PHYSICAL REVIEW B VOLUME 49, NUMBER 8 15 FEBRUARY 1994-II

Direct evidence of photoinduced electron transfer in conducting-polymer–C_{60} composites by infrared photoexcitation spectroscopy

Kwanghee Lee, Rene A. J. Janssen, N. S. Sariciftci, and A. J. Heeger
Institute for Polymers and Organic Solids, University of California at Santa Barbara, Santa Barbara, California 93106

(Received 8 November 1993)

We report direct spectral evidence of photoinduced electron transfer from the excited state of poly(3-octylthiophene), P3OT, onto C_{60} by infrared photoexcitation spectroscopy, 0.01 eV (100 cm^{-1}) to 1.3 eV (11 000 cm^{-1}). The photoinduced absorption spectrum of P3OT, characterized by subgap electronic absorptions and associated infrared-active vibrational modes, is significantly enhanced in magnitude upon adding a few percent of C_{60}. Two new peaks are found in the photoexcited spectrum of the P3OT/C_{60} composite and assigned to the allowed HOMO (T_{1u})-LUMO (T_{1g}) transitions of $C_{60}{}^-$ with energies, 1.15 and 1.25 eV, in good agreement with calculated values. The photoinduced charge transfer from P3OT onto C_{60} enhances the quantum efficiency for photogeneration of charge carriers resulting in charge separation in the excited state. As a result, the lifetime of the excited-state configuration, $(P3OT)^+$ and $C_{60}{}^-$, is extended; thereby leading to both the enhanced photoinduced response of P3OT and the appearance of the 1.15- and 1.25-eV signatures associated with $C_{60}{}^-$.

In conducting polymers, the quasi-one-dimensional electronic structure is strongly coupled to the chemical (geometrical) structure. As a result, the nonlinear excitations (solitons, polarons, and bipolarons) are self-localized around local structural distortions with electronic states within the energy gap.[1] Therefore, when such excitations are created, the symmetrical (Raman-active) modes become infrared-active vibrational (IRAV) modes. These nonlinear excitations can be studied spectroscopically (excitation spectroscopy) either by injecting charges into the system through chemical (or electrochemical) doping or by direct optical pumping above the energy gap with an intense external light source.[1,2]

Photoinduced electron transfer from the excited state of conducting polymers onto C_{60} has been recently reported.[3–6] The quenching of the photoluminescence[3,4] and the subpicosecond time-resolved photoinduced absorption[5] 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 π-π^* gap. Since charge transfer occurs nearly 10^3 times faster than any competing process, the quantum efficiency for photoinduced electron transfer is of order unity. Early time recombination is inhibited by the spatial separation of the electron and hole on the C_{60} acceptor (A) and the conducting polymer donor (D), respectively. The high quantum efficiency for charge transfer and charge separation stimulated the fabrication of D-A thin-film heterojunction diodes and photovoltaic cells.[7,8]

Charge separation in the excited state, facilitated (and stabilized) by carrier delocalization and by structural relaxation, leads to enhanced efficiency for photogeneration of free charge carriers and to enhanced lifetimes for those carriers.[4–6] As a result, the magnitude of the steady-state photoinduced absorption signals in conducting polymer/C_{60} composites is expected to be enhanced over those observed in the conducting polymer alone. Furthermore, 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 excitation spectroscopy (photomodulation) measurements.[3,4] We have, therefore, initiated photoinduced absorption measurements using Fourier-transform infrared (FTIR) interferometry on P3OT/C_{60} composites.

We have obtained direct spectral evidence of photoinduced electron transfer from the excited state of the conducting polymer, poly(3-octylthiophene), P3OT, onto C_{60} through infrared (IR) photoexcitation spectroscopy in the spectral range from 0.01 eV (100 cm^{-1}) to 1.3 eV (11 000 cm^{-1}). The photoinduced absorption spectrum of P3OT, characterized by subgap electronic absorptions and associated IRAV modes, is significantly enhanced in magnitude upon adding a few percent of C_{60}. Moreover, two new peaks are found in the excitation spectrum of P3OT/C_{60}, at 1.15 and 1.25 eV, which correspond to the allowed HOMO (T_{1u})-LUMO (T_{1g}) transitions of $C_{60}{}^-$ (HOMO is the highest occupied molecular orbital, LUMO is the lowest unoccupied molecular orbital). The results indicate long-lived photoinduced electron transfer between the two systems.

The poly(3-octylthiophene) and the P3OT/C_{60} samples were cast from solution as described previously.[4] The solutions were drop cast onto sapphire substrates for photoinduced absorption in the near-IR, onto cadmium telluride (CdTe) substrates for the mid-IR, and onto silicon wafer substrates 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.

Thin films of C_{60} (for comparative measurements) were prepared by evaporating purified C_{60} powder from a

0163-1829/94/49(8)/5781(4)/$06.00

quartz crucible, heated to 450 °C at a pressure of 5×10^{-6} Torr onto KBr substrates. The C_{60} was kept oxygen free; after preparation, the sample was transferred into the measuring system without exposure to air, and mounted onto the cold finger of the cryostat in nitrogen atmosphere.

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.[8] A Nicolet Magna 750 FTIR system was used for frequencies from 100 cm^{-1} (0.01 eV) to 11 000 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 technique probes spectral changes due to long-lived photoexcitations. The measurements are carried out at 80 K with samples in vacuum (10^{-5} Torr).

Direct IR absorption spectra of P3OT and P3OT/C_{60}(5%) are compared for frequencies between 400 and 2000 cm^{-1} in Fig. 1. For P3OT, six characteristic IR modes are found at 721 (C-H deformation of methylene group of the hexyl chain), 822 (out-of-plane C-H deformation), 1377 (methyl deformation), and 1462, 1512, and 1562 cm^{-1} (ring-stretching modes). After adding 5% C_{60} by weight into the P3OT, we observed all the above modes, essentially unchanged. The four characteristic IR modes of C_{60} can be observed as weak peaks (526 and 572 cm^{-1}) or shoulders (1182 and 1429 cm^{-1}) superimposed on the vibrational modes of P3OT. Thus, the IR spectrum of P3OT/C_{60} is a 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 P3OT/C_{60}(5%) for frequencies from 0.01 to 1.3 eV upon photoexcitation with the 2.41-eV line of an Ar^{+}-ion laser at 50 mW/cm^{2}. For quantitative comparison (since the thicknesses of the different films are not identical), the spectra are normalized by the ratio of the oscillator strengths of the linear absorption of the samples. The photoinduced absorption spectrum of pure P3OT is characterized by 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 energy bipolaron transitions, respectively.[9] Notice that there are relatively strong broad bands at 0.1 eV (with the IRAV modes superimposed) and at 0.21 eV. These two peaks were observed in early work by Kim *et al.*[9] and attributed to a polaronlike defect having a different physical origin from two bipolaron electronic transitions (0.3 and 1.3 eV).

In recent photomodulation studies[4] of P3OT, an electronic absorption was observed in the excitation spectrum at 1.05 eV and assigned to a triplet-triplet transition. Our IR photoinduced absorption measurements show no indication of this 1.05-eV absorption. Since the steady-state photoexcitation technique probes the spectral changes due to photocarriers over long times (10 s on and 10 s off), these spectra are dominated by excitations with the longest lifetimes; i.e., the long-lived charged polarons or bipolarons which remain after separation of the early neutral singlet or triplet excitations.

Upon photoexcitation of P3OT/C_{60}(5%), the photoinduced IR spectra change dramatically. First, the overall strength of the photoinduced absorption spectrum (both the electron subgap absorptions and the associated IRAV modes) is increased by almost one order of magnitude, as shown in Fig. 2. Second, new peaks are observed at 1.15 and 1.25 eV together with a bleaching around 1 eV.

The remarkable increase in oscillator strength of the IRAV modes and the subgap electronic excitations in P3OT/C_{60} results from the photoinduced electron transfer from P3OT onto C_{60}. Ultrafast photoinduced electron transfer[4,5] improves the quantum efficiency for

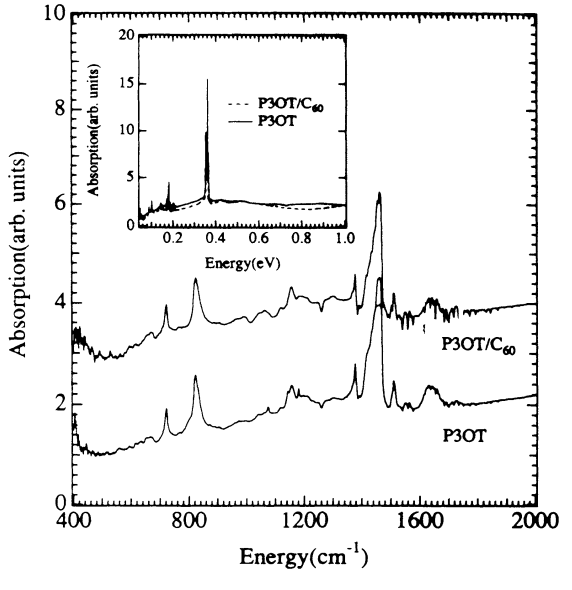

FIG. 1. Infrared absorption spectra of P3OT and P3OT/C_{60}(5%) films at 80 K. The inset shows the data over the whole IR range up to 1.0 eV.

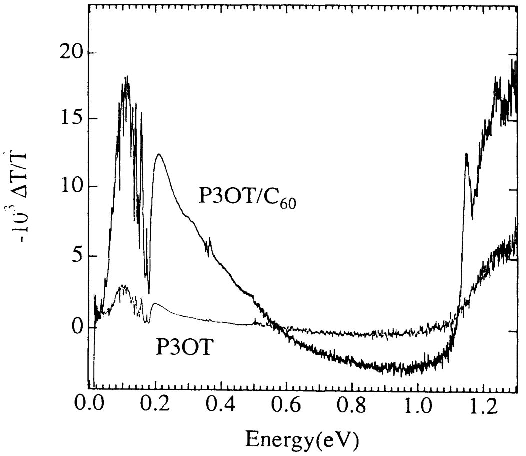

FIG. 2. Photoinduced IR absorption spectra of P3OT and P3OT/C_{60}(5%) at 80 K obtained by pumping with an Ar^{+} laser at 2.41 eV with 50 mW/cm^{2}.

charge carrier generation and suppresses recombination; both effects were demonstrated by photoconductivity measurements.[6] 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 $(P3OT)^+$ and $C_{60}{}^-$: light-induced electron spin resonance (ESR) studies[3,4] have identified the two separate ESR signals with g values characteristic of $(P3OT)^+$ and $C_{60}{}^-$, respectively. The charge separated excited state is stabilized through a combination of effects, including delocalization of the electron on the C_{60}, structural relaxation around the hole to form a positive polaron on the P3OT (and subsequent formation of bipolarons through $P^+ + P^+ \rightarrow B^{2+}$). Therefore, the dominant photogenerated charge carriers on the P3OT host in P3OT/C_{60} are positive polarons and bipolarons, while both positive and negative polarons (and bipolarons) are photogenerated in pure P3OT. The identical electronic absorptions and IRAV modes in P3OT and P3OT/C_{60}, demonstrated in Fig. 3, imply electron-hole symmetry in P3OT, as in a number of conducting polymers.[1]

The enhanced magnitude of the IRAV modes in P3OT/C_{60} enables us to analyze the IRAV spectrum with better definition and better resolution. The photoinduced IRAV spectra of P3OT and P3OT/C_{60}(5%) are shown in detail in Fig. 3, and compared with the doping-induced IRAV spectrum of P3OT. The spectrum obtained from P3OT/C_{60}(5%) and from P3OT are essentially identical, except for the increased strength of all spectral features in P3OT/C_{60} due to the enhanced photogeneration efficiency and the extended lifetime of the photocarriers. The four localized IRAV modes at 1047, 1119, 1182, and 1254 cm^{-1} are associated with the uniform translation of the bipolaron (T modes). The ring-bending modes (R) arising from the weak coupling of the injected charges to the thiophene ring deformations are observed at 594, 687, 717, and 800 cm^{-1}.[9] The prominent IRAV mode associated with the nonuniform translation (shape oscillation) of the bipolaron[10,11] is found at 1393 cm^{-1} in P3OT. Although all the IRAV modes in P3OT/C_{60} correspond to those of P3OT without any new features due to C_{60}, we note that the concentration of C_{60} is small, only 5%, so any such signals would be correspondingly weaker.

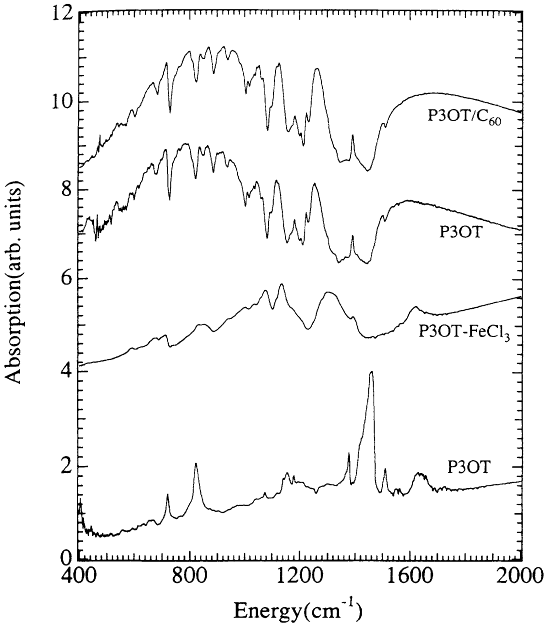

FIG. 3. Infrared spectra in the IRAV range. (top) Detailed photoinduced IR spectrum of P3OT/C_{60}(5%); (second from top) detailed photoinduced IR spectrum of P3OT; (second from bottom) IR spectra of P3OT doped with $FeCl_3$; (bottom) infrared spectra of P3OT. For clear comparison, the P3OT spectrum is multiplied six times.

The one-to-one correspondence between the photoinduced and doping-induced spectral changes is evident in Fig. 3, as is the redshift of the photoinduced IRAV modes with respect to the doping induced IRAV modes. These features are typical of conducting polymers and have been explained in complete detail by the amplitude mode formalism.[12]

The 1.15-eV and 1.25-eV peaks in the photoinduced absorption spectrum are the only new features that appear in P3OT/C_{60}. Figure 4 shows the 1.15- and 1.25-eV peaks from P3OT/C_{60} together with the photoinduced absorption spectrum obtained from a pure C_{60} film. The 1.15- and 1.25-eV 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 spectroelectrochemical absorption studies[13] of $C_{60}{}^-$ and in the absorption spectra of $C_{60}{}^-$ generated by γ-ray irradiation.[14] In these earlier studies, the two absorption peaks were assigned to the allowed HOMO (T_{1u})-LUMO (T_{1g}) transitions of $C_{60}{}^-$, with energies in agreement with calculated values.[15] The explicit appearance of these peaks demonstrates the appearance of $C_{60}{}^-$ subsequent to photoexcitation of

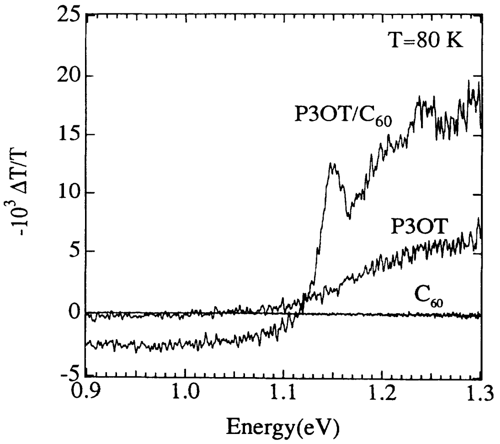

FIG. 4. Photoinduced absorption spectra of P3OT and P3OT/C_{60}(5%) in the near IR at 80 K obtained by pumping with an Ar^+ laser at 2.41 eV (514 nm) with 50 nW/cm^2. For comparison, the photoinduced absorption spectrum of a pure C_{60} film is shown under the same experimental conditions.

P3OT/C_{60}; an independent and unambiguous proof of photoinduced electron transfer.

The C_{60}^{-} in P3OT/C_{60} does not arise from the photoexcitation of C_{60} itself, as shown above, see Fig. 4. We have extended the IR photoexcitation studies on pure C_{60} films from 0.05 to 1.3 eV. There are no corresponding photoinduced absorption features in pure C_{60} up to 1.3 eV, consistent with the early study by Kim, Li, and Diederich.[16] The absence of photoinduced response in pure C_{60} implies that the photoexcitation lifetime is too short to enable detection of the excitation spectrum using the on/off FTIR method.

In conclusion, the increased magnitude of the IR photoinduced response and the spectroscopic evidence of C_{60}^{-} subsequent to photoexcitation of P3OT/C_{60} indicate photoinduced electron transfer from the excited state of poly(3-octylthiophene) onto C_{60}. The results are consistent with the ultrafast photoinduced charge transfer observed in time-resolved measurements[5] and with the metastability of the charge separated state as inferred from light-induced electron spin resonance[3] measurements.

We thank V. I. Srdanov for supplying the pure C_{60} film and L. Smilowitz, B. Kraabel, and C. H. Lee for helpful discussions. This work was supported by the Department of Energy under a grant from Advanced Energy Projects, DOE-93ER12138.

---

[1] A. J. Heeger, S. Kivelson, J. R. Schrieffer, and W. P. Su, Rev. Mod. Phys. **60**, 781 (1988).

[2] *Handbook of Conducting Polymers,* edited by T. A. Skotheim (Dekker, New York, 1986).

[3] N. S. Sariciftci, L. Smilowitz, A. J. Heeger, and F. Wudl, Science **258**, 1474 (1992).

[4] L. Smilowitz, N. S. Sariciftci, R. Wu, C. Gettinger, A. J. Heeger, and F. Wudl, Phys. Rev. B **47**, 13 835 (1993).

[5] B. Kraabel, C. H. Lee, D. McBranch, D. Moses, N. S. Sariciftci, and A. J. Heeger, Chem. Phys. Lett. **213**, 389 (1993).

[6] C. H. Lee, G. Yu, D. Moses, K. Pakbaz, C. Zhang, N. S. Sariciftci, A. J. Heeger, and F. Wudl, Phys. Rev. B **48**, 15 425 (1993).

[7] N. S. Sariciftci, D. Braun, C. Zhang, V. Srdanov, A. J. Heeger, and F. Wudl, Appl. Phys. Lett. **62**, 585 (1993).

[8] For example, see G. B. Blanchet, C. R. Fincher, T.-C. Chung, and A. J. Heeger, Phys. Rev. Lett. **50**, 1938 (1983).

[9] Y. H. Kim, D. Spiegel, S. Hotta, and A. J. Heeger, Phys. Rev. B **38**, 5490 (1988).

[10] H. E. Schaffer and A. J. Heeger, Solid State Commun. **59**, 415 (1986).

[11] Y. H. Kim, S. Hotta, and A. J. Heeger, Phys. Rev. B **36**, 7486 (1987).

[12] B. Horovitz, Solid State Commun. **41**, 729 (1982); E. Ehrenfrund, Z. Vardeny, O. Brafman, and B. Horovitz, Phys. Rev. B **36**, 1535 (1987).

[13] M. A. Greaney and S. M. Gorun, J. Phys. Chem. **95**, 7142 (1991); T. Kato *et al.*, Chem. Phys. Lett. **186**, 35 (1991); S. Nonell, J. Arbogast, and C. Foote, J. Phys. Chem. **96**, 4169 (1992).

[14] T. Kato *et al.*, Chem. Phys. Lett. **180**, 446 (1991).

[15] S. Larsson, A. Volosov, and A. Rosen, Chem. Phys. Lett. **137**, 501 (1987).

[16] Y. H. Kim, F. Li, and F. Diederich, Phys. Rev. B **45**, 10 169 (1992).