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Protonation-induced modulation of one- and two-photon absorption properties for quadripolar dyes

Hong-Juan Ding, Jie Sun, Yu-Jin Zhang, Chuan-Kui Wang [*]

College of Physics and Electronics, Shandong Normal University, Jinan 250014, China

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A B S T R A C T

The time-dependent hybrid density functional theory (TD-DFT) in combination with analytical response theory is used to explore the one-photon absorption (OPA) and emission as well as two-photon absorption (TPA) properties of quadripolar compounds with hydroxyl, amino or pyridyl end groups upon (de)protonation process. Both their one-photon absorption and emission as well as two-photon absorption properties show obvious changes upon passing from their neutral to their doubly (de)protonated state. The intramolecular charge-transfer (ICT) analysis demonstrates the variation of the electronic properties of the terminal groups by the (de)protonation process. The computational results are in reasonable agreement with the experimental ones.

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1. Introduction

The simultaneous absorption of two photons by a molecule excited to a higher energy state is a nonlinear optical process that has various applications in photonics and biophotonics, such as optical limiting [1–4], photodynamic therapy [5–8], up-converted lasing [9,10], three-dimensional optical data storage [6,11,12], two-photon excitation microscopy imaging [13,14], and microfabrication [15,16]. These applications are greatly dependent on the two-photon absorption (TPA) cross section. Thus, developing new organic TPA materials with strong TPA ability is an important issue pursued by both experimental and theoretical researchers. Up to now, the studies have demonstrated that the TPA activities are closely related to molecular factors such as the conjugation length, the π center properties, the symmetrical or asymmetrical arrangement of electron-donors (D) and electron-acceptors (A) attached to the π center and their strength to push and pull electrons, coplanarity, and the molecular dimensionality.[17,18].

On the purpose of forming sensitive two-photon excited fluorescence molecular probes, chromophores are required to have not only high TPA behaviors, but also strong response in terms of their photophysical properties to the external stimuli, such as polarity, pH, ion concentration, and temperature. Recently, significant modulation of photophysical properties of chromophores in response to protons and metal cations has been explored [19–25]. Werts et al. synthesized two quadripolar dyes and measured the one- and two-photon absorption characteristics as well as fluorescence properties upon passing from their neutral to their doubly (de)protonated state [23]. They found that their fluorescence properties have strongly response to pH values of solution while maintaining large TPA cross sections.

A fluorescent probe consists of the fluorophore and receptor. When the receptor interacts with the detected object (e.g. metal cation or proton), the electron donating or accepting ability of the receptor will be modified, leading to a charge redistribution that induces a change of their optical properties. To the best of our knowledge, there are few theoretical investigations on two-photon pH fluorescent probes. Here, we provide a theoretical study on these systems' optical properties including the one-photon absorption (OPA) and TPA as well as fluorescence upon (de)protonation by means of the time-dependent hybrid density functional theory (TD-DFT) in combination with response theory. Moreover, the available experimental measurements are elucidated. The main purpose of this letter is to investigate the mechanism for these quadripolar two-photon pH fluorescent probes with fluorene center and different auxochromic groups.

2. Computational details

The transition probability of one-photon absorption and emission is described by the oscillator strength,

$$\delta_{op} = \frac{2\omega_f}{3}\sum_{\alpha}|\langle 0|\mu_\alpha|f\rangle|^2 \tag{1}$$

where $|0\rangle$ and $|f\rangle$ denote the ground state and the final state separately, ω_f represents the corresponding excitation energy, and μ_α is the Cartesian component of the electronic dipole moment operator. The summation is performed over the molecular x, y, and z axes: $\alpha \in \{x, y, z\}$.

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[*] Corresponding author. Fax: +86 531 8618 2521.
E-mail address: ckwang@sdnu.edu.cn (C.-K. Wang).

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The two-photon absorption cross-section that can be directly compared with the experimental results is defined as

$$\sigma_{tp} = \frac{(2\pi)^3 a_0^5 \alpha}{c_0 \pi} \times \frac{\omega^2 g(\omega)}{\Gamma_f} \delta_{tp}. \tag{2}$$

.Here a_0 is the Bohr radius, c_0 is the speed of light, α is the fine structure constant, ω is the photon frequency of the incident light, and $g(\omega)$ denotes the spectrum line profile, which is assumed to be a δ function here, Γ_f is the lifetime broadening of the final state, which is commonly assumed to be 0.1 eV. δ_{tp} is the orientation average value of the two-photon absorption probability,

$$\delta_{tp} = \frac{1}{30} \sum_{\alpha\beta} [F \times S_{\alpha\alpha} \times S^*_{\beta\beta} + G \times S_{\alpha\beta} \times S^*_{\alpha\beta} + H \times S_{\alpha\beta} \times S^*_{\beta\alpha}] \tag{3}$$

where F, G, and H are coefficients depending on the polarization of the light. For the linearly polarized light, F, G and H are 2, 2, 2, and for the circularly case, they are -2, 3, 3. In the present letter, we only consider the case excited by a linearly polarized monochromatic beam. $S_{\alpha\beta}$ is the two-photon transition matrix element. For the absorption of two photons with the frequency $\omega_f/2$ it can be written as,

$$S_{\alpha\beta} = \sum_i \left[\frac{\langle 0|\mu_\alpha|i\rangle\langle i|\mu_\beta|f\rangle}{\omega_i - \omega_f/2} + \frac{\langle 0|\mu_\beta|i\rangle\langle i|\mu_\alpha|f\rangle}{\omega_i - \omega_f/2} \right] \tag{4}$$

where ω_i and ω_f denote the excitation frequency of the intermediate state $|i\rangle$ and final state $|f\rangle$ respectively, $\alpha, \beta \in \{x, y, z\}$ and the summation goes over all the intermediate states including the ground state $|0\rangle$ and the final state $|f\rangle$.

In this letter, the ground-state geometrical structures are fully optimized using the GAUSSION09 package [26] at the HF level. At the same level, frequency calculations are carried out to verify the stability of the optimized structures. On the basis of each optimized ground-state structure, the OPA properties are systematically investigated by using TD-DFT at the DFT/B3LYP level. The one-photon emission (OPE) properties are obtained by using TD-DFT at the DFT/B3LYP level after optimizing the first excited state structures. In addition, the quadratic response theory implemented in the Dalton package [27] is used to calculate the TPA cross section of molecules, providing an analytical solution for the TPA cross section.

In order to simulate the protonation of the amino and pyridyl end groups, we use a hydrogen atom with the basis restricted to only the *s* orbital to couple with each nitrogen atom, and the exponent factor of the basis function is enlarged until the hydrogen atom has very little negative charge [28,29]. As a result, the end groups are protonated in the solution. To mimic the deprotonation of the hydroxyl end groups, we remove the hydrogen atom attached to the oxygen atom in the hydroxyl group and simultaneously put an electron in the molecule. Due to the high electronegative property of the oxygen atom, the most part of the electron charge is held by it. Moreover, the solvent effect caused by the surrounding ethanol (CH_3CH_2OH) solvent is considered with the polarized continuum model (PCM) approach for all the calculations. The basis set of 6-31G(d) is chosen for the work. The molecular electrostatic potential (MEP) maps are visualized for charge analysis in the ground state of the molecules. The charge difference between the charge-transfer (CT) and ground states is calculated using Mulliken population analysis.

3. Results and discussions

3.1. Molecular structures

The studied molecular structures and the reversible (de)protonation processes of the compounds are presented in Figure 1. In comparison with the compounds synthesized in experiments, we use ethyl groups to replace the aliphatic side chains for considering the computational resource, and the simplification would have little effect on optical properties of the compounds. All the studied compounds have fluorene as π center. In order to study the influence of conjugation bridge, we design the T series (T1–3) with —C≡C— bridge, replacing the —C=C— bridge in D series (D1–3). Three kinds of terminal groups, where hydroxyl group and amino group act as donor while pyridyl group plays a role of acceptor, are considered. As one knows, both the amino group and the pyridyl group are favorable to get one proton, while the hydroxyl group is favorable to lose one. Thus, when the compounds are in different pH-value solution, the protonation or (de)protonation process would take place.

Some selective bond lengths and the dihedral between phenyl and fluorene center of the optimized molecules are displayed in Table 1. When the compound D1 is deprotonated, the bond length of $O_1—C_2$ is contracted from 1.351 to 1.255 Å, enhancing the electron donating ability of hydroxyl group after deprotonation. As the compounds D2 and D3 are protonated, the bond length of $N_1—C_2$ is stretched from 1.394 to 1.458 Å, while $C_1—C_2$ is contracted from 1.487 to 1.479 Å, reducing the electron donating ability of the amino group and enhancing the electron accepting ability of the pyridyl group after protonation. From Table 1, one can see that the bond length alternation parameter defined as $d_{BLA} = (R_{C3-C4} + R_{C5-C6})/2 - R_{C4-C5}$ has a larger variation for D1 compared to D2 and D3 as these molecules are in corresponding solutions. This indicates the deprotonation process induces a relative larger modulation on the molecular structure. The similar situation exists for the T series compounds. Concerning on the dihedral angle, one can see from Table 1 that the T series compounds have better planarity than the D series. When the compounds are (de)protonated, planarity of D1 (D2) compound except for D3 compound is improved, but planarity of the T series compounds becomes slightly worse.

The frontier orbital energies and energy gaps (ΔE_{H-L}) between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are shown schematically in Figure 2. For deprotonated molecules $D1-2H^+$ and $T1-2H^+$, their HOMO and LUMO energies move up compared with those of the neutral forms D1 and T1. While for protonated $D2+2H^+$, $D3+2H^+$, $T2+2H^+$ and $T3+2H^+$, their HOMO and LUMO energies move down compared with those of the corresponding neutral forms. It is noteworthy that the ΔE_{H-L} values of $D1-2H^+$ and $D3+2H^+$ become smaller while that of $D2+2H^+$ is larger in comparison with those of their corresponding neutral forms. This observation is understandable because the electron donating or accepting ability of the end groups for $D1-2H^+$ or $D3+2H^+$ is stronger, while the electron donating ability of the end groups for $D2+2H^+$ is weaker compared with their counterparts. The similar situation for T series compounds is observed. In addition, the ΔE_{H-L} values of the T series compounds are larger than those of the corresponding D series ones. In order to view the influence of (de)protonation process on the electronic charge distribution of compounds, we show the molecular electrostatic potentials (MEPs) in Figure 3. It is shown that the deprotonation of D1 induces a significant negative charge density at the end groups, and the protonation of D2 or D3 induces a significant positive charge density at the end groups.

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