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Theoretical studies of one- and two-photon absorption properties for two series of three-branched fluorenylene–vinylene compounds with different centers (B, N) and peripheral substituted groups

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ABSTRACT

Two series of three-branched fluorenylene–vinylene compounds with different centers (B, N) and peripheral substituted groups were investigated. The equilibrium geometries and electronic structures were obtained by using the density functional theory B3LYP and 6-31G basis set. The one- and two-photon absorption properties of all the molecules were studied theoretically with a ZINDO–SOS method in detail. It can be seen that the maximum one-photon absorption (OPA) intensities and the maximum two-photon absorption (TPA) cross sections values δ_{max} are gradually increased with the stronger electron-donating capability [H < OH < N(CH$_3$)$_2$] or electron-accepting one (H < CHO < NO$_2$). This indicates that intramolecular charge transfer from the center to the peripheral substituted groups (or vice versa) plays a very important role on the TPA.

1. Introduction

Two-photon absorption (TPA) is one of the third-order nonlinear absorption processes involving the simultaneous absorption of two photons, either degenerate or nondegenerate. TPA responses have various applications, such as three-dimensional (3D) optical data storage, 3D optical imaging for biological systems, 3D microfabrication and early corrosion detection, optical power limiting and photodynamic therapy, to name just a few [1–5]. To search for molecules endowed with large TPA cross sections, researchers are examining various design strategies, including the linear (dipolar and quadrupolar) compounds, octupolar compounds, multi-branched compounds, oligomeric strategy, organometallic compounds and macromolecular architectures [6–10], which show the TPA cross sections can be enhanced by these factors. The studied results indicate that increasing donor and acceptor strength, extending the conjugated length, increasing the molecular dimensionality and changing the character of the conjugated bridge were in favor of enhancing the magnitude of the molecular TPA cross section.

Zyss et al. have recognized octupolar molecule as a new field of research in nonlinear optics in the early 1990s [11–13]. As it is known that for molecules belonging to octupolar space groups, the vector part of the molecular hyperpolarizability $\beta_{(J=1)}$ is canceled so that only the octupolar contribution $\beta_{(J=3)}$ remains [14]. Compared with the traditional dipolar linear molecules, octupolar compounds have many advantages: they possess more rounded-off shapes, which ease their packing in a single crystalline lattice as opposed to less favorable elongated dipolar rodlike molecule; the absence of dipolar moments in the excited as well as ground state makes them more suitable in various optical applications; they resolve the inherent conflict between the transparency and nonlinearity existing in traditional dipolar molecules. It is also known that the intramolecular charge transfer within the π-conjugated system is effective in enhancing the two-photon absorptivity irrespective of the direction of the transfer (from the ends to the center of the molecule or from the center to the ends). Furthermore, more charge transfer during the excitation will certainly lead to enhanced TPA response. So in this paper, we herein design two series of three-branched fluorenylene–vinylene molecules with different centers (B, N) and peripheral substituted groups. All the two series of molecules have a propellerlike structure with C_{3h} symmetry, which can be regarded as an assembly of three branches like arms. Despite the C_{3h} point groups of these molecules deviating from these types given above by Zyss and Ledoux about purely octupolar molecules [13], the general trend of the NLO properties are not significantly altered by these structural differences. So the two series of molecules can be called pseudo-octupolar molecules. The two series of molecules have D(-π-A)$_3$ and A(-π-D)$_3$ structural design, where D

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is an electron-donating group, A an electron-accepting group and π a conjugating moiety. Their systems of the fluorene moieties might lead to strong electronic coupling of charge transfer (CT) excitations involving the attached substituents. We have investigated their molecular geometries, one-photon absorption (OPA) and two-photon absorption (TPA) properties using density functional theory B3LYP/6-31G associated with ZINDO–SOS methods.

2. Theoretical methodology

The TPA process corresponds to simultaneous absorption of two photons. The TPA efficiency of an organic molecule, at optical frequency $\omega/2\pi$ can be characterized by the TPA cross-section $\delta(\omega)$. It can be directly related to the imaginary part of the second hyperpolarizability $\gamma(-\omega;\omega,\omega,-\omega)$ by [15,16]

$$\delta(\omega)=\frac{3\hbar\omega^2}{2n^2c^2\varepsilon_0}L^4 Im[\gamma(-\omega;\omega,-\omega,\omega)] \tag{1}$$

where $\gamma(-\omega;\omega,-\omega,\omega)$ is the third-order molecular polarizability, $\hbar\omega$ the energy of the incoming photons, and ε_0 the vacuum electric permittivity. n denotes the refractive index of the medium and L corresponds to the local-field factor. In the calculations presented here, these two quantities are set to one (isolated molecule in vacuum).

The sum-over-states (SOS) expression to evaluate the components of the second hyperpolarizability $\gamma_{\alpha\beta\gamma\delta}$ can be induced out using perturbation theory. By considering a Taylor expansion of the energy with respect to the applied field, the methodology adopted here to calculate the second hyperpolarizability are given in the form shown in the literatures [17,18].

To compare the calculated δ value with the experimental value, the orientationally averaged (isotropic) value of γ is evaluated, which is defined as

$$\langle\gamma\rangle=\frac{1}{15}\Sigma_{ij}(\gamma_{iijj}+\gamma_{ijij}+\gamma_{ijji}), \quad i,j=x,y,z. \tag{2}$$

whereafter $\langle\gamma\rangle$ is taken into Eq. (1), and then the TPA cross section δ is obtained.

Generally, the position and relative strength of the two-photon resonance are to be predicted using the following simplified form of the SOS expression:

$$\delta\propto\frac{M_{0k}^2M_{kn}^2}{(E_{0k}-E_{0n}/2)^2\Gamma}+\frac{M_{0n}^2\Delta\mu_{0n}^2}{(E_{0n}/2)^2\Gamma} \tag{3}$$

where the subscripts 0, k and n refer to the ground state S_0, the intermediate state S_k, and the TPA final state S_n, respectively; M_{0k} and M_{kn} are the transition dipole moment from S_0 to S_k and from S_k to S_n, respectively; E_{0k} and E_{0n} are the corresponding excitation energy from S_0 to S_k and from S_0 to S_n, respectively; $\Delta\mu_{0n}$ is the dipole moment difference between S_0 and S_n, which is neglected in the molecule with a reverse center. So for molecule with a reverse center, expression (3) becomes the following formula [19,20]:

$$\delta\propto\frac{M_{0k}^2M_{kn}^2}{(E_{0k}-E_{0n}/2)^2\Gamma} \tag{4}$$

In principle, any kind of self–consistent field molecular orbital procedure combined with configuration interaction can be used to calculate the physical values in the above expression. In this paper, the molecular equilibrium geometries are calculated using the density functional theory with B3LYP functional and 6-31G basis set. Then the properties of electronic excited states were obtained by using ZINDO method, the CI employed here includes single (S) excitations between 14 occupied orbital and 14 unoccupied orbital, and double (D) excitations among the two highest occupied and two lowest unoccupied molecular orbital, thus including 196 singlet configurations and 11 doubly configurations. Furthermore, either UVVis (groundstate one-photon absorption) spectra or the transition dipole moment and the corresponding transition energy which were needed to predict TPA were provided. Then, by using formulas (1), (2) and SOS expression, we calculated the second hyperpolarizability γ and TPA cross section δ.

3. Results and discussion

3.1. Geometry optimization and electronic structure

The geometrical structures of the pseudo-octupolar molecules were optimized with the density functional theory B3LYP method and the 6-31G basis set in the Gaussian 03 package. We have shown the chemical structures of the studied compounds in Fig. 1. The optimized results show that all of these compounds possess C_{3h} point symmetry. The fluorene building block was used in the design of the molecules studied because fluorene can provide good planarity and high electron delocalization through increased overlap of π molecular orbitals between the rings. B and N atoms are the central atoms of the two series of molecules. Because the order of the Pauling's electronegativity for B, C and N is B(2.04) < C(2.55) < N(3.04), the B atom and N atom have the positive and negative net charge in the ground state, respectively. Thus, the electron-withdrawing B will facilitate its acceptability during the excitation while the electron-pushing N is likely to donating electrons during the excitation. Comparing the end substituent groups, the electron-donating capability is in the order $N(CH_3)_2$ > OH > H, and NO_2 > CHO > H for the electron-accepting capability. These different substituent groups will have great effect on the OPA and TPA.

Table 1 shows the energies of some frontier orbitals obtained by B3LYP/6-31G method. As seen from Table 1, for the series 1 molecules, the energies of the HOMO and LUMO are increased with the stronger electron-donating capabilities of the peripheral substituted groups, i.e., H < OH < $N(CH_3)_2$. Meanwhile, for the series 2 molecules, the energies of the HOMO and LUMO are decreased with the stronger electron-accepting capabilities of the peripheral substituted groups, i.e., H < CHO < NO_2. It is also obvious that the energy gaps ($\Delta E_{\mathrm{H-L}}$) between HOMO and LUMO are gradually decreased with the stronger electron-donating or electron-accepting capabilities of the peripheral substituted groups mentioned above. In addition, for the series 1 molecules, the HOMO are degenerate with the next occupied orbital HOMO − 1, while there are large energy gaps between the LUMO and the LUMO + 1. In contrast, for the series 2 molecules, the LUMO are almost degenerate with the next unoccupied orbital LUMO + 1, while there are also large energy gaps between the HOMO and the HOMO − 1. The most possible cause of the interesting results for the frontier orbital energy might be the different electronic structure in the two series of molecules. The essential reason should be investigated in the farther research.

Observing the molecular orbital contour plot of HOMO and LUMO for B-1 and N-1 in Fig. 2, it can be seen that the electron clouds of HOMO and LUMO of B-1 are concentrated on the branch parts and the central moieties of the molecule, respectively. On the contrary, the electron clouds of HOMO and LUMO of N-1 mainly distribute in the central moieties and the branch parts of the molecule, respectively. The reason for this phenomenon can be due to the different molecular structure. Specifically, the B-1 and N-1 molecules have the central atom – B and N with the electron-accepting and electron-donating properties, respectively. Simultaneously, there are the electron-donating group – $N(CH_3)_2$ and electron-accepted one – NO_2 in the end of B-1 and N-1 molecules.

3.2. One-photon absorption

The OPA properties of all molecules have been calculated by using the ZINDO program on the basis of geometric structures