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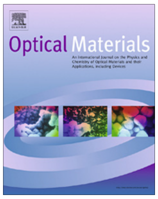

Effective regulation of second-order nonlinear optical properties of macrocyclic thiophene-based derivatives with dipole structure

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ABSTRACT

The static second-order nonlinear optical susceptibilities (β_0) of a series of macrocyclic thiophene-based derivatives with strong donor/acceptor (D/A) substituents were studied in detail on the basis of the stability of the equilibrium geometries calculated at density functional theory (DFT) level. The research results show that the type of substituent, the pair number and the position of D/A group all have important influence on the value of β_0. The molecule $4A_{1-4}D_{5-8}$ with four pairs of electron donor ($-NH_2$) and acceptor ($-CN$) located at contraposition has larger value of β_0 (-338.88×10^{-30}/esu), which is close to 50 times larger than that of SII. And the absolute value of β_0 enlarges as increasing the ring size or the pair number. Moreover, the effects of BLA and charge transfer are analyzed to explain the significant enlargement of β_0 for the molecules with stronger D/A group, besides the influence factors of f, $\Delta\mu$ and W in the two-level approximation formula. In addition, it indicates an approximately proportional relationship between the values of β_0 and $\delta_{\max}$ for most studied molecules.

1. Introduction

Over the past two decades, the development of materials with outstanding nonlinear optical (NLO) properties has continued to be in the limelight [1,2]. In particular, organic molecules have many advantages, such as easy chemical modifications for structural diversity, easy fabrication, mechanical flexibility, and low cost. The prospective applications of NLO materials include optical data-manipulations, data-storage, data-transmission and electro-optic modulators for optical telecommunication [3]. Materials with large hyperpolarizabilities will be good candidates for the use in optoelectronics, optical-switching devices and signal-processing devices [4–9].

Recent years, the major interest lies in the organic materials duo to their larger second-order NLO polarizability, high laser damage thresholds, low dielectric constants, fast NLO response times and so on [10]. Till now, a significant amount of work has been carried out on organic materials with different conventional strategies to enhance the NLO response [11–14]. As we know, increasing the length of chain-like molecules or increasing the number of branch for branch-like molecules can remarkably enhance the second-order polarizability (β) duo to the cooperative enhancement of the charge transfer. However, organic materials have several disadvantages, for example, the enhancement of the NLO efficiency with low energy transitions during the UV–Vis region will result in a trade-off between nonlinear efficiency and optical transparency, and the thermal stability will reduce simultaneously [15]. Therefore, it is extremely important to search for suitable organic materials with larger NLO response, excellent optical transparency and thermal stability.

It is well known that the NLO property can be enhanced through adopting suitable design strategies, such as donor–π-bridge–acceptor structure (D–π–A), donor–π-bridge–donor structure (D–π–D) and acceptor–π-bridge–acceptor structure (A–π–A) [16]. In our previous researches [17,18], a series of macrocyclic thiophene-based derivatives were investigated in theory, and the influence of the ring size, the type of substitution, the substituted position and the pair number on the one- and two-photon absorption properties were analyzed in detail. The results indicate that the one-photon absorption (OPA) wavelength maxima $\left(\lambda_{\max}^{(1)}\right)$ of the designed molecules with D or A group show red-shifts compared with original molecule SII. And the values of two-photon absorption (TPA) cross-section ($\delta_{\max}$) increase with increasing the number of D/A pair. The $\delta_{\max}$ values of D–π–A type of molecules are close to

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that with A–π–A structure, and larger than that with D–π–D structure and SII molecule. Moreover, the molecules show larger values of $\delta_{\max}$ when electron donor and acceptor located at contraposition. In summary, the previous researches have provided a useful guideline for the design of novel D–π–A molecules with large TPA cross-section via enhancing the strength, enlarging the number and changing the position of electron donor and acceptor substituents based on the circular π-conjugated skeleton, besides enlarging the ring size.

In this way, what about the second-order nonlinear optical properties with regard to the designed macrocyclic molecules with stronger push–pull group? In this work, systematic studies on the static second-order nonlinear polarizabilities (β_0) of the series of macrocyclic thiophene-based derivatives will be investigated in theory. And the influences of the type for the substitution, substituted position and pair number on their NLO properties will be analyzed in detail. Moreover, the effects of BLA and charge transfer are investigated to explain the significant enlargement of β_0 for the molecules with stronger D/A group, besides the influence factors of f, $\Delta\mu$ and W in the two-level approximation formula. In addition, the relationship between the values of $\delta_{\max}$ and β_0 will be predicted in the end.

2. Theoretical methods

A quantitative description of molecular NLO response is derived from a power-series expansion of the molecular polarization upon interaction with an external electromagnetic field by Eq. (1)

$$P_i = \sum_j \alpha_{ij}E_j + \sum_{j\geq k}\beta_{ijk}E_jE_k + \sum_{j\geq k\geq l}\gamma_{ijkl}E_jE_kE_l + \ldots\ldots \tag{1}$$

where P_i is the molecular polarization induced along the ith axis; E_j is the jth component of the applied electric field; α, β and γ denote the linear polarizability, the first hyperpolarizability or the second-order polarizability, and the second hyperpolarizability or the third order polarizability, respectively.

α, β and γ describe the susceptibility of the molecule to an electromagnetic perturbation and are constants for a given molecular geometry and external electromagnetic field. And β and γ are responsible for the second-harmonic and third-harmonic generation.

The SOS expression for the individual components of the second-order polarizability tensor has been given by perturbation theory [19,7,20,21]:

$$\beta_{ijk}+\beta_{ikj} = -\frac{e^3}{4\hbar^2}\left\{\begin{array}{l} \displaystyle\sum_{\substack{n\neq n'\\ n'\neq g\\ n'\neq g}}\left[\begin{array}{l} \left(r^j_{gn'}r^i_{n'n}r^k_{gn}+r^k_{gn'}r^i_{n'n}r^j_{gn}\right)\times\left(\frac{1}{(\omega_{n'g}-\omega)(\omega_{ng}+\omega)}+\frac{1}{(\omega_{n'g}+\omega)(\omega_{ng}-\omega)}\right)+\\ \left(r^i_{gn'}r^j_{n'n}r^k_{gn}+r^i_{gn'}r^k_{n'n}r^j_{gn}\right)\times\left(\frac{1}{(\omega_{n'g}-2\omega)(\omega_{ng}-\omega)}+\frac{1}{(\omega_{n'g}+2\omega)(\omega_{ng}+\omega)}\right)+\\ \left(r^j_{gn'}r^k_{n'n}r^i_{gn}+r^k_{gn'}r^j_{n'n}r^i_{gn}\right)\times\left(\frac{1}{(\omega_{n'g}-\omega)(\omega_{ng}-2\omega)}+\frac{1}{(\omega_{n'g}+\omega)(\omega_{ng}+2\omega)}\right) \end{array}\right]+\\ 4\displaystyle\sum_{n\neq g}\left[r^j_{gn}r^k_{gn}\Delta r^i_n\left(\omega^2_{ng}-4\omega^2\right)+r^i_{gn}\left(r^k_{gn}\Delta r^j_n+r^j_{gn}\Delta r^k_n\right)\left(\omega^2_{ng}+2\omega^2\right)\right]\frac{1}{(\omega^2_{ng}-\omega^2)(\omega^2_{ng}-4\omega^2)} \end{array}\right\} \tag{2}$$

where the summations are over the complete sets of eigenstates $|n\rangle$ and $|n'\rangle$ of the unperturbed molecular system. The quantities $r^i_{gn'}$ ($\langle g|r^i|n\rangle$) and $r^i_{nn'}$ ($\langle n|r^i|n'\rangle$) are matrix elements of the position operator r^i (along the ith coordinate axis) between the unperturbed ground state (g) and excited states (n), or between the two excited states (n, n'), respectively; $\Delta r^i_n = r^i_{nn} - r^i_{gg}$ is the dipole moment difference between the excited state (n) and ground state (g). Although all 27 components of the β tensor can be computed, only the vector component in the dipolar direction (β_μ) is sampled by electric-field-induced second-harmonic generation experiments. And β_μ is given by:

$$\beta_\mu = (\mu_x\beta_x + \mu_y\beta_y + \mu_z\beta_z)\Big/(\mu_x^2+\mu_y^2+\mu_z^2)^{1/2} \tag{3}$$

where

$$\beta_i = \beta_{iii} + 1/3\sum_{i\neq j}(\beta_{jii}+\beta_{iji}+\beta_{iij}) \quad i,j\in(x,y,z) \tag{4}$$

The ZINDO program was employed to provide the transition dipole moment and the transition energy needed in Eq. (2) on the next step, since the reliability of ZINDO–SOS method has been proven for the description of molecular NLO property [7,22]. In our previous work, the second-order and third-order NLO polarizabilities have been reported for dozens of molecules [23–28]. In this study, the configuration interaction (CI) active spaces include 20 highest occupied and 20 lowest unoccupied π-orbitals in single CI, and 5 highest occupied and 5 lowest unoccupied π-orbitals in double CI. There are in all 826 configuration states in the CI calculation using ZINDO program.

During the computation of β value with the SOS expression in ZINDO program, the truncation problem should be considered. As clearly seen in Eq. (2), the summation is over the complete sets of eigen states $|n\rangle$, $|m\rangle$ and $|g\rangle$ of the unperturbed system. And the denominator of each term includes ω_{ng} and $\omega_{n'g}$, which will increase gradually as the energy differences between the ground state and the excited states increase through enlarging the values of n and n′. It means that the higher excited state will make less contribution to the value of β. As the values of n and n' reach certain ones, the higher excited states will be neglected. Namely, the calculated β value will reach a limiting value as the number of the excited states increases gradually. Usually, the summation over 25–400 excited states is adequate for the convergence of β value [29–31]. With regard to the macrocyclic thiophene derivatives reported in our previous work, 300 excited states were considered for the calculation of β_0 values, which converge when the number of excited states exceeds 290 [32]. So that 300 excited states were chosen to the ZINDO-SOS calculation for the molecules studied in this paper.

In the SOS formula of β_{ijk} shown in Eq. (2), if only considering an important excited state which possesses a low-energy excited state with large oscillator strength, and combining with Eqs. (3) and (4), two-level approximate formula Eq. (5) [7,19,33] will be gained, which is still a good model in chemical interpretation of NLO response.

$$\beta_\mu = \frac{3e^2\hbar^2}{2m}\frac{Wf\Delta\mu}{\left[W^2-(2\hbar\omega)^2\right]\left[W^2-(\hbar\omega)^2\right]} \tag{5}$$

where ω is the frequency of the laser field, and $W = \hbar\omega_{1g}$ is the transition energy from ground state to the excited state; f is the oscillator strength for the transition; $\Delta\mu$ is the difference of the dipole