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Photoinduced electron transfer processes in oligothiophene/C$_{60}$ composite films

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We present near steady-state photoinduced absorption (PIA) spectroscopy and steady-state light-induced electron spin resonance (LESR) studies on photoinduced electron transfer reactions in composite films of well defined α-oligothiophenes (T_n, $n=6$, 7, 9, and 11) as electron donor with buckminsterfullerene (C$_{60}$) and a methanofullerene derivative (1-(3-cholestanoxycarbonyl)-propyl-1-phenyl-[6.6]C$_{61}$) as electron acceptors. Dispersion on a molecular level of these fullerenes in oligothiophene films causes quenching of both the photoluminescence and intersystem crossing after photoexcitation across the $\pi-\pi^*$ energy gap as a result of a fast electron transfer reaction. The PIA spectra exhibit bands due to $T_n^{+\bullet}$ radical cations, fullerene radical anions and electroabsorption oscillations of the $\pi-\pi^*$ band edge resulting from strong local electric fields set up by the photoinduced charges. LESR spectra give additional unambiguous evidence of the photoinduced electron transfer reaction. Using PIA and LESR, we do not observe an effect of the conjugation length of the photoinduced electron transfer reaction or on the metastability of the charge-separated state. © *1995 American Institute of Physics.*

INTRODUCTION

Recently, photoinduced electron transfer from π-conjugated polymers onto buckminsterfullerene, C$_{60}$, has been reported.[1] Time-resolved photoinduced absorption (PIA) spectroscopy has revealed that this process is extremely fast; forward electron transfer occurs on a 300 fs time scale after excitation of the polymer across the $\pi-\pi^*$ energy gap.[2] The fact that photoluminescence of the conjugated-polymer/C$_{60}$ films is almost completely quenched,[1,3] implies that in the composite films there is a process that is competing with radiative emission, consistent with the fast electron transfer from the photoexcited polymer onto C$_{60}$ which reduces the lifetime of the initial singlet excited state significantly. The rate for back electron transfer (i.e., the recombination of photogenerated holes and electrons) is, however, many orders of magnitude lower, as evidenced from the observation of the absorptions of the radical ions of the conjugated polymer and C$_{60}$ using (near) steady-state PIA spectroscopy and light-induced electron spin resonance (LESR).[1,4] Additional evidence for fast forward and slow back electron transfer has been provided by the increase of both transient and steady-state photoconductivity.[5,6] The metastability of the charge-separated state is proposed to arise from the excellent acceptor properties of C$_{60}$ and the π-electron delocalization on the conjugated polymer.

Photoinduced electron transfer onto C$_{60}$ has now been observed for a variety of conjugated polymers, viz. poly(3-alkylthiophene)s, poly(2,5-dialkoxy-1, 4-phenylene vinylene)s, poly(9,9-dihexylfluorene) and poly(o-trimethylsilylphenylacetylene).[1–8] The extended π-conjugation associated with these materials enhances the stabiliza-

tion of positively charged photogenerated polarons and/or bipolarons via delocalization and mobility along the polymeric chain, reducing the back electron transfer rate. In order to assess the role of the π-conjugation length of the donor, we set out to study photoinduced electron transfer in a series of composite films of well-defined medium-sized α-oligothiophenes (T_n, $n=6$, 7, 9, 11; Fig. 1) with C$_{60}$.

Oligothiophenes are among the most extensively studied type of conjugated oligomers. It has been shown that their oxidation potential correlates linearly with the reciprocal of the number of thiophene rings, consistent with the simple rationale that longer conjugation lengths stabilize radical cations via increased delocalization.[9] In photoinduced electron transfer reactions ($D^*+A\rightarrow D^{+\bullet}+A^{-\bullet}$), however, the electron is transferred in the excited state and the formation of the radical ions does not occur unless $I_{D^*}-A_A-U_C<0$, where I_{D^*} is the ionization potential of the excited state donor (D^*), A_A the electron affinity of the acceptor, and U_C is the Coulomb energy of the separated radical ions (including polarization effects). In general, the excited state energy of π-conjugated materials depends on the conjugation length; for the oligothiophenes used in this study the $\pi-\pi^*$ band gap is inversely proportional to the number of thiophene rings.[10,11] Since low oxidation potentials in the ground states are accompanied by low excitation energies and vice versa, the ionization potential of the excited state (I_{D^*}), is affected by two opposite effects, both depending on the chain length. I_{D^*} could therefore end up to be fairly insensitive to the conjugation length of the oligomer. In fact, it has been shown recently that photoinduced electron transfer in solution can occur from the photogenerated triplet states of oligo- and polythiophenes onto tetracyanoethylene (TCNE) for donors in the range from terthienyl to poly(3-alkylthiophene).[12–15] Triplet-energy transfer from the photogenerated triplet oligothiophene to C$_{60}$ (i.e., photosensitization of C$_{60}$ to form
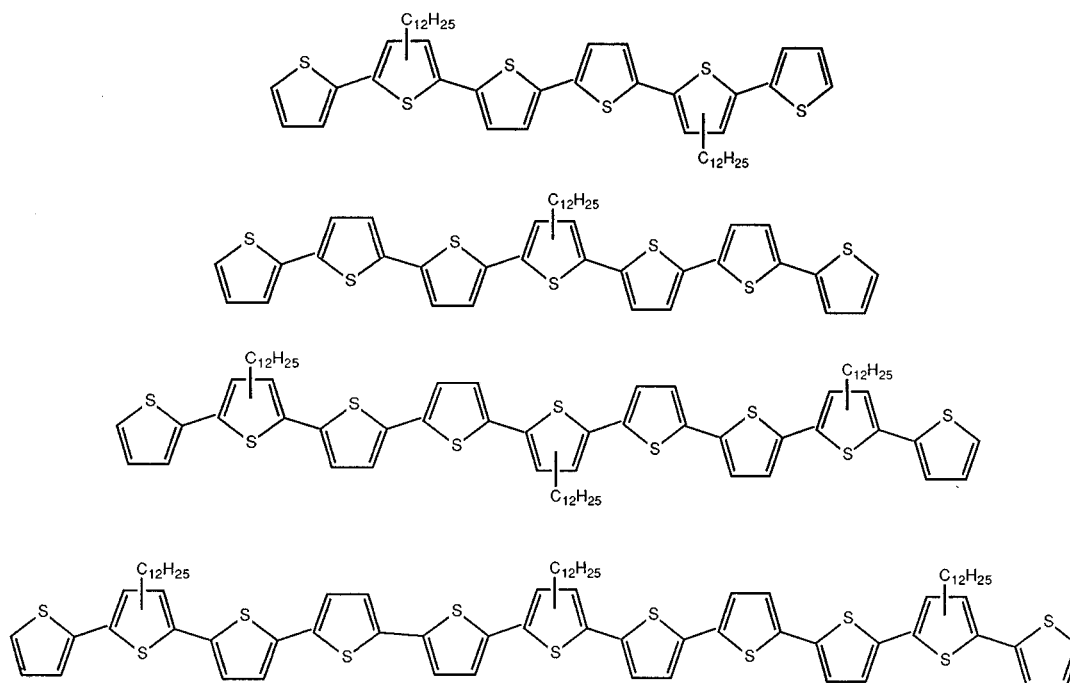
FIG. 1. Molecular structure of T$_n$ oligomers investigated in this study.

^{3}C$_{60}$) in solution has been found to be less efficient for longer oligothiophenes.[14] This has been attributed to a slight decrease of the triplet state energy level with respect to the ground state for longer conjugation lengths, concomitant with the decreasing $\pi-\pi^*$ energy gap.

In this paper we report the results of near steady-state PIA spectroscopy and steady-state LESR studies of oligothiophenes (donor) and fullerenes (acceptor) in composite films to investigate the effect of conjugation length on photoinduced electron transfer reactions. In contrast to the results of the same donor–acceptor couple in solutions,[14] the studies in the films clearly show a rapid photoinduced electron transfer from the conjugated oligothiophenes onto fullerenes, provided that mixing on a molecular level is achieved.

EXPERIMENT

The synthesis of the oligothiophenes used in the present study has been described by Ten Hoeve *et al.*[16] The preparation and characterization of 1-(3-cholestanoxycarbonyl)-propyl-1-phenyl-[6.6]C$_{61}$ ([6.6]PCBCa) will be described elsewhere.[17]

PIA experiments were performed using an argon-ion cw laser as a pump beam (458 nm, 25 mW, 2 mm pump diameter) and a tungsten–halogen probe beam. The pump beam was mechanically chopped (typically at 275 Hz) and the resulting modulation of the probe light transmission (ΔT) was phase-sensitively recorded after dispersion by a grating monochromator using a lock-in amplifier and a two-color (Si/PbS) detector. The probe beam transmission (T) was recorded separately, and the PIA ($-\Delta T/T \approx \Delta \alpha \cdot d$) was obtained after correction for luminescence. Pure T$_n$ films and composite films of T$_n$ with C$_{60}$ or [6.6]PCBCa in a molar ratio of 75:25 for PIA were prepared by casting from xylenes solution onto sapphire substrates. As a result of the limited solubility of T$_7$ and T$_{11}$ in xylenes at ambient temperature, solutions were heated to 100 °C to obtain films of o.d.$\approx$1 (at the $\pi-\pi^*$ transition). The uv/vis absorption spectra of the mixed films show a linear superposition of T$_n$ and C$_{60}$ or [6.6]PCBCa spectra without new absorptions below the $\pi-\pi^*$ energy gap. The substrates were mounted on a cryostat held at 80 K under a dynamical vacuum on the order of 10^{-5} Torr.

LESR experiments utilized a Bruker ESP300 *X*-band ESR spectrometer equipped with an Oxford ITC4 variable temperature unit. Excitation was provided by an argon-ion cw laser operating at 488 nm and 150 mW. The light was transmitted into the microwave cavity through a 50% transmission grid. LESR spectra were typically recorded at 25 K and lowest microwave power (10 μW) attainable to prevent saturation while ensuring sufficient S/N ratio. In these experiments care was taken to avoid "background" signals caused by the ambient light of fluorescent lamps which was found to produce readily detectable LESR signals. Frequencies were recorded using a HP5225A frequency counter and reported g values are calibrated against DPPH (g=2.0036). Samples for LESR experiments were prepared from T$_n$ and T$_n$/C$_{60}$ (75:25 mol %) solutions in xylenes by evaporation of the solvent from a suprasil quartz tube. This procedure provides films and mixed films on the inner wall of the tube. The tubes were subsequently flame sealed under a vacuum of 5×10^{-6} Torr.
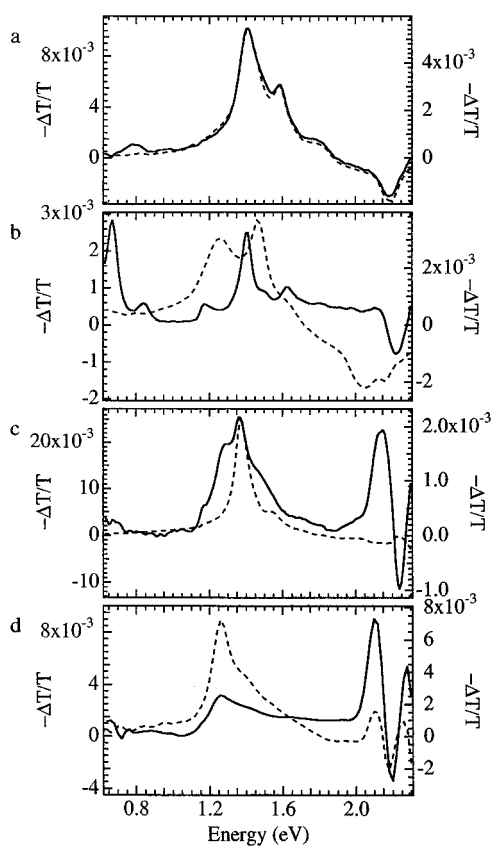
FIG. 2. PIA spectra of T$_n$ films (dashed line, left axis) and T$_n$/C$_{60}$ films (75:25 mol %) (solid line, right axis) (a) T$_6$, (b) T$_7$, (c) T$_9$, (d) T$_{11}$. Spectra were recorded at 80 K by pumping at 2.71 eV with 25 mW and a modulation frequency of 275 Hz.

RESULTS AND DISCUSSION

Photoinduced absorption of pristine T$_n$ films

The PIA spectra of the pristine oligomer films recorded at 80 K are shown in Fig. 2 and reveal a number of transitions in the 0.6–2.4 eV region. The PIA signals of the pure T$_n$ oligomers are assigned to a vibronically coupled dipole-allowed transition within the triplet manifold, i.e., the T→T* absorption of a triplet photoexcited state that has been formed via intersystem crossing from the singlet excited state.[11] The number of resolved vibronic transitions and their relative intensities vary for the different oligomers. This has been attributed to different levels of crystallinity in the oligomer films.[11] The PIA spectra increase sublinearly with pump intensity ($-\Delta T \sim I^\alpha$, $\alpha=0.55$–0.68) which demonstrates the contribution of a bimolecular process in the decay of the triplet photoexcited state in addition to a monomolecular relaxation process. By recording $\Delta T/T$ as function of the modulation frequency ω (Fig. 3), the relaxation of the triplet photoexcited state can be studied in more detail; we deduce the excitation lifetime from fitting the theoretical expressions for mono- and bimolecular decay to the experimental data. This analysis yields lifetimes on the order of 100 μs.[11] The partly bimolecular decay in the films and the reduced lifetime of the triplet state photoexcitation as compared to the lifetime under matrix isolated conditions in a
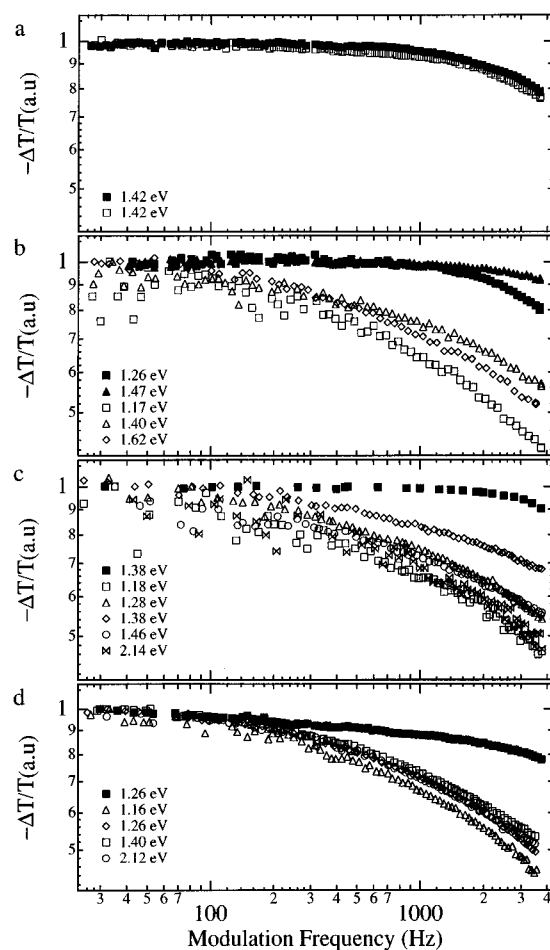
FIG. 3. Normalized frequency dependence of the PIA signals shown in Fig. 2 (peak positions are shown in the insets). Solid markers represent pristine T$_n$ films; open markers composite T$_n$/C$_{60}$ (75:25 mol %) films. (a) T$_6$, (b) T$_7$, (c) T$_9$, (d) T$_{11}$. The relaxation behavior was recorded at 80 K by pumping at 2.71 eV with 25 mW.

2-methyltetrahydrofurane glass at the same temperature, have been attributed to intermolecular interactions.[11]

Photoinduced absorption of mixed T$_n$/C$_{60}$ films

The PIA spectra of the mixed T$_n$/C$_{60}$ (75:25 mol %) films are also shown in Fig. 2 for direct comparison with the results of pristine T$_n$ films. Except for the T$_6$/C$_{60}$ mixed film, the PIA spectra of the T$_n$/C$_{60}$ composite films differ dramatically from those obtained for the pristine T$_n$ films.

As shown in Fig. 2(a), only minor changes occur for the PIA spectrum of T$_6$ after introduction of C$_{60}$ (T$_6$/C$_{60}$ 75:25 mol %); the PIA intensity reduces by a factor of approximately two and a small additional PIA band appears in the NIR region centered at 0.79 eV. This 0.79 eV band is assigned to the low-energy absorption of a T$_6^{+\bullet}$ radical cation (polaron) corresponding to a transition from the highest doubly occupied molecular orbital (HDOMO) to the singly occupied molecular orbital (SOMO). This assignment is in agreement with PIA results on (pristine) α-sexithienyl films.[18] The corresponding high-energy polaron band for T$_6^{+\bullet}$ is expected at about 1.54 eV,[18] but is apparently con-

cealed by the much stronger triplet PIA bands. The PIA bands at 1.42 eV of the T$_6$ and T$_6$/C$_{60}$ films show identical relaxation behavior [Fig. 3(a)], strongly suggesting that they represent the same photoexcited state. Although incorporation of C$_{60}$ into films of poly(3-alkylthiophene)s and poly(2,5-dialkoxy-1,4-phenylene vinylene)s is known to cause an effective quenching of the photoluminescence efficiency,[1,3] we do not observe such a strong effect for T$_6$/C$_{60}$ mixed films. From the PIA spectra and the persistence of the photoluminescence of T$_6$/C$_{60}$ we conclude that photo-induced electron transfer from T$_6$ to C$_{60}$ in composite T$_6$/C$_{60}$ films does not occur to the same extent as previously found for conjugated-polymer/C$_{60}$ films. The small T$_6^{+\bullet}$ PIA band at 0.79 eV indicates that some photoinduced electron transfer takes place, but the rate for this process does not compete efficiently with intersystem crossing and luminescence.

In case of T$_7$, introduction of C$_{60}$ (25 mol %) causes a complete quenching of the triplet PIA spectrum and reveals a number of new and well-resolved PIA features [Fig. 2(b)]. The maximum intensity ($-\Delta T/T$) of the spectrum increases slightly. The new PIA band at 1.17 eV corresponds to the absorption of the C$_{60}^{-\bullet}$ radical anion[19] and several of the remaining bands are attributed to the T$_7^{+\bullet}$ radical cation (polaron) resulting from a redistribution of energy levels analogous to the creation of states in the gap upon oxidation (*p*-doping) of conjugated polymers.[20] The molecular symmetry of T$_7$ (pseudo-C_{2v}), results in two dipole allowed electronic transitions among the frontier orbitals corresponding to HDOMO→SOMO and SOMO→LUMO (lowest unoccupied molecular orbital) excitations. These two excitations are readily attributed to the two most intense bands in the PIA spectrum at 0.67 and 1.40 eV, respectively. The additional peaks at 0.84 and 1.63 eV are assigned to vibrational replicas. This assignment is in agreement with recent results on the generation of T$_7^{+\bullet}$ radical cations in solution via electron transfer from the triplet photoexcited state to TCNE.[14] The principal absorption bands of T$_7^{+\bullet}$ in solution are found at 0.77 and 1.52 eV, with vibrational side bands at 0.94 and 1.72 eV. The observed ~0.1 eV redshift of the T$_7^{+\bullet}$ spectrum in the T$_7$/C$_{60}$ film at 80 K as compared to the solution spectrum obtained at ambient temperature is similar to the well-known thermochromic and solvatochromic effects on the linear absorption of poly(3-alkylthiophene)s.[21] The full width at half maximum of the T$_7^{+\bullet}$ PIA bands is remarkably small (<0.08 eV), likely to be caused by an increased quinoid character of the wave function, giving rise to a more rigid structure of the T$_7^{+\bullet}$ radical cation than of the neutral T$_7$ oligothiophene, and hence less inhomogeneous broadening of the absorption spectrum.

The spectral features assigned to the T$_7^{+\bullet}$ and C$_{60}^{-\bullet}$ radical ions increase with pump intensity with near square root behavior ($-\Delta T \sim I^{\alpha}$, $\alpha = 0.48$–0.52), characteristic of a bimolecular relaxation mechanism. The bimolecular decay suggests that the recombination of electrons and holes is the major relaxation pathway. The existence of a common decay mechanism for T$_7^{+\bullet}$ and C$_{60}^{-\bullet}$ is also supported by the uniform relaxation behavior of the 1.27, 1.40, and 1.63 eV lines [Fig. 3(b)]. When the ΔT vs ω data are fitted to the theoretical
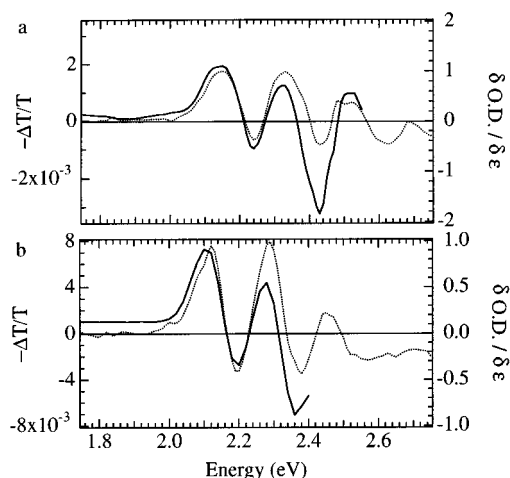

FIG. 4. PIA spectra (solid line, left axis) and first derivative of optical density (O.D.) (dashed line; right axis) at the π–π^* band edge region. (a) T$_9$, (b) T$_{11}$. PIA and linear absorption spectra were recorded on the same sample spot at 80 K.

expression for bimolecular decay,[22] we find a lifetime of about 0.8 ms.

All PIA results are consistent with the occurrence of a photoinduced electron transfer reaction from T$_7$ to C$_{60}$, producing T$_7^{+\bullet}$ and C$_{60}^{-\bullet}$ radical ions. Simultaneously, we observe a significant reduction of the photoluminescence intensity. The efficient quenching of both the luminescence and intersystem crossing (absence of the triplet T$_7$ PIA band) indicates that the photoinduced electron transfer reaction must occur promptly after excitation.

The PIA spectrum of a T$_9$/C$_{60}$ (75:25 mol %) composite film [Fig. 2(c)] reveals that the intensity of the strong triplet T$_9$ PIA band at 1.38 eV has decreased by an order of magnitude. At the same time, a number of new PIA bands and shoulders emerge at 1.18, 1.28, 2.14, and 2.33 eV. In addition, there is an onset of a new absorption at ~0.64 eV. The shoulder at 1.18 eV is assigned to C$_{60}^{-\bullet}$. The feature at 0.64 eV is most likely due to T$_9^{+\bullet}$; a vibronic transition of the low-energy HDOMO→SOMO excitation. The PIA bands at 1.28 and 1.46 eV exhibit approximately a square root pump intensity dependence ($-\Delta T \sim I^{0.54}$ and $-\Delta T \sim I^{0.59}$) and are assigned to the high-energy SOMO→LUMO transition of T$_9^{+\bullet}$ and its vibronic replica. In addition, the PIA spectrum of the mixed T$_9$/C$_{60}$ film shows a number of oscillatory features near the onset of the π–π^* transition of T$_9$ with peaks at 2.14 and 2.33 eV. The energy difference of 1.19 eV indicates a vibronic origin of the splitting between these transitions. These oscillations follow the first derivative of the absorption spectrum [Fig. 4(a)] but with a small redshift of approximately 0.01 eV. The negative offset of the PIA as compared to the first derivative of the absorption which appears at higher energies, is due to photobleaching of the π–π^* absorption arising from a transfer of oscillator strength to the intragap transitions associated with the triplet and charged photoexcitations. The PIA spectrum in this region is reminiscent of electroabsorption (EA) spectra of conjugated polymers. We attribute these bands to modulation of

the $\pi-\pi^*$ absorption band due to strong local electric fields resulting from photoinduced charged excitations in the film. Since these oscillations are absent in the spectrum of the pristine films and were found to increase steadily upon increasing the amount of C_{60} in the film, it is likely that these charges are associated with $T_9^{+\bullet}$ and $C_{60}^{-\bullet}$ radical ions. The absence of this band in the PIA spectrum of the pristine material and its steady increase with higher C_{60} concentrations argue against the alternative explanation that this band originates from the excitation of the ^1B_u exciton in the present case. We propose that the modulated space-charge field caused by photoinduced charges results in a PIA spectrum which exhibits EA, similar to EA phenomena caused by externally applied electrical fields. In general, EA spectra of conjugated materials are found to follow the first[23] or second[24] derivative of the linear absorption or combinations thereof.[25] A first-derivative behavior of the field modulated absorption signal is expected for a quadratic Stark effect of an excited state energy level[26] and is usually associated with more highly ordered materials. The quadratic Stark effect of the ^1B_u in this case is dominated by an increase in the localization length of the exciton which causes a redshift of the $\pi-\pi^*$ absorption and first-derivative behavior. A second-derivative like EA can arise from a broadening of the vibronic transitions.[25] It is noteworthy that in a recent PIA study of unsubstituted α-sexithienyl, similar EA phenomena have been observed which were, unlike in the present case, related to the second derivative of the absorption spectrum.[18] This result is in contradiction with the expectation that highly ordered materials such as small oligothiophenes usually exhibit first-derivative behavior. For poly(3-octylthiophene) on the other hand, the EA spectrum closely matches the first derivative of the absorption.[27]

The relaxation behavior of all bands in the T_9/C_{60} PIA spectrum [Fig. 3(c)] is basically identical and analogous to the behavior observed in T_7/C_{60} films, except for the residual 1.38 eV triplet band which deviates somewhat. Although the PIA spectrum of the T_9/C_{60} mixture still exhibits the triplet T_9 PIA band at 1.38 eV as a prominent feature, it is clear that the spectrum has changed considerably as compared to the PIA spectrum of the pristine T_9 film, and all new features are consistent with a photoinduced electron transfer reaction from T_9 to C_{60}. Another demonstration of the dramatic changes due to C_{60} is the quenching of the photoluminescence which is reduced to approximately 5% and slightly blueshifted with respect to the pristine T_9 film.

The PIA spectrum of a T_{11}/C_{60} (75:25 mol %) mixed film differs from the PIA spectrum of a pristine T_{11} film [Fig. 2(d)]. The changes are similar to those observed between T_9/C_{60} and T_9; the PIA spectrum of T_{11}/C_{60} shows a considerable decrease of the triplet T_{11} PIA band at 1.26 eV and new absorptions appear in the NIR region and near the $\pi-\pi^*$ band edge at 2.11 and 2.28 eV. In addition, a small shoulder at 1.18 eV suggests the presence of $C_{60}^{-\bullet}$. The oscillating PIA features at the band edge agree fairly well with the first derivative of the absorption spectrum [Fig. 4(b)] although they appear slightly redshifted by 0.01–0.02 eV and exhibit a negative offset at higher energies due to photobleaching of the $\pi-\pi^*$ absorption. Following our assignment of the cor-

responding bands observed in the T_9/C_{60} film, we attribute these bands to the modulation of the $\pi-\pi^*$ band edge due to the presence of $T_{11}^{+\bullet}$ and $C_{60}^{-\bullet}$ as charged sites causing local electric fields in the sample.

The relaxation behavior of the T_{11}/C_{60} PIA spectrum clearly indicates a different decay mechanism as compared to that in pristine T_{11} [Fig. 3(d)]. Analogous to the T_7/C_{60} and T_9/C_{60} composite films, we also observe a quenching of the photoluminescence for the mixed T_{11}/C_{60} films and conclude that the results for T_{11}/C_{60} are consistent with the occurrence of a photoinduced electron transfer reaction.

We conclude that the PIA spectrum for composite films of T_7, T_9, and T_{11} with C_{60} reveal characteristic features associated with the formation of $T_n^{+\bullet}$ radical cations and $C_{60}^{-\bullet}$ radical anions and that photoluminescence and intersystem crossing to the triplet states as observed in the pristine materials are quenched to a large extent. We note that the prominent EA bands attributed to photoinduced charges in the films of T_9/C_{60} or T_{11}/C_{60} are not observed in the T_7/C_{60} composite film, despite the fact that the absorptions due to $T_7^{+\bullet}$ and $C_{60}^{-\bullet}$ are clearly present in the PIA spectrum. The origin of this difference is not completely clear, but might be associated with the fact that EA is a third-order nonlinear process and hence increases strongly with increasing conjugation length. The fact that the EA band in T_{11}/C_{60} is three to four times more intense than in T_9/C_{60} is consistent with this explanation. On the other hand, significant differences in $\Delta T/T$ intensity of the triplet states are also observed in the films of the pristine oligomers, which makes direct comparison of intensities less straightforward.

Light-induced electron spin resonance

LESR spectra of mixed T_n/C_{60} (75:25 mol %) films recorded at 25 K while irradiating at 488 nm are shown in Fig. 5. Consistent with the PIA spectra, we observe a significant difference between the T_6/C_{60} films on one hand and the $T_7, T_9, T_{11}/C_{60}$ films on the other hand. For the latter three mixed films two different transitions are present, one at $g=1.9994(2)$ and one at $g=2.0021(2)$. The $g=1.9994$ signal corresponds to $C_{60}^{-\bullet}$,[28] while the signal at $g=2.0021$ can be attributed to the $T_n^{+\bullet}$ radical cations. In addition to these clear $C_{60}^{-\bullet}$ and $T_n^{+\bullet}$ features a third absorption at higher field can be distinguished. This signal does not readily saturate with increasing microwave power, in contrast to the $T_n^{+\bullet}$ and $C_{60}^{-\bullet}$ signals. The nature of this absorption, however, is at present unknown. In contrast to the other oligomers, we observe a relatively weak signal at $g=1.9994$ ($C_{60}^{-\bullet}$) for the T_6/C_{60} mixture, which is not accompanied by a $T_6^{+\bullet}$ absorption.

LESR spectra of pristine T_n films also reveal weak signals due to $T_n^{+\bullet}$ radical cations, except for T_6 where no LESR can be detected. The LESR intensities of the pristine films are, however, at least ten times less than those of the composite films and demonstrate that the generation of $T_n^{+\bullet}$ is much more efficient in the presence of C_{60}.

The LESR results are consistent with our conclusion from the PIA studies that photoinduced electron transfer in T_n/C_{60} films occurs for $n=7$, 9, and 11, but is absent or at least not very efficient for T_6/C_{60}. Such consistency is not
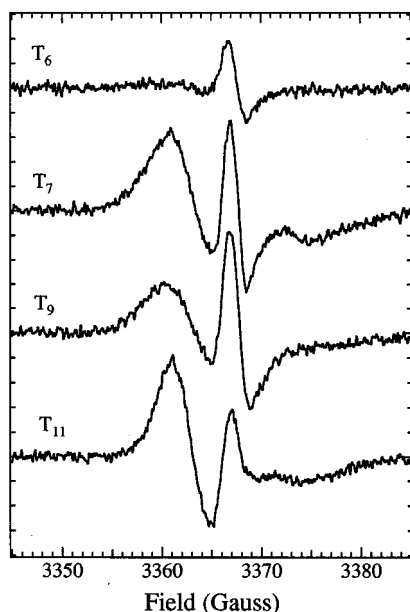
FIG. 5. LESR spectra of T$_n$/C$_{60}$ composite films ($n=6, 7, 9, 11$). Spectra (25 cumulative scans) were recorded at 25 K, while continuously irradiating the sample at 488 nm with 150 mW through a 50% transmission grid and corrected for dark signal. Microwave power was 10 μW.

necessarily to be expected because the LESR experiments probe the steady-state concentration of (long-lived) radicals formed upon continuous photoexcitation and thus probe a different time regime than our PIA experiment which detects species with lifetimes in the microsecond and millisecond domains. Although we cannot unambiguously exclude the possibility of a rapid forward and rapid back electron transfer in T$_6$/C$_{60}$ composites, both the absence of luminescence quenching as well as the absence of triplet quenching argue against this mechanism.

Photoinduced absorption of mixed T$_6$/[6.6]PCBCa films

Both PIA and LESR studies clearly indicate that photo-induced electron transfer from T$_6$ to C$_{60}$ in a mixed film does not take place to the same extent as for T$_7$, T$_9$, or T$_{11}$ under similar conditions. The question arises whether this is due to the reduced conjugation length of T$_6$, since the extended conjugation of the longer oligomers is expected to increase the stabilization of the corresponding radical cations (polarons). On the other hand, the $\pi-\pi^*$ band gap is larger for T$_6$, which results in a higher energy of the first excited singlet state, which is beneficial for transferring an electron to C$_{60}$ after excitation. Moreover, it has been shown that T$_6^{+\bullet}$ radical cations can readily be photogenerated in solution via electron transfer from the triplet photoexcited state to TCNE or from the singlet excited state to a suitable solvent molecule.[13,14] The absence of photoinduced electron transfer in the T$_6$/C$_{60}$ films may then be due to another effect than the somewhat different energies of T$_6$ as compared to T$_7$, T$_9$, or T$_{11}$. One explanation might be the absence of intimate molecular mixing of the two components T$_6$ and C$_{60}$ as a result
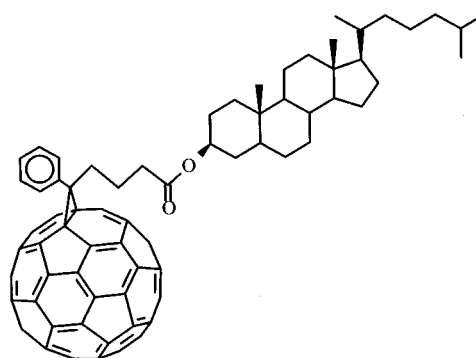

FIG. 6. Molecular structure of [6.6]PCBCa.

of phase segregation due to the tendency of T$_6$ and C$_{60}$ to crystallize in separate domains. In this respect it is important to note that x-ray studies have shown that films of pristine T$_6$ are more crystalline than films of the longer oligomers.[10]

We have recently shown that certain methanofullerene (C$_{61}$R$_1$R$_2$) derivatives (with a cyclopropane ring across a 6,6 ring junction) and 58 instead of 60π electrons are equally suited as C$_{60}$ to act as an electron acceptor in photoinduced electron transfer reactions with conjugated polymers.[29] The advantage of these methanofullerenes, however, is the fact that their solubility and miscibility with conjugated polymers and oligomers can be enhanced via chemical modification of the substituents on the bridgehead carbon. A particularly efficient compound in this respect is [6.6]PCBCa (Fig. 6).

Figure 7 shows the PIA spectrum of a T$_6$/[6.6]PCBCa (75:25 mol %) composite film at 80 K. The PIA spectrum has changed dramatically as compared to the spectra of T$_6$ and T$_6$/C$_{60}$ [Fig. 2(a)]. The T$_6$ triplet band at 1.42 eV is completely quenched and new bands appear at 0.79 and 1.53 eV, in full agreement with the expected positions for the T$_6^{+\bullet}$ radical cation (polaron)[18] and shoulders at 1.00 and 1.73 eV are assigned to vibronic overtones of these polaron bands. The small feature at 1.20 eV is most likely due to [6.6]PCBCa$^{-\bullet}$. We do not observe EA bands in the T$_6$/[6.6]PCBCa composite films. The relaxation behavior (Fig. 8) of the PIA bands at 1.20, 1.53, and 1.72 eV is almost identical but clearly different from the 1.42 eV band in the
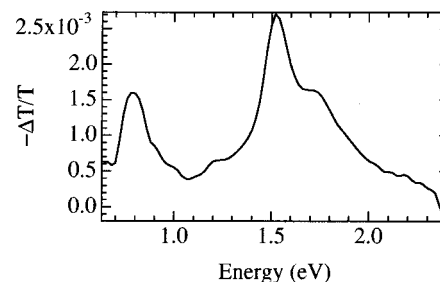

FIG. 7. PIA spectrum of a T$_6$/[6.6]PCBCa (75:25 mol %) mixed film, recorded at 80 K by pumping at 2.71 eV with 25 mW and modulation frequency of 275 Hz.
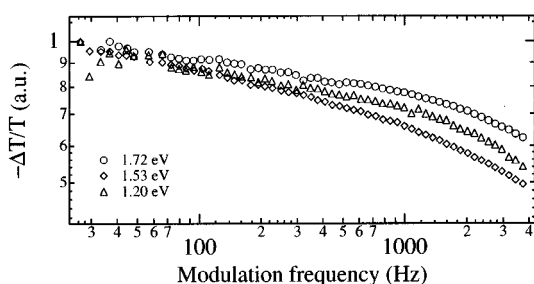
FIG. 8. Normalized frequency dependence of the PIA signals shown in Fig. 7 on the modulation frequency for T$_6$/[6.6]PCBCa mixed films (peak positions are shown in the inset). The relaxation behavior was recorded at 80 K by pumping at 2.71 eV with 25 mW.

pristine T$_6$ film. From this PIA spectrum and the bimolecular characteristics of the relaxation, we conclude that in contrast to a T$_6$/C$_{60}$ composite film, photoinduced electron transfer does occur efficiently in T$_6$/[6.6]PCBCa films giving rise to metastable T$_6^{+\bullet}$ and [6.6]PCBCa$^{-\bullet}$ radical ions.

CONCLUSION

We have shown that incorporation of C$_{60}$ or a C$_{61}$-methanofullerene in films of alkyl substituted oligothiophenes changes the photophysical properties dramatically. The typical decay process observed upon photoexcitation of the pristine oligomers such as intersystem crossing to a metastable triplet state and photoluminescence to the ground state is effectively quenched in the presence of these electron acceptors. Instead, a photoinduced electron transfer reaction from the oligothiophene to the electron acceptor occurs, as evidenced from PIA and LESR spectra of the corresponding radical ions. The fact that photoluminescence is quenched to a large extent indicates a singlet photoexcited state as the origin of the transferred electron and that the electron transfer is extremely fast. The contrasting results of T$_6$/C$_{60}$ and T$_6$/[6.6]PCBCa films demonstrate that dispersion of the acceptor in the oligomer film on a molecular level is required for this process to occur efficiently.

We do not observe a consistent chain length effect on the photoinduced electron transfer of the oligothiophenes; this process occurs for the shortest (T$_6$) as well as for the longest (T$_{11}$) oligomers, but some differences can be noted. In the T$_6$/[6.6]PCBCa and T$_7$/C$_{60}$ PIA spectra we observe clear bands in the NIR and the VIS regions that are associated with the T$_n^{+\bullet}$ radical cations, whereas there is no clear evidence for EA-like phenomena near the $\pi-\pi^*$ band edge. For the longer two oligomers, on the other hand, the oscillations in the PIA spectra associated with EA are prominent, whereas the T$_n^{+\bullet}$ radical cation PIA bands are less intense. Considering the fact that significant differences exist in the PIA intensities of the triplet bands of the four pristine oligomers (Fig. 2), it is difficult to speculate on the reasons for the differences in the relative intensities of the radical cation and EA bands in the composite films. The appearance of the prominent EA bands in the longer oligomers is, however, consistent with the fact that EA is a third-order nonlinear process. Since $\chi^{(3)}$ is known from experiment and theory to depend strongly on the localization length of the eigenstates,[30] EA is expected to be stronger for oligomers with longer conjugation lengths, consistent with its more prominent appearance in T$_9$/C$_{60}$ and T$_{11}$/C$_{60}$.

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