Third- and fifth-order optical nonlinearities in organic materials

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Abstract

We measure the nonlinear optical properties of solutions of a bisbenzethiozole-substituted thiophene compound (BBTDOT) and didecyloxy substituted polyphenyl (DDOS) using the Z-scan technique with 532 nm picosecond pulses. Both compounds exhibit two-photon absorption (2PA) and excited-state absorption (ESA) from the 2PA generated excited states. We measure the magnitude and sign of the real (refractive) and imaginary (2PA) parts of the third-order hyperpolarizability, and the excited-state absorptive and refractive cross sections. We observe third-order self-focusing in BBTDOT and self-defocusing in DDOS while both show excited-state defocusing. All these effects were previously observed and modeled in semiconductors giving insight into the nonlinearities occurring in these organic materials.

In the last decade, organic materials have emerged as potentially viable media for optical switching and limiting. Many researchers have been involved in the investigation of the nonlinear optical properties of various types of organics [1–6]. In this Letter, we study the nonlinear optical properties of two organic compounds, a bisbenzethiozole-substituted thiophene compound (BBTDOT) [7] and a didecyloxy substituted polyphenyl compound (DDOS) [8] using the Z-scan technique with picosecond pulses at 532 nm and compare the nonlinearities to those we have previously studied in semiconductors [9,10]. As in semiconductors, we observe two-photon absorption (2PA), ultrafast nonlinear refraction (NLR) and excited-state nonlinearities induced by 2PA [10]. The existence of 2PA in DDOS was also observed by Zhao

et al. [8], where 400 fs pulses at a wavelength of 602 nm were used in a degenerate four-wave mixing (DFWM) experiment. We compare the information obtained from these different methods. The molecular structures of these compounds are shown in Fig. 1.

We employed the Z-scan experimental method where a sample is scanned in Z through the focus of a Gaussian beam to investigate the nonlinearities in these compounds [11,12]. As discussed more fully in Refs. [11,12], the normalized transmittance of an aperture placed in the far field is measured as a function of the position Z with respect to focus. Such a 'closed aperture' Z-scan gives a measure of the NLR including nonlinear absorption (NLA). If the aperture is removed ('open aperture'), the Z-scan is only sensitive to NLA. A division of the 'closed' by 'open' aperture data gives a signal dependent only on the NLR under approximations outlined in Ref. [12].

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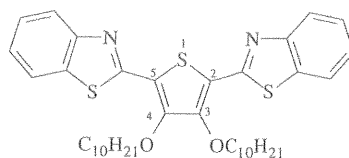
2,5-bis(2-benzothiazoyl)-3,4-didecyloxy-thiophene

(BBTDOT)
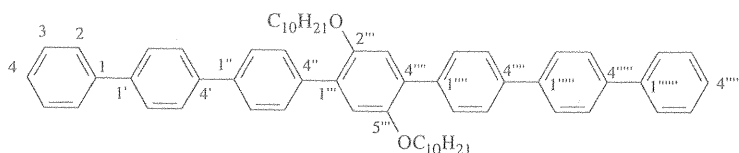
2''',5'''-Didecyloxy-1,1':4',1'':4'',1''':4''',1'''':4'''',1''''':4''''',1''''''-septiphenyl

(DDOS)

Fig. 1. The chemical structure of BBTDOT and DDOS.

Examples of closed and open aperture, and divided Z-scans are shown later in Fig. 2.

Measurements were performed on samples of BBTDOT and DDOS dissolved in tetrahydrofuran (THF). We use a 0.02 M solution of BBTDOT and a 5×10^{-3} M solution of DDOS. The lower concentration is used for DDOS as it precipitates at concentrations in excess of 0.01 M. The linear absorption for
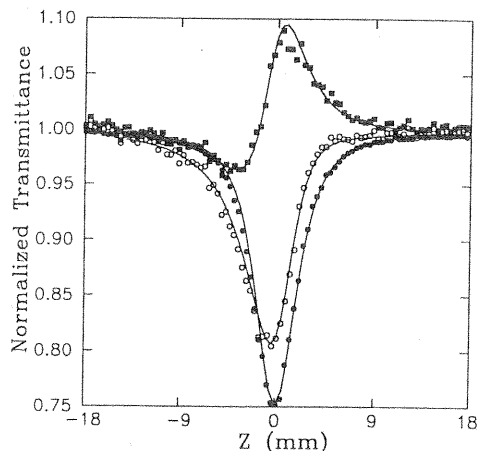
the 2 mm path length spectroscopic cells was too low to measure ($< 2\%$ loss) for both solutions. This is consistent with the maxima in the linear absorption occurring at ≈ 400 nm for BBTDOT and ≈ 300 nm for DDOS. Linear spectra for these materials are given in Refs. [7,13]. Our experiments were performed using the second harmonic of a Q-switched and mode-locked Nd:YAG laser, producing pulses of 32 ps (fwhm) duration at a wavelength of 532 nm and a 10 Hz repetition rate. The Gaussian beam was focused to a 19 µm (hw1/e^2m in irradiance) spot size. Z-scans were performed at several irradiances for each sample to enable determination of the order of the nonlinearities. Fig. 2 shows a typical series of open-aperture, closed-aperture and divided Z-scans for DDOS at a fixed input energy ($I_0 \approx 36$ GW/cm^2). In all, we performed six such series of Z-scans on BBTDOT and five on DDOS at varying peak-on-axis input irradiances, I_0, from 1 to 36 GW/cm^2.

We initially calculate an effective 2PA coefficient, β_{eff}, for each input irradiance where the change in irradiance with depth, $dI/dz = -\beta_{eff}I^2$. Experimentally we measure the incident energy, E_i, and the transmitted energy, E_t. The change in energy transmittance at focus, $\Delta T = (E_i - E_t)/E_i$, is determined experimentally from which we can calculate β_{eff}.

Fig. 2. Typical open aperture (●), closed aperture (○), and divided (■) Z-scan data for sample DDOS in THF at $I_0 \approx 36$ GW/cm^2.

Plotting β_{eff} for BBTDOT in Fig. 3a gives a straight line of positive slope showing that the effective non-linear absorption increases linearly with I. This suggests that a higher order effect, such as excited-state absorption (ESA) accessed via 2PA, is contributing to the NLA. The behavior of this material is similar to semiconductors irradiated in the 2PA regime, and hence we may use an analysis similar to that of Ref. [9]. In the case of semiconductors, the NLA is caused by 2PA and by the absorption due to free carriers generated via this 2PA. The propagation equation for the irradiance within the sample is given by

$$\frac{dI}{dz} = -\beta I^2 - \sigma_{\text{a}} N_{\text{e}} I , \qquad (1)$$

where β is the actual 2PA coefficient, σ_{a} is the ESA cross section and N_{e} is the density of excited states created by 2PA. The carrier generation rate is [14]

(a)

$$\frac{dN_{\text{e}}}{dt} = \frac{\beta I^2}{2\hbar\omega} , \qquad (2)$$

were $\hbar\omega$ is the incident photon energy. The data of Fig. 3a are described well by Eqs. (1) and (2) giving a value for β and σ_{a}. The ESA from the 2PA generated excited states acts as a fifth-order nonlinearity [15]. The solid line for the open aperture Z-scan of Fig. 2 is a fit for β and σ_{a}.

The hyperpolarizability given in Table 1 comes from the following definitions. Defining the third-order polarization as $P^{(3)} = \frac{3}{4}\chi^{(3)}|E|^2 E$, in terms of the electric field $E(t) = \frac{1}{2}E e^{-i\omega t} + \text{c.c.}$, the corresponding imaginary part of the third-order susceptibility $\chi_{\text{I}}^{(3)}$ is

$$\chi_{\text{I}}^{(3)} = \frac{n_0^2}{4\pi^2\mu_0} \lambda\beta , \qquad (4)$$

where λ is the free-space wavelength, μ_0 is the permeability of free space, and n_0 is the linear index of refraction ($n_0 \approx 1.41$ for THF). Here $\chi^{(3)}$ is in Gaussian units (i.e. $\text{cm}^2/\text{statvolt}^2$), while all other parameters are in MKS. The imaginary part of the hyperpolarizability, γ_{I}, is then given by [1]

$$\gamma_{\text{I}} = \frac{1}{[\frac{1}{3}(n_0^2+2)]^4 N} \chi_{\text{I}}^{(3)} , \qquad (5)$$

where N is the molecular density in cm^{-3}. Hence the units for γ are $\text{cm}^5/\text{statvolt}^2$. A corresponding equation may be written to relate the real parts of γ and $\chi^{(3)}$. Table 1 shows the average γ_{I} and σ_{a} obtained from the different inputs, I_0, for the two samples.

The closed aperture Z-scan of Fig. 2 shows positive NLR. The NLR may be caused by both the solute, solvent and the glass windows of the spectroscopic cell. By performing a Z-scan on a cell containing only the solvent, significant NLR is observed which we
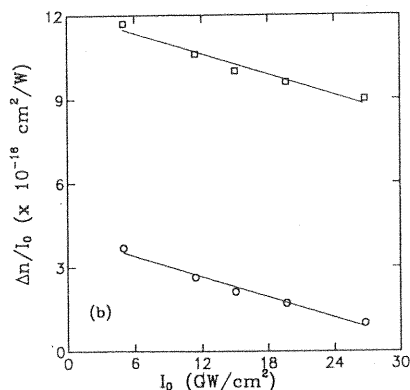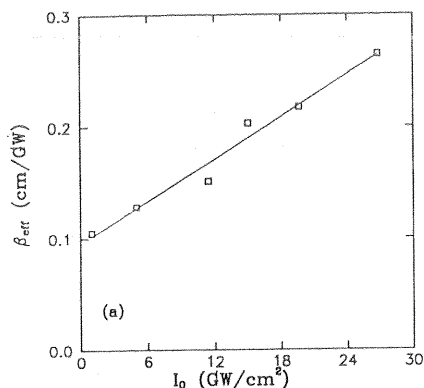

(b)

Fig. 3. (a) $\Delta\alpha/I_0$ versus I_0 for the BBTDOT sample with least-squares fit (solid line); (b) $\Delta n/I_0$ versus I_0 with solvent n_2 present and subtracted along with fits (solid lines).

Table 1
List of measured nonlinear coefficients for bound electronic and excited state processes in BBTDOT and DDOS, along with estimated experimental uncertainties

Sample	BBTDOT	DDOS	Errors
γ_{I}	4.8×10^{-34} esu	1.1×10^{-33} esu	22%
γ_{R}	4.8×10^{-34} esu	-4.5×10^{-34} esu	30%
σ_{a}	6.2×10^{-18} cm^2	4.2×10^{-18} cm^2	30%
σ_{r}	-1.9×10^{-18} cm^2	-1.2×10^{-18} cm^2	36%

subtract from all the NLR data to obtain the contribution from the solute alone. No NLA or higher order effects are observed in the solvent.

Upon examining the NLR data of BBTDOT at several input irradiance levels, we observe a trend similar to the NLA data. The sample exhibits both positive third- and positive fifth-order contributions to the NLR. We attribute this to a third-order bound-electronic contribution of coefficient n_2, and to a fifth-order effect due to a change in index caused by the production of excited states by 2PA. Hence, the change in the refractive index is,

$$\Delta n = n_2 I + k\sigma_r N , \qquad (6)$$

where $k = 2\pi/\lambda$ and σ_r is the excited state refractive index cross section. Using the same procedure as in the nonlinear absorption case, we plot Δn divided by the input irradiance as a function of I_0 in Fig. 3b [9]. Also shown is the total index change before subtraction of the NLR from the cell and solvent.

The real part of the hyperpolarizability, γ_R, given in Table 1 is determined after fitting the closed aperture Z-scan or divided data (examples shown in Fig. 2) using Eq. (5) and

$$\chi_R^{(3)} = \frac{n_0^2}{\mu_0 \pi} n_2 , \qquad (8)$$

where again $\chi^{(3)}$ is in Gaussian units and n_2 is in MKS. The fits use temporal and spatial averages of Eq. (6) as described in Ref. [9] and result in the values for γ_R and σ_r given in Table 1. The values in Table 1 are the averages of the fits for the different I_0s.

The sample DDOS also shows increasing NLA with increasing I_0 as seen in BBTDOT. From the closed aperture data for DDOS we determine a negative intercept for a plot of $\Delta n/I_0$ versus I_0 leading to a negative n_2 and γ_R. The slope of this plot is negative, indicating that σ_r is also negative for DDOS.

Both these materials had been previously studied using DFWM, DDOS in Ref. [7] and BBDOT in Ref. [8]. The fact that for DDOS, the nonlinear refractive index of the solute and solvent have opposite signs allows the determination and identification of 2PA via DFWM, by measuring the concentration dependence of the DFWM signal [7]. Hence our conclusions for DDOS are similar to those of Ref. [7]. However, if the solvent and solute have the same sign of n_2, DFWM cannot distinguish between the real and

imaginary parts of $\chi^{(3)}$. For this reason, the previous study of BBTDOT was unable to separate the NLA and NLR contributions to the DFWM signals, and the signal was attributed entirely to NLR. Additionally, the Z-scan is able to distinguish the third- and fifth-order NLR separately from these contributions to the NLA at low concentrations ($\approx 5 \times 10^{-3}$ M) where the nonlinear refraction is dominated by the cell and solvent.

In summary, we use the Z-scan technique to determine NLA and NLR in solutions of BBTDOT and DDOS. Third- and fifth-order nonlinearities are observed for both the NLA and NLR, but NLA dominates in each sample. A list of the measured optical parameters is found in Table 1. The third order nonlinear refraction in BBTDOT is positive while that of DDOS is negative. The excited-state refraction which is caused by 2PA generation of excited states is negative in both BBTDOT and DDOS solutions. The nonlinear optical properties of these organic materials are strikingly similar to those of semiconductors when the latter are probed in the 2PA regime [9]. In semiconductors the fifth-order effect is caused by the free carriers generated via 2PA while in these organic compounds the fifth-order nonlinearity is due to excited states created by 2PA.

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