

Nonlinear absorption in charge transfer films

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ABSTRACT

Nonlinear optical absorption in solid films of poly(3-octyl thiophene) (P3OT) sensitized with methanofullerene was investigated for wavelengths from 620 to 960 nm. The nonlinear absorption is enhanced over that in either of the component materials by more than two orders of magnitude at 760 nm. The large nonlinearity results from efficient photoinduced intermolecular charge transfer from P3OT to methanofullerene, followed by absorption in the charge separated excited state. P3OT/fullerene films are promising as reverse saturable absorbers and the optical limiting performance is demonstrated at 760 nm.

1. INTRODUCTION

When C₆₀ or C₆₀ derivatives are mixed with a semiconducting polymer, the composite shows efficient photoinduced charge transfer; photoexcited electrons are transferred from the polymer to the fullerene molecule in less than a picosecond.¹⁻⁵ Charge transfer and charge separation (with electron on the C₆₀ and hole on the conducting polymer) were demonstrated by photoinduced electron spin resonance which exhibits g-value labeled signatures of both the semiconducting polymer cation and the C₆₀ anion.¹ Spectroscopic signatures of the C₆₀ anion have been observed in photoinduced absorption (PIA) measurements.² Sub-picosecond time-resolved PIA data show that charge transfer occurs within 300 femtoseconds after photo-excitation.^{4,5} Since the charge transfer rate is more than 1000 times faster than any competing process, the quantum efficiency for charge separation approaches unity.¹⁻⁵

The photoinduced charge transfer is metastable; the back transfer (recombination) occurs on a much longer time scale; the charge separated state persists to times in the microsecond and even the millisecond regime.¹⁻⁷ Thus, the photoinduced charge transfer is analogous to artificial photosynthesis; photoinduced charge separation with unit quantum efficiency and inhibited back transfer. As a result, the photoinduced charge transfer and charge separation can be used to create novel high performance nonlinear optical (NLO) materials.

NLO phenomena in such charge transfer composites are of particular interest.⁸ Photoinduced absorption measurements indicate large shifts in oscillator strength following photoexcitation.^{4,5} The spectrum persists to the millisecond time scale, consistent with the metastability of the charge separated state. The high quantum efficiency and metastability of photoinduced charge separation in combination with the large photoinduced absorption suggested to us the possibility of nonlinear absorption in conjugated polymer/C₆₀ blends. If this nonlinear absorption were large enough, the photoinduced charge transfer mechanism could be a route to materials for optical limiters.

In this paper, we report the NLO absorption of P3OT/fullerene-derivatives in solid films using nanosecond laser pulses at wavelengths from 620 nm to 960 nm (1.3 eV to 2.0 eV). We find a large nonlinearity, enhanced over that in either of the component materials by more than two orders of magnitude at 760 nm, which results from efficient photoinduced intermolecular charge transfer followed by absorption in the charge separated excited state. We find that the NLO absorption of P3OT/methanofullerene blends is sufficiently large that photoinduced charge transfer films are

promising as optical limiters (optical surge protectors). When pumped at 760 nm, the transmitted energy saturates at an average fluence of approximately 0.1 J/cm².

2. SAMPLE PREPARATION

Because of the tendency for C₆₀ to phase separate and crystallize, there is limited solubility of C₆₀ in the conjugated polymers. To achieve efficient charge separation and a high concentration of metastable excited states following photoexcitation, one needs to extend the solubility range. To accomplish this, a series of soluble functionalized C₆₀ derivatives has been developed.⁹ The molecular structure of one of these, denoted as (6,6)PCBCR (phenyl-C₆₁-butyric acid cholesteryl ester; MW = 1164) is shown in Figure 1. With these soluble C₆₀-derivatives, one can make homogeneous, stable, optical quality films containing 1:1 by weight methanofullerenes (approximately 1 acceptor for every 5 repeat units of P3OT). The molecular structure of the conducting polymer, P3OT is also shown in Figure 2.

For comparative studies, solid films were made of pure (6,6)PCBCR, pure P3OT, and a 1:1 (by weight) mixture. Each material was dissolved in xylene. Thick films (20~30μm) for NLO absorption experiments at off-resonant wavelengths were cast from filtered solution onto fused silica substrates. Thin films (0.1~0.2 μm thick) for measurements near resonance and for third harmonic generation (THG) experiments were prepared by spin coating.

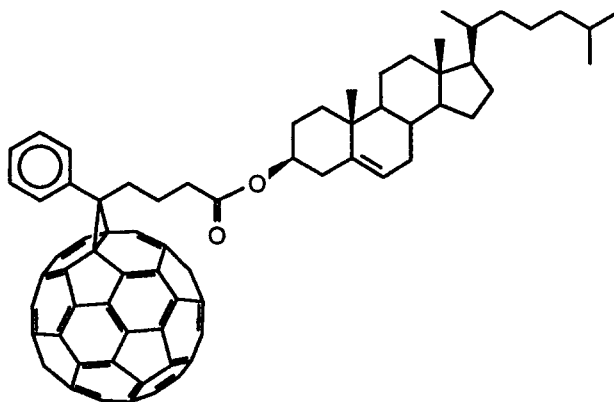


Fig.1 Molecular structure of (6,6) PCBCR (phenyl-C₆₁-butyric acid cholesteryl ester)

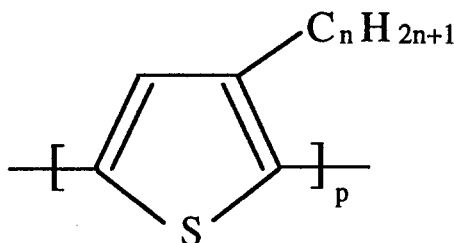


Fig.2 Chemical structure of P3OT (n=8)

3. LINEAR AND NONLINEAR OPTICAL EXPERIMENTS

Linear transmission (T) and NLO absorption were measured for wavelengths from 620 nm to 960 nm using a pulsed dye laser pumped by the second harmonic of a Q-switched Nd:YAG laser. The full width at half maximum of the dye laser pulse was about 8 ns with a repetition rate of 10 Hz. Open aperture Z-scan technique¹⁰ was employed to obtain the nonlinear change in transmission ($\Delta T/T$ vs Z). The Gaussian beam radius at focus (radius at $1/e$ of the maximum electric field) was estimated to be $\sim 25 \mu\text{m}$. Closed aperture Z-scans were also tried; however, nonlinear refraction could not be observed because the nonlinear absorption was dominant. The experimental setup and typical open aperture Z-scan data are shown in Figure 3.

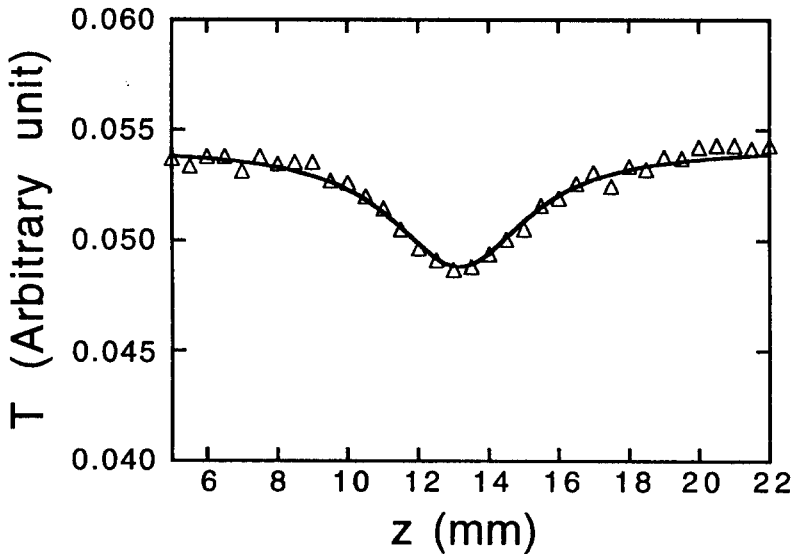
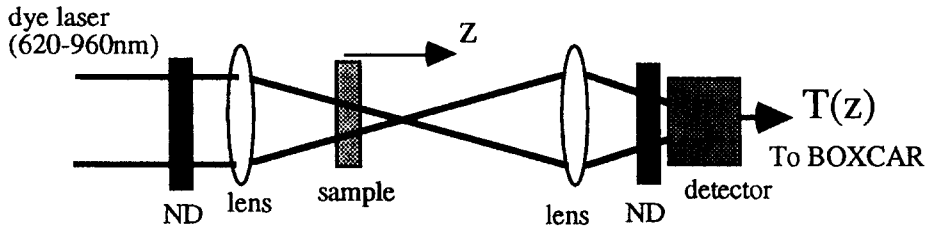


Fig.3 Experimental setup for open aperture Z-scan (upper) and typical data at 760 nm for the composite film (P3OT/(6,6)PCBCR) (lower). NDs are neutral density filters.

4. DATA ANALYSIS AND DISCUSSION

As a first approximation we fitted the open aperture Z-scan data to a model based on pure two-photon absorption (TPA) assuming Gaussian spatial and temporal pulse intensity profiles.¹⁰ The "effective" TPA coefficient, β_{eff} , provides a good description of the nonlinear absorption, $\Delta\alpha(I) = \beta_{\text{eff}}I$ where I is the intensity. The β_{eff} values obtained from the fits are summarized in Table 1. We found that β_{eff} is weakly dependent on the input optical pulse energy, decreasing slightly at higher input pulse energies; the β_{eff} in Table 1 were obtained in the low input energy regime ($\Delta T/T \leq 0.2$) where the values are constant within the experimental error. At 760 nm, the NLO absorption is enhanced by more than two orders of magnitude in the composite film over that in the films of pure P3OT or pure (6,6) PCBCR.

λ (nm)	620	700	760	810	860	910	960
P3OT	(-)	5.6±1	0.76±0.1	1.3±0.1	0.8±0.2	0.6±0.3	<0.3
(6,6)PCBCR	no data	<60 *	0.6±0.1	0.3±0.2	<0.2	<0.3	<0.3
Composite	(-)	220±30	140±16	44±4	17±2	5.3±0.5	1.6±0.2

Table 1 Effective two photon absorption coefficients, β_{eff} (cm/MW) of the three films.
(-) negative value (nonlinear bleaching), * intensity-dependent

In Figure 4, the spectral dependence of β_{eff} for the composite film is compared with the linear absorption coefficient, α , of the same thick film. The spectral dependence of β_{eff} follows the absorption coefficient which decreases with increasing wavelength (in the tail of the π - π^* absorption). We observed nonlinear bleaching at 620 nm (Table 1). This arises from the shift in oscillator strength from the interband transition characteristic of the ground state to the absorption from the charge transferred excited state.⁴⁻⁶

The NLO absorption does not arise from a Kerr-type $\chi^{(3)}$ process. The values for β_{eff} are too large ($\sim 10^4$ times) compared with typical TPA coefficients obtained from similar organic systems with physically reasonable oscillator strengths.^{11,12} Moreover, THG measurements of P3OT and of the P3OT/(6,6) PCBCR composite show no enhancement of any two-photon resonance.

We propose that the nonlinear absorption arises from photoinduced charge transfer followed by absorption from the charge transferred excited state. Although 760 nm is below the principal π - π^* absorption, there exists a small residual absorption coefficient ($\sim 270 \text{ cm}^{-1}$), mainly from the P3OT component, which is large enough to initiate the process. We have re-analyzed the Z-scan data using this model. The rate equation for the excited state population can be written as follows:

$$\frac{dN}{dt} = \alpha I / h\nu - N / \tau \quad (1)$$

where $N = N(r, z, t)$ is the number density of charge separated excited states generated by linear absorption with absorption coefficient α , $I = I(r, z, t)$ is the intensity of the laser pulse at time t and coordinate (r, z) inside the medium, $h\nu$ is the photon energy, and τ is the decay time of the charge separated excited states. The last term can be neglected when the decay time is much longer than the optical pulse width, which is the case in our experiments. To calculate the nonlinear energy transmission, the propagation equation

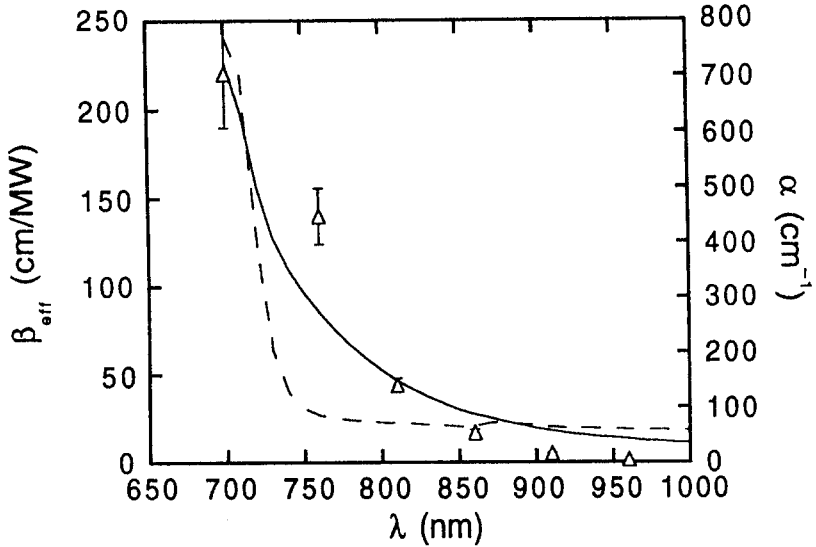


Fig.4 Dispersion of β_{eff} (open circles; refer to the right vertical axis) compared with the linear absorption spectra of a thick film of the composite and the (6,6)PCBCR (solid curve and dashed curve, respectively; refer to the left vertical axis)

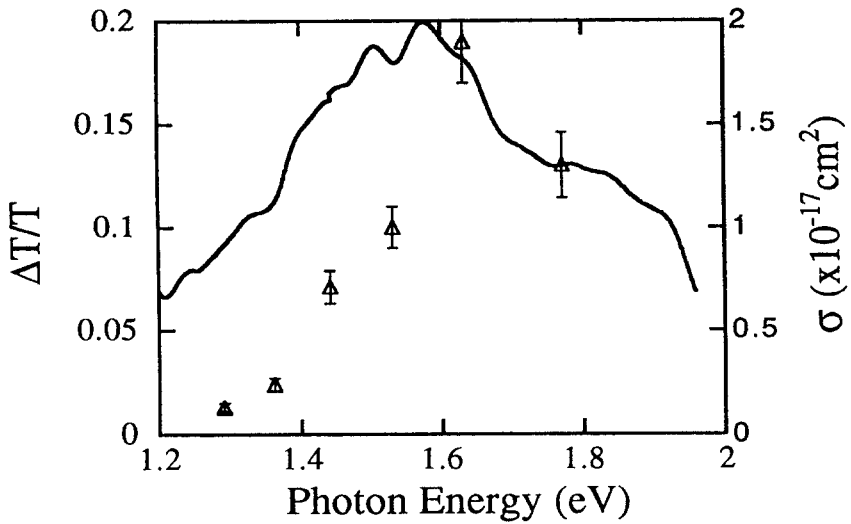


Fig.5 Dispersion of excited state absorption cross section (σ) is compared with the picosecond PIA spectrum (see ref. 5).

Fitting the nonlinear absorption data to eqns. 1 and 2 gave the spectrum of the excited state cross section shown in Figure 5. The peak at 760 nm (1.63 eV) indicates a resonance in the excited state absorption.^{4,5} The peak cross-section, $\sigma \approx 1.9 \times 10^{-17} \text{ cm}^2$, is in order of magnitude agreement with values obtained from the picosecond photoinduced absorption^{4,5} (the Z-scan would generate an average over times less than the 8 ns pulse width) and much larger than the linear absorption cross section as required for reverse saturable absorption.¹³ The spectrum of the picosecond PIA is shown for comparison as the solid curve in Figure 5. The general agreement between the magnitude and spectral dependence of σ as obtained indirectly from the Z-scan data (using eqns. 1 and 2) and as obtained directly from the PIA confirms the proposed mechanism.

$$dI/dz = -\alpha I - \sigma NI \quad (2)$$

was numerically solved simultaneously with eqn. 1, where σ is the cross-section for absorption from the charge separated excited state to a higher lying state. The second term produces nonlinear fluence-dependent loss due to the integration of $I(r,z,t)$ in eqn. (1) with time.

5. OPTICAL LIMITING APPLICATION AND CONCLUSION

Utilizing this large nonlinear absorption, optical limiting was demonstrated; for 30 μm films, there is both a large excited state absorption cross section and a reasonable linear transmission (44 %) at 760 nm. The photoinduced charge transfer blend film was placed at the focus and the input pulse energy was varied. The data are plotted in Figure 6. The limiting function of the P3OT/[6,6]PCBCR blend is clearly established; at 5 $\mu\text{J}/\text{pulse}$ (0.3 J/cm^2 average fluence) the transmission is reduced to half of the linear transmission. Saturation occurs at $E_{\text{out}} < 2 \mu\text{J}/\text{pulse}$ ($\sim 0.1 \text{ J}/\text{cm}^2$) for higher inputs.

The measured E_{out} is somewhat greater than that predicted using eqns. 1 and 2 (solid curve in Fig. 6) due to the weak intensity dependence of β_{eff} . The origin of such an intensity dependence can be a higher order negative nonlinearity, possibly nonlinear bleaching due to the thermochromic effect in P3OT.¹⁴ The damage threshold was around 15 $\mu\text{J}/\text{pulse}$ ($\sim 1 \text{ J}/\text{cm}^2$ in average fluence), above which there is a permanent change in the linear transmission.

Although materials containing metallophthalocyanines and C_{60} have been demonstrated as reverse saturable absorbers, most were in the form of solutions.¹⁵⁻²² Comparable optical limiting was reported for thick bulk of polymethyl methacrylate containing C_{60} or metallophthalocyanine when pumped at 532 nm.²³

To improve the performance of photoinduced charge transfer materials as optical limiters, the challenge will be to further increase the methanofullene content and to select stable semiconducting polymers with significantly higher laser damage thresholds. To increase the useful spectral range for the optical limiting materials well into the visible part of the spectrum, one must use conjugated polymers with a larger energy gap. The latter is straightforward, for there exists a deep understanding of how to control the $\pi\text{-}\pi^*$ gap in conjugated polymers through changes in the molecular structure.

5. ACKNOWLEDGMENT

This research was supported by the U.S. Air Force Office of Scientific Research under AFOSR93-1-0191 (Dr. Charles Lee, Program Officer).

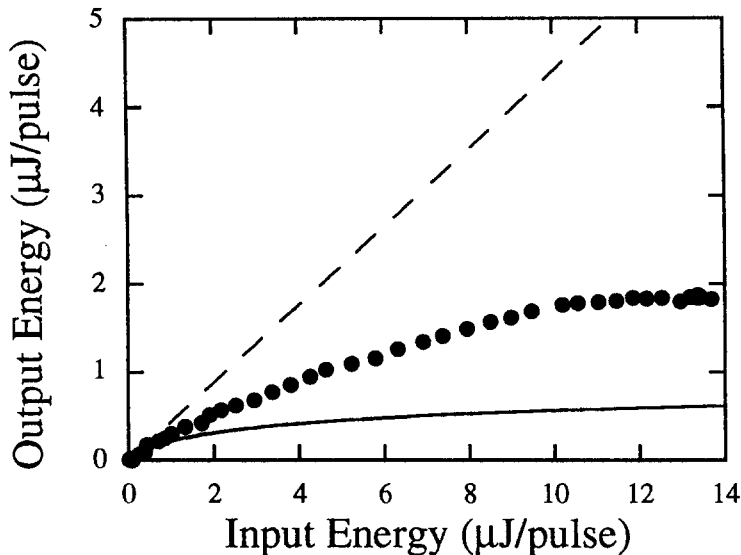


Fig.6 Performance of an optical limiter made of the charge transfer film at 760 nm with a beam radius of 23 μm (half width at $1/e^2$ maximum). Closed circles: experimental data, Dashed line: linear transmission line (44%) Solid curve: calculated response using the excited cross section obtained from the Z-scan experiment at low input energy levels.

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