Two-Photon Absorption Cross Sections of Dithienothiophene-Based Molecules

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We performed nonlinear transmission measurements and quantum-chemical calculations on dithienothiophene (DTT)-based molecules to gain insight into the effect of acceptor and donor groups on two-photon absorption (TPA) properties. The TPA intensity showed dispersion characteristics of the single-photon absorption spectrum. When the molecules included an asymmetric donor-acceptor pair, the single- and two-photon absorption maximum wavelengths were red-shifted more than when the molecules had a symmetric donor-donor structure. We interpreted this result as indicating that the S_2 state plays the dominating role in the absorption process of molecules with a symmetric structure. The experimental TPA δ values at the absorption peak wavelength showed a dependence on the structural variations. We found the self-consistent force-field theory and Hartree-Fock Hamiltonian with single configuration interaction formalism to be valid for evaluating TPA δ. Although the quantum-chemical calculations slightly underestimated the experimental δ values obtained from nonlinear transmission measurements, they reasonably predicted the dependence of the δ value on the structural variations. We confirmed the role of molecular symmetry by observing that donor-donor substituted structure gave the highest experimental and theoretical TPA δ values and that the donor-acceptor substituted structure showed a greater red-shift in the TPA absorption maximum wavelength. Overall, the theoretical δ values of DTT-based molecules were in the order of 10^{-46} cm$^4 \cdot$ s $\cdot$ photon^{-1} and are higher than that of AF-50 by nearly two orders of magnitude.

I. INTRODUCTION

Molecules can simultaneously absorb two or more photons to access excited states in the presence of intense laser pulses [1]. Since the probability of excitation by two-photon absorption (TPA) is proportional to the squared intensity of the incident light, the excitation and two-photon induced photochemical processes can be confined to the vicinity of the focal point of a beam [1], [2]. Molecules with large TPA cross sections (δ) can be easily applied in the fields of three-dimensional optical memory [3], two-photon fluorescence microscopy [2], [4], optical power limiting [5], [6], and two-photon absorbed photopolymerization for three-dimensional microfabrication [7]. However, the relatively small δ values of existing nonlinear organic molecules have deferred their practical applications. The development of molecules with large δ values requires more detailed studies on the structure-property relationships for third-order nonlinear optics.

Recently, we observed distinct roles of dithienothiophene (DTT); it acts as both an electron bridge in charge transfer of nonlinear optical molecules and an electron modulator in redox reaction of light-emitting molecules [8]. DTT has also been used as the π-center of the TPA molecules, and the DTT-based molecules have shown a large enhancement in δ [9]. In an effort to get higher δ values from DTT, we synthesized DTT-based molecules attached with various functional moieties and measured the TPA dispersion properties. We also theoretically calculated δ values to gain insight into the effect of donor and acceptor groups on the TPA properties of DTT-based molecules and report the results in this paper.

The chemical structures of the DTT-based molecules under study are shown in Fig. 1. In (a) and (b) the central DTT is symmetrically end-capped with donor groups (9-ethylcarbazol-
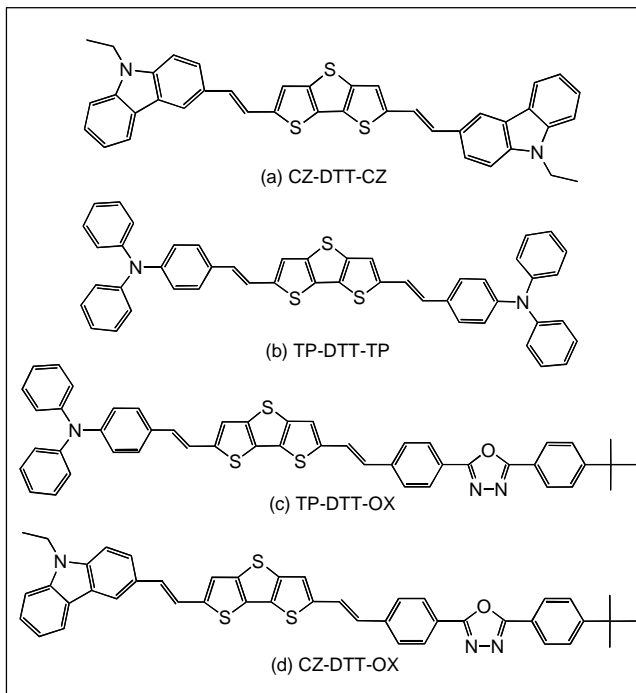
Fig. 1. Chemical structures of the TPA molecules based on DTT as π–center [9].

3-ylmethyl and *N,N*-diphenyl-*p*-benzyl, respectively), while in (c) and (d) the central DTT is functionalized asymmetrically with a donor and an acceptor ([2-(*p-tert*-butylphenyl-3,4-oxadiazol-5-yl)]-benzyl) at each end [9].

II. MEASUREMENT OF TPA δ

We measured the TPA dispersion properties and TPA coefficients for DTT-based molecules. The TPA coefficients were measured by direct nonlinear optical transmission in which the transmission of a sample was measured as a function of incident intensity. Measurements were made on 1-cm path length solutions in THF with a Nd:YAG pumped dye laser with a pulse duration of about 7 ns at 800 nm. TPA δ values were obtained from the measured TPA coefficients with the standard expressions described in [10] for a pure TPA process. As Ehrlich et al. noted [10] the TPA δ values that we report here should be effective values because of contributions from higher-order nonlinearities to the measured TPA coefficients.

III. THEORETICAL CALCULATION OF TPA δ

We theoretically calculated δ values to gain insight into the effect of donor and acceptor groups on the TPA properties of DTT-based molecules. Full geometry optimizations were performed with the self-consistent force-field theory. The energies and transition dipole moments for the ground state and multiple excited states were calculated by combining the Hartree-Fock (HF) Hamiltonian with a single configuration interaction (SCI) formalism. The TPA δ at an optical field frequency is related to the imaginary part of the third-order polarizability Im $\gamma(-\omega;\omega,\omega,-\omega)$ by

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

where $\hbar$ is Planck's constant divided by 2π, c is the speed of light, L is a local field factor ($L = 1$ for vacuum), and n denotes the refractive index of the medium ($n = 1$ for vacuum). Im $\gamma(-\omega;\omega,\omega,-\omega)$ was calculated using the sum-over-states expression with a damping factor of 0.1 eV as suggested by Albota et al [11]. Although we considered up to twenty excited states, we found six excited states to be sufficient for obtaining the saturated values with negligible deviations.

IV. RESULTS AND DISCUSSION

We measured both the single- and two-photon absorption spectrums of all DTT-based molecules. The TPA intensity showed dispersion characteristics of the single-photon absorption spectrum (Fig. 2). However, as Table 1 reveals, the two-photon absorption maximum wavelength (TPA $\lambda_{\max}$) did not coincide with the single-photon absorption maximum wavelength ($\lambda_{\max}$), implying that single- and two-photon absorption peaks are not in close relationship for these molecules. A fluorene derivative *N,N*-diphenyl-7-[2-(4-pyridinyl)ethenyl]-9,9-di-*n*-decylfluorene-2-amine (AF-50) showed a close relationship of single- and two-photon absorption peaks [12]. The $\lambda_{\max}$ and TPA $\lambda_{\max}$ of the molecules including an asymmetric D/A pair (3 and 4) were
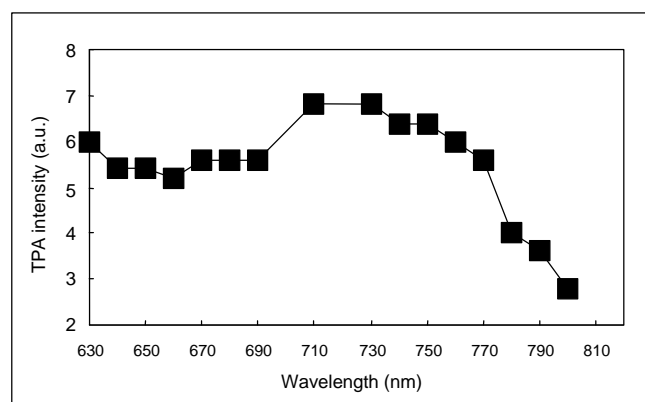

Fig. 2. Wavelength dependence of the TPA intensity for 1 in THF ([M] = 0.5×10^{-2} mol/l). See [9] for linear absorption spectrum.

Table 1. Single- and two-photon absorption data of DTT-based molecules.

Molecules	λ_{max} [a] (nm)	λ_{edge} (nm)	Energy$_{edge}$ (eV)	TPA λ_{max} [b] (nm)
1	440	511	2.42	720
2	453	537	2.31	780
3	456	546	2.27	970
4	446	539	2.30	940

a. Single-photon absorption maximum wavelength
b. Two-photon absorption maximum wavelength

red-shifted more than the molecules with the symmetric D/D structure (1 and 2). The partial charge transfer in the excited state of the asymmetric molecules could have contributed to the red shifts. For molecules with symmetrical arrangements, due to the different parity selection rules between single- and two-photon absorption processes, the S_2 state becomes the dominating TPA state, and hence the location of the maximum TPA state should be higher than that for asymmetrical arrangements [13]. The shift of TPA λ_{max} with structural variation may enable us to tune the TPA peak wavelength through the controlled modification of the chemical structure.

We obtained the experimental TPA δ values at the peak wavelength (δ^a) from the experimental δ values at 800 nm and the ratio of the TPA intensity at the maximum wavelength to that at 800 nm. Table 2 shows that there were differences in the δ^a value of the molecules according to the structural variation. Although we anticipated much larger δ^a values for D-π-D structures than that for D-π-A structures, we did not find any particular tendencies according to the structural variation supporting the dominant role of DTT in the enhancement of δ. The largest δ^a value of 1 may be explained by the substantial

Table 2. Calculated and experimental values of two-photon cross-section for DTT-based molecules.

Molecule	Experimental δ^a at λ_{max} (cm$^4 \cdot$ s $\cdot$ photon^{-1})	Calculated δ^b (cm$^4 \cdot$ s $\cdot$ photon^{-1})
1	3.3×10^{-45}	8.3×10^{-46}
2	7.9×10^{-46}	3.4×10^{-46}
3	1.4×10^{-45}	7.3×10^{-46}
4	3.9×10^{-46}	1.8×10^{-46}

symmetric charge redistribution upon excitation proposed by Albota et al. for the D-π-D structure [11]. We expected a larger TPA value for 2 than for 1 because the stronger donor seemed to be more effective. On the contrary, the δ^a value of 1 was lager than that of 2 and this could be attributed to the better planarity of the CZ groups resulting in the better delocalization of π-electrons.

Prior to applying the self-consistent force-field theory and HF-SCI schemes to the DTT-based molecules, we calculated the TPA δ of AF-50 based on these schemes. The calculation gives a δ of 370×10^{-50} cm$^4 \cdot$ s $\cdot$ photon^{-1}, which is slightly higher than that based on the random phase approximation response theory (142×10^{-50} cm$^4 \cdot$ s $\cdot$ photon^{-1}) [13] and is slightly lower than the experimental δ value obtained using the background-free fluorescence technique (658×10^{-50} cm$^4 \cdot$ s $\cdot$ photon^{-1}) [12]. This result suggests the validity of the calculation schemes used in this work.

Table 2 lists the theoretical TPA cross sections (δ^b) of DTT-based molecules calculated by HF-SCI schemes and on the basis of assumptions suggested by Albota et al. [11] together with the experimental values. The calculations slightly underestimated the experimental results and reasonably predicted the dependence of the δ value on the structural variation. The use of relatively long laser pulses (about 7 ns) could have contributed to the experimental overestimations. Considering the sensitivity of TPA δ on measurement conditions such as solvent, intensity level, and the pulse duration of the laser beam, we consider the δ^b values acceptable. The δ^b values of DTT-based molecules were in the order of 10^{-46} cm$^4 \cdot$ s $\cdot$ photon^{-1} and higher than that of AF-50 by nearly two orders of magnitude. Very recently, Wang et al. theoretically examined a series of DTT-based molecules using the *ab initio* response theory. They calculated the δ value of *N,N*-diphenylamine substituted DTT (TP-DTT-TP) and obtained a value of 1727×10^{-50} cm$^4 \cdot$ s $\cdot$ photon^{-1}, which is lower than that of our result by 20 times. The discrepancy could have been caused by different calculation schemes. However, at least at present, it is hardly possible to judge which one is the right calculation scheme for lack of a standard measuring method of absolute TPA δ value and standard samples. The higher δ^b value of D/D paired 1 compared with that of D/A paired 4 confirms both the experimental result (this study) and theoretical results on the role of the molecular symmetry [13]. Understanding the contribution of sulfur *d* orbital associated with the enhancement in molecular two-photon absorption and the detailed electronic role of DTT as a π-center could provide us with the design strategies required for the development of DTT-based molecules with a more enhanced δ value.

V. SUMMARY

We obtained both experimental and theoretical TPA δ values

of DTT-based molecules from nonlinear transmission measurements and quantum-chemical calculations. The experimental TPA δ values at the absorption peak wavelength showed a dependence on the structural variations. The self-consistent force-field theory and HF-SCI calculation schemes were valid for evaluating TPA δ. Although the quantum-chemical calculations slightly underestimated the experimental δ values obtained from nonlinear transmission measurements, they reasonably predicted the dependence of the δ value on the structural variations. We confirmed the role of molecular symmetry by observing that the donor-donor substituted structure gives the highest experimental and theoretical TPA δ values and that the donor-acceptor substituted structure shows a greater red-shift in TPA λ_{max}. Overall, the theoretical δ values of DTT-based molecules are in the order of 10^{-46} cm$^4 \cdot$ s $\cdot$photon^{-1} and are higher than that of AF-50 by nearly two orders of magnitude.

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