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Photoinduced absorption spectroscopy of oligothiophene/C₆₀ mixtures in films and solutions

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Abstract

We present spectral evidence for the formation of triplet-state photoexcitations in T₇ films and solutions. Introduction of C₆₀ affects the photophysical processes dramatically via electron transfer (film) or energy transfer (solution) from photoexcited T₇ to C₆₀.

1. INTRODUCTION

Photoinduced electron transfer from conducting polymers to buckminsterfullerene has recently been reported for poly(3-octylthiophene)/C₆₀ and poly[2-methoxy-5-(2'-ethylhexyloxy) 1,4-phenylene vinylene]/C₆₀ composite films.^{1–3} It has been shown from time resolved photoinduced absorption (PIA) spectroscopy that the forward electron transfer from the conjugated polymer to C₆₀ occurs on a sub picosecond time scale after excitation across the π - π^* energy gap.³ The back electron transfer rate, however, is orders of magnitude smaller and the radical ions of conjugated polymer and C₆₀ have been detected using steady state light-induced ESR.^{1–2} In this contribution, we present spectroscopic studies on the effect of C₆₀ on the photophysical processes of monododecyl- α -heptathiophene (T₇) in composite films and solution. We provide evidence that both electron transfer (in films) and energy transfer (in solution) from T₇ to C₆₀ occur.

2. EXPERIMENTAL

Near steady-state PIA spectra were recorded by exciting with a mechanically modulated Ar-ion laser (458 nm, 2.71 eV) pump beam and monitoring the resulting change in the transmission of the sample (ΔT) with a phase sensitive lockin amplifier after dispersion by a grating monochromator. The PIA, $-\Delta T/T \equiv \Delta\alpha/\alpha$, is obtained from the normalized changes in transmission after correction for the luminescence.

The synthesis of T₇ has been described by Ten Hoeve et al.⁴ Films were cast from xylenes and studied at 80 K in vacuum (on the order of 10⁻⁵ Torr). Solutions were prepared in oxygen-free p-xylene and studied at ambient temperature in 1 mm cuvettes.

3. RESULTS AND DISCUSSION

3.1. T₇/C₆₀ films

The PIA spectrum of a T₇ film (Figure 1) at 80 K reveals two subgap absorptions at 1.36 and 1.47 eV which have been attributed to the (0-0) and (0-1) vibronics transitions of a metastable triplet state photoexcitation exhibiting a dipole allowed transition within the triplet manifold.⁵ The monomolecular lifetime of this triplet-state photoexcitation, as determined from the spectrum intensity dependence on the modulation frequency, is on the order of 120 μ s.⁵

Figure 1. PIA spectra of T₇ and T₇/C₆₀ films at 80 K

The PIA spectrum of a T₇/C₆₀ composite film (75:25 mol%) (Figure 1) shows a number of well-resolved PIA features. The PIA band centered at 1.17 eV corresponds to the absorption of the C₆₀^{•-} radical anion. Several of the other bands can be attributed to the T₇^{•+} radical cation (polaron). Removal of one electron from T₇ produces the T₇^{•+} radical cation and causes a redistribution of the energy levels, analogous to the creation of states in the gap upon oxidation (p-doping) of conjugated polymers.^{6,7} The molecular symmetry of T₇ (pseudo C_{2v}), restricts the dipole allowed electronic transitions among the frontier orbitals to HOMO→SOMO and SOMO→LUMO excitations.⁸ These two excitations are readily attributed to the

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two most intense bands in the PIA spectrum at 0.67 and 1.40 eV respectively (compare 0.80 and 1.54 eV for T_6^{+*}).⁹ The additional peaks at 0.84 eV and 1.63 eV are assigned to vibrational replicas. The full width at half maximum of the T_7^{+*} PIA bands is remarkably small (< 0.08 eV). This indicates a well-defined geometry for the T_7^{+*} radical cation, which is likely to be caused by an increased quinoid character of the wave function (i.e. partial double bonds between the thiophene rings). The shoulder at 1.49 eV is a remnant of the triplet spectrum of T_7 .

The derivative-like features at 2.22 and 2.34 eV are probably due to the combined effects of bleaching and electric and/or thermal modulation of the band edge.

The spectral features assigned to T_7^{+*} and C_{60}^{+*} all increase with pump intensity (I) according to $\Delta T \propto I^\alpha$, with $\alpha = 0.48$ –0.52. This square-root behavior is characteristic of a bimolecular decay mechanism and suggests that recombination of electrons and holes is the major relaxation pathway. The existence of a common relaxation mechanism is also supported by the identical dependence of the 1.17, 1.40 and 1.63 eV lines on the modulation frequency in the range from 20 to 4000 Hz. When fitted to the theoretical expression for bimolecular decay, we find an estimate of the lifetime on the order of 800 μ s.

3.2. T_7/C_{60} solutions

The PIA spectrum of T_7 (Figure 2) in deoxygenated p-xylene (10^{-4} M) at 295 K shows a strong PIA band at 1.71 eV with an additional shoulder at 1.86 eV. The PIA is due to the 3T_7 state, which decays monomolecularly ($\Delta T \propto I$) and has a lifetime of less than 50 μ s.

Figure 2. PIA spectra of T_7 , $T_7/TCNE$ (both left axis) and T_7/C_{60} solutions at 295 K.

Adding C_{60} (3×10^{-3} M) to the solution results in a strong decrease of the 3T_7 triplet band. New PIA features that can be attributed to T_7^{+*} or C_{60}^{+*} are not observed (Figure 2). Apparently, the quenching of the 3T_7 state by C_{60} in the mixed solution is not a result of an electron transfer reaction as observed in the composite film, but the result of an energy transfer reaction between 3T_7 and C_{60} . This conclusion is supported by the observation of a PIA band at 1.65 eV, the expected position for $^3C_{60}$.¹⁰ By studying C_{60} in p-xylene, we confirm that the main intensity of the band at 1.65 eV in the mixed solution is not due

to direct excitation and intersystem crossing of C_{60} , but rather the result of photosensitization via 3T_7 .

When instead of C_{60} , tetracyanoethylene (TCNE), is added (10^{-2} M) to a 10^{-4} M solution of T_7 in dichloromethane, we do observe an electron transfer reaction in solution: The PIA spectrum reveals the appearance of absorptions due to T_7^{+*} at 0.77 and 1.52 eV with vibrational side bands at 0.94 and 1.72 eV respectively. The persistence of the luminescence indicates that in dichloromethane electron transfer occurs between 3T_7 and TCNE.

4. CONCLUSION

We have presented spectral evidence of: (1) The efficient formation of (3T_7) triplet states in T_7 films and solutions. (2) Photoinduced electron transfer in a T_7/C_{60} mixed film, resulting in T_7^{+*} polarons (radical cations) and C_{60}^{+*} radical anions. (3) Triplet-triplet energy transfer between 3T_7 and C_{60} in mixed solutions, resulting in photosensitization of C_{60} . (4) Photoinduced electron transfer between 3T_7 and TCNE in solution.

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