



Photoinduced Electron Transfer from a Conducting Polymer to Buckminsterfullerene

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- at strategic nodes beneath the rise axis so that paths pass to the correct side of the magma lens. Because the nodes of near-zero velocity strongly influence the placement of paths, the asymmetric displacement of the low-velocity zone to the west in the delay-time tomographic velocity model (6) and in multichannel reflection data [J. C. Mutter *et al.*, *Nature* **336**, 156 (1988)] is not reflected in the approximate paths.
20. The smoothest model inversion algorithm [A. N. Tikhonov and V. Y. Arsenin, *Solutions of Ill-Posed Problems* (Wiley, New York, 1977); S. C. Constable, R. L. Parker, C. G. Constable, *Geophysics* **52**, 289 (1987)] minimizes the weighted sum of the misfit to the data and the roughness of the model measured with the use of first-order differences
- $$(t_o - t_m)^T R_{tt}^{-1} (t_o - t_m) + \mu (q_a - q_m)^T \Delta^T \Delta (q_a - q_m)$$
- where t_o is a vector of the t^* observations, t_m is the model predictions, R_{tt} is a diagonal matrix of the estimated data variances, μ is the weight of the smoothing constraint, q_a is the vector of the $\ln(Q^{-1})$ nodal values in the starting model, q_m is the current model, Δ is an operator that calculates the first-order differences between all adjacent nodes, and T denotes transpose.
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33. We thank the officers and crew of the R.V. *Thomas Washington* and members of the scientific party for their assistance. Supported by the Office of Naval Research grant N00014-89-J-1257, the National Science Foundation grants OCE-8615797 and OCE-8615892 (for the original data collection), and WHOI Contribution 8150.

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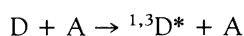
Photoinduced Electron Transfer from a Conducting Polymer to Buckminsterfullerene

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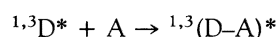
Evidence for photoinduced electron transfer from the excited state of a conducting polymer onto buckminsterfullerene, C_{60} , is reported. After photo-excitation of the conjugated polymer with light of energy greater than the π - π^* gap, an electron transfer to the C_{60} molecule is initiated. Photoinduced optical absorption studies demonstrate a different excitation spectrum for the composite as compared to the separate components, consistent with photo-excited charge transfer. A photoinduced electron spin resonance signal exhibits signatures of both the conducting polymer cation and the C_{60} anion. Because the photoluminescence in the conducting polymer is quenched by interaction with C_{60} , the data imply that charge transfer from the excited state occurs on a picosecond time scale. The charge-separated state in composite films is metastable at low temperatures.

Photoinduced electron transfer has been extensively investigated in physics, chemistry, and biology (and in the interdisciplinary areas of overlap between the traditional disciplines) because of fundamental interest in the photophysics and photochemistry of excited states in organic molecules and because such studies provide a synthetic approach to a deeper understanding of solar energy conversion in green plants (1). A basic description of intramolecular or intermolecular photoinduced electron transfer is as follows:

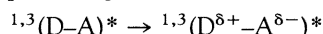
Step 1, excitation on D:



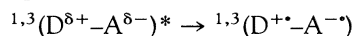
Step 2, excitation delocalized on the D-A complex:



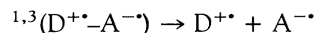
Step 3, charge transfer initiated:



Step 4, ion radical pair formed:



Step 5, charge separation:



In these equations the donor (D) and acceptor (A) units are either covalently bonded (intramolecular) or spatially close but not covalently bonded (intermolecular); 1 and 3 denote singlet or triplet excited states, respectively. At each step, the D-A system can relax back to the ground state either by releasing energy to the "lattice" (in the form of heat) or by emitting light (provided the radiative transition is allowed). Permanent changes that may occur from ion radical reactions beyond step 5 are not considered here,

even though their importance in photochemical reactions has been established. The electron transfer (step 4) describes the formation of an ion radical pair; this does not occur unless $I_{D^*} - A_A - U_C < 0$, where I_{D^*} is the ionization potential of the excited state (D^*) of the donor, A_A is the electron affinity of the acceptor, and U_C is the Coulomb energy of the separated radicals (including polarization effects). The charge separation (step 5) can possibly be stabilized by carrier delocalization on the D^+ (or A^-) species and by structural relaxation.

The possibility of using such charge separation in molecular information storage and optoelectronics has been suggested (2). Donor-bridge-acceptor-type "supermolecules" have been proposed as bistable "molecular information storage units," in which the separated ion radical pair state is visualized as one logic state and the ground state is the second logic state (3). For intramolecular photoinduced electron transfer, the requirements on the spacer between the donor and acceptor units are important (and demanding); for metastability, the molecular orbitals of the D and A components must be decoupled so as to retard the back electron transfer process (4-6).

The discovery of conducting polymers and the ability to dope these polymers over the full range from insulator to metal have resulted in the creation of a class of new materials that combines the electronic and optical properties of semiconductors and metals with the attractive mechanical properties and processing advantages of polymers (7). Moreover, the ability to control the energy gap and electronegativity through molecular design has made possible the synthesis of conducting polymers with a range of ionization potentials and electron affinities (7-9). The extended π -orbitals of conjugated polymers result in a quasi-one-dimensional electronic structure with associated novel nonlinear excitations (solitons, polarons, bipolarons) (7-14). The unique combination of electronic, electrochemical, and mechanical properties of these synthetic metals and semiconductors plus the ability to expand the class of materials and control their properties through rational chemical synthesis have made conjugated polymers a promising field of interdisciplinary research.

As a new form of carbon, buckminsterfullerene, C_{60} , has generated considerable recent interest in the scientific community (15-17). This molecule is an excellent electron acceptor capable of taking on as many as six electrons (18, 19); C_{60} , therefore, forms charge transfer salts with a variety of strong donors. The discovery of important solid-state properties in such charge-transfer salts of C_{60} has opened

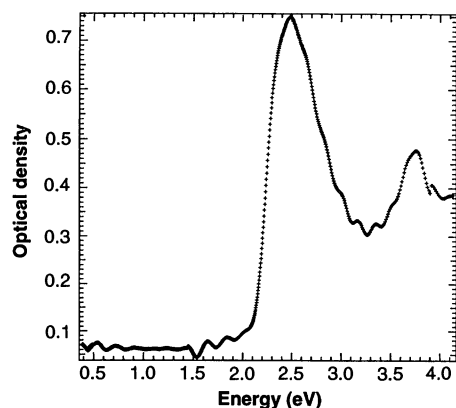


Fig. 1. Absorption spectrum of the (MEH-PPV)- C_{60} composite at room temperature.

exciting new directions of research activity; examples include the metallic state and superconductivity in salts with alkali metal ions (20, 21) and soft ferromagnetism in an organic salt with $(C_{60})^-$ (22).

We report the observation of reversible photoinduced electron transfer from poly[2-methoxy,5-(2'-ethyl-hexyloxy)-*p*-phenylene vinylene], hereafter referred to as MEH-PPV (23), onto C_{60} . The charge-separated configuration is long-lived as inferred from studies of the spectroscopy, the excitation spectroscopy (photoinduced absorption, PIA), the steady-state and time-resolved luminescence, and the light-induced electron spin resonance (LESR). Ion radicals originating from charge separation, $D + A \rightarrow D^+ + A^-$, are photo-generated. Although the DA complex is the stable ground state, the photoinduced charge transfer occurs because $I_{D^+} - A_A - U_C < 0$. The metastability of the charge-separated configuration may arise from structural relaxation to form positive polarons on the MEH-PPV chains.

Thin films of the (MEH-PPV)- C_{60} composite were prepared for optical studies by spin casting or drop casting from concentrated solutions onto quartz or sapphire substrates. We prepared the solutions by dissolving MEH-PPV and C_{60} (1:1 by weight) in toluene at a total typical concentration of 6 mg per 0.3 ml. For LESR experiments, ESR tubes were filled with the same solutions, dried under vacuum, and subsequently sealed.

Photoinduced changes in the absorption (α) spectra were recorded by mechanical chopping of the pump beam output from an argon ion laser (2.41 eV, 50 mW) at 273 Hz and coherent detection of the resulting changes in transmission (T) with a lock-in amplifier. The photoinduced absorption is directly calculated from the normalized changes in transmission ($-\Delta T/T \approx \delta\alpha d$, where d is the film thickness). With this

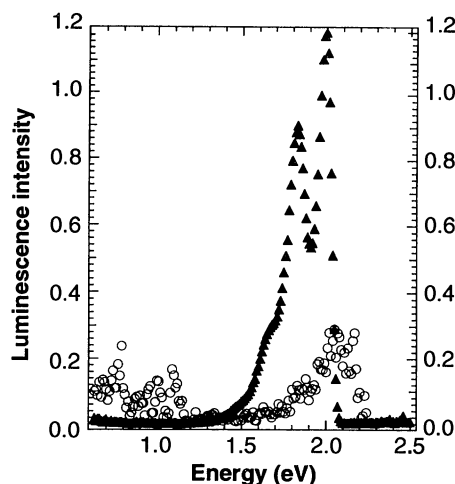


Fig. 2. Luminescence of MEH-PPV (▲) (left axis, $\times 10^{-2}$) and of the (MEH-PPV)- C_{60} composite (○) (right axis, $\times 10^{-4}$). The unit for luminescence in this figure is the output voltage of the detector.

method, the system response is automatically divided out; independent measurements were carried out to check for any contribution from luminescence emission to the photoinduced signal. Unless stated otherwise, all optical data reported were obtained with the samples at 80 K and at pressures of $\sim 10^{-5}$ torr.

In the LESR experiments we used a Bruker 200D ESR spectrometer equipped with a variable-temperature cryostat. The sample was illuminated with an optical fiber to bring the output beam from an argon ion laser (2.41 eV, 150 mW) into the microwave cavity. Steady-state ESR spectra were

recorded with the beam on and off and compared.

The $\pi \rightarrow \pi^*$ absorption (peak at 2.5 eV) of MEH-PPV and the 3.7-eV transition of C_{60} are clearly observed in the absorption spectrum (Fig. 1); the spectrum is simply a linear superposition of the two. Because there are no additional features, the composite can be regarded as $D + A$, where D = (MEH-PPV) and $A = C_{60}$, indicating no significant mixing of the electronic wave functions in the ground state.

The intense photoluminescence of MEH-PPV is, however, almost completely quenched, implying a strong interaction of the two components in the excited state (Fig. 2); the intensity is reduced in the composite by nearly three orders of magnitude (and there is a small blue shift). Independent measurements of the time decay of the photoluminescence demonstrate a reduction in the photoluminescent lifetime from approximately 550 ps in MEH-PPV to less than 60 ps (the pulse width of the excitation laser) in the (MEH-PPV)- C_{60} composite (24). The quenching of the photoluminescence intensity as well as the lifetime of MEH-PPV [and other conjugated polymers (25)] by interaction with C_{60} imply that in the (MEH-PPV)- C_{60} composite there is a process that is competing with the radiative emission of MEH-PPV, consistent with charge transfer from the π^* band of the photoexcited MEH-PPV to C_{60} . An estimate of the transfer rate, $1/\tau_{ct}$, is given by the decay rate of the photoluminescence in the (MEH-PPV)- C_{60} composite (charge transfer will cut off the radiative decay). Because the photolumines-

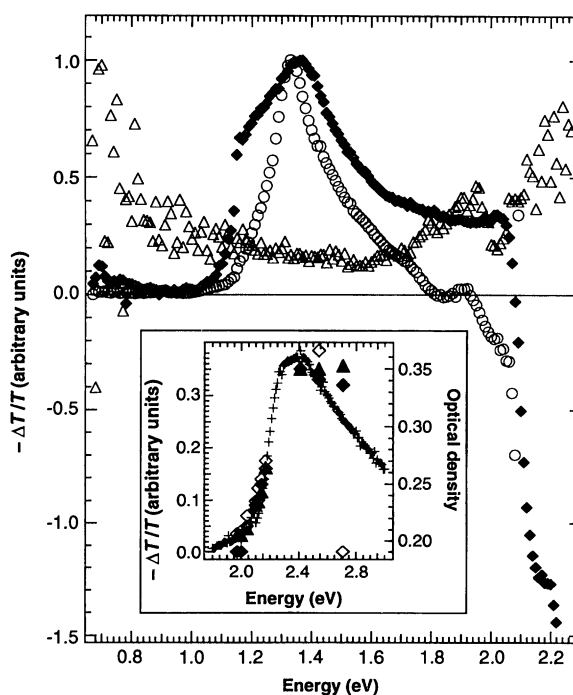


Fig. 3. Normalized photoinduced absorption spectra of MEH-PPV (○), C_{60} (△), and the (MEH-PPV)- C_{60} composite (◆). The inset shows the excitation profile (left axis) of the PIA peak at 1.33 eV (▲), PIA edge at 1.15 eV (◆), and PIA plateau at 1.8 eV (◇) as a function of the photon energy ($\hbar\omega$) of the laser pump, compared with the MEH-PPV absorption spectrum (right axis).

cence decay in the composite is unresolved within the 60-ps excitation pulse, we use the ratio of the intensities to estimate $1/\tau_{ct}$:

$$1/\tau_{ct} \sim (1/\tau_{rad})I_0/I_{comp} \quad (1)$$

where $1/\tau_{rad}$ is the radiative decay rate and I_0 and I_{comp} are the integrated photoluminescence intensities of MEH-PPV and the (MEH-PPV)- C_{60} composite, respectively. The data imply, therefore, that $1/\tau_{ct} \sim 10^{12}$; electron transfer occurs on a picosecond time scale. Because the charge-transfer rate is more than two orders of magnitude faster than competing radiative and nonradiative recombination processes, the quantum efficiency for charge transfer is close to unity.

The photoinduced changes in the absorption of the (MEH-PPV)- C_{60} composite are displayed in Fig. 3 and compared with those of MEH-PPV and C_{60} ; the data are normalized (the PIA of C_{60} is $\sim 10^{-3}$ of that of the composite). A sharp PIA edge at 1.15 eV and a plateau around 1.8 to 2.1 eV distinguish the composite from the pure MEH-PPV. On the basis of earlier work on MEH-PPV (26, 27), the PIA band with peak near 1.35 eV observed in the composite is to be assigned to the excited state of MEH-PPV, in either a triplet or a bipolaron (or polaron) configuration. Although the origin of the sharp PIA edge at 1.15 eV is less clear, the first absorption of C_{60}^- anion (28, 29) occurs at 1.1 to 1.2 eV. The sharp turnover in the PIA spectrum of the (MEH-PPV)- C_{60} composite at 2 eV (this is not due to photoluminescence) indicates a bleaching of the π - π^* interband transition of MEH-PPV, consistent with charge transfer; similar bleaching is observed, for example, on *p*-type doping. As shown in the inset of Fig. 3, in the excitation profile all the PIA features observed in the (MEH-PPV)- C_{60} composite follow the absorption profile of pure MEH-PPV, demonstrating that the initial step in the photoinduced electron transfer from the conducting polymer onto C_{60} is the π - π^* absorption of MEH-PPV. Because photo-excited C_{60} is a stronger acceptor than C_{60} in the ground state (30), any absorption by the C_{60} further enhances the probability of charge transfer.

Definitive evidence of electron transfer is observed in the LESR experiments (Fig. 4). Upon irradiation at 80 K, two photoinduced spin signals can be resolved; one at $g \approx 2.0000$ (where g is the electron g -factor) with $\Delta H_{pp} = 7.2$ G (where ΔH_{pp} is the peak-to-peak linewidth) and the other at $g \approx 1.9955$ with $\Delta H_{pp} = 6$ G. The higher g -value line is assigned to the (MEH-PPV) $^+$ cation and the lower g -value line to $(C_{60})^-$, in accord with earlier reports on the $(C_{60})^-$ ESR (31). At 80 K, the intensity of the ESR signal increases during successive light on-off cycles, indi-

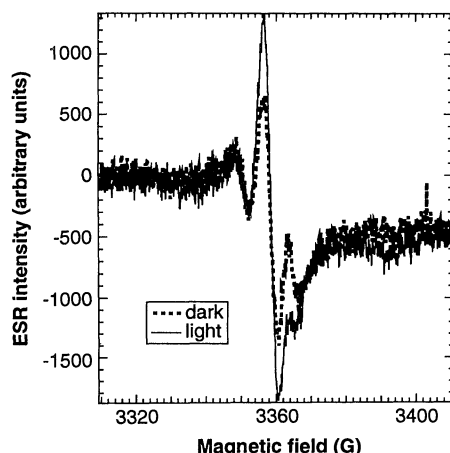


Fig. 4. LESR spectra of the (MEH-PPV)- C_{60} composite on successive illumination cycles.

cating the accumulation of photogenerated spins associated with the (MEH-PPV) $^+$ and $(C_{60})^-$ species. At 200 K, however, the LESR signal has nearly vanished, demonstrating the reversibility of the photoinduced electron transfer and ruling out permanent spins from photochemical reaction products. The relatively long lifetime (milliseconds at 80 K, estimated from relaxation of the photoinduced absorption) is particularly interesting (32); metastability of the photoinduced charge transfer might arise from delocalization of the positive polarons on the semiconducting MEH-PPV chains, thereby stabilizing the charge-transferred configuration.

The implications from the photoinduced electron transfer reported here are far-reaching. The charge-separated state could be used in photoelectrochemistry and in molecular optoelectronics; virtual excitations (in the sense of perturbation theory) may provide a mechanism for non-linear optical response. Thin layers of MEH-PPV and C_{60} , separately spun on top of one another to form a heterojunction, show luminescence quenching, indicating photoinduced charge transfer at the interface. Such heterostructures might, therefore, be useful as photovoltaic junctions. Indeed, we have observed photovoltaic phenomena in initial heterojunction devices (33). When illuminated, the devices (with rectification ratios in the current versus voltage characteristics that exceeded 10^4) exhibit a large photoresponse as a result of photoinduced electron transfer across the heterojunction interface from the semiconducting polymer (donor) onto C_{60} (acceptor).

Quite clearly, the observed photoinduced electron transfer and related phenomena are not limited to MEH-PPV; for example, preliminary experiments on (β -carotene)- C_{60} composites indicate photoinduced charge transfer. The wide range of

possible conducting polymers and conjugated oligomers available as donors and C_{60} derivatives (for example in polymeric form) as acceptors implies an important scientific opportunity.

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