Theoretical elaboration about excited state behaviors and fluoride anion sensor mechanism for 2-{[2-(2-Hydroxy-phenyl)-1H-benzoimidazo-5-yl]-phenyl-methylene} malononitrile

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Abstract. In view of the enormous potential of fluorescence chemosensors in recent years, more and more people focus on their developments. In the present work, we theoretically investigate a novel fluorescence sensor 2-{[2-(2-Hydroxy-phenyl)-1H-benzoimidazo-5-yl]-phenyl-methylene}-malononitrile (HBPMM) [*J. Lumin. 2016, 173, 165*] about its excited state intramolecular proton transfer (ESIPT) and probe response mechanism. Based on density functional theory (DFT) and time-dependent density functional theory (TDDFT) methods, we focus on the S_0-state and S_1-state hydrogen bonds dynamical behaviors and confirm that the strengthening intramolecular hydrogen bond in the S_1 state may promote the ESIPT reaction. In view of the photoexcitation, we find that the charge redistribution around hydroxyl moiety plays important roles in providing driving force for ESIPT. And the constructed potential energy curves further verify the ESIPT process of HBPMM should be ultrafast. That is the reason why the normal HBPMM fluorescence cannot be detected in previous experiment. Further, with the addition of fluoride anions, the exothermal deprotonation process occurs spontaneously along with the intermolecular hydrogen bond O-H•••F. It reveals the uniqueness of detecting fluoride anion using HBPMM molecule. As a whole, the fluoride anion inhibits the initial ESIPT process of HBPMM, which results in different fluorescence behaviors. This work presents the clear ESIPT process and fluoride anion sensing mechanism for the novel HBPMM chemosensor.

Keywords: Intramolecular hydrogen bond; Fluoride anion; Charge transfer; ESIPT; MOs.

1. Introduction

In recent years, fluorescence chemosensors have been largely designed and developed due to their tremendous potentials for selective detection about biological and chemical species [1-5]. It is well known that the most important feature of fluorescence sensors should be the changed fluorescence emission in the UV-Vis region, since the observable fluorescence intensities or wavelengths can be affected based on the interactions with surroundings [6-10]. Fluoride anion, a type of essential trace element in human lives, is very important and widely used in industrial process, health, medical, and so on [11-14]. It is also a useful chemical in dental care and treatment of osteoporosis. Although fluoride anions could play important roles in nature, the excessive fluoride ions can result in immune system disruption, environmental pollution, kidney damage, and even cancer [15]. In other words, the detection about fluoride anions should be significant in our life. Given the fluorescence chemosensors have apparent advantages, namely, low cost, high sensitivity, high selectivity, rapid implementation, and so on [16-20], the

designing and developing new fluoride ion chemosensors have attracted lots of attention in solution phase in recent years.

Generally, the fluorescence sensors could convert the discrimination of fluoride ions into the fluorescence emission signals. And most of the current fluoride ion chemosensors have been developed via fluoride mediated desilylation of Si-O bond using tert-butyldiphenylsilyl (TBDPS) and tert-butyldimethylsilyl (TBDMS) groups, fluoride anion induced deprotonation via pre-existing intra- or inter- molecular hydrogen bond, and so forth [21-30]. And in the aspect of experiment, the corresponding photophysical and
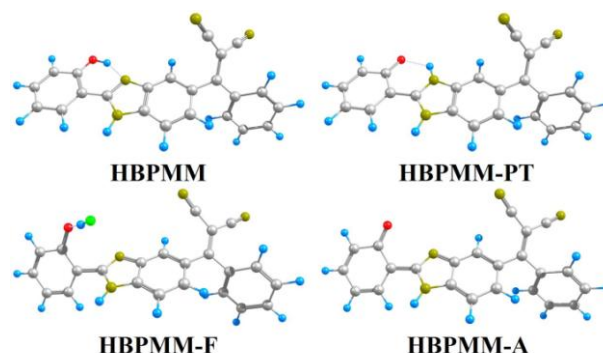
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Figure 1: The relative structures of the optimized HBPMM, the proton-transfer HBPPM (HBPPM-PT), the fluoride-anion complex form HBPMM-F, and the anion form HBPMM-A.

photochemical characteristics are generally revealed via 1HNMR spectra, time-resolved absorption and emission spectra. And as a kind of complement to experimental techniques, theoretical simulations can be suitable for further exploring the sensor response mechanism.

Recently, a novel fluorescence sensor 2-{[2-(2-Hydroxy-phenyl)-1H-benzoimidazo-5-yl]-phenyl-methylene}-malononitrile (HBPMM) has been designed and synthesized by Gupta and coworkers [31]. Due to the withdrawing -dicyano groups exist in HBPMM molecule, it showed the broad absorption at 370 nm and fluorescence band centered at 505 nm [31]. And the emission spectrum of 505 nm was predicted to be the facilitation of ESIPT phenomenon. While with the addition of fluoride anions, the fluorescence band changes a lot with response the fluoride anion. They suggested that the added fluoride anion may lead to the inhibition of the ESIPT process and the release of initial fluorescence and the anion-form emission [31]. The HBPMM structure has been shown in Figure 1. As far as we know, the theoretical investigations about this type sensors are limited [21-30]. In experiment, just the indirect information about the structural and photochemical properties can be infrared based on experimental manner. Particularly, the mechanism about the uniqueness for detecting fluoride anion cannot be revealed experimentally. It is well known that the chemical reaction mechanism is very important for HBPMM molecule, which can facilitate understanding and controlling the probe response in future. While the quantum chemical calculations about the excited states for HBPMM system might be a reasonable way to clarify the fundamental aspects about its response mechanism for fluoride anion, which can further explain the uniqueness for fluoride anions.

In this present work, therefore, we mainly focus our attention on the excited state dynamical behaviours of HBPMM and its fluoride anion response mechanism. Based on density functional theory (DFT) and time-dependent density functional theory (TDDFT) methods, we verify the validity for fluoride anion response. We deem that the elaborating probe mechanism for HBPM in this work should be useful for design and synthesis novel fluorescent chemosensors in future.
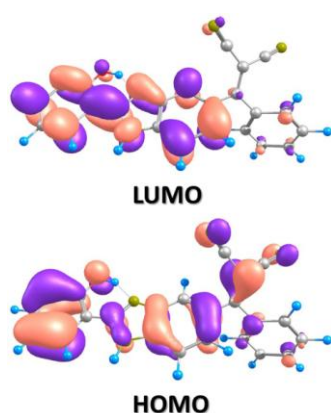
2. Computational Methods

In this work, all the calculations have been performed via Gaussian 09 program suit [32]. As mentioned above, within the framework of DFT and TDDFT methods, the hybrid exchange-correlation functional B3LYP and the triple-ζ valence quality with one set of polarization functions (TZVP) basis set have been selected in all calculations [33-39]. Given the solvent surrounding in previous experiment [31], the tetrahydrofuran (the dielectric constant: 7.426) solvent has been used in this work with the model of Polarizable Continuum Model (PCM) using the integral equation formalism variant (IEFPCM) [40-42], which considers the solute in the cavity of overlapping solvent that own apparent charges to reproduce the electrostatic potential because of the polarized dielectric within the cavity. PCM models mitigate the computational burden of explicitly modeling solvent molecules and the specific interactions with the solute. The solvent is treated as a constant dielectric reaction field where the charge density of the solute is projected onto a grid on the surface of a solvent cavity and polarized based on the value of the solvent dielectric. The resulting polarized charges on the cavity affect the charge density of the molecule and so on until self-consistency is achieved.

The S_0-state geometries were optimized without constraint for all the species in this work. And the vibrational frequencies have been analyzed at the optimized structures to verify that all these forms correspond to the local minima on the S_0-state potential energy surface. Harmonic vibrational frequencies with normal mode force constants, anharmonic vibrational frequencies with normal mode force constants, dipole moments, and dipole moment first derivatives were calculated for all solvent phase optimized structures. In view of the vertical excitation energy calculations, they can be carried out from the S_0-state optimized structure using TDDFT method with default solvation (i.e., linear reaponse and non-equilibrium). And six low-lying excited states have been predicted in this work. The S_1-state geometries were optimized with constraint based on the ground-state optimized
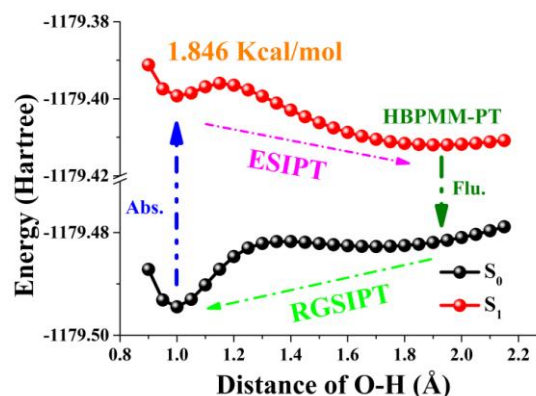

Figure 2: The theoretical frontier molecular orbitals (HOMO and LUMO) for HBPMM system.

Figure 3: The constructed S_0-state and S_1-state potential energy curves for HBPMM molecule along with the proton-transfer reaction path. The potential energy barrier for the S_1-state proton transfer process is also shown in this figure.