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Photoinduced absorption of conjugated polymer/ C_{60} solutions: Evidence of triplet-state photoexcitations and triplet-energy transfer in poly(3-alkylthiophene)

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We present spectral evidence of the efficient photogeneration of triplet-state excitations in poly(3-alkylthiophene), P3AT, solutions. The steady-state photoinduced absorption spectra display a PIA band centered at 1.50 eV which is attributed to a dipole-allowed triplet-triplet transition. Photoexcitation of P3AT solutions containing C_{60} , results in an efficient energy transfer reaction and provides an estimate for the P3AT triplet-state energy of 1.57–1.72 eV.

INTRODUCTION

Both band-based models (weak electron-hole correlation) and exciton-based models (strong electron-hole correlation) have been invoked to describe the spatial extent of the transient singlet excited state of π -conjugated polymers obtained via photoexcitation across the π - π^* energy gap. The transient singlet excited state can decay via various mechanisms, e.g., luminescence (radiative recombination of electrons and holes), intersystem crossing to form a metastable triplet, or via creation of long-lived polarons and bipolarons through an interchain transfer mechanism.

Polarons and bipolarons are the charged nonlinear excitations of nondegenerate ground state π -conjugated polymers. Such excitations are self-localized on the polymer chain as a result of the strong coupling of the quasi-one-dimensional π electrons to the polymer backbone, and are characterized by electronic states within the energy gap.^{1,2} Photoinduced absorption (PIA) spectroscopy has been extensively used to determine the electronic energies of the polaron, bipolaron, and triplet-state photoexcitations and the associated structural distortions of the polymer backbone.^{3–6}

PIA spectra of conjugated polymers in solution were first detected in poly(3-hexylthiophene), P3HT.^{7,8} After photoexcitation of P3HT (in solution in dichloromethane) across the π - π^* energy gap (onset at ~ 2.3 eV), two PIA bands were observed, centered at 0.6 and 1.5 eV, and attributed to originate from photogenerated bipolarons.^{7,8} Recent studies on poly(3-alkylthiophene), P3AT, solutions have shown that the creation of charged photoexcitations (polarons and/or bipolarons) critically depends on the nature of the solvent.^{9–12} Photoexcitation of poly(3-decylthiophene) in chloroform, for example, produces bipolarons exhibiting subgap PIA bands at 0.55 and 1.55 eV, whereas in benzene or toluene no PIA activity was observed.¹⁰ To account for the solvent-dependent formation of charged photoexcitations, it has been proposed that a weak reversible charge transfer between the photoexcited polymer, and the solvent takes place.^{10,12} The key parameter in the proposed solvent mediated mechanism is the ground state electron affinity of the solvent.

We demonstrate, for the first time, that the principal

long-lived photoexcitation of P3AT in solution is a triplet excited state, which is characterized by a single PIA band and which is readily observed in various solvents. Furthermore, we explore the effect of the addition of C_{60} to the P3AT solution. Photoinduced electron transfer from conducting polymers onto C_{60} has been recently reported for solid films.^{13–17} Subpicosecond time-resolved PIA¹⁵ and the efficient quenching of the photoluminescence,^{13,14} have demonstrated that electron transfer occurs within a picosecond after photoexcitation across the π - π^* energy gap. We show that in solution, however, the primary reaction of C_{60} with the photoexcited polymer does not result in electron transfer, but rather in an efficient transfer of excitation energy.

EXPERIMENT

The experiments were performed on poly[3-(2-(3-methylbutoxy)ethyl)thiophene], P3MBET (Fig. 1), synthesized following McCulloughs procedure (slightly modified).^{18–20} This polymerization technique yields typically highly regioregular poly(3-alkylthiophene), with no detectable irregularities (head-to-tail coupling $\geq 99\%$), and an average molecular weight $\bar{M}_n = 17\,000$ g/mol with a dispersity index of 1.4 (determined by GPC against polystyrene standards). Dry deoxygenated solvents are used in all PIA experiments; samples were prepared under an argon atmosphere and placed in sealed 1 mm cuvettes. Direct transmission (T) spectra are recorded in the spectral region from 0.64 to 2.4 eV using a tungsten-halogen probe source, a grating monochromator, and a two color Si/PbS detector. Photoexcitation is provided by the 457.9 nm (2.71 eV) line of a cw argon-ion laser. The photoinduced change in transmission (ΔT) of the sample is measured by mechanically chopping the pump beam and the resulting modulation of the probe beam is detected using a phase-sensitive lockin amplifier. The PIA, $-\Delta T/T \cong \Delta \alpha d$, is directly calculated from the change in transmission.

RESULTS AND DISCUSSION

The steady state PIA spectrum of a 0.5 mg/mL solution of P3MBET in *p*-xylene (Fig. 2) exhibits one strong, well-defined, PIA band centered at 1.50 eV. This PIA band increases linearly with the pump intensity (Fig. 3) and does not

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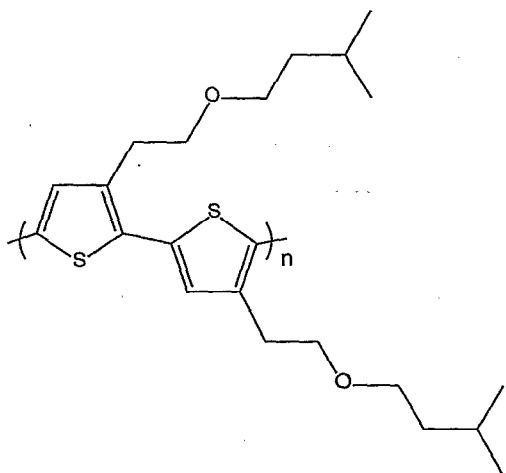


FIG. 1. Molecular structure of poly[3-(2-(3-methylbutoxy)ethyl)thiophene], P3MBET.

decrease in intensity upon increasing the modulation frequency (ω) of the pump beam from 20 to 4000 Hz (Fig. 4). This behavior is consistent with monomolecular decay of the photoexcited state. The intrinsic lifetime, τ , however, cannot be determined from this experiment because the characteristic transition from the $\omega\tau \ll 1$ region (where $\Delta T/T$ is independent of ω) to the $\omega\tau \gg 1$ regime (where $\Delta T/T$ decreases as ω^{-1}),³ does not occur for frequencies up to 4000 Hz. Accordingly, the lifetime is estimated to be less than 50 μs . The presence of a single PIA band in the spectral region from 0.64 to 2.40 eV and the associated monomolecular decay are

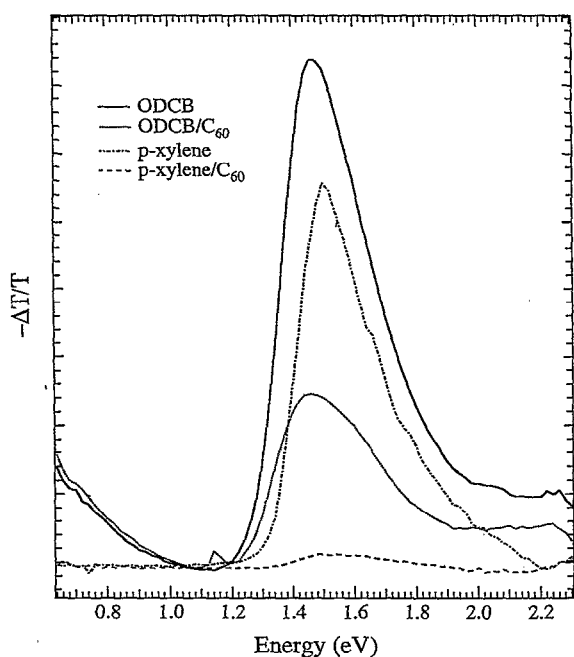


FIG. 2. PIA spectra of 0.5 mg/mL P3AT solutions. Spectra were recorded at 295 K by pumping with an argon-ion laser at 2.71 eV with 75 mW and a modulation frequency of 25 Hz.

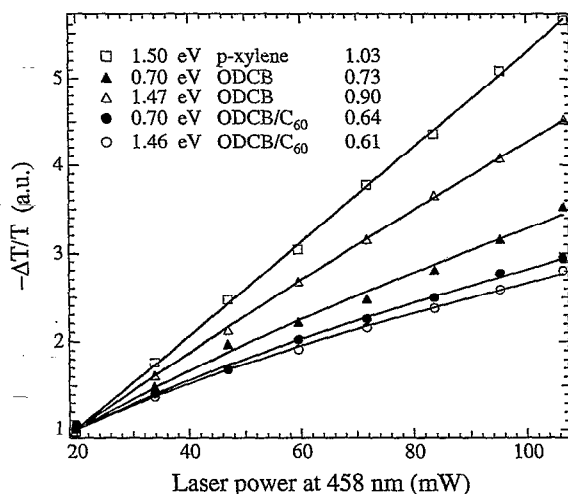


FIG. 3. Normalized $\Delta T/T$ of the PIA bands shown in Fig. 2 vs the intensity of the pump beam. Solid lines are best fits assuming power-law dependences with exponents as indicated in the inset. The experiment was performed at 295 K with a 25 Hz modulated pump beam at 2.71 eV.

clear signatures of a triplet-state photoexcitation; hence we attribute the PIA band at 1.50 eV to a dipole allowed $T_1 \rightarrow T_2$ absorption. The observation that the PIA band at 1.50 eV is completely quenched after exposing the solution to air, gives strong support to our assignment that it originates from a triplet-state photoexcitation, since a triplet would be expected to be readily quenched by molecular oxygen.²¹

The PIA spectrum of a 0.5 mg/mL solution of P3MBET in 1,2-dichlorobenzene (ODCB) is significantly different from the spectrum obtained from a *p*-xylene solution (Fig. 2). In this more polar solvent ($\epsilon=9.93$ vs $\epsilon=2.27$ for *p*-xylene), we observe two PIA bands; a strong transition centered at 1.47 eV and the onset of a second, less intense, band in the low-energy region with an absorption maximum below 0.64 eV; i.e., beyond our detection limit. The low-

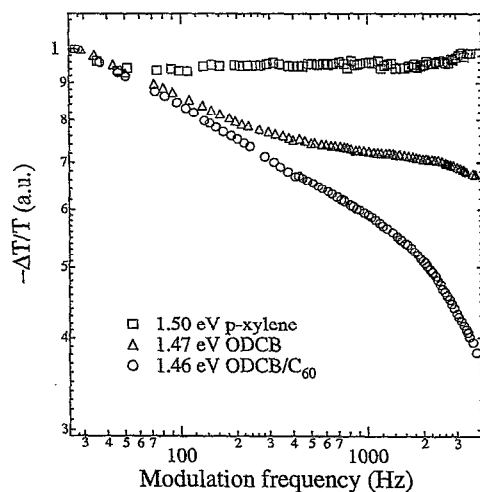


FIG. 4. Normalized $\Delta T/T$ of the PIA bands shown in Fig. 2 vs the modulation frequency. Curves were recorded by pumping at 2.71 eV with 75 mW.

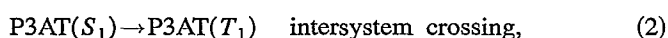
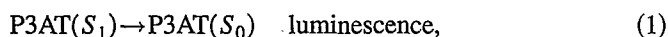
energy PIA band increases sublinearly ($I^{0.73}$) with pump intensity, as determined at 0.70 eV. In contrast, the high-energy PIA band increases according to $I^{0.90}$ (Fig. 3), i.e., intermediate to that of the low-energy PIA band (<0.64 eV) in ODCB and the PIA band at 1.50 eV in *p*-xylene. This suggests that the PIA band at 1.47 eV observed in an ODCB solution of P3MBET results from overlapping absorptions of two different photoexcitations, one exhibiting a linear and one a sublinear intensity dependence.

Additional support for this conclusion comes from the chopping frequency dependence of the PIA band at 1.47 eV (Fig. 4); after an initial decay according to $\omega^{-0.12}$, $\Delta T/T$ becomes almost independent on ω ($\omega^{-0.04}$ dependence) at approximately 200 Hz. This complex decay behavior is characteristic of a PIA band that consists of two overlapping absorptions with different decay kinetics. Accordingly, the PIA band at 1.47 eV of P3MBET in ODCB is attributed to the superposition of a PIA signal due to a triplet-state photoexcitation and the high-energy PIA band of a charged polaron and/or bipolaron photoexcitation. The PIA band exhibiting a peak below 0.64 eV is attributed to the associated low-energy feature of the charged photoexcitation. The slow time response of the PbS detector in the NIR region precluded, however, a detailed modulation frequency analysis of the low-energy PIA band.

In addition to photoinduced absorption, photoexcitation of P3MBET in solution produces intense, vibronically resolved, luminescence in both solvents. The 0–0 vibronic transitions in the luminescence spectrum (not shown) are found at 2.15 eV in *p*-xylene and at 2.11 eV in ODCB.

Although we focus our attention to *p*-xylene and ODCB as solvents, we note that the triplet-state photoexcitations of the P3ATs can be detected in a variety of (deoxygenated) organic solvents, whereas the creation of charged photoexcitations is only observed in more polar solvents.^{9–12} Moreover, the formation of a triplet-state photoexcitation is not restricted to regioregular P3ATs and can readily be observed for conventionally prepared P3ATs, with various side chains.

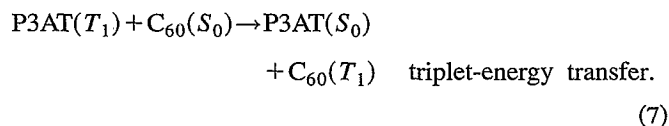
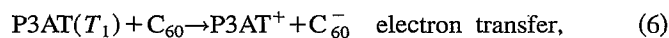
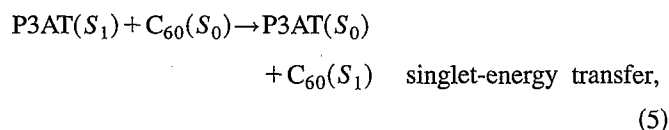
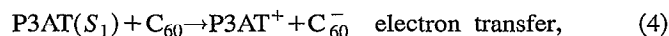
Excitation of P3MBET in solution at 2.71 eV by pumping across the π – π^* band (absorption maximum 2.74 eV (ODCB), 2.77 eV (*p*-xylene)) produces initially a singlet excited state [P3AT(S_1)]. Our experiments show that, apart from radiative decay (photoluminescence, 1) via electron–hole recombination, the singlet excited state can decay non-radiatively via intersystem crossing to a triplet state (2), or via transfer of an electron to a suitable acceptor (3)



The results presented here constitute the first experimental evidence that *intersystem crossing is efficient in P3AT solutions and produces readily observable triplet-state photoexcitations in various solvents*, in accordance with observations for oligothiophenes.^{22–24} Preliminary time-resolved PIA experiments in our laboratory indicate that intersystem crossing occurs within a few nanoseconds following excitation.

To account for the formation of charged excitations a solvent mediated mechanism has recently been proposed.^{9–12} Our data are consistent with this mechanism. Electron transfer from the singlet photoexcited state requires the immediate proximity of a suitable electron acceptor (*A*) in order to compete with the efficient luminescence and intersystem crossing processes. In dilute P3AT solutions only solvent molecules fulfill this requirement,²⁵ because molecular diffusion is slow compared to the lifetime of the singlet excited state. The fact that charged excitations are present in ODCB but not in *p*-xylene, demonstrates that the nature of the solvent can be detrimental. A solvent with high electron affinity (low reduction potential) can act as an electron acceptor and the increased solvent polarity (high ϵ) will stabilize the charged reaction products. The charged photoexcitation is attributed to polarons and/or bipolarons. Although the low-energy and high-energy PIA bands of P3AT are usually interpreted as originating from bipolarons, we note that in PIA experiments of oligothiophenes we observe clear signatures of monoradical cations (polarons).

Electron transfer from a photoexcited polymer onto C_{60} has been recently reported for solid films.^{13–17} Here we investigate the effect of C_{60} in solution. In a solution containing a mixture of a poly(3-alkylthiophene) and C_{60} , we might expect several different interactions after photoexcitation



Processes (4) and (5) occur from the P3AT(S_1) state and can only take place within the short lifetime of this transient species. As indicated above, interactions (4) and (5) are unlikely to occur in dilute solution where the average distance between the polymer and C_{60} molecules is large compared to the molecular dimensions. Electron transfer (6) or energy transfer (7) from a metastable triplet state, however, seem to be viable options due to the longer lifetime of the triplet state and because C_{60} has a high electron affinity^{26,27} and a relatively low triplet energy.^{28,29}

The PIA spectrum obtained from a 0.5 mg/mL solution of P3MBET in *p*-xylene containing 5×10^{-4} M C_{60} is shown in Fig. 2. Compared to the spectrum recorded without C_{60} , the intensity of the triplet-state photoexcitation of P3MBET has dramatically decreased in *p*-xylene/ C_{60} , by nearly 2 orders of magnitude. This indicates that the P3MBET triplet-state photoexcitation is effectively quenched by introducing C_{60} into the solution. The fact that no signals of charged excitations emerge in the spectrum demonstrates that in *p*-xylene, triplet-energy transfer (7) is favored over electron transfer (6). The luminescence intensity, however, is not no-

ticeably affected by the presence of C_{60} , indicating that processes (4) and (5) are not of major importance in solution.

In a separate experiment, we measured the PIA spectrum of a 5×10^{-4} M solution of C_{60} . Photoexcitation at 2.71 eV of C_{60} in *p*-xylene (or ODCB) at 295 K, produces the corresponding C_{60} triplet state, characterized by a PIA band at 1.65 eV and an additional shoulder at 1.83 eV, in excellent agreement with photomodulation and ODMR studies on C_{60} /polystyrene glasses at 4 K.³⁰ The intensity of the triplet C_{60} PIA band in solution is, however, orders of magnitude less than the triplet PIA band of P3MBET, and does not interfere with the spectra shown in Fig. 2.

The PIA spectrum of a P3MBET (0.5 mg/mL)/ C_{60} (5×10^{-4} M) mixture in ODCB exhibits two principal PIA bands, one centered at 1.46 eV and the other below 0.64 eV (Fig. 2). Compared to the PIA spectrum recorded in ODCB without C_{60} , the band at 1.46 eV has decreased considerably, but is not completely suppressed in contrast with the results obtained in *p*-xylene. The intensity of the PIA band at <0.64 eV, on the other hand, is not affected by the introduction of C_{60} . Therefore, we conclude that C_{60} quenches the triplet-state photoexcitation of P3MBET in ODCB, analogous to a *p*-xylene solution via triplet-energy transfer, and that the remaining PIA signal at 1.46 eV in ODCB/ C_{60} must be attributed to the high-energy absorption band of the charged photoexcitation. This charged state is not affected by introduction of C_{60} , as evidenced from the constant intensity of the associated low-energy feature at 0.64 eV.

The low-energy and high-energy PIA bands of P3MBET in ODCB/ C_{60} increase sublinearly with pump intensity, following $I^{0.64}$ and $I^{0.61}$, respectively (Fig. 3), thus supporting the conclusion that both bands originate from the same charged polaron and/or bipolaron photoexcitation. The frequency dependence measured for the high-energy PIA band is shown in Fig. 4. The signature of the decay curve is reminiscent of a bimolecular decay mechanism.¹² The initial decay follows $\omega^{-0.15}$ and, at approximately 2000 Hz, a transition to a faster decay occurs. From this transition we estimate the lifetime to be on the order of 0.5 ms.

In addition to the features of the charged photoexcitation due to P3MBET, the PIA spectrum of the P3MBET/ODCB/ C_{60} solution exhibits a small absorption at 1.14 eV. This signal lags in phase considerably with respect to the PIA bands of the charged photoexcitation. The PIA band at 1.14 eV is characteristic of the C_{60}^- anion radical; this band has been observed in absorption studies of chemically³¹ and electrochemically³² generated C_{60}^- , as well as in the absorption spectra of C_{60}^- generated by γ irradiation.³³ This band has generally been assigned to the $T_{1u} \rightarrow T_{1g}$ transition of C_{60}^- , though recent calculations suggest that the 1.14 eV peak corresponds to a $T_{1u} \rightarrow H_g$ transition.³⁴ The presence of C_{60}^- in P3MBET/ODCB/ C_{60} in solution can either be the result of an electron transfer reaction (6), or C_{60} might act as an electron acceptor to solvent anion radicals formed via (3). Without additional information, it is not possible to discern between the two processes. However, as indicated above, the importance of electron transfer from the P3MBET triplet state onto C_{60} is limited,

since no significant increase of the PIA band at 0.64 eV is observed.

The efficient energy transfer from P3MBET to C_{60} in both *p*-xylene and ODCB, can only occur when the $S_0 \rightarrow T_1$ energy of C_{60} is less than the energy released in the P3MBET $T_1 \rightarrow S_0$ process. The energy of $C_{60}(T_1)$ is estimated to lie 1.57 eV above $C_{60}(S_0)$ ^{26,27} and gives an indication of the lower limit on the energy of the triplet state of P3MBET. The triplet energy of α -terthienyl determined by heavy-atom induced optical absorption has been reported;³⁵ the value of 1.72 ± 0.05 eV serves as an upper limit to the triplet energy of P3MBET.

CONCLUSION

We have presented the first observation and characterization of a metastable triplet-state photoexcitation of a poly(3-alkylthiophene), P3MBET, in solution. The PIA spectrum of P3MBET in various solvents reveals a strong band centered at 1.50 eV which is attributed to a dipole allowed triplet-triplet absorption. The P3MBET triplet-state photoexcitation exhibits efficient energy transfer to C_{60} . We estimate that the triplet state of P3MBET lies 1.57–1.72 eV above the ground state. Our experiments support recent observations that the creation of charged photoexcitations follows an electron transfer reaction in which the solvent is actively involved. The formation of charged polaron and/or bipolaron excitations is, however, a minor process compared to the generation of the metastable triplet state, even in favorable solvents.

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