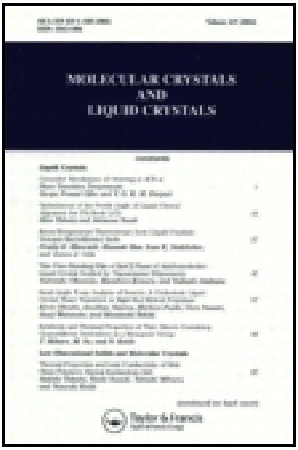

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Theoretical Two-Photon Absorption Cross-Sections of Dithienothiophene-Based Molecules

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Theoretical Two-Photon Absorption Cross-Sections of Dithienothiophene-Based Molecules

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Abstract We have calculated TPA cross section δ value of dithienothiophene (DDT)-based molecules to gain insight into the origin of the large δ values. The energy and transition dipole moments for the ground state and multiple excited states were calculated by combining the Hartree-Fock Hamiltonian with single configuration interaction formalism. For the calculation of the imaginary part of the third-order polarizability the sum-over-state expression was used. There are some differences between theoretical and experimental values. However the theoretical calculation reasonably estimates the δ values of the DTT-based molecules roughly 2-10 times larger than those fluorene- as well as stilbene-based ones.

INTRODUCTION

Molecules with large two-photon absorption (TPA) cross-sections (δ), can be easily applied on two-photon fluorescence microscopy, optical limiting [1,2], 3D-optical memory [3,4], and two-photon-induced biological caging studies [5]. However, most known organic molecules have relatively small δ values. The development of molecules with large δ requires more detailed studies on the structure-property relationship.

In this paper we have calculated TPA cross-sections of dithienothiophene (DTT)-based molecules that were already reported to give large δ values [6]. To look into the relationship between structure and TPA cross section values triphenylamine (TP), ethylcarbazole (CZ), and 2-phenyl-5-(4-*ter*-butyl)-1,3,4-oxadiazole (OX) were attached to DTT. The chemical structures of molecules under study are shown in

Fig. 1. **1** and **2** are symmetrically end-capped with donor groups while **3** and **4** are functionalized asymmetrically with donor and acceptor at each end.

Full geometry optimizations were performed with the self-consistent force-field theory. We calculated the energy and transition dipole moments for the ground state and multiple excited states by combining the Hartree-Fock Hamiltonian with single configuration interaction formalism. The TPA at an optical field frequency is related to the imaginary part of the third-order polarizability $\mathrm{Im}\gamma(-\omega;\omega,\omega,-\omega)$ by

$$\delta(\omega)=\left(\frac{8\pi\hbar\omega^2}{n^2c^2}\right)L^4\,\mathrm{Im}\gamma(-\omega;\omega,\omega,-\omega) \qquad (1)$$

where *c* is the speed of light, L is a local field factor (equal to 1 for vacuum), and *n* denotes the refractive index of the medium (vacuum assumed for the calculations). We calculated $\mathrm{Im}\gamma(\omega;\omega,\omega,-\omega)$ using the sum-over-states (SOS) expression (the damping factor Γ has been set to 0.1eV in all cases in this study) as suggested by Brédas *et. al* [7].

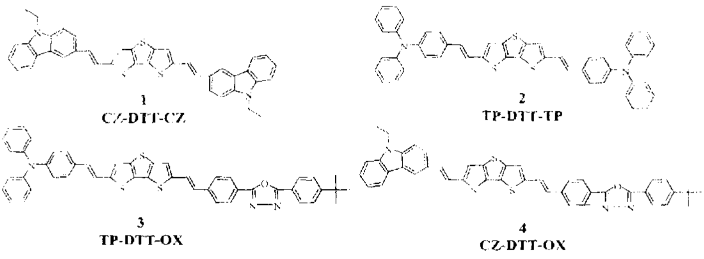

Figure 1. Chemical structure of the DDT based molecules.

RESULTS AND DISCUSSION

The calculated (δ^b) and experimental cross-sections (δ^a) of DTT-based molecules are listed in Table 1. The δ^a values were derived from the

TPA dispersion curves obtained from the non-linear transmission experiment (uncertainty range is ± 15%). From the ratio of the intensity at TPA maximum to that at 820nm the first column in Table 1 was obtained. More detailed experimental conditions are to be described elsewhere.

As can be seen in Table 1, the quantum-chemical calculation estimates reasonably the experimental values with respect to the structural variation. The δ^b values are slightly less than δ^a values. **1** and **3** show relatively larger δ values than **2** and **4**. The results of the calculations, as shown in Fig. 2, indicate that both the $S_0 \rightarrow S_1$ and $S_1 \rightarrow S_2$ transition dipole moments contribute to the larger δ values of **1** and **3**. Larger δ values were expected for molecules functionalized with TP than with CZ due to better delocalization of the π-electron in TP. However δ^b for CZ-DTT-CZ is larger than that for TP-DTT-TP. It would be attributed to the better planarity of the CZ groups. It is not easy to evaluate the molecular TPA efficiency among different chromophores through direct comparison of their δ values. Considering the sensitivity of TPA on experimental conditions, the calculated TPA δ values are acceptable. The δ values of the DTT were turned out to be about 2-10 times larger than those fluorene- as well as stilbene-based ones [8].

Table 1. Calculated and experimental values of two-photon cross-section and experimental peak positions (TPA λ_{max}).

Molecules	λ_{max} (nm)	δ^a (cm^4 sec)	δ^b (cm^4 sec)
1. CZ-DTT-CZ	720	3.3×10^{-45}	8.3×10^{-46}
2. TP-DTT-TP	780	7.9×10^{-46}	3.4×10^{-46}
3. TP-DTT-OX	970	1.4×10^{-45}	7.3×10^{-46}
4. CZ-DTT-OX	940	3.9×10^{-46}	1.8×10^{-46}

[a] Experimental value of TPA cross section by measuring the transmission method.

[b] For the calculation of the third-order polarizability (γ) the SOS expression was used [7].

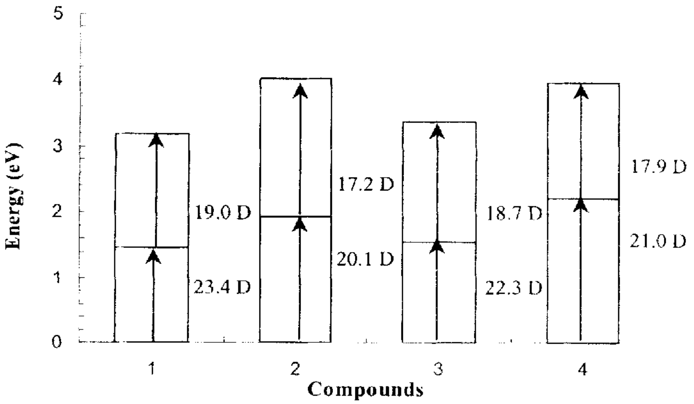

Figure 2. Scheme of the calculated energy and transition dipole moments (in debyes).

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