

Two-photon absorption in two-dimensional conjugated quadrupolar chromophores

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We present ultrafast *z*-scan measurements of the two-photon absorption (TPA) spectra of a pair of two-dimensionally conjugated quadrupolar donor/acceptor (D/A) chromophores. The all-donor substituted species displays a peak TPA cross section [$\sigma^{(2)} = 520 \pm 30 \text{ GM}$] that is more than twice that of the D–A species [$\sigma^{(2)} = 240 \pm 20 \text{ GM}$]. Unlike previous structure–property studies that have evaluated TPA behavior for D/A molecules through the comparison of dipolar and quadrupolar compounds, both molecules investigated herein are quadrupolar, ultimately providing a more consistent evaluation of the effects of donor and/or acceptor substitution on the TPA of conjugated chromophores. © 2006 Optical Society of America
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Two-photon absorption (TPA) is a primary process of interest in various emergent photonics applications.¹ To be of use, TPA materials must display large absorptive nonlinearities tuned within specific spectral regions.² At present, conjugated organic molecules with high π -electron densities are at the forefront of TPA research,¹ but there remains considerable need in establishing structure–property relationships.^{1–4} Early studies on quasi-one-dimensional molecular architectures have shown that incorporating strong donor (D) and/or acceptor (A) groups across a conjugated backbone ($-\pi-$) can lead to substantial increases in the molecular two-photon cross section, $\sigma^{(2)}$.¹ In particular, the structure–property relationship of quasi-one-dimensional molecules that have quadrupolar structures such as D- π -D or A- π -A have been extensively studied.^{1,5–7} Recent studies have also explored higher-dimensional D–A systems.^{2,8,9} However, despite these efforts, a comprehensive picture for this structure–property relationship has yet to be fully unveiled. For example, some studies find that D- π -D schemes show larger cross sections than D- π -A schemes,^{5,10} while other studies show them to be equivalent.¹¹

The comparison between D- π -D and D- π -A schemes is not always straightforward due to the fact that D- π -D molecules are often quadrupolar, and D- π -A analogues are dipolar, resulting in different parity selection rules for the TPA transition in addition to differing factors such as the importance of both one-photon-allowed intermediate states in the quadrupolar systems and permanent dipole(s)

strength in the dipolar systems. Thus the best way to establish structure–property TPA relationships would be to allow for the two aspects—D/A substitution and symmetry—to be treated independently.

A solution to this issue is found in the use of two-dimensionally conjugated molecules^{12,13} such as the cruciform tetrakis(phenylethynyl)benzenes (TPEBs, Fig. 1).¹⁴ Electron donor and/or acceptor substitution of the four terminal TPEB groups provides an ideal framework for studying the intrinsic effects of the symmetry and the electron distribution on TPA. Although these molecules have been studied theoretically,¹⁵ their experimental TPA spectra have not been reported. Herein, we present and compare the TPA characteristics of an all-donor- and a D–A-substituted TPEB (Fig. 1).

The two chromophores under study possess inversion symmetry and thus have no net permanent dipole moment in the ground state. Despite being quadrupolar, the compounds differ in charge distribution and conjugation path arrangements: TD-TPEB has two equivalent straight conjugation paths (D- π -D) through the *para*-linkage of the central phenyl ring; whereas *para*-TPEB has two nonequivalent linear-conjugation paths (D- π -D and A- π -A). Furthermore,

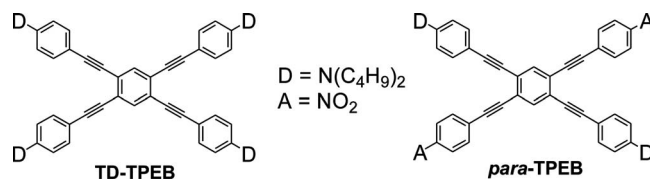


Fig. 1. Compounds studied in this work.

the bent-conjugation paths through the *ortho*-linkage are D- π -D for TD-TPEB but D- π -A for *para*-TPEB.

We present the TPA spectra of dilute TPEBs in tetrahydrofuran (THF) solutions (5–11 mM) obtained with a *z*-scan technique using ultrafast (~ 125 fs) amplified pulses with a near-Gaussian spatial profile.¹⁶ TPA cross sections, $\sigma^{(2)}$, are determined at each measurement wavelength from fits to the laser-power dependence of the two-photon absorbance, q_0 , obtained from open-aperture traces, using $q_0 = (I_0 L_{\text{eff}} N_c \sigma^{(2)}) / (\hbar \omega)$, where I_0 is the peak on-axis optical intensity, L_{eff} is the effective path length (~ 1 mm), and N_c is the number density of the sample.¹⁷ The Rayleigh range is 4–8 mm, depending on wavelength, and is longer than L_{eff} in fulfillment of the thin sample condition.¹⁸ I_0 was varied through the range of 10–150 GW/cm². Good linearity between q_0 and I_0 was displayed at all wavelengths, suggesting that contributions from the excited-state absorption shown previously to exist at longer time scales in these systems is negligible for the present *z*-scan measurements.¹⁹ For comparability of our obtained $\sigma^{(2)}$ values to others reported in the literature, we also measured iteratively (at each wavelength) MPPBT¹⁷ and/or 1,4-bis(*p*-dibutylaminostyryl)-2,5-dimethoxybenzene (compound 8 in Ref. 3) under the same experimental conditions.²⁰

Figure 2 presents the observed TPA spectrum overlapped with the one-photon absorption (OPA) spectrum and the measured OPA at the TPA-measurement concentrations for each of the compounds. TD-TPEB has a TPA peak at 710 nm with $\sigma^{(2)} = 520 \pm 30$ GM (1 GM = 10^{-50} cm⁴ s photon⁻¹ molecule⁻¹), and *para*-TPEB has a peak at 750 nm with $\sigma^{(2)} = 240 \pm 20$ GM. Thus TD-TPEB yields a peak cross section that is both blueshifted and more than double the magnitude of that in *para*-TPEB, in contrast to previous theoretical results for linear quadrupolar molecules.²¹

The TPA spectrum of *para*-TPEB displays a sharp increase when the laser frequency approaches the OPA edge (hatched area, Fig. 2) in a fashion similar to that reported for some other symmetric molecules.^{17,22} This is attributed to the tuning of a double resonance condition. At the lowest measured wavelength (586 nm), *para*-TPEB shows considerable TPA (~ 600 GM) while still maintaining one-photon transparency. On the other hand, the rise in $\sigma^{(2)}$ for TD-TPEB is not significant in the same wavelength region. This is most likely because the lowest-energy OPA peak is blueshifted for TD-TPEB in comparison with *para*-TPEB.

The low-energy peak TPA cross section in quadrupolar systems is typically described in terms of a three-level model, which represents the simplest approximation within the essential-state approach to the full sum-over-states treatment.²³ In this model, absorption from the ground state (*g*) to the two-photon-allowed (one-photon-forbidden) excited state (*e'*) is mediated by an intermediate one-photon-allowed (two-photon-forbidden) level (*e*). The peak

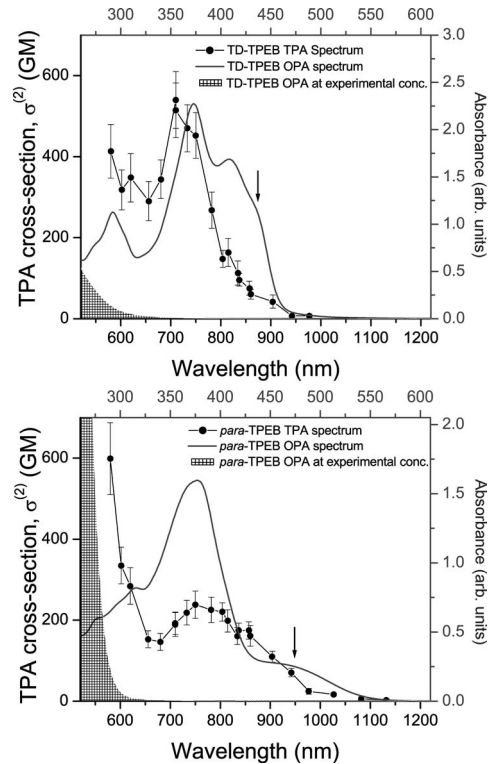


Fig. 2. OPA and TPA spectra of the all-donor TD-TPEB (top) and D-A *para*-TPEB (bottom). The OPA spectrum (solid gray curves) scale is top and right; the TPA scale is bottom and left. The measured OPA spectrum at the TPA experimental concentration is included (hatched area; scales are bottom and right) to indicate the tuning of TPA to the residual OPA absorption below 600 nm. Arrows indicate the lowest-energy OPA peak-shoulder.

TPA cross section is thus proportional to the magnitude of transition dipoles M_{ge} and $M_{ee'}$, and is given by

$$\sigma_{3\text{-level}}^{(2)} = C \frac{E_{ge}^2 M_{ge}^2 M_{ee'}^2}{(2E_{ge} - E_{eg'})^2 \Gamma_{ge'}}, \quad (1)$$

where it is assumed that, on peak, $E_{ge'} \approx 2\hbar\omega$, and $(E_{ge} - \hbar\omega) \gg \Gamma_{ge}$ (i.e., far from double resonance). Here $\hbar\omega$ is the photon energy; E_{ge} and $E_{ge'}$ are the one- and two-photon transition energies, respectively; $\Gamma_{ge'}$ is the damping factor (linewidth) for the transition; and C is a numerical prefactor.

Inspection of the relative positions of the lowest OPA and TPA peaks in the two compounds, as shown in Fig. 2, suggests that TD-TPEB has a larger detuning factor $(2E_{ge} - E_{eg'})$ than *para*-TPEB and should thus display a lower ($\sim 25\%$) TPA cross section. Experimentally, however, TD-TPEB displays a twofold increase in TPA than *para*-TPEB. This difference must therefore originate from transition dipole terms, M_{eg} and $M_{ee'}$, in Eq. (1). In practice, M_{eg} is often approximated from the integrated OPA oscillator strength. TD-TPEB does display a considerably larger absorption than *para*-TPEB¹⁴ and might therefore be expected to have a larger M_{eg} . The respective linewidths, however, are not similar, and a valid approximation of M_{eg} is thus problematic. Esti-

mations of $M_{ee'}$ are difficult to obtain experimentally and must be calculated quantum chemically. Thus the roles of M_{eg} and $M_{ee'}$ remain to be confirmed.

A recent theoretical report did not identify any two-photon resonances for TPEBs at wavelengths greater than 520 nm.¹⁵ This clearly contradicts our experimental results in which both TPEBs display a continuum of TPA commencing at ~ 900 nm with large cross-section peaks in the near-IR. Furthermore, our observation that the all-donor species shows a higher TPA cross section than the D-A compound further disagrees with the predictions of Ref. 15. The large TPA cross section of TD-TPEB may stem from large transition dipoles arising from the central tetraethynylbenzene core acting as an acceptor, thus leading to a favorable D- π -A- π -D arrangement.¹

In conclusion, we report the differences in the TPA spectra of two quadrupolar D- π -D/A chromophores. The lowest-energy TPA peak in the all-donor-substituted TD-TPEB presents a considerably larger cross section in comparison with that with D- π -A *para*-TPEB. Thus the incorporation of donor groups more strongly increases peak TPA than does acceptor substitution. By using the two-dimensionally conjugated TPEB framework, we are able to confirm this structure-property relationship without resorting to comparisons between molecules of disparate ground-state polarity.

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20. For example, at a wavelength of 733 nm, we obtained $\sigma^{(2)} = 720 \pm 90$ GM and 870 ± 110 GM for MPPBT and 1,4-bis(*p*-dibutylaminostyryl)-2,5-dimethoxybenzene, respectively, which agrees with the previously reported literature values of ~ 700 and ~ 900 GM, respectively, at 730 nm. See Refs. 17 and 4.
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