ELECTRON TRANSFER AND ENERGY TRANSFER REACTIONS IN PHOTOEXCITED α-NONATHIOPHENE/C60 FILMS AND SOLUTIONS

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Abstract Photoexcitation of a nonathiophene in film or solution across the π-π* energy gap produces a metastable triplet state. In the presence of C60, on the other hand, an ultra fast electron transfer from the photoexcited nonathiophene onto C60 is observed in films, whereas in solution C60 is involved in an efficient energy transfer reaction with the triplet-state nonathiophene.

INTRODUCTION

Photoinduced electron transfer from conducting polymers onto C60 has recently been reported for solid films.1-5 The efficient quenching of luminescence and subpicosecond photoinduced absorption (PIA) spectroscopy have demonstrated that electron transfer occurs within a picosecond after photoexcitation across the π-π* energy gap.1-3 In this paper we extend these studies using a well-defined α-nonathiophene (T9, Figure 1) and explore the effect of C60 upon photoexcitation of this oligomer in films and solutions.

![Molecular structure of T9](image)

FIGURE 1 Molecular structure of T9.

EXPERIMENTAL

Near-steady-state PIA spectroscopy was performed with a mechanically modulated pump-and-probe technique, which has been described in more detail in previous publications.1-2

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Excitation was provided by the 457.9 nm line of an Ar-ion laser at 25 mW (film) or 75 mW (solution). The synthesis of α-nanonathiophene (T₉) has been described elsewhere.⁶

RESULTS AND DISCUSSION

The PIA spectrum of a T₉ film, cast from p-xylene, at 80 K (Figure 2) exhibits a single subgap absorption centered at 1.38 eV with a small vibronic band at 1.54 eV. The PIA signal increases sublinearly with pump intensity (ΔT/T ~ I⁰.⁶⁸), intermediate to the theoretical values for monomolecular (~I) and bimolecular (~I⁰.⁵) decay.⁷ The relaxation behavior of the PIA band at 1.38 eV was determined by monitoring the intensity of the PIA band as function of the chopping frequency (Figure 3). A fit of the data to theoretical curves for mono- and bimolecular decay gives 70-120 μs as an estimate for the lifetime of the photoexcitation.⁷ The presence of a single subgap absorption and the associated relatively long lifetime are the clear signatures of a metastable triplet-state photoexcitation. Apart from intersystem crossing to the triplet manifold, photoexcitation of T₉ produces luminescence, characterized by three vibronic transitions at 2.04, 1.89, and 1.72 eV, corresponding to the 0-0, 0-1, and 0-2 emissions (Figure 4).

![PIA spectra of T₉ and T₉/C₆₀ composite films at 80 K.](image)

The PIA spectrum of T₉ in deoxygenated p-xylene solution (10⁻⁴ M) at 295 K shows a well-defined band at 1.59 eV with an additional shoulder at 1.75 eV (Figure 5). The PIA spectrum of the solution is very similar to that of the film, although broadened and blue-shifted. The PIA band at 1.59 eV increases linearly with pump intensity (~I⁰.⁹₈) and is almost invariant to the modulation frequency in the range from 20 to 4000 Hz (Figure 3),
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\[ -\Delta I/T (\text{a.u.}) \]

FIGURE 3  The dependence of the PIA bands shown in Figures 2 and 5 on the modulation frequency.

consistent with monomolecular decay kinetics and an intrinsic lifetime below 50 µs. The fact that the signals at 1.59 and 1.75 eV are completely lost upon exposing the solution to air, supports our assignment as due to a triplet-state photoexcitation, which is effectively quenched by molecular oxygen.8 Luminescence of T9 in p-xylene solution at 295 K is observed at 2.25, 2.09 and 1.93 eV (Figure 4).

\[ \text{Energy (eV)} \]

FIGURE 4  Absorption/luminescence spectra of T9 film (dashed line/dot-dashed line) at 80 K and T9 solution (dotted line/solid line) at 295 K.
The luminescence intensity of a T9 film containing 25 mol% C60 at 80 K is strongly reduced to approximately 5%, compared to the pristine T9 film and slightly blue-shifted by 0.02 eV. At the same time, the PIA spectrum has changed dramatically; the triplet-triplet absorption at 1.38 eV is almost lost, and a number of new PIA bands and shoulders emerge at 2.14, 1.46, 1.28, 1.18, and -0.64 eV (Figure 2). The shoulder at 1.18 eV is readily attributed to C60.9,10 The PIA band at -0.64 eV is the characteristic low-energy feature of a charged T9 polaronic and/or bipolaronic excitation. The PIA bands at 1.28 and 1.46 eV are attributed to the corresponding high-energy feature of the same polaron/bipolaron. The 1.28 and 1.46 eV bands exhibit similar pump intensity ( -0.54, -0.59) and modulation frequency (Figure 3) characteristics, and therefore probably originate from the same species. The position of the PIA band at 2.14 eV coincides with the band edge of the linear π-π* absorption of T9 (Figure 4) and possesses a different pump intensity ( -0.40). We tentatively attribute the band at 2.14 eV as caused by a modulation of the band edge due to local electric fields resulting from photoinduced charges (T9+, C60+) in the films, analogous to electroabsorption phenomena.

These results demonstrate that photoexcitation of a T9/C60 film gives rise to an efficient electron-transfer reaction, similar to the previously reported photoprocess of conjugated polymer/C60 mixtures.1-5 This conclusion is supported by the direct spectral observation of T9+ and C60+, as well as by electroabsorption features at the band edge. The efficient quenching of the luminescence and intersystem crossing, indicate that the photoinduced electron transfer reaction occurs at very early stages after initial excitation.

The PIA spectrum of a 10⁻⁴ M T9 p-xylene solution, containing C60 (3x10⁻³ M) shows a strong decrease of the T9 triplet PIA band at 1.59 eV, to approximately 10% of
the initial level and concurrently the maximum shifts to 1.64 eV. In a separate experiment we found that photoexcitation of C₆₀ in p-xylene (3×10⁻³ M) produces the same PIA band at 1.64 eV resulting from triplet state C₆₀, in excellent agreement with photomodulation and ODMR studies on C₆₀/polystyrene glasses at 4 K.¹⁴ Compared to the same amount of C₆₀ alone, however, the PIA intensity of the band at 1.64 eV is somewhat enhanced in T₉/C₆₀ solution. In contrast to the luminescence of a T₉/C₆₀ composite film, the luminescence of a T₉ solution is not affected by introduction of C₆₀.

These results indicate that C₆₀ affects the evolution of photoexcited T₉ in solution via a different mechanism as compared to a film. We propose that in solution, C₆₀ is involved in a triplet energy transfer reaction, where the triplet state of T₉ acts as a sensitizer to C₆₀. The persistence of the luminescence in T₉ solutions containing C₆₀ supports our view that interaction of C₆₀ with the singlet photoexcited state of T₉ in solution is unlikely at the concentrations employed, because the lifetime of the singlet excited state is short compared to the molecular diffusion rate. For triplet state T₉, on the other hand, the lifetime is much longer and in principle both electron and energy transfer from triplet T₉ to C₆₀ can be anticipated because C₆₀ has a high electron affinity¹¹ and a low triplet energy level.¹²,¹³ The fact that no PIA bands due to T₉⁺ or T₉²⁺ are observed upon photoexcitation of T₉/C₆₀ in p-xylene solution, rules out that the triplet of T₉ acts as an electron donor to C₆₀. The observation of a PIA band at 1.64 eV, however, is consistent with the proposed energy transfer, although this band partly results from direct excitation and intersystem crossing of C₆₀.

CONCLUSION

In T₉ films and p-xylene solution, luminescence and intersystem crossing to metastable triplet-state photoexcitations follow photoexcitation across the π-π* energy gap:

\[ T₉(S₁) \rightarrow T₉(S₀) \quad \text{luminescence} \quad (1) \]
\[ T₉(S₁) \rightarrow T₉(T₁) \quad \text{intersystem crossing} \quad (2) \]

The 0-0 emissions occur at 2.04 eV and 2.25 eV for film and p-xylene solution respectively. The triplet-state photoexcitation of T₉ exhibits vibrationally resolved absorption bands centered at 1.38 eV (film) and at 1.59 eV (p-xylene).

Addition of C₆₀ strongly affects the observed photoprocess, but the mechanisms are distinctively different in film and solution. In a T₉/C₆₀ film at 80 K we observe a fast electron transfer reaction:
\[ T_9(S_1) + C_{60} \rightarrow T_9^+ + C_{60}^- \]  
\text{electron transfer (3)}

Both \( T_9^+ \) and \( C_{60}^- \) can be identified in the PIA spectrum, concurrently luminescence and intersystem crossing are quenched. In a \( T_9/C_{60} \) p-xylene solution, on the other hand, the luminescence and intersystem crossing are not affected, but the \( T_9 \) triplet state photoexcitation is quenched in an energy transfer reaction:

\[ T_9(T_1) + C_{60}(S_0) \rightarrow T_9(S_0) + C_{60}(T_1) \]  
\text{energy transfer (4)}

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