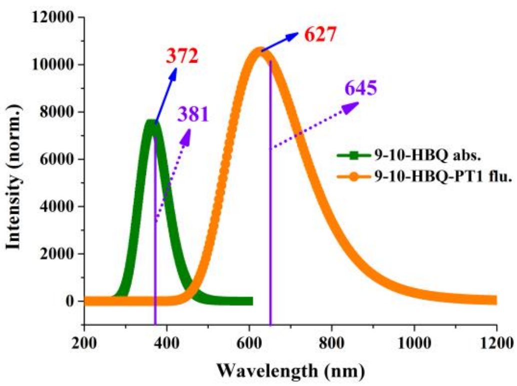

Figure 3: The calculated absorption and fluorescence spectra of 9-10-HBQ and 9-10-HBQ-PT1 at the TDDFT/B3LYP/TZVP theoretical level. Herein, vertical lines denote experimental results.

Furthermore, we also calculated the absorption and fluorescence spectra of 9-10-HBQ system to verify the validity of our calculations. The simulation results are displayed in **Figure 3**, and the vertical lines denote experimental results reported by Chen *et al*. [28]. It should be noted that our calculated absorption peak for 9-10-HBQ is located at 372 nm, which is in consistent with experimental result (381 nm) [28]. Due to no stable S_1-state 9-10-HBQ configuration, we can only provide the fluorescence peak of 9-10-HBQ-PT1 structure. Also the calculated emission peak (627 nm) is in good agreement with experiment (645 nm). The good consistence between our simulation results and experimental data shows that the theoretical level we adopted can delineate the excited-state properties of

9-10-HBQ system well. Furthermore, as a well-known photochemical phenomenon, charge distribution over the studied molecule should be changed within the framework of photo excitation, which has an important effect on excited-state dynamical process [5-8]. Particularly, the frontier molecular orbitals (MOs) could provide information about properties of excited-state structures on qualitative discussion of charge distribution. For 9-10-HBQ, it can be assigned as a dominant $\pi\pi^*$ type transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) with the percentage of 95.42% as shown in **Figure 4**. It should be noticed that the electron density of N_5 atom increases, while those of both O_1 and O_3 atoms decreases upon the transition from HOMO to LUMO. That is to say, from the viewpoint of valence bond theory, the increased electron density of N_5 atom could enhance intramolecular hydrogen bond (O_3-H_4···N_5), which promotes the ESIPT process of 9-10-HBQ depicted in **Figure 2**.

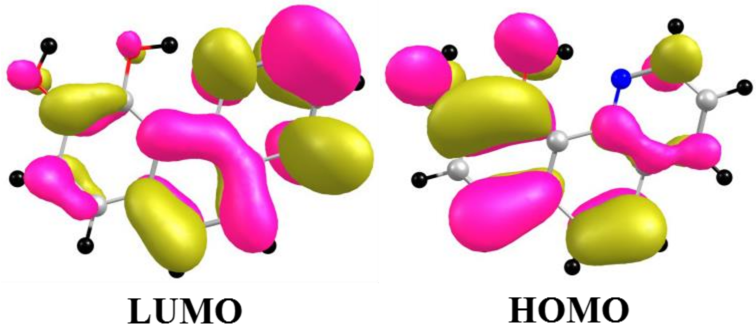

Figure 4: View of frontier molecular orbitals (HOMO and LUMO) for 9-10-HBQ system.

It is noteworthy that even though the ESIPT process via O_3-H_4···N_5 is smooth without barrier; the charge variation on O_1 atom should not be neglected. Just as the changes of electron density on O_1 (see **Figure 4**), upon the excitation, charge population drops from HOMO to LUMO orbital. Therefore, it is also necessary to consider the second hydrogen bond (O_1-H_2···O_3) of 9-10-HBQ-PT1 structure. To judge whether the second proton transfer occurs, we have constructed the potential energy curve as function of O_1-H_2 bond length (shown in **Figure 5**). In the S_1-state potential curve, we found a barrier (around 7.69 kcal/mol) crossing the proton (H_2) from O_1 to O_3. This low potential barrier is reasonable for completing ESIPT process on the excited state potential energy surfaces. In addition, we optimized the 9-10-HBQ-PT2 form and found an about 819 nm fluorescence peak with low oscillator strength (0.0749). Noticing this little oscillator strength, we believe that it is different to be observed by experimental measurement. And we have to mention that the 819 nm fluorescence peak is close to the near infrared region, which is also a difficulty for experimental observations. Also, the previous experimental maximum UV-Vis region is 750 nm, we speculate it is not enough to detect the emission peak of 9-10-HBQ-PT2 form. Our calculation results here it to be proven by further experiments. Till now, we could show the excited state dynamical process of 9-10-HBQ system in **Figure 6**. It is confirmed that 9-10-HBQ could occur stepwise excited state dual proton transfer process, and then radiate back to the S_0 state with reversed ground state dual proton transfer reaction.

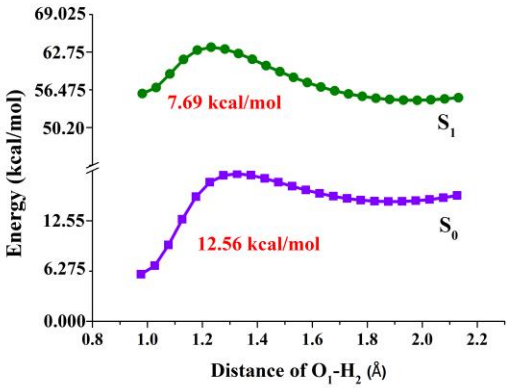

Figure 5: The constructed potential energy curves of both S_0 and S_1 states starting from 9-10-HBQ-PT1 form to 9-10-HBQ-PT2 form as functions with keeping O_1-H_2 bond length in steps of 0.05 Å.

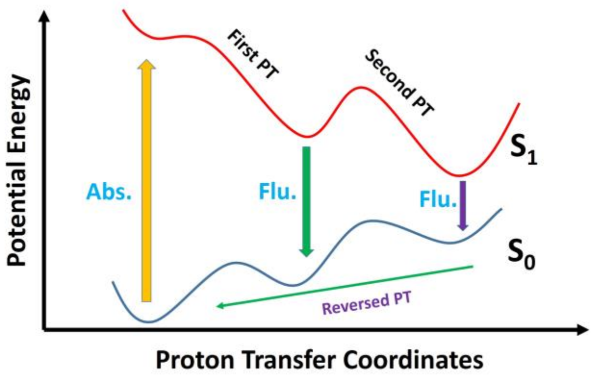

Figure 6: A schematic diagram indicating the stepwise excited-state and ground-state dual proton transfer process.

In summary, in this present work, within the framework of DFT and TDDFT methods with B3LYP/TZVP theoretical level, we have investigated the ESIPT mechanism for 9-10-HBQ system. It is undeniable that the intramolecular hydrogen bond (O_3-$H_4\cdots N_5$) is strengthened in the S_1 state, which facilitates the ESIPT reaction. Due to the ESIPT process without potential energy barrier, only the 9-10-HBQ-PT1 form can be optimized based on

9-10-HBQ structure. Then along with the hydrogen bond O_1-H_2···O_3, 9-10-HBQ-PT form occurs ESIPT process forming 9-10-HBQ-PT2 structure with a low potential energy barrier (7.69 kcal/mol). We put forward a new ESIPT mechanism for 9-10-HBQ system that double proton transfer process could occur step by step. After finishing excited state dynamical process, the 9-10-HBQ-PT2 radiates an around 819 nm fluorescence back to the S_0 state. Then the reversed ground-state double proton transfer takes place from S_0-state 9-10-HBQ-PT2 back to initial 9-10-HBQ structure.

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