

CHAPTER 4

Conclusions

Theoretical studies of ESPT reactions of HBO and its derivatives have been systematically studied both static and dynamics calculations. The concluding remarks are summarized as follows.

From Chapter 1, the appropriate positions of the proton donor and acceptor play an important role in promoting the ESPT of the molecule. Either ESIntraPT or ESInterPT possibly occurs depending on the nature of chemical structures. The photo-tautomerization of ESPT molecules driven by an increase of the acidity of the proton donor can take place through an intrinsic intramolecular hydrogen bond. To utilize the HBO and its derivatives as a fluorescent sensor, the detailed information of HBO with and without interacting with water molecule are performed using dynamics simulations at high accurate level of ADC(2). The ADC(2) excited-state energies similar to that obtained at CC2 level can provide accurate excitation energies for the excited-state dynamics simulations of HBO with small clusters of water. For predicted photophysical properties of HBO and its derivatives as a representative system for the ESPT, cost-effective methods at DFT and TD-DFT calculations are utilized as a screening tool to validate methods that give small deviation from the experimental data. DFT and TD-DFT calculations are accurate and adequate to simulate the photophysical properties of the HBO and its derivatives.

From Chapter 2, different conformations of ground-state geometries of free HBO and its hydrated clusters were calculated at MP2 level of theory. For free HBO, the lowest energy (most stable) geometry is *syn*-HBO which is confirmed by our calculations and previous studies at B3LYP [76] and MP2 [33] levels. The static calculations at MP2 level can be used to support and to confirm structures responsible for its spectral peak from the experiment. While, the stable structures of its hydrated clusters are the intramolecular hydrogen-bonded and intermolecular hydrogen-bonded

HBO. In addition, the intramolecular hydrogen-bonded HBO is more stable than the intermolecular hydrogen-bonded HBO and their optimized energies are slightly different for about 1 kcal.mol⁻¹.

So, they were chosen as starting conformations for excited-state dynamics simulations at ADC(2). For free HBO, ESIntraPT takes place through the intrinsic intramolecular hydrogen bond in timescale of 28 fs. While HBO with one water, two possible pathways (ESIntraPT or ESInterPT) may occur depending on the initial structures. Two different types of cluster structures in the ground state can be envisaged: in the first, the intramolecular hydrogen bond in HBO is surrounded by a water molecule (intramolecular hydrogen-bonded HBO); in the second, the intramolecular hydrogen bond in HBO is broken, and the -OH group and the -N atom of HBO are connected through a network of water (intermolecular hydrogen-bonded HBO). A water molecule in the HBO(H₂O) systems makes PT time slower than in free HBO. The hydrogen bond rearrangement of the intermolecular hydrogen-bonded structure takes place to form the intramolecular hydrogen bonding and complete PT. This slow process of PT occurs because of the competition between the formations of intramolecular and intermolecular hydrogen bonds of HBO and a water molecule. The PT times of the starting intramolecular hydrogen-bonded HBO, the starting intermolecular hydrogen-bonded HBO and the hydrogen bond rearrangement of the intermolecular hydrogen-bonded HBO are about twice, thrice and sixth times lower than that of free HBO, respectively. Therefore, the excited-state dynamics simulations of HBO and its clusters provide clear pictures of facilitating and delaying reaction mechanisms and can be used for further studies in the target systems with solvents.

From Chapter 3, we reveal the effect of electron donating and withdrawing groups introducing into HBO. To validate our method of choice, geometry optimization and enol absorption of HBO were calculated using five different DFT and TD-DFT calculations. From method of choice, TD-B3LYP calculation in the gas and cyclohexane was found to provide the best results in predicting the enol absorption of HBO with the smallest deviation from the experiment. So, B3LYP and TD-B3LYP were performed to predict photophysical properties of HBO derivatives. For enol

absorption, maxima of HBO having electron-withdrawing groups give red-shift corresponding to their lower HOMO-LUMO energy gaps compared to that of HBO.

For keto emission, blue-shift or red-shift emission depends on position and substituent. Either electron-donating or withdrawing groups on the phenyl ring give blue-shift as well as electron-donating group substituted in benzoxazole moiety. While, electron-withdrawing groups on the benzoxazole moiety give red-shift compared to HBO. In addition, HOMO-LUMO energy gaps of HBO derivatives can explain the blue-shift and red-shift emission corresponding to that of HBO. The substituents on HBO affect both HOMO and LUMO energy levels. Electron-donating groups lift LUMO energy level up rather than lower HOMO energy level resulting in larger HOMO-LUMO gaps but these gaps are slightly different in some HBO derivatives. Whereas, electron-withdrawing groups lower both HOMO and LUMO energy levels especially lower LUMO energy level, resulting in narrower HOMO-LUMO energy gaps than that of HBO. Blue- to red-shift emissions are ranged by the increase of the electron-withdrawing ability of substituents. Thus, to make HBO derivatives as candidates for use as fluorescent sensors that provide high intensity of emission, large Stokes shift, and emission in the longer wavelength, HBO having strong electron-withdrawing groups substituted on the benzoxazole moiety is recommended.

To conclude, utilizing the unique photophysical properties of HBO and its derivatives is very useful for the molecular design for the ESIntraPT molecules. The prediction from the computational calculations is helpful to interpretation of experimental results and can be used as a screening tool to guide chemists for synthesizing new HBO derivatives.