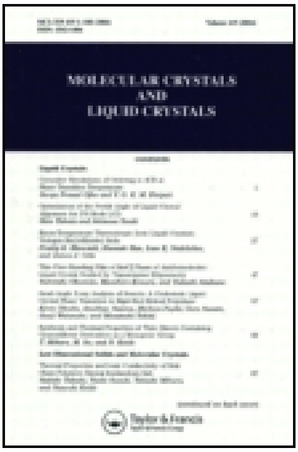

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INFRARED PHOTOEXCITATION SPECTROSCOPY OF CONDUCTING POLYMER AND C_{60} COMPOSITES : DIRECT EVIDENCE OF PHOTO-INDUCED ELECTRON TRANSFER

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Abstract We report direct spectral evidence of photoinduced electron transfer from the excited state of conducting polymer onto C_{60} by infrared photoexcitation spectroscopy, from 0.01 eV (100 cm^{-1}) to 1.3 eV (11,000 cm^{-1}). The photoinduced absorption spectra of poly(3-octylthiophene) (P3OT) and poly[2-methoxy, 5-(2'ethyl-hexyloxy)-p-phenylene vinylene] (MEH-PPV) are characterized by subgap electronic absorptions and associated infrared-active vibrational modes. Upon adding a few percent of C_{60} into both conducting polymers, the photoinduced absorption spectra are significantly enhanced in magnitude and two new peaks are found at 1.15 eV and 1.25 eV. The photoinduced charge transfer from conducting polymer onto C_{60} enhances the quantum efficiency for photogeneration of charge carriers, resulting in the enhanced photoinduced response of conducting polymer and the appearance of 1.15 eV and 1.25 eV signatures associated with C_{60}^-.

I. INTRODUCTION

Photoinduced electron transfer from the excited state of conducting polymers onto C_{60} has been recently reported.[1-4] The quenching of the photoluminescence[1,2] and the subpicosecond time-resolved photoinduced absorption[3] demonstrate that electron transfer from the excited state of the conducting polymer to C_{60} occurs within 10^{-12} s after photoexcitation with $\hbar\omega$ greater than the $\pi-\pi^*$ gap. Although the signatures of photoinduced electron transfer from conducting polymers onto C_{60} are unambiguous, direct spectral evidence of C_{60}^- was not observed in previous photomodulation excitation spectroscopy measurements.[1,2] We have, therefore, initiated photoinduced absorption measurements using Fourier transform infrared (FTIR) interferometer on conducting polymer/C_{60} composites.

We have obtained direct spectral evidence of photoinduced electron transfer from the excited state of conducting polymer onto C_{60} by infrared photoexcitation spectroscopy, from 0.01 eV (100 cm^{-1}) to 1.3 eV (11,000 cm^{-1}). The photoinduced absorption spectra of poly(3-octylthiophene) (P3OT) and poly[2-methoxy, 5-(2'ethyl-hexyloxy)-p-phenylene vinylene] (MEH-PPV) are significantly enhanced in magnitude upon adding a few percent of C_{60}. Moreover, two new peaks are found in the excitation spectra of conducting polymer/C60, at 1.15 eV and 1.25 eV, associated with C_{60}^{-}. The results indicate long lived photoinduced electron transfer between the two systems.

II. EXPERIMENT

The P3OT, MEH-PPV, and their composites with C_{60} were cast from solution as described previously.[2] The solutions were drop cast onto sapphire substrates for photoinduced absorption in near-IR, onto cadmium telluride (CdTe) substrates for the mid-IR and onto silicon wafer substrate for the far-IR. Since all these single crystal substrates are good thermal conductors, experimental artifacts arising from sample heating do not contaminate the spectra. Films with 5% C_{60} in the conducting polymer appear uniform and without segregation of the less soluble C_{60} component.

Photoinduced absorption spectra were obtained by measuring changes (ΔT) in the IR transmission (T) in response to the external pumping source (Ar^+ laser) incident on the sample; $\Delta(\alpha d) \approx -\Delta T/T$, where α is the absorption coefficient and d is the sample thickness.[5] A Nicolet Magna 750 FTIR was used for frequencies from 100 cm^{-1} (0.01 eV) to 11000 cm^{-1} (1.35 eV); ΔT was measured by recording spectra for 10 s intervals with the excitation source on and then with the sample in the dark. This steady-state photoexcitation technique probes the spectral changes due to long-lived photoexcitations. The measurements are carried out at 80 K with samples in vacuum (10^{-5} Torr).

III. RESULTS AND DISCUSSION

Direct IR absorption spectra of conducting polymers and conducting polymer/C_{60}(5%) are compared in Figure 1. For pure P3OT and MEH-PPV, characteristic IR modes are found throughout the mid-IR. After adding 5% of C_{60} by weight into the conducting polymer host, we observed all the above modes, essentially unchanged. The four characteristic IR

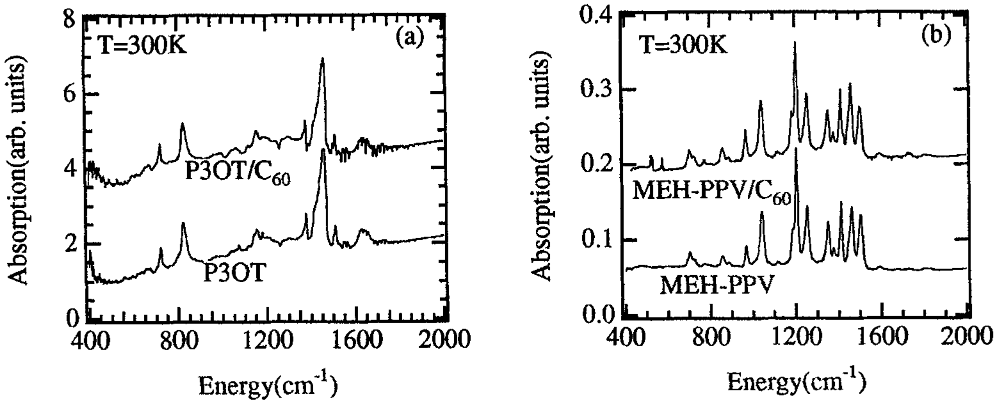

FIGURE 1 (a) Infrared absorption spectra of P3OT and P3OT/C_{60} (5%) and (b) MEH-PPV and MEH-PPV/C_{60} (5%) at 80K.

modes of C_{60} can be observed as weak peaks (526, 572 cm^{-1}) or shoulder (1182, 1429 cm^{-1}) superimposed on the infrared vibration modes of P3OT and MEH-PPV, respectively. Thus, the IR spectra of conducting polymer/C_{60} are simple superposition of the two components, implying relatively weak mixing of the ground state electronic wave functions.

Figure 2 shows the photoinduced changes in the IR spectrum of P3OT and

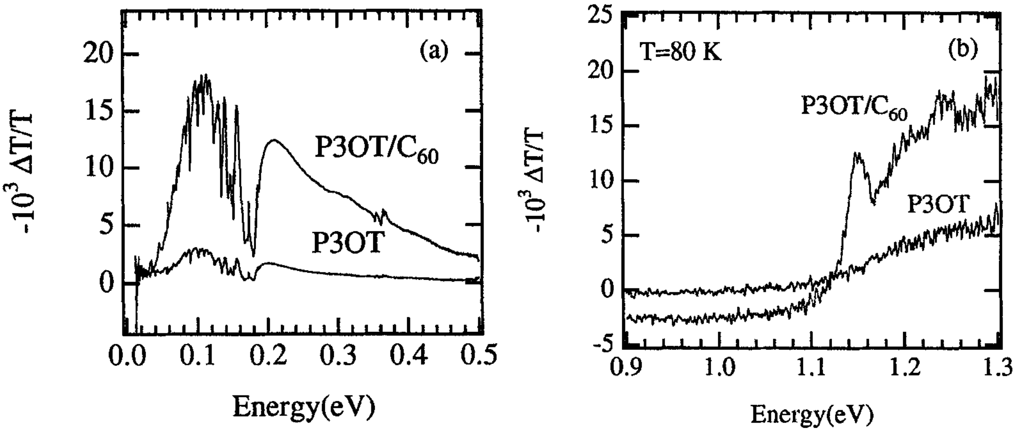

FIGURE 2 Photoinduced IR absorption spectra of P3OT and P3OT/C_{60}(5%) at 80K obtained by pumping with an Ar^+ laser at 2.41 eV with 50 mW/cm^2.

P3OT/C_{60}(5%) for frequencies from 0.01eV to 1.3 eV upon photoexcitation with the 2.41 eV line of an Ar^+ ion laser at 50 mW/cm^2. The photoinduced absorption spectrum of pure P3OT is characterized by the subgap electronic absorptions (a lower energy feature peaked at 0.3 eV and a higher energy feature with onset at 1.1 eV) together with the prominent IRAV modes superimposed on the lower energy electronic absorption peak. These two broad electronic features share the same physical origin and have been assigned to the lower and upper bipolaron transitions, respectively.[6] Notice that there are relatively strong broad bands at 0.1eV (with the IRAV modes superimposed) and at 0.21 eV. These two peaks were observed in early work by Kim et. al. and attributed to a polaron-like defect having a different physical origin from two bipolaron electronic transitions (0.3 and 1.3 eV).[6]

Upon photoexcitation of the P3OT/C_{60} composite, the photoinduced infrared spectra change dramatically. First, the overall strength of the photoinduced absorption spectrum (both the electronic subgap absorptions and the associated IRAV modes) is increased by almost one order of magnitude, as shown in Figure 2. Second, new peaks are observed at 1.15 eV and 1.25 eV together with a bleaching around 1 eV.

Figure 3 is the photoinduced absorption spectra of MEH-PPV and MEH-PPV/C_{60}(5%) for frequencies from 0.01 eV to 1.3 eV with the same experimental

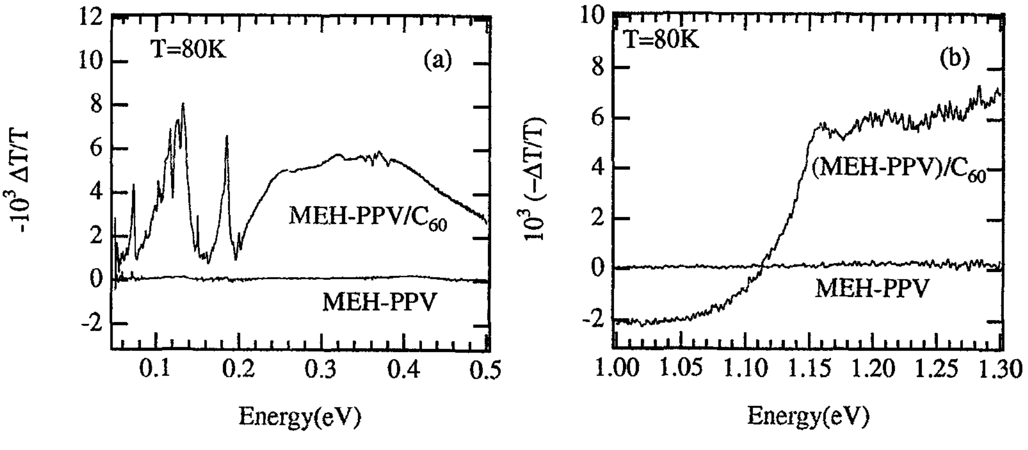

FIGURE 3 Photoinduced absorption spectrum of MEH-PPV and MEH-PPV /C_{60}(5%) at 80K obtained by pumping with an Ar^+ laser at 2.41 eV with 50 mW/cm^2.

conditions as P3OT. The photoinduced absorption spectra of pure MEH-PPVare characterized by subgap electronic absorptions with a lower energy feature superposed with two peaks at 0.25 eV and 0.4 eV and a higher energy feature with onset at 1.1 eV together with IRAV modes below the lower energy electronic absorption feature. The 0.4 eV and 1.1 eV features are assigned to the lower and upper energy bipolaron transitions, respectively.[7] Another lower energy peak at 0.25 eV, which is absent in photoinduced absorption spectrum of PPV,[7] can be assigned to lower polaron transition. The magnitude of spectral response is smaller than that of P3OT by a factor of 10. These results arise from the weak interchain coupling in MEH-PPV due to the large side group. As a result, interchain transport is inhibited by large interchain separation leading to the suppression of bipolaron formation, and the early time recombination is enhanced, resulting in weak spectral response. Upon addition of five percent of C_{60} to MEH-PPV, the photoinduced absorption spectra are significantly enhanced in nearly two orders of magnitude. In addition, two new peak are evident at 1.15eV and 1.25eV, consistent with P3OT/C_{60}.

The remarkable increase in oscillator strength of the IRAV modes and the subgap electronic excitations in polymer/C_{60} results from the photoinduced electron transfer from conducting polymer onto C_{60}. Ultrafast photoinduced electron transfer,[2,3] improves the quantum efficiency for charge carrier generation and suppresses recombination; both effects were demonstrates by photoconductivity measurements.[4] As a result, more charged excitations live for longer times, thereby leading to an increase in the strength of the photoinduced absorption signals by an order of magnitude upon adding only a few percent C_{60}.

The photoinduced electron transfer is complete; charge is transferred from the excited state of polymer to the C_{60} acceptor, resulting in the formation of both $(\text{polymer})^+$ and C_{60}^- : light induced electron spin resonance (LESR) studies[1,2] have identified the two separate ESR signals with g-values characteristics of $(\text{polymer})^+$ and C_{60}^-, respectively. The charge separated excited state is stabilized through a combination effects, including delocalization of the electron on the C_{60}, structural relaxation around the hole to form a positive polaron on the conducting polymer (and subsequent formation of bipolarons through $P^+ + P^+ \rightarrow B^{2+}$). Therefore, the dominant photogenerated charge carriers on the polymer host in polymer/C_{60} are positive polarons and bipolarons, while both positive and negative polarons (and bipolarons) are generated in pure conducting polymer. The identical electronic absorptions and IRAV modes in conducting polymer and polymer/C_{60} imply electron-hole symmetry in conducting polymers.

The 1.15 eV and 1.25 eV peaks in the photoinduced absorption spectra are the only new features that appear in polymer/C_{60}. These features are not seen in pure C_{60}. The 1.15 and 1.25 eV absorption bands are characteristic of C_{60}^- ; both were observed in electrochemical absorption studies[8] of C_{60}^- and in the absorption spectra of C_{60}^- generated by γ-ray irradiation.[9] In these earlier studies, the two absorption peaks were assigned to the allowed HOMO (T_{1u})-LUMO (T_{1g}) transitions of C_{60}^-, with energy in agreement with calculated value.[10] The explicit appearance of these peaks demonstrate the appearance of C_{60}^- subsequent to photoexcition of polymer/C_{60} ; an independent and unambiguous proof of photoinduced electron transfer.

In conclusion, the increased magnitude of the IR photoinduced response and the spectroscopic evidence of C_{60}^- subsequent to photoexcitation of polymer/C_{60} indicate photoinduced electron transfer from the excited state of conducting polymers onto C_{60}. The results are consistent with the ultrafast photoinduced charge transfer observed in time resolved measurements[3] and with the metastability of the charge separated state as inferred from light induced electron spin resonance[1] measurements.

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