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Infrared photoexcitation spectra of conducting polymer/methanofullerene films

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Abstract

We report photoinduced absorption (PIA) and photoinduced reflectance (PIR) spectra of poly(3-octyl thiophene)-methanofullerene films. As a result of the efficient photoinduced intermolecular charge transfer, the PIA and PIR spectra of the composite films are significantly enhanced in magnitude over those in either of the component materials. From the PIA and PIR spectra, the corresponding changes in the complex refractive index, $\Delta N = \Delta n(\omega)+i\Delta\kappa(\omega)$, are obtained. The results indicate that the PIA spectra are dominated by $\Delta\kappa(\omega)$, while the PIR spectra are dominated mainly by $\Delta n(\omega)$. The implications of these photoinduced changes in the index resulting from photoexcitations are discussed in terms of potential optoelectronic and nonlinear optical applications of these materials.

Keywords: Photoinduced absorption spectroscopy, Non-linear optical methods, Fullerene derivatives

The recent discovery of photoinduced charge transfer in composites of conjugated polymers and fullerenes (C_{60}) has opened exciting new directions of research activity[1]. One such opportunity is utilizing nonlinear optical (NLO) properties of these materials which are important in potential photonics applications. Indeed, nonlinear absorption and optical limiting have been demonstrated in these systems[2].

The mechanism responsible for the NLO response in the conjugated polymer/C_{60} composites is inherently different from that of conventional NLO materials[2,3]. The nonlinear response arises from efficient photoinduced charge transfer from conjugated polymers onto C_{60} followed by absorption from the charge separated excited state. Thus, deeper understanding of the photophysical phenomena requires detailed studies of steady-state photoexcitation spectra to determine the corresponding changes in the frequency dependence of the complex index of refraction, $\Delta N = \Delta n(\omega) + i\Delta\kappa(\omega)$.

We have utilized steady-state infrared (IR) photoexcitation methods to measure the photoinduced absorption (PIA) and photoinduced reflectance (PIR) spectra of composite films of poly(3-octyl thiophene), P3OT, mixed with methanofullerene, phenyl-C_{61}-butyric acid cholesteryl ester, denoted as (6,6)PCBCR. Using such soluble functionalized C_{60}-derivatives[4], we obtained homogeneous, stable films of proper thickness(6-7μm) with good optical quality containing 1:1 by weight methanofullerenes.

The PIA spectra were obtained by measuring spectral changes (ΔT) in the IR transmission between 0.01 eV and 1.7 eV in response to the external pumping source (514 nm line of an Ar^+ ion laser) incident on the sample. The PIR spectra were determined by measuring the change in specular reflectance (ΔR) at near-normal incidence (≈10°) for incident photon energies from 0.05 eV to 0.5 eV. Identical laser pumping conditions were used for PIA and PIR measurements.

The PIA spectra of a P3OT/(6,6)PCBCR composite and pure P3OT films are shown in Figure 1 in the energy range from 0.01 eV to 1.7 eV. Consistent with previous results[5] using C_{60}, the PIA spectrum of the composite film has two subgap electronic absorptions; a lower energy feature (superposed on the enhanced IRAV modes) with a peak around 0.1 eV and a higher energy feature which onsets at approximately 1.1 eV. The PIA is significantly enhanced in magnitude over that in either of the component materials.

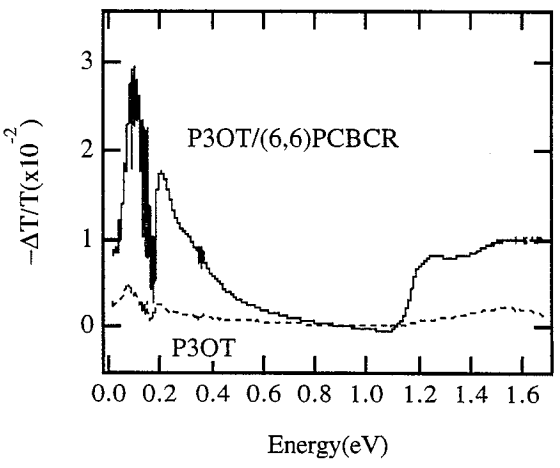

Figure 1. PIA spectra of P3OT (dashed) and P3OT/(6,6)PCBCR composite (solid) films from 0.01eV to 1.7eV at 50K obtained by pumping with an Ar^+ laser at 514 nm with 50mW/cm^2.

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The PIR spectra of P3OT and the composite films are shown in Figure 2 for the spectral range between 0.08 to 0.5 eV. The PIR signal of the composite film is negative (decreased reflectance) above 0.11 eV with a minimum around 0.15 eV. There is a zero-crossing at 0.11 eV with $\Delta R/R$ positive and increasing with decreasing frequency. As in the PIA spectra, the PIR spectra exhibit spectral features associated with the IRAV modes between 0.1 and 0.2 eV. The magnitude of the photoinduced reflectance of the composite film is significantly enhanced over that of the pure P3OT film, consistent with the PIA measurements.

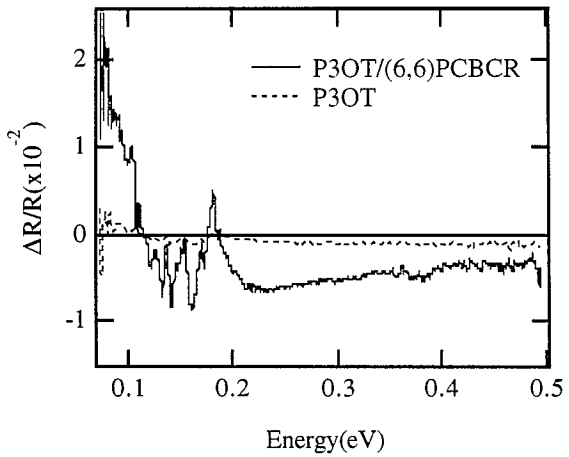

Figure 2. PIR spectra of P3OT (dashed) and P3OT/(6,6)PCBCR composite (solid) films in the IR range from 0.08eV to 0.5eV at 50K with laser pump intensity 50mW/cm^2 at 514 nm.

The large increase in oscillator strength of the photoinduced signals and the appearance of the 1.2 eV feature associated with the (6,6)PCBCR anion in the composite film unambiguously prove the existence of photoinduced charge transfer from P3OT onto (6,6)PCBCR[3,5]. The increase in oscillator strength arises from a combination of enhanced quantum efficiency for photogeneration of charge carriers and extended lifetime of excited states.

Determining both PIA and PIR spectra enables one to obtain the corresponding changes in the real and imaginary components of the index of refraction, $\Delta n(\omega)$ and $\Delta\kappa(\omega)$, without any additional calculation as described elsewhere in detail [3].

Figure 3 shows Δn and $\Delta\kappa$ directly obtained from the PIA and PIR spectra. As expected, the spectral response of $\Delta\kappa$ resembles the PIA spectrum, remaining positive over the energy range below 0.5 eV with a peak at 0.1 eV; whereas Δn has a derivative-like spectral shape with a zero-crossing at 0.1 eV, similar to the PIR spectrum. Qualitatively, the spectral shapes of the Δn and $\Delta\kappa$ suggest the Kramers-Kronig consistency between the two spectra.

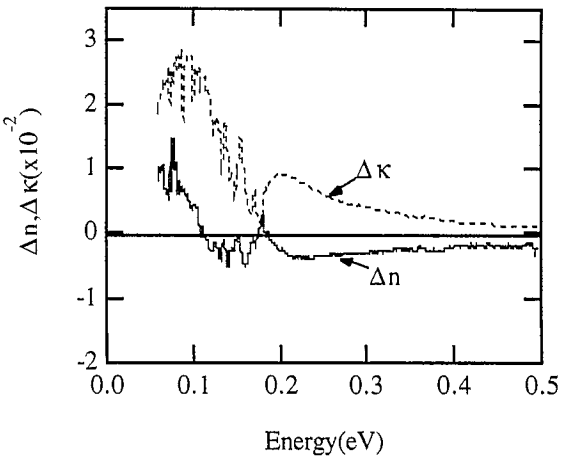

Figure 3. Photoinduced changes of the components of the refractive index, $\Delta n(\omega)$ (solid line) and $\Delta\kappa(\omega)$ (dashed line), for P3OT/(6,6)PCBCR composite film as obtained directly from the PIA (Fig.1) and PIR (Fig.2) spectra.

In summary, photoinduced absorption and photoinduced reflectance spectra were obtained for P3OT/methanofullerene composite films in the IR. The data enable direct evaluation of the corresponding changes in the components of the complex refractive index, $\Delta n(\omega)$ and $\Delta\kappa(\omega)$. As a result of the efficient photoinduced intermolecular charge transfer, the magnitudes of $\Delta n(\omega)$ and $\Delta\kappa(\omega)$ are significantly enhanced in the P3OT-methanofullerene composites, with Δn and $\Delta\kappa \approx 10^{-2}$ in the far IR at laser pump intensity of only 50mW/cm^2. Thus, the P3OT/methanofullerene composites offer potential as fast, optically driven "switches" for far IR radiation.

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