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Theoretical investigation on proton-induced intramolecular charge transfer of a D-π-A dye for a pH molecular switch

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ABSTRACT

The ground and excited state properties of the neutral and protonated dye molecule, 3-(dicyanomethylene)-5,5-dimethyl-1(4-[(2-hydroxy-ethyl)-methyl-amino]-styryl) cyclohexene (DCDHC), for a pH fluorescent switch have been investigated using density functional theory (DFT) and time-dependent DFT (TDDFT) in combination with polarizable continuum models (PCM) and compared with experimental absorption and fluorescence spectra. The global-hybrid B3LYP and global-hybrid meta-generalized gradient approximations functional M06 have been used. The calculations have reproduced both the UV–Vis absorption and fluorescent emission spectra of the experimental observations. It has been found that the N atom of the amino group should be the major site to accept a proton. Upon the addition of protons, proton-induced intramolecular charge transfer occurred from the electronic donor to acceptor resulting in the fluorescence quenching. The mechanism on the operation of the pH molecular switch has been given.

1. Introduction

Organic functional dyes with the donor-π-acceptor (D-π-A) structure have attracted much attention for their inherent intramolecular charge transfer (ICT) characters, which lead to various applications in organic photonics and biochemistry [1]. A typical D-π-A molecule, 3-(dicyanomethylene)-5,5-dimethyl-1(4-[(2-hydroxy-ethyl)-methyl-amino]-styryl) cyclohexene (DCDHC), was synthesized [2,3] as a red emitter in organic light emitting diodes (OLED) [2,4]. Specially, DCDHC was constructed as a pH molecular switch because of its proton-induced ICT property [3]. It has the potential to be used as fluorescent molecular switches and efficient sensors for the detection of volatile organic compounds [3].

DCDHC dye showed interesting spectroscopic properties in the ethanol solvent of different pH values [3]. For the absorption spectrum, DCDHC had an intense band at 510 nm (2.43 eV) in the ethanol solvent [3]. Upon the addition of protons, the band at 510 nm progressively decreased, meanwhile a new band with a peak at 370 nm (3.35 eV) developed [3]. The DCDHC dye produced a strong fluorescence emission at 650 nm (excitation at 460 nm) in ethanol at room temperature [3]. When adding protons, the fluorescent emission peak at 650 nm (1.91 eV) progressively decreased and finally quenched [3].

The properties of the absorption and emission are closely related to the electronic structure of the emitting molecule, especially the structure of the excited state. Having short lifetimes, the excited state is not easy to describe directly by experimental observations. Theoretical calculation is a powerful tool to explore the excited state. During the last 25 years, linear response time-dependent (TD) density functional theory (DFT) [5] has become one of the most widely used quantum chemical methods to study excited states of medium sized to large molecules [2,6–16]. However, both for the ground and excited states, the choice of the exchange–correlation functional form, which is the only approximated term in DFT, plays a key role in reaching chemically sound results [17].

B3LYP, a global-hybrid with 20% Hartree Fock (HF) exchange, has de facto become a standard for DFT calculations. Ref. [17] M06 [18], with 27% HF exchange, is a global-hybrid meta-generalized gradient approximations functional. In a benchmark calculation [19] on the performance of the M06 family of density functionals, it was found that the M06 functional yielded average deviations for valence excitations similar to those obtained with other popular hybrid functionals, such as B3LYP, and that for the majority of the investigated excited states, M06 emerged as the most accurate functional for π–π^* transitions among the tested functionals. The present authors also performed theoretical investigations on the electronic and geometrical structures of the neutral DCDHC [2,4,20]. The experimental UV–Vis absorption and fluorescence emission spectra in various solvents were reproduced [4]. In addition, the performances of 10 theoretical strategies were accessed and M06 in the frame of DFT [21] and TDDFT [22] with polarizable continuum models (PCM) [23,24] as well as 6-31G(d) basis set [25,26] emerged as one of the most effective strategies for DCDHC [4].

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In the present paper, the electronic structure of DCDHC and its protonated forms will be investigated. The protonated location will be specially analyzed. The mechanism on the operation of the pH molecular switch will be discussed.

2. Computational details

The calculations have been carried out with the Gaussian 09 [27] program package. Geometrical optimizations for the ground (S_0) and lowest excited states (S_1) of the neutral and protonated DCDHC were performed by means of DFT/PCM and TDDFT/PCM methods, respectively. Absorption and fluorescence transitions were calculated from the Frank–Condon geometries of the S_0 and S_1 states, respectively, at the TDDFT/PCM level of theory, and the lowest six excited states were calculated in order to describe the lowest one. The M06 functional was used for the calculations since it has been proved to be one of the best methods to describe DCDHC in our earlier study [4]. Moreover, the standard local exchange functional B3LYP was also used for compares. All the calculations were carried out using the 6-31G(d) basis set [25,26] and the 6-311+G(d) basis set [28] was also used to check the basis set convergence.

3. Results and discussions

As illustrated in Fig. 1, it can be seen that there are four possible sites of DCDHC for accepting protons. Therefore, four types of structures accepting one proton, i.e. DCDHC-H^+(a), DCDHC-H^+(b), DCDHC-H^+(c), and DCDHC-H^+(d), and six geometries with two protons, i.e. DCDHC-H_2^{2+}(ab), DCDHC-H_2^{2+}(ac), DCDHC-H_2^{2+}(ad), DCDHC-H_2^{2+}(bc), DCDHC-H_2^{2+}(bd), and DCDHC-H_2^{2+}(cd), may be constructed when protons were added to DCDHC.

Computational transition energies and oscillator strengths of absorption and emission spectra as well as the experimental results are collected in Table 1. It can be seen that both TD-B3LYP and TD-M06 methods reproduce the experimental transition energies for the neutral DCDHC molecule within 0.2 eV, which is in the acceptable error range. The difference of the same transition energies computed by TD-B3LYP and TD-M06 is no more than 0.1 eV, in most cases less than 0.05 eV. Therefore, in the following part, results by M06 functional will be mainly discussed.

For DCDHC, the calculated absorption and emission energies in ethanol (see Table 1) are 2.48 eV and 2.11 eV, respectively, which are in good agreement with the experimental observations [3], 2.43 eV for absorption and 1.91 eV for emission. When a larger basis set 6-311 + G(d) was used, the transition energies were 2.44 eV for UV–Vis absorption and 2.06 eV for fluorescence emission, which improve the agreements with the experimental values. Such good agreement indicates that the computational strategy is suitable for the DCDHC system.

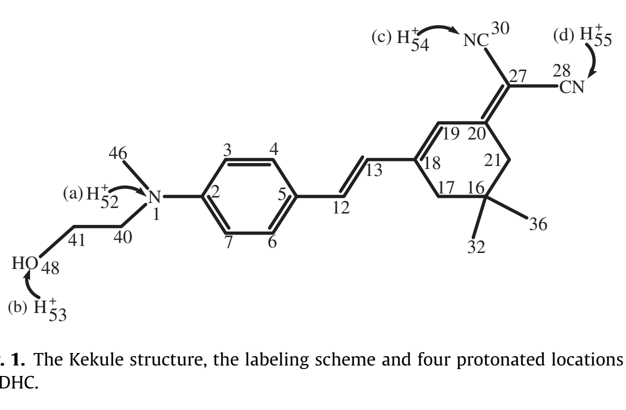

Fig. 1. The Kekule structure, the labeling scheme and four protonated locations of DCDHC.

In the experimental observation of Wang and Kim [3], when proton was added to DCDHC in the ethanol solvent, the absorption band at 2.43 eV progressively decreased, while a new band with a peak at 3.35 eV developed. The presence of an isosbestic points indicated that only two species coexisted at the equilibrium [3]. Wang and Kim [3] proposed that the spectral changes had been due to the interaction of the proton and the electron of the N atom of the amino moiety. According to our computed absorption spectra of the protonated species, DCDHC-H^+(a) and DCDHC-H_2^{2+}(ab) with the absorption energies of 3.09 eV and 3.11 eV (see Table 1), respectively, which were largely blue-shift compare with the transition energy of DCDHC, 2.48 eV, seem to be the major protonated forms. On the contrary, the absorption bands of DCDHC-H^+(c), DCDHC-H^+(d), DCDHC-H_2^{2+}(bc), DCDHC-H_2^{2+}(bd), and DCDHC-H_2^{2+}(cd) underwent red-shift relative to that of DCDHC. Meanwhile, the absorption bands of DCDHC-H^+(b), DCDHC-H_2^{2+}(ac), and DCDHC-H_2^{2+}(ad) were slightly blue-shifted compare with that of DCDHC. These results indicate that such species may not be the main protonated forms in solution. We have also calculated the absorption maximum of DCDHC-H^+(a) using 6-311 + G(d), a small difference of 0.03 eV was found compared with the result obtained by 6-31G(d). Such small variation indicates that the calculation convergence has been reached.

For experimental emission spectra [3], an intense emission at 1.91 eV was observed. Upon adding protons, the fluorescence progressively decreased then totally quenched [3]. It should be mentioned that the experimental observation was in the region between 1.65 eV (750 nm) and 2.25 eV (550 nm). It can be seen from Table 1 that the emission transition energies of DCDHC-H^+(a), DCDHC-H_2^{2+}(ab), DCDHC-H_2^{2+}(ac), and DCDHC-H_2^{2+}(ad) are out of this region and largely overlap with the absorption, which indicate the disappearance of the fluorescence in the experimental observation. However, the fluorescence maxima of DCDHC-H^+(c), DCDHC-H^+(d), DCDHC-H_2^{2+}(bc), DCDHC-H_2^{2+}(bd), and DCDHC-H_2^{2+}(cd) underwent red-shift compare with that of DCDHC but that of DCDHC-H^+(b) was a small blue-shift. These fluorescence emissions can be observed in the experiment. When a larger basis set 6-311 + G(d) was used to calculate the emission energy of DCDHC-H^+(a), a small deviation of 0.05 eV was found relative to the result of 6-31G(d).

Based on the above results of calculations, it can be proposed that DCDHC-H^+(a) and DCDHC-H_2^{2+}(ab) should be the equilibrium forms of protonated DCDHC and other protonated species may not be constructed when the pH value of the solution decreases. After more detailed analysis, it has been found that the protonation of the O atom of the hydroxyl unit had obviously less effect on the property than that of the N atom of the amino group had. According to the experimental absorption spectra, the presence of an isosbestic points indicated that only two species coexisted at the equilibrium [3]. It can be deduced that the dominant form of protonated structure should be DCDHC-H^+(a) and a minor DCDHC-H_2^{2+}(ab) form can also be constructed when the pH value is quite small. That is, the major site to accept a proton should be the N atom of the amino group, which is in agreement with the hypothesis of Wang and Kim [3]. This is not surprising because the double cyano groups are good at accepting an electron and the ability to accept a proton is the weakest. Meanwhile, amino is a better electron donating group [6] than the hydroxyl unit, thus the N atom of the amino group can be the optimal place for protonation.

The computed absorption and emission spectra of the neutral and protonated DCDHC using the M06 hybrid are presented in Fig. 2, which reproduce the profiles of the experimental spectra in Fig. 5 of Ref. [3]. The difference of the computed and experimental wave peaks is within the acceptable error range. The only obvious difference is that the calculated emission spectrum of