

New Class of Two-Photon-Absorbing Chromophores Based on Dithienothiophene

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Two-photon absorption (TPA) offers the advantage of high transmission at low incident intensity for fundamental optical frequencies well below the band gap frequency. Rentzepis in his pioneer work^{1,2} demonstrated the application of TPA for 3-D data storage. Webb introduced the two-photon approach for 3-D confocal microscopy and 3-D microfabrication.^{3,4} Many new applications have become reality,^{5,6} some of which include two-photon upconverted lasing,^{5,7} two-photon optical power limiting,^{8–10} and two-photon photodynamic therapy.¹¹ Multiphoton microscopy appears to be of great value as an imaging technique for numerous biological applications¹² as well as for nondestructive evaluation of organic paints and coatings.¹³

A number of nonlinear optical (NLO) chromophores including commercial dyes have been reported to display TPA behavior but most known two-photon absorptivities were too small to find usage in practical applications. Unfortunately, design criteria for the molecules with large TPA cross section, σ_{TPA} , have not been well

developed. Recent reports^{14,15} from two different groups disclosed their design strategies for efficient TPA molecules by a systematic investigation of chromophores with various electron-donor (D) and electron-acceptor (A) moieties, which are attached symmetrically or asymmetrically to a conjugated linker (π -center); D- π -D or A- π -A. The typical difference in their approaches is that one¹⁴ deals with *trans*-stilbene as π -center with various D/A pairs, and the other¹⁵ does with chromophores bearing fluorene as π -center, which is asymmetrically coupled with D and A; D- π -A. While the former emphasizes the importance of conjugation length, D/A strength, and molecular symmetry, the latter stresses planarity of π -center (fluorene), the donor strength, and molecular asymmetry. It seems to be that there must be more crucial molecular factors other than structural symmetry and donor strength. One of the largest σ_{TPA} values^{15,16} so far was obtained with an asymmetric structure, D- π -A (where D, A, and π -center are *N,N*-diphenylamino, 4-ethenylpyridine, and 9-di-alkylfluorenyl, respectively), known to be AF-50.

Recently, we have observed a distinct role of dithienothiophene (DTT) as an electron relay in charge transfer (CT) of nonlinear optical chromophores¹⁷ and as an electron modulator in redox reaction of light-emitting chromophores.¹⁸ Those are some of the novel features of DTT. In this communication, we report another feature of DTT as π -center of TPA molecules, in that DTT induces a large enhancement of TPA, compared with benzenoids counterpart,^{6,10,16} such that one of the DTT-centered chromophores produces one of the largest σ_{TPA} values ever known (Tables 1 and 2). Part of the role played by DTT is considered to be contributed by electron-rich heterocycles involving sulfur atoms, known¹⁹ to possess enhanced $\chi^{(3)}$ effects. An enhanced TPA can be also expected as it represents the imaging part of $\chi^{(3)}$.

In the present TPA molecules (Figure 1), the central DTT is attached through conjugation to either a D/D or a D/A pair at the ends, forming a D- π -D (**101** and **103**) or D- π -A (**102** and **104**) sequence. In this case, D is carbazole or *N,N*-diphenylamine unit and A is 2-phenyl-5-(4-*ter*-butyl)-1,3,4-oxadiazole. These chromophores were synthesized by Wittig reaction of dithieno[3,2-*b*:2'3'-*d*]thiophene-2,6-dicarboxaldehyde (DTT-2CHO) with a triphenylphosphonium functional end of D or A moiety such as 9-ethylcarbazol-3-ylmethyl (D), *N,N*-diphenyl-*p*-benzyl (D), or [2-(*p*-*tert*-butylphenyl)-3,4-oxadiazol-5-yl]-benzyl (A). Ultrapure products were obtained through

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(1) Parthenopoulos, D. A.; Rentzepis, P. M. *Science* **1989**, *249*, 843.

(2) Dvornikov, A. S.; Rentzepis, P. M. *Opt. Commun.* **1995**, *119*, 341.

(3) (a) Denk, W.; Strinkler, J. H.; Webb, W. W. *Science* **1990**, *248*, 73. (b) Xu, C. M. J.; Webb, W. W. *Opt. Lett.* **1995**, *20*, 2532.

(4) Wu, En, S.; Strickler, J. H.; Harrell, W. R.; Webb, W. W. *SPIE Proc.* **1992**, *1674*, 776.

(5) Bhawalkar, J. D.; He, G. S.; Prasad, P. N. *Rep. Prog. Phys.* **1996**, *59*, 1041.

(6) Cumpston, B. H.; Ananthavel, S. P.; Barlow, S.; Dyer, D. L.; Ehrlich, J. E.; Erskine, L. L.; Heikal, A. A.; Kuebler, S.; Lee, I.-Y. S.; McCord-Maughon, D.; Qin, J.; Roedel, H.; Rumi, M.; Wu, X.-L.; Marder, S. R.; Perry, J. W. *Nature* **1999**, *398*, 51.

(7) (a) He, G. S.; Zhao, C. F.; Bhawalkar, J. D.; Prasad, P. N. *Appl. Phys. Lett.* **1995**, *67*, 3703. (b) Zhao, C. F.; He, G. S.; Bhawalkar, J. D.; Park, C. K.; Prasad, P. N. *Chem Mater.* **1995**, *7*, 1979.

(8) Fleitz, P. A.; Sutherland, R. A.; Strogkendl, F. P.; Larson, F. P.; Dalton, L. R. *SPIE Proc.* **1998**, *3472*, 91.

(9) He, G. S.; Bhawalkar, J. D.; Zhao, C. F.; Prasad, P. N. *Appl. Phys. Lett.* **1995**, *67*, 2433.

(10) Ehrlich, J. E.; Wu, X. L.; Lee, L.-Y.; Hu, Z.-Y.; Roedel, H.; Marder, S. R.; Perry, J. W. *Opt. Lett.* **1997**, *22*, 1843.

(11) Bhawalkar, J. D.; Kumar, N. D.; Zhao, C. F.; Prasad, P. N. *J. Clin. Laser Med. Surg.* **1997**, *15*, 201.

(12) Caylor, C. L.; Dobrianov, I.; Kimme, C.; Thorne, R. E.; Zipfel, W.; Webb, W. W. *Phys. Rev. E* **1999**, *59* (4), R3831.

(13) Bhawalkar, J. D.; Pan, S. J.; Shih, A.; Samarbandu, J. K.; Swiatkiewicz, J.; Reinhardt, B. A.; Prasad, P. N.; Cheng, P. C. *Polym. Commun.* **1997**, *38*, 4551.

(14) Albota, M.; Beljonne, D.; Bredas, J.-L.; Ehrlich, J. E.; Fu, J.-Y.; Heikal, A. A.; Hess, S. E.; Kogej, T.; Levin, M. D.; Marder, S. R.; McCord-Maughon, D.; Perry, J. W.; Rumi, H. R. M.; Subramaniam, G.; Webb, W. W.; Wu, X.-L.; Xu, C. *Science* **1998**, *281*, 1653.

(15) Reinhardt, B. A.; Brott, L. L.; Clarson, S. T.; Dillard, A. G.; Bhatt, J. C.; Kannan, R.; Yuan, L.; He, G. S.; Prasad, P. N. *Chem. Mater.* **1998**, *10*, 1863.

(16) He, G. S.; Yuan, L.; Cheng, N.; Bhawalkar, J. D.; Prasad, P. N.; Brott, L. L.; Clarson, S. J.; Reinhardt, B. A. *Opt. Soc. Am. B* **1997**, *14*, 1079.

(17) Kim, O.-K.; Fort, A.; Barzoukas, M.; Blanchard-Desce, M.; Lehn, J.-M. *J. Mater. Chem.* **1999**, *9*, 2227.

(18) Kim, O.-K.; Heuer, W. B.; Woo, H. Y.; Lee, K.-S. Manuscript in preparation.

(19) Prasad, P. N.; Reinhardt, B. A. *Chem. Mater.* **1990**, *2*, 60.

Table 1. TPA Cross-Section Values Measured under Nanosecond Pulses for DTT-Based Chromophores (101–104) in Comparison with Other Chromophores Based on Fluorene and Stilbene

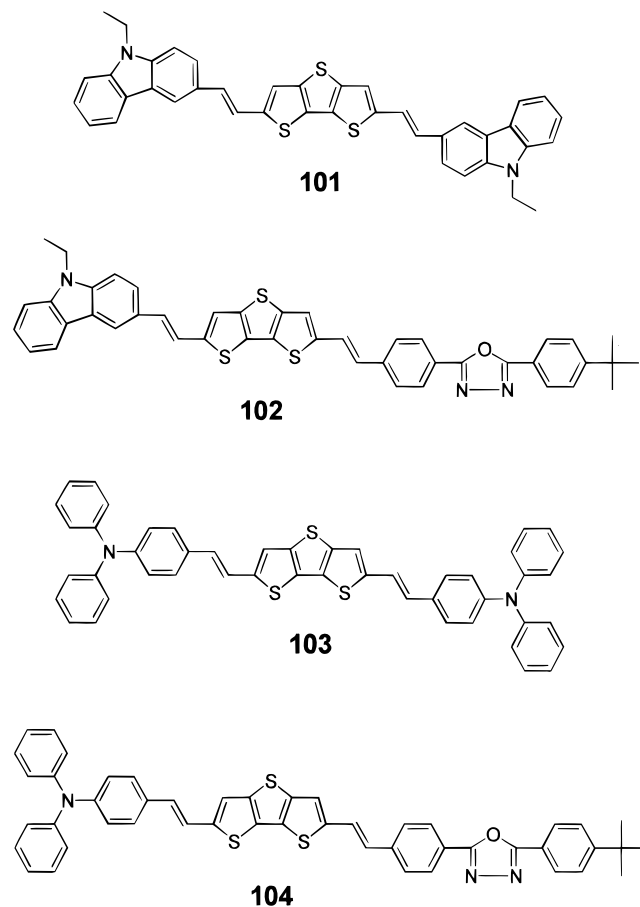
	chromophore						
	101	102	103	104	AF-50 ^a	BDBAS ^b	BDPAS ^c
solvent	TCE	TCE	TCE	TCE ^d	benzene	acetone	toluene
concentration (10 ⁻² mol/L)	0.74	0.91	0.97	0.74	4.5	5	5
wavelength (nm)	810	810	810	810	800	600	700
pulse duration (ns)	8	8	8	8	8	5	5
NLO absorption Coeff. β (cm/GW)	19	7.5	47	19	21		
σ'_{TPA} (10 ⁻²⁰ cm ⁴ /GW)	428	136	810	483	78		
σ_{TPA} (10 ⁻⁴⁶ cm ⁴ s)	10.5	3.35	19.9	11.9	1.94	1.77 (0.93) ^e	1.30 (1.0) ^f
reference	this work	this work	this work	this work	15, 16	10	10

^a *N,N*-Diphenyl-7-[2-(4-pyridinyl)ethenyl]-9,9-di-*n*-decylfluorene-2-amine. ^b 4,4'-Bis(di-*n*-butylamino)stilbene. ^c 4,4'-Bis(diphenylamino)stilbene. ^d 1,1,2,2-Tetrachloroethane. ^e In toluene. ^f Perry, J. W.; et al. *Nonlinear Opt.* **1999**, *21*, 225.

Table 2. TPA Cross-Section Values Measured for Chromophore 103 and AF-50 under 160 fs Pulse

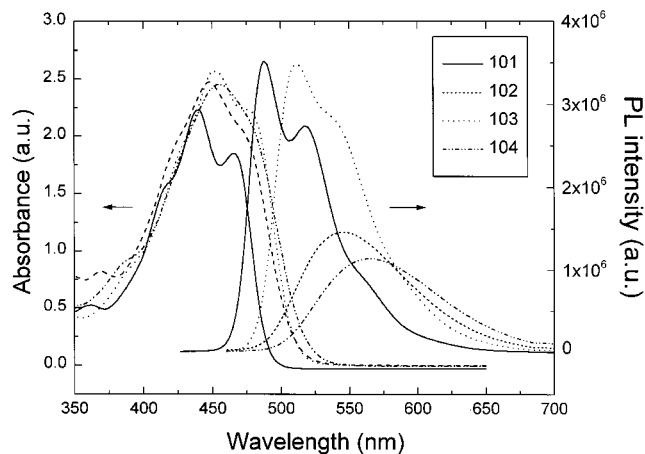
	chromophore	
	103	AF-50
solvent	TCE ^a	benzene
concentration (10 ⁻² mol/L)	0.5	4.5
wavelength (nm)	796	796
pulse duration (fs)	160	160
irradiance range (GW/cm ²)	up to 20	up to 20
σ'_{TPA} (10 ⁻²⁰ cm ⁴ /GW)	1.1	0.12
σ_{TPA} (10 ⁻⁴⁸ cm ⁴ s)	2.7	0.30

^a 1,1,2,2-Tetrachloroethane.

**Figure 1.** Chromophore structures based on DTT as π -center.

purifications by repeating the column chromatography and confirmed by NMR, electronic spectra, and elemental analysis.

As shown in Figure 2, when the chromophores comprise an asymmetric D/A pair of mixed components in

**Figure 2.** Absorption and emission spectra of chromophores bearing DTT as π -center (refer to the chromophore numbers to the chemical structures in Figure 1).

the molecule (**102** and **104**), their absorption maximum, λ_{max} (of single photon absorption), is slightly red-shifted (~ 5 nm) relative to that of their symmetric D/D pair counterpart (**101** and **103**). This is due to a partial CT in the excited state of the asymmetric molecule. These compounds are highly fluorescing (for example, Φ_f of **101** is 0.47), particularly when DTT is linked by a symmetric D/D pair. The emission intensity (of single photon excitation) of the chromophores with the asymmetric structure is significantly smaller relative to the symmetric counterpart. This is probably due to a partial quenching²⁰ associated with intramolecular CT.

TPA cross section (σ_{TPA}) values (the uncertainty range is $\pm 15\%$) were determined from experimentally measured two-photon absorption coefficient (β), which was obtained by measuring the nonlinear transmissivity (T_i) of chromophores (in solution) for a given input intensity, I_0 , and a given thickness of a sample solution, l_0 , from the following relationships:^{16,21}

$$T_i = [\ln(1 + \beta I_0 l_0)] / \beta I_0 l_0 \quad (1)$$

$$\sigma_{\text{TPA}} = h\nu\beta / N_0 = 10^3 h\nu\beta / N_A C \quad (2)$$

where N_0 and N_A are the density of assumed absorptive centers and Avogadro number, respectively, and C is the molar concentration of solute.

(20) Kim, O.-K.; Lehn, J.-M. *Chem. Phys. Lett.* **1996**, *255*, 147.

(21) Tutt, L. W.; Boggess, T. F. *Prog. Quantum Electron.* **1993**, *17*, 2279.

The β values of DTT-based chromophores were measured in tetrachloroethane using 810 nm and 8 ns pulse laser beam at the intensity level of several hundreds of megawatts per square centimeter. For a comparison, additional TPA measurements were carried out at 160 fs using a 796 nm pulsed laser in an irradiance range of 0–20 gigawatts per square centimeter. Both nanosecond and femtosecond nonlinear transmission methods and the femtosecond Z-scan methods were used to investigate the effect of pulse width and hence the relative contribution of excited-state absorption to the two-photon absorption.

The σ_{TPA} values measured in nanoseconds are given Table 1. There are significant differences in σ_{TPA} values of the chromophores, depending on the structural variations; the symmetric structure (**101** and **103**) exhibits relatively larger values compared to the respective asymmetric ones (**102** and **104**) and the stronger donor (triphenylamine > *N*-ethylcarbazole)^{18,22} seems to be more effective. When a comparison is made among chromophores differing in the π -center, the σ_{TPA} values of DTT-based chromophores are roughly 2–10 times larger than that based on fluorene as well as on stilbene. When the comparison is made with respect to the asymmetric chromophores (e.g., AF-50 and **104**) with a nearly comparable A strength (referring to pyridine and oxadiazole moieties),^{23,24} the σ_{TPA} value of chromophore **104** is 6 times larger than that of AF-50. The σ_{TPA} value of DTT-based asymmetric chromophore **104**, for example, is much larger than that of symmetric stilbene-based BDBAS and BDPAS.

It is not simple to assess the molecular TPA efficiency among different chromophores from a direct comparison of their σ_{TPA} values because TPA coefficients can vary significantly with the measurement conditions such as the solvent employed¹⁶ as well as the intensity level and the pulse duration^{10,25} of the laser beam. It has been pointed out that even for the same medium, the measured values of β and σ_{TPA} might be different if the intensity level and the pulse duration are changed on a large scale.^{10,25} The σ_{TPA} values measured by using femtosecond laser pulses are orders of magnitude smaller than those measured by using nanosecond laser pulses.²⁵ Femtosecond time-resolved pump-probe studies have suggested²⁵ that excited-state absorption contributes to the effective nonlinear absorption. The relative contribution of excited-state absorption becomes more manifested when longer time scale pulses are

used. Therefore, for comparison sake, we used femtosecond data which provide a more accurate assessment of the true two-photon absorption.

Table 2 summarizes σ_{TPA} values measured with femtosecond pulses for chromophore **103** and AF-50 which we use as a benchmark. When compared with the nanosecond measurement values, femtosecond values are roughly 2–3 orders of magnitude lower. A similar trend was found in a recent study.²⁵ However, even under the femtosecond measurement, the σ_{TPA} value of chromophore **103** is nearly 1 order of magnitude greater relative to AF-50, as was observed by the nanosecond measurement.

Such a distinct role of DTT in the molecular two-photon absorptivity may be associated with desirable electronic properties^{26,27} such as polarizability brought about by the rigid, planar fused-terthiophene structure which contributes a great deal to the reduction of band gap and the extended π -electron delocalization, where sulfur d orbitals are effectively mixing with π -electrons. Earlier, we have investigated the electronic properties of DTT as an electron relay in push–pull nonlinear chromophores and found that DTT is significantly more efficient as compared to phenyls and other oligothiophenes.^{17,20} It is worth noting that there is no marked difference in σ_{TPA} values between the symmetric and asymmetric structures of the chromophores (**103** and **104**, for example). This seems to suggest that the importance of structural symmetry (**101** and **103**) in chromophores may be a valid argument for the larger σ_{TPA} values but even more important is electronic properties of individual segments and their combination as indicated in chromophores **101** and **104**. The σ_{TPA} value of the latter with an asymmetric structure is even larger than that of the former with a symmetric structure.

In conclusion, we have synthesized a novel class of TPA chromophores bearing dithienothiophene (DTT) as π -center, which comprise a three-component structure: D- π -D and D- π -A. Their TPA cross section (σ_{TPA}) values were measured to be nearly 1 order of magnitude larger than that of AF-50. The structural symmetry of the molecule and donor strength of the D component are important parameters for the enhanced TPA but the crucial role is played by the π -center, DTT.

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(22) On the contrary, cyclic voltammetry (in DMF) indicated that the donor strength of chromophore **1** ($E_1^{\text{ox}} = 0.65$ V) is greater than chromophore **3** ($E_1^{\text{ox}} = 0.69$ V).

(23) Redox potentials of 2-(4-biphenyl-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (a closest relative of 1,3,4-oxadiazole) and 1,4-di(4-pyridyl)-benzene are -1.94^{18} and -1.98^{24} V (vs SCE), respectively.

(24) Takahashi, K.; Nihira, T. *Bull. Chem. Soc., Jpn.* **1992**, *65*, 1855.

(25) Swiatkiewicz, J.; Prasad, P. N.; Reinhardt, B. A. *Opt. Commun.* **1998**, *157*, 135.

(26) Roncali, J.; Thobie-Gautier, C. *Adv. Mater.* **1994**, *6*, 846.

(27) Blanchard, P.; Brisset, H.; Riou, A.; Hierle, R.; Roncali, J. *J. Org. Chem.* **1998**, *63*, 8310.