Nonlinear Optical Properties of Nanostructured Supramolecular Organic Semiconductor

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Abstract. Resonant third-order optical susceptibility and hyperpolarizability of donor polymer in chloroform were revealed to be \( \sim 2.5 \times 10^{-20} \text{ m}^2/\text{V}^2 \) and \( \sim 8.6 \times 10^{-42} \text{ m}^5/\text{V}^2 \) by degenerate four-wave mixing in nanosecond scale at 532 nm, which was attributed to the resonant enhancement.

1. Introduction

Organic materials are attractive because of their ultrafast, broad band response as well as low absorption. Conjugated organic molecules and polymers, which have large and fast optical nonlinearities due to a delocalized \( \pi \) electron system, have potential applications in nonlinear optical devices. The optical nonlinearities are expected to increase by substituting electron donors through the electric-induced effects and the charge transfer effects. Compounds with an intramolecular charge transfer have large optical nonlinearities due to the transfer of electron density between the donor (D) and acceptor (A). The block copolymer is a single material where donor and acceptor components are covalently linked by non \( \pi \)-conjugate chains. D and A are physically different from each other and therefore have the tendency to nano-phase separation. "Perfect" nano-scale morphology is achieved via judicial design of the material structure.

The third-order nonlinearities of the donor, acceptor and the corresponding block copolymer were investigated at 532 nm for photonic nonlinear applications. In this article, we reported our preliminary results on both the donor and acceptor polymer in chloroform. The results showed that the donor had much larger third-order nonlinearity than that of the acceptor because of the stronger resonant absorption at the excitation wavelength at 532 nm of the donor than that of the acceptor. The block copolymer is expected to have larger nonlinearity than that of the donor because of the possible contribution from the intramolecular charge transfer effect.

2. Molecular Structures and Linear Absorption
The molecular structures of the donor, acceptor, and the block copolymer were shown in figure 1. In the block copolymer case, an effective charge separation can be obtained through photoexcitation of the donor component. Thus, this kind of supramolecular system is an ideal candidate for the investigation of the charge transfer caused optical nonlinearities.

![Figure 1. Structure of the donor, acceptor, and the block copolymer.](image)

The typical linear absorption spectrum of both the donor and acceptor were shown in figure 2. At the wavelength of 532 nm, the absorption coefficient of the donor in chloroform with a weight concentration of 0.5% is about 3.7 cm\(^{-1}\), which is 24 times larger than that of the acceptor with the same concentration. The absorption peaks of the first absorption bands are at 468 nm and 444 nm for the donor and acceptor, respectively. These absorption bands were assigned to the absorption from the ground state to the first excited state. The lifetimes of these states can be estimated by the simple time-resolved luminescent measurements.

![Figure 2. Absorption spectra of the acceptor (left) and donor (right) samples. Weight concentrations of the copolymers are given in the figure.](image)

### 3. Nonlinear Optical Properties

Forward degenerate four-wave mixing (DFWM) was used to measure the third-order nonlinearity. The light source was a Nd:YAG laser operated at 532 nm with 8 ns pulse width and 10 Hz repetition rate. Two laser beams with wave vectors \(k_1\) and \(k_2\) were focused in coincidence on the sample, whose thickness was 1 mm, at a small angle of 2°. The laser beam passed through an attenuator for intensity adjustment. The two spatially and temporally overlapped beams wrote a dynamic grating in the sample
and then the beams themselves were diffracted by the grating in directions of 2k₁-k₂ and 2k₂-k₁, respectively. Since beam k₁ is much stronger than beam k₂, the signal in the 2k₁-k₂ direction is much stronger than that in the 2k₂-k₁. The diffracted signal in the 2k₁-k₂ direction, which was proportional to the third-order nonlinear susceptibility \( \chi^{(3)} \), was detected by a photomultiplier and boxcar averager system.

As shown in figure 3, a cubic dependence of the signals of the donor samples on the total input intensity was obtained which indicates that only third-order nonlinearity contributes to the diffracted signal. Thus, the third-order nonlinearity of the samples can be safely extracted from the degenerate four-wave mixing measurement in this intensity range.

The third-order nonlinear optical susceptibility, \( \chi^{(3)} \), of each donor sample was estimated to be \( \approx 2.5 - 9.1 \times 10^{-20} \text{ m}^2/\text{V}^2 \) \( \approx (1.8 - 6.5) \times 10^{-12} \text{ esu} \) from its measured intensity of the phase conjugate signal, \( I_s \), relative to that of CS₂ under the same conditions using the following expression [1]

\[
\chi^{(3)}_{S} = \frac{I_S}{I_R} \left( \frac{n_S}{n_R} \right)^2 \left( \frac{L_R}{L_S} \right) \left( \frac{\alpha L}{1 - e^{-\alpha L}} \right) \chi^{(3)}_{R},
\]

where, \( I \) is the signal intensity of the DFWM signal beam, \( n \) is the refractive index \( (n_{CS^2} \approx 1.46, n_{GO} \approx 1.63) \) [2], \( L \) is the sample path length \( (L_s = L_R \approx 1 \text{ mm}) \), \( \alpha \) is the linear absorption coefficient at 532 nm \( (\alpha = 2.3 \text{ A/cm for } 3.86, 3.69, 2.44, 2.26, 1.93, 1.40 \text{ cm}^{-1}, d=1 \text{ cm}) \) for different concentrations of the sample, and \( S \) and \( R \) indicates sample and reference. The excellent and stable third-order optical response solvent, carbon disulfide \( \text{(CS}_2, 99+ \text{%, spectrophotometric grade, Aldrich)} \), was selected as a reference. It has been assumed that the reference has no linear absorption at the excitation wavelength at 532 nm. The third order nonlinear susceptibility of \( \text{CS}_2 \) was reported to be \( \approx 9.5 \times 10^{-21} \text{ m}^2/\text{V}^2 \) \( \approx (6.8) \times 10^{-13} \text{ esu} \) in the nanosecond time-scale [3].

The third-order nonlinear susceptibility of the donor in chloroform is correlated to the donor concentration and the effect of the dielectric confinement [4]

\[
\chi^{(3)} = f^4 N_d a_f^h C \quad \text{(SI)}
\]

where \( f = (2 + n^2) / 3 \) is the simplified local field, \( n \) is the refractive index \( n \approx 1.46 \), \( N_d \) is the Avogadro’s number, and \( C \) is the concentration of donor in chloroform. The third-order nonlinear susceptibility of the donor in chloroform has a linear dependence as expected in equation (2). The hyperpolarizability \( \gamma_f \) of donor samples was extrapolated from the slope \( f^4 N_d a_f^h \) of the third-order nonlinear susceptibility as a function of concentration plot as shown in figure 3. The hyperpolarizability of the donor sample was estimated to be \( \approx 8.6 \times 10^{-42} \text{ m}^5/\text{V}^2 \) \( \approx (6.0 \times 10^{-28} \text{ esu}) \).
The third-order nonlinearity from the acceptor polymer in chloroform was not observed, while that of the donor polymer in chloroform exhibited large third-order nonlinearity ($\sim 2.5 \times 9.1 \times 10^{-20} \text{m}^2/\text{V}^2$) at the input intensity level of $\sim 100 \text{MW/cm}^2$, as shown in figures 3 and 4. This is mainly due to the relatively smaller linear absorption of acceptors at 532 nm for a given excitation intensity level than that of a donor polymer in chloroform. The large third-order nonlinear susceptibility of the donor polymer in chloroform is attributed to resonance enhancement. The nonlinearity of the block copolymer is expected to be even larger at the higher intensity level or ultrafast time scale because of the following reasons. First, the overall photon-induced charge-transfer (CT) efficiency reaches unity since every donor block is ensured to have interaction with an acceptor block. Second, the distance between D and A can be tuned to a certain level so that the charge recombination rate is greatly reduced, while the CT process is still significantly faster than the decay of the exciton. Third, the charge recombination is further suppressed in the D/A nanometer-level phase-separated self-assembled structure, since the strongest D-A interaction, i.e. $\pi-\pi$ stacking between D and A, can be eliminated through judicious selection of side-chains of donor and acceptor blocks. Fourth, $\pi$-stacking of donor (acceptor) blocks produced an effect similar to that in discotic liquid crystals: greatly enhanced hole or electron mobility. Fifth, the charge collection efficiency can be optimized through realization of continuous paths for both electrons and holes in block copolymers in several types of known morphologies such as the ordered bi-continuous double diamond phase and the gyroid phase. Therefore we expect that the block copolymer is a very good candidate for nonlinear optical device application, such as nonlinear transmission limiting and optical switching.

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