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An investigation of excited-state intramolecular proton transfer mechanism of new chromophore

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Abstract. Based on the time-dependent density functional theory (TDDFT), the excited state intramolecular proton transfer (ESIPT) mechanism of a new compound 1 chromophore synthesized and designed by Liu *et al.* [Journal of Photochemistry and Photobiology B: Biology., 138 (2014), 75-79] has been investigated theoretically. The calculations of primary bond lengths, angles and the IR vibrational spectra verified the intramolecular hydrogen bond was strengthened. The fact that reproducing the experimental absorbance and fluorescence emission spectra well theoretically demonstrates that the TDDFT theory we adopted is reasonable and effective. In addition, intramolecular charge transfer based on the frontier molecular orbitals demonstrated the indication of the ESIPT reaction. The constructed potential energy curves of ground state and the first excited state based on keeping the O-H distance fixed at a serious of values have been used to illustrate the ESIPT process. A little barrier of 2.45 kcal/mol in the first excited state potential energy curve provided the transfer mechanism. Further, the phenomenon of fluorescence quenching has been explained reasonably based on the ESIPT mechanism.

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Key words: Hydrogen bond; ESIPT; TDDFT; Potential energy curve.

1 Introduction

The hydrogen bonding interaction has formed the nucleus of intensive research for years due to its pivotal roles in physics, chemistry, and biology [1-14]. Proton transfer (PT), as

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one fundamental class of photochemistry, has attracted more and more attentions along hydrogen bonding in recent years [15-30]. In fact, in the middle of the last century, the investigation of the excited-state intramolecular proton transfer (ESIPT) reaction has been a new arena of research in the field of photochemistry since the experimental observation of the phenomenon reported by Weller *et al.* firstly [31, 32]. PT occurs containing both acidic and basic groups in close proximity, which could rearrange structures in the electronic excited state via a proton or hydrogen atom transfer. After photo-excitation, the molecules could be projected on a potential energy surface, which could make the position of a proton unstable. The driving force for the transformation could be provided based on the energy difference between the locally excited state and the relaxed excited state. In turn, the slope of the surface connecting these two points determines the relative kinetics. The stationary fluorescence spectroscopy provides important indications of the occurrence of proton transfer in the excited state. The observation of a nearly mirror symmetry between absorption and fluorescence spectra demonstrates that the nuclear configuration of the molecule and its surrounding medium remains close to that of the ground state over the timescale of the excited state lifetime. And the effect of the proton transfer on the Frank-Condon factors is enough to result in the break-up of the mirror symmetry. The light emission originating from the proton-transferred state occurs at longer wavelength with a red shift with respect to absorption ranging. It is hence possible to interpret the normal, shorter wavelength emission as originating from the locally excited state, and to associate the red shifted long wavelength emission with the product of the proton transfer.

Recently, a new compound 1 chromophore has been synthesized and designed by Liu *et al.* [33], which shows high selectivity for some biologically ions. Based on the absorption spectra, fluorescence spectra, ^{1}HNMR and more experiment measures, Liu *et al.* offered the important spectrum properties of 1 chromophore and inferred the ESIPT mechanism. However, only the indirect information about photo-physical properties could be provided based on spectroscopic techniques. Therefore, in order to give a clear and detailed picture of this proton transfer mechanism, in the present work, a theoretical investigation based on the density functional theory (DFT) and the time-dependent density functional theory (TDDFT) method have been applied to study both the ground and the excited state of molecular relevant to the transfer mechanism, respectively. We mainly forced our attention on the configurations of ground state and the first excited state, and further calculated and analyzed the vertical excitation energies, the frontier molecular orbitals and homologous ground state and the first excited state potential energy curves to elaborate the proton transfer mechanism.

2 Computational details

In the present work, the DFT and TDDFT methods have been adopted to optimize the ground state and the first excited state structures, respectively [34-38]. Becke's three-