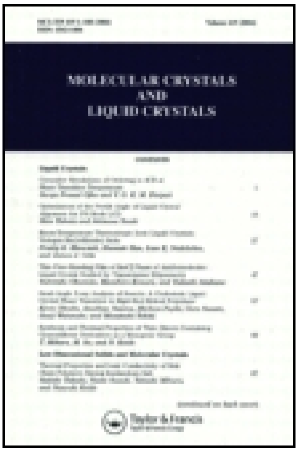

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Electron Transfer and Energy Transfer Reactions in Photoexcited α-Nonathiophene/C_{60} Films and Solutions

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ELECTRON TRANSFER AND ENERGY TRANSFER REACTIONS IN PHOTOEXCITED α-NONATHIOPHENE/C_{60} 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 C_{60}, on the other hand, an ultra fast electron transfer from the photoexcited nonathiophene onto C_{60} is observed in films, whereas in solution C_{60} is involved in an efficient energy transfer reaction with the triplet-state nonathiophene.

INTRODUCTION

Photoinduced electron transfer from conducting polymers onto C_{60} 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 (T_9, Figure 1) and explore the effect of C_{60} upon photoexcitation of this oligomer in films and solutions.

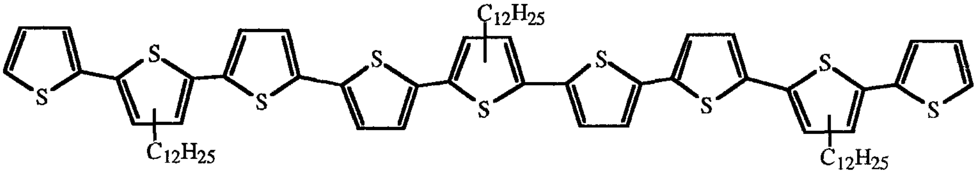

FIGURE 1 Molecular structure of T_9.

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-nonathiophene (T_9) has been described elsewhere.[6]

RESULTS AND DISCUSSION

The PIA spectrum of a T_9 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 ($\Delta T/T \sim I^{0.68}$), intermediate to the theoretical values for monomolecular (~I) and bimolecular ($\sim I^{0.5}$) 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 T_9 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).

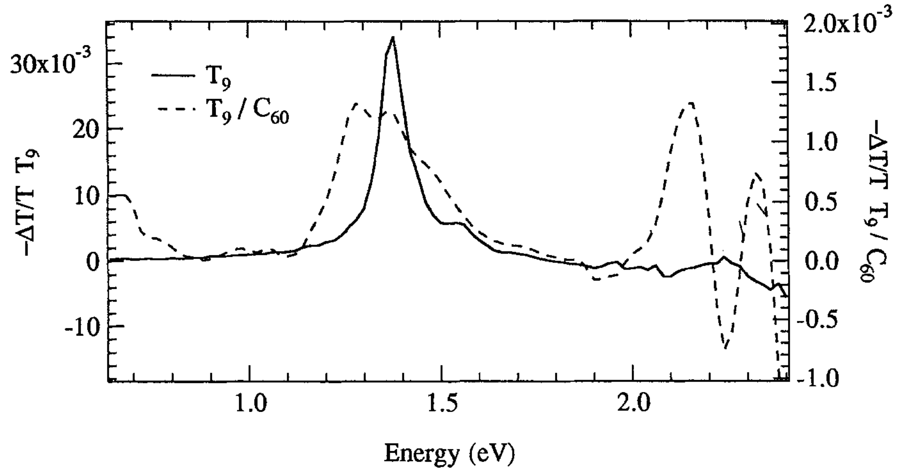

FIGURE 2 PIA spectra of T_9 and T_9/C_{60} composite films at 80 K.

The PIA spectrum of T_9 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 ($\sim I^{0.98}$) and is almost invariant to the modulation frequency in the range from 20 to 4000 Hz (Figure 3),

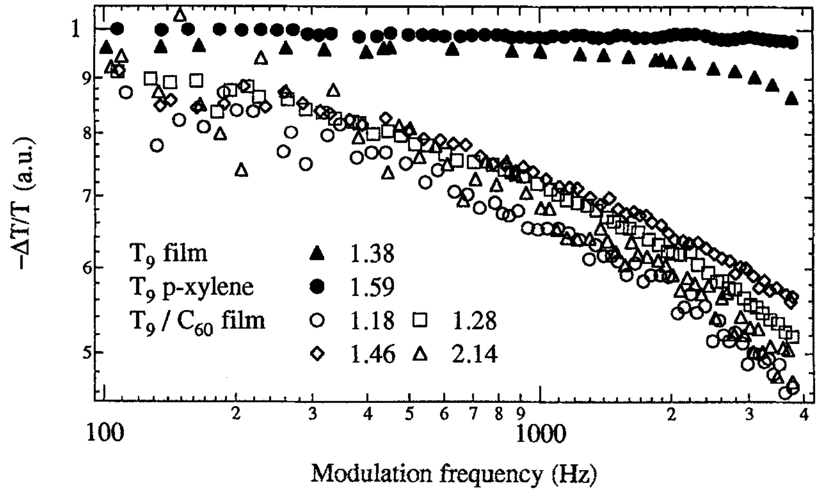

FIGURE 3 The dependence of the PIA bands shown in Figures 2 and 5 on the modulation frequency.

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 T_9 in p-xylene solution at 295 K is observed at 2.25, 2.09 and 1.93 eV (Figure 4).

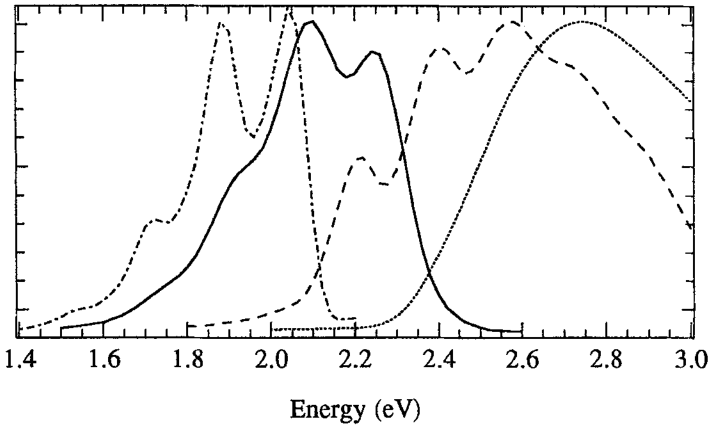

FIGURE 4 Absorption/luminescence spectra of T_9 film (dashed line/dot-dashed line) at 80 K and T_9 solution (dotted line/solid line) at 295 K.

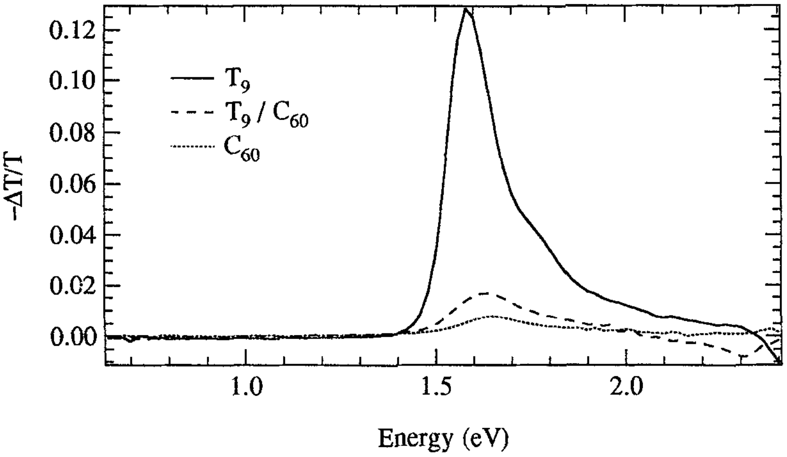

FIGURE 5 PIA spectra of T_9; T_9/C_{60}; and C_{60} in p-xylene solution at 295 K.

The luminescence intensity of a T_9 film containing 25 mol% C_{60} at 80 K is strongly reduced to approximately 5%, compared to the pristine T_9 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 C_{60}^-.[9,10] The PIA band at ~0.64 eV is the characteristic low-energy feature of a charged T_9 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 ($\sim I^{0.54}$, $\sim I^{0.59}$) 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 T_9 (Figure 4) and possesses a different pump intensity ($\sim I^{0.40}$). 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 (T_9^+, C_{60}^-) in the films, analogous to electroabsorption phenomena.

These results demonstrate that photoexcitation of a T_9/C_{60} film gives rise to an efficient electron-transfer reaction, similar to the previously reported photoprocess of conjugated polymer/C_{60} mixtures.[1-5] This conclusion is supported by the direct spectral observation of T_9^+ and C_{60}^-, 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 T_9 p-xylene solution, containing C_{60} (3×10^{-3} M) shows a strong decrease of the T_9 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 C_{60} in p-xylene ($3x10^{-3}$ M) produces the same PIA band at 1.64 eV resulting from triplet state C_{60}, in excellent agreement with photomodulation and ODMR studies on C_{60}/polystyrene glasses at 4 K.[14] Compared to the same amount of C_{60} alone, however, the PIA intensity of the band at 1.64 eV is somewhat enhanced in T_9/C_{60} solution. In contrast to the luminescence of a T_9/C_{60} composite film, the luminescence of a T_9 solution is not affected by introduction of C_{60}.

These results indicate that C_{60} affects the evolution of photoexcited T_9 in solution via a different mechanism as compared to a film. We propose that in solution, C_{60} is involved in a triplet energy transfer reaction, where the triplet state of T_9 acts as a sensitizer to C_{60}. The persistence of the luminescence in T_9 solutions containing C_{60} supports our view that interaction of C_{60} with the singlet photoexcited state of T_9 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 T_9, on the other hand, the lifetime is much longer and in principle both electron and energy transfer from triplet T_9 to C_{60} can be anticipated because C_{60} has a high electron affinity[11] and a low triplet energy level.[12,13] The fact that no PIA bands due to T_9^+ or T_9^{2+} are observed upon photoexcitation of T_9/C_{60} in p-xylene solution, rules out that the triplet of T_9 acts as an electron donor to C_{60}. 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 C_{60}.

CONCLUSION

In T_9 films and p-xylene solution, luminescence and intersystem crossing to metastable triplet-state photoexcitations follow photoexcitation across the π-π^* energy gap:

$T_9(S_1) \rightarrow T_9(S_0)$ luminescence (1)

$T_9(S_1) \rightarrow T_9(T_1)$ intersystem crossing (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 T_9 exhibits vibrationally resolved absorption bands centered at 1.38 eV (film) and at 1.59 eV (p-xylene).

Addition of C_{60} strongly affects the observed photoprocess, but the mechanisms are distinctively different in film and solution. In a T_9/C_{60} film at 80 K we observe a fast electron transfer reaction :

$$T_9(S_1) + C_{60} \rightarrow T_9^{+} + C_{60}^{-} \qquad \text{electron transfer} \qquad (3)$$

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:

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

ACKNOWLEDGMENTS

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REFERENCES

1. N. S. Sariciftci, L. Smilowitz, A. J. Heeger, and F. Wudl, Science, 258, 1474 (1992).
2. L. Smilowitz, N. S. Sariciftci, R. Wu, C. Gettinger, A. J. Heeger, and F. Wudl, Phys. Rev. B, 47, 13835 (1993).
3. B. Kraabel, C. H. Lee, D. McBranch, D. Moses, N. S. Sariciftci, and A. J. Heeger, Chem. Phys. Lett., 213, 389 (1993)
4. C. H. Lee, G. Yu, D. Moses, K. Pakbaz, C. Zhang, N. S. Sariciftci, A. J. Heeger, and F. Wudl, Phys. Rev. B, 48, 15425 (1993).
5. K. H. Lee, R. A. J. Janssen, N. S. Sariciftci, and A. J. Heeger, Phys. Rev. B (1994), in press.
6. W. ten Hoeve, H. Wynberg, E. E. Havinga, and E. W. Meijer, J. Am. Chem. Soc., 113, 5887 (1991), and references therein.
7. G. Dellepiane, C. Cuniberti, D. Comoretto, G. F. Musso, G. Figari, A. Piaggi, and A. Borghesi, Phys. Rev. B , 48, 7850 (1993).
8. N. J. Turro, Modern Molecular Photochemistry (University Science Books, Mill Valley, 1991).
9. M. A. Greaney and S. M. Gorun, J. Phys. Chem., 95, 7142 (1991).
10. T. Kato, T. Kodama, T. Shida, T. Nakagawa, Y. Matsui, S. Suzuki, H. Shiromaru, K., Yamauchi, and Y. Achiba, Chem. Phys. Lett., 180, 446 (1991).
11. P.-M. Allemand, A. Koch, F. Wudl, Y. Rubin, F. Diederich, M. M. Alvarez, S. J. Anz, and R. L. Whetten, J. Am. Chem. Soc., 113, 1050 (1991).
12. Y. Zeng, L. Biczok, and H. Linschitz, J. Phys. Chem., 96, 5237 (1992).
13. S. P. Sibley, S. M. Argentine, and A. H. Francis, Chem. Phys. Lett., 188, 187 (1992).
14. X. Wei, Z. V. Vardeny, D. Moses, V. I. Srdanov, and F. Wudl, Synth. Met., 54, 273 (1993)