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Triplet-state photoexcitations of oligothiophene films and solutions

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We present studies of steady-state photoinduced absorption (PIA) spectroscopy on photoexcitations in a series of well-defined α -oligothiophene (T_n , $n=6, 7, 9$, and 11) films and solutions. The PIA spectra and the excited state lifetimes are consistent with the signatures of a photoexcited triplet state. The PIA spectra consist of a strong vibronically resolved subgap absorption, which is readily observed in solid-state films and in solutions at ambient and cryogenic temperatures. The transition energy is linearly dependent on the reciprocal chain length and shifts to lower energy for longer oligomers. Variation of the modulation frequency and the pump intensity under matrix-isolated conditions reveals that the photoexcitation is created via an intrachain mechanism and decays nonradiatively with monomolecular kinetics. In solid films we find a significant contribution of a bimolecular decay process to the relaxation rate.

I. INTRODUCTION

Conjugated polymers attract considerable attention because of their interesting molecular and physical properties and their potential application as new materials for electronic and optical technology.¹⁻³ The electronic and optical properties of π -conjugated polymers are associated with nonlinear soliton, polaron, and bipolaron excitations.^{4,5} Such excitations result from the coupling of the quasi-one-dimensional π -electron system to the structure of the polymer backbone via the electron-phonon interaction. This coupling causes structural relaxation which results in a self-localization of the electronic excitations around the local structural distortions; giving rise to electronic states within the gap.

Nonlinear excitations can be generated either by injecting charges into the system through (electro) chemical doping or by optical excitation. Direct optical pumping results in the formation of transient and metastable excitations which can be studied spectroscopically. Photoinduced absorption (PIA) spectroscopy has been successfully applied to characterize the gap states of the nonlinear excitations and the associated structural relaxation in the bond alternation pattern for various conjugated polymers.¹⁻⁵

In this study we focus on steady-state PIA studies of four well-defined substituted α -oligothiophenes, with, respectively, 6, 7, 9, and 11 thiophene units (Fig. 1). These medium-sized oligomers are among the largest well-defined oligothiophenes synthesized and have been studied in relation with their linear absorption, conductivity, and their third-order nonlinear optical susceptibilities.⁶⁻⁸ The oligothiophenes carry a number of dodecyl side chains that ensure solubility. Their limited number, however, and their nonadjacent positions on the oligomer chain decrease steric hindrance and minimize conformational disorder.

The general picture that emerges from previous PIA experiments on conjugated polymers suggests that intrachain excitation above the energy gap initially produces a neutral nonlinear excitation, a singlet-polaron exciton (which is also

referred to as neutral bipolaron), in an intrachain mechanism. Models of interband and excitonic excitation have been invoked to describe the phenomena following the initial absorption of light in conjugated polymers. In the interband model, excitation provides weakly correlated electron-hole pairs along the chain, whereas in an exciton, the electron-hole pair is bound and strongly correlated. In either case, recombination of electron and holes can result in radiative decay (photoluminescence). Photogeneration of long-lived (trapped) charged excitations requires an interchain mechanism to prevent geminate recombination of electrons and holes. Alternatively, the primary excitation can decay via intersystem crossing to form a neutral intrachain metastable triplet-state excitation.

Polythiophene (PT) and poly(3-alkylthiophene) derivatives (P3AT) have been studied extensively during the past decade.⁹⁻¹³ Photoexcitation of PT or P3AT with alkyl chains incorporating up to ten carbon atoms results in the formation of long-lived charged photoexcitations, exhibiting two subgap electronic absorptions and a series of infrared active vibrational (IRAV) modes. These excitations have been attributed to bipolarons formed by coalescence of two polarons. In contrast, for poly(3-dodecylthiophene) a single subgap absorption band has been reported and tentatively assigned to an intrachain triplet exciton.¹¹ The latter result has been explained in terms of a poor contact between the π -conjugated backbone of the polymers due to the long alkyl chains, that prevents interchain charge separation. On the other hand, PIA studies for poly(*p*-phenylene vinylene), PPV, and various dialkoxy PPV derivatives, reveal the formation of triplet excitons in addition to doubly charged bipolarons.¹⁴⁻²⁰ The signature of the triplet excitons is characterized by a single subgap dipole-allowed triplet-triplet ($T_1 \rightarrow T_2$) absorption and the absence of IRAV modes.

Recently, it has been reported that in pure and highly ordered conjugated polymers the formation of long-lived charged photoexcitations is reduced in favor of neutral metastable triplet excitons. For carefully purified and fractionated poly(3-octylthiophene), the PIA spectrum is considerably different from the PIA spectrum reported earlier, and exhibits a band, among others, at 1.05 eV attributed to a triplet

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FIG. 1. Molecular structure of T_{11} α -oligothiophene [$T_{11}d(2,6,10)$].

exciton.²¹ A similar shift in steady-state PIA states from trapped charged photoexcitations to metastable triplet excitons has been observed in MEH-PPV when going from a disordered film to an oriented blend and in PPV by using an improved synthesis technique yielding a highly ordered material.^{22–25} These differences have been attributed to the lower defect level and increased order, reducing the stabilization of trapped charged excitations and to decreased inter-chain interactions.

Because of their uniform degree of polymerization and their well-defined chemical structure, oligomers are instrumental to access properties of π -conjugated systems that critically depend on the conjugation length. In addition, several of the basic features of conjugated materials can be explained by the molecular characteristics of small subunits. Optical spectra and PIA studies of phenylene vinylene oligomers have been reported recently and reveal the sole formation of triplet excited states, in accordance with highly ordered phenylene vinylene polymers.²⁶

Oligothiophenes have been studied extensively in recent years. High-resolution fluorescence and fluorescence excitation spectra have been reported for T_n ($n=2–4$) α -coupled oligothiophenes.^{27–29} A large number of studies has concentrated on the redox states of the oligothiophenes with a particular focus on the optical properties of cations, cation dimers, and dications in solution.^{30–38} In general, an inverse correlation is established between the transition energies of subgap absorptions and the chain length. Only few studies have addressed the characterization of photoinduced excitations. Using time-resolved fluorescence and pump-and-probe transient spectroscopy in the femto- and picosecond time domain, the early time evolution of excitations in small oligothiophenes (T_n , $n=2–6$) in solution has been studied.^{39–42} The picosecond transient photoinduced absorption, ranging from 2.49 eV for T_2 to 1.36 eV for T_6 , has been attributed to the lowest excited singlet-state absorption. Triplet states, on the other hand, have been characterized for terthiophene and tetrathiophene in solution in relation to their photobiological effects.⁴³

In this paper we present the linear absorption, luminescence, and photoinduced absorption of a series of medium-sized oligothiophenes in solution (at ambient and cryogenic temperatures) as well as in solid films. Strong PIA spectra exhibiting a single vibronically resolved transition are observed and their frequency and intensity dependence are determined. We demonstrate that the PIA bands are associated with the $T_1 \rightarrow T_2$ absorption of a metastable triplet-state photoexcitation. Having a series of well-defined oligomers, we explore the effect of increasing conjugation length on the

linear and nonlinear optical properties. The energy of the PIA band decreases linearly with the inverse number of thiophene units. We find that under matrix-isolated (single chain) conditions the photoexcitation decays with monomolecular kinetics. However, in solid films or when chains aggregate, we observe the signatures of bimolecular decay. Long-lived charged excitations are detected in specific solvents at ambient temperature, but are absent in solid films.

II. EXPERIMENT

The oligothiophenes used in the present study carry a number of dodecyl substituents on different thiophene rings and are designated as $T_6d(2,5)$; $T_7d(4)$, $T_9d(2,5,8)$, and $T_{11}d(2,6,10)$ (Fig. 1). The synthesis of the oligothiophenes has been described previously.^{6,7} Dry deoxygenated solvents were used to study the oligomers in solution. Solution samples were prepared under oxygen-free argon atmosphere and placed in sealed cuvettes. Cuvette path lengths were 1 mm for ambient and 3 mm for cryogenic temperature experiments. Unless stated otherwise, concentrations were 10^{-4} M in dichloromethane (CH_2Cl_2) for experiments at 295 K. For experiments on frozen solutions 2-methyltetrahydrofuran (2MeTHF) has been used, since it forms a clear transparent glass at 80 K. To suppress chain aggregation at 80 K, the concentration of the oligothiophenes is on the order of 10^{-5} – 10^{-6} M in 2MeTHF. The cuvette containing the glassy 2MeTHF matrix is cooled by placing it in a transparent double walled Dewar vessel filled with liquid nitrogen.

Oligothiophene films were freshly prepared by dip coating (T_6, T_9) or drop casting (T_7, T_{11}) from chloroform solutions on sapphire substrates. The sapphire substrates are mounted on the cold finger of a cryostat held at 80 K under a dynamical vacuum on the order of 10^{-5} Torr.

Absorption spectra are obtained with a Perkin Elmer Lambda 9 spectrophotometer. The transmission spectra for PIA experiments are recorded from 2.5 to 0.65 eV using a tungsten-halogen white light source (probe), a grating monochromator, and Si (VIS region) or PbS (NIR region) detectors; for a direct transmission (T), the probe beam is mechanically chopped and the signal is detected using a lock-in amplifier. Photoexcitation is provided by the 457.9 nm (2.71 eV) line of a cw argon-ion laser (pump). The pump power incident on the sample is in the range of 5 to 120 mW at a pump diameter of 2 mm. The photoinduced change in transmission (ΔT) of the sample is measured by chopping the pump beam and the resulting modulation of the probe beam transmission is detected using a phase-sensitive lock-in amplifier, referenced to the chopping frequency. The

FIG. 2. (a) Normalized absorption spectra of oligothiophenes in CH_2Cl_2 solution (10^{-4} M T_6 , T_7 , and T_9 ; 3×10^{-5} M T_{11}) at room temperature. (b) Normalized absorption spectra of oligothiophene films at 80 K. Spectra are offset for clarity of presentation.

pump beam is modulated between 20 and 4000 Hz. The photoinduced absorption $-\Delta T/T \approx \Delta \alpha d$ is directly calculated from the normalized changes in transmission. In order to avoid contamination of the PIA signal by luminescence, the light emission of the sample is recorded in a separate experiment. Luminescence and photoinduced absorption

spectra are obtained with the pump beam in an almost anti-parallel direction to the probe beam.

III. RESULTS AND DISCUSSION

A. Optical absorption

The electronic absorption spectra of the oligothiophenes in CH_2Cl_2 solution at 295 K exhibit a well-defined $\pi-\pi^*$ absorption band [Fig. 2(a)] corresponding to a $S_0 \rightarrow S_1$ transition. The $\pi-\pi^*$ absorption band does not show any resolvable vibronic fine structure. The absorption maximum is shifted to lower energies for the longer oligomers and its energy is inversely proportional to n , the number of thiophene units [Fig. 3(a)].

The absorption spectra of the solution cast films at 80 K reveal three distinct vibronic peaks separated by 0.16–0.18 eV and an additional shoulder at higher energy [Fig. 2(b)]. The energy separation indicates strong coupling of the $\text{C}=\text{C}$ stretch mode to the electronic structure. The 0–0 transition is less intense than the 0–1, 0–2, and 0–3 transitions. Each vibronic peak shifts linearly with $1/n$ to lower energy for the longer oligomers. The absorption edge of the oligothiophene films is shifted by 0.05 eV on decreasing the temperature to 80 K as compared to the spectra at ambient temperature, and the vibrational structure appears more clearly as result of line narrowing.

Figure 3(a) depicts the absorption maxima observed in CH_2Cl_2 solution (295 K) as well as the energies of the first three vibronic transitions of the oligothiophene films (80 K) vs the reciprocal number of thiophene units in the oligomer.

FIG. 3. Transition energies of the linear optical absorption of oligothiophenes in film at 80 K (solid markers), CH_2Cl_2 solution at 295 K (asterisks), and 2MeTHF glass at 80 K (open markers) vs $1/n$, where n is the number of thiophene units. (a) Linear absorption; (b) luminescence; (c) photoinduced absorption. All positively identified vibronic transitions of the spectra are included in the graph.

Poly(3-alkylthiophene) solutions exhibit thermochromism and solvatochromism,^{44–48} at lower temperatures, or by adding a nonsolvent, a transformation to a more ordered (planar) structure is induced with a concurrent aggregation of the chains, resulting in a substantial red shift of the π - π^* absorption band. The distinct red shift of the onset of the band edge observed for the oligothiophene films relative to the solution spectra [Fig. 3(a)], suggests that such effects also occur in oligomers. In preparing frozen solutions, dilute solutions on the order of 10^{-5} to 10^{-6} M were used in order to suppress aggregation of chains. The absorption spectra of these dilute oligomer solid solutions in a 2MeTHF glass at 80 K (prepared by rapid cooling in liquid nitrogen) are red shifted by 0.22–0.28 eV with respect to the room-temperature spectra. This red shift indicates a longer conjugation length at lower temperatures. We interpret this result in terms of a more planar molecular conformation which results in increased π conjugation.^{44–48} The π - π^* absorption band, however, remains solution-like, i.e., without any resolvable vibronic structure. However, for more concentrated solutions in 2MeTHF, the electronic absorption at 80 K is virtually identical to that of the corresponding film, exhibiting an additional 0.16 eV shift of the band edge to lower energy and well resolved vibrational structure.

These results suggest that in dilute 2MeTHF glassy solutions the oligomers are present in a more planar molecular conformation but that microcrystallization has not yet taken place. At the employed concentrations of 10^{-5} – 10^{-6} M the average intermolecular distance is on the order of several hundreds of angstroms and, hence, we can describe the dilute frozen solutions as matrix-isolated oligothiophene chains.

B. Photoluminescence

Photoluminescence spectra of oligothiophenes in CH_2Cl_2 solution at 295 K are shown in Fig. 4(a) together with the spectra of samples in 2MeTHF at 80 K. In both cases excitation was provided by the 457.9 nm line of an argon-ion laser. Two to three vibronic emissions are observed in CH_2Cl_2 solution at room temperature with an average energy spacing of 0.14–0.17 eV, similar to the separation of the vibronic absorptions of the solution cast films. The presence of vibrational structure indicates a strong electron-phonon coupling. In an earlier study, it was shown that the photoluminescence spectrum of these oligothiophenes is invariant to the excitation wavelength as long as it lies within the π - π^* absorption band.⁷ The luminescence is assigned to an emission from the lowest vibrational level of the first excited singlet state to the vibrational manifold of the ground state ($S_1 \rightarrow S_0$). The energy difference of the highest energy emission (0–0 phonon transition) of the oligothiophenes in CH_2Cl_2 solution and the π - π^* absorption maximum amounts to 0.47–0.52 eV.

The structureless absorption and the vibrationally resolved luminescence suggest that the excited-state geometry is more ordered than the ground-state conformation. The rotational energy barrier of the interring band is smaller in the ground state and contributes to the molecular disorder at 295 K, giving rise to inhomogeneous broadening and hence a structureless absorption. The vibrationally resolved lumines-

FIG. 4. (a) Normalized photoluminescence spectra of oligothiophenes in CH_2Cl_2 solution at 295 K (dashed line) and in a 2MeTHF glass at 80 K (solid line). Concentrations are 10^{-4} M T_6 , T_7 , and T_9 in CH_2Cl_2 ; 3×10^{-5} M T_{11} in CH_2Cl_2 ; 10^{-5} M T_6 , T_7 , and T_9 in 2MeTHF; 10^{-6} M T_{11} in 2MeTHF. (b) Normalized photoluminescence spectra of T_n oligothiophene films at 80 K (solid lines) and for T_{11} in a 2MeTHF glass at 10^{-5} M (dashed line). Excitation was provided by a 457.9 nm (2.71 eV) line of an argon-ion laser. Spectra are offset for clarity of presentation.

cence, on the other hand, indicates a narrow distribution of excited-state molecular geometries, characterized by a more rigid planar conformation of the thiophene rings, due to the increased contribution of a quinoid canonical electronic structure to the singlet excited-state configuration.

The photoluminescence spectra of the oligothiophenes in dilute 2MeTHF glassy solutions exhibit an even more pronounced vibrational structure due to line narrowing at low temperature; four distinct peaks or shoulders can be seen [Fig. 4(a)]. There is, however, virtually no shift in energy of the emission spectra for T_6 , T_7 , and T_9 as compared to the spectra recorded in CH_2Cl_2 at 295 K. This indicates that the excited-state geometry from which the emission occurs is similar at both temperatures. In contrast, T_{11} exhibits an energy shift, probably as a result of an onset of aggregation in the frozen solution which will be discussed in more detail in conjunction with the PIA spectrum.

The fact that the fluorescence at 80 and 295 K are energetically almost identical contrasts with the 0.22–0.28 eV energy shift of the absorption spectra at these temperatures. Apparently, ground-state and excited-state geometries are much more alike at 80 K than at 295 K. This result is consistent with a more planar ground-state geometry at low temperatures. The more defined vibrational structure of the luminescence as compared to that of the absorption, originates from conformational relaxation of the excited state to a more rigid molecular structure prior to the radiative decay. Our data are consistent with a reduction of the interring torsional angle as the major change in geometry of the excited state. An alternative explanation for the similarity of the luminescence spectra in CH_2Cl_2 at 295 K and in 2MeTHF at 80 K is the occurrence of spectral diffusion.⁴⁹ Spectral diffusion implies the migration of a singlet exciton along a conjugated polymer chain to a geometry of minimum energy (longest conjugation length), from which emission occurs. Since absorption is fast on the time scale of vibrational motion, it is insensitive to the molecular geometry and will occur for a wide distribution of conformations. These two processes explain the observation that identical luminescence spectra can be obtained from photoexcitation of two samples with different absorption spectra. However, for the medium-sized oligomers, spectral diffusion seems less likely due to the confinement of the singlet excitation onto the short oligomer chain.

The luminescence of the films at 80 K [Fig. 4(b)] is red-shifted by about 0.20 eV as compared to the solution spectra. The oligomer films show a shoulder at the 0–0 phonon transition, except for T_{11} where a distinct 0–0 emission peak is observed. The average vibrational frequency observed in the emission spectra of the films at 80 K is 0.145 eV, and less than the average of 0.174 eV observed for the absorption. This result agrees with recent observations for MEH-PPV⁵⁰ and highly ordered PPV.⁴⁹ The reduction of the spacing of the vibronic transitions in emission relative to absorption indicates a shallower potential energy surface at the ground state as compared to that at the first excited state, consistent with the more rigid geometry of the first excited singlet state suggested above.

Finally, in Fig. 3(b) we depict the energies of the various vibronic emissions as a function of the reciprocal chain length ($1/n$). As can be seen all lines shift to lower energy for longer conjugation lengths, although the decrease is less than expected from a linear relation with $1/n$.

C. Photoinduced absorption in solution

PIA spectra of conjugated polymers in solution have first been detected for poly(3-hexylthiophene) in dichloromethane.^{51,52} The PIA spectrum of poly(3-hexylthiophene) displays two equally intense spectral features at about 0.6 and 1.5 eV which were attributed to bipolarons. The assignment was based on the close similarity of the PIA spectra of poly(3-hexylthiophene) in solution and in solid-state films at cryogenic temperature.¹⁰ However, more recent studies seem to indicate that both the intensity and the number of transitions in the PIA spectrum of poly(3-alkylthiophene) in solution depend on the nature of the solvent. Poly(3-decylthiophene) in chloroform solution exhibits two bands at 0.55 and 1.55 eV,^{12,13,53} whereas in benzonitrile, a nonsolvent for poly(3-alkylthiophene), an additional band at 1.75 eV has been reported and attributed to long-lived trapped photoexcitations confined to aggregated chains. Interestingly, however, PIA activity was only observed in a few solvents such as chloroform and benzonitrile, but not in benzene or toluene. To account for the solvent-dependent formation of charged photoexcitations a mechanism of photoinduced doping in which the solvent is actively involved has been invoked. This mechanism is referred to as weak solvent–polymer charge transfer.^{13,53}

It has been shown that small oligothiophenes, e.g., terthiophene, are capable of generating reactive singlet oxygen upon photoexcitation.^{54–57} In order to avoid effects of oxygen we used carefully deoxygenated solvents for measuring the photoinduced absorption of the oligothiophene solutions.

Figure 5(a) shows the PIA spectra of the oligomers in CH_2Cl_2 solution. The spectra reveal strong PIA signals with $\Delta T/T$ on the order of 10^{-2} . The most prominent band in the PIA spectra shifts gradually to lower energy for the longer oligomers, ranging from 1.80 eV for T_6 to 1.54 eV for T_{11} [Fig. 3(c)]. The PIA bands exhibit partially resolved shoulders on the high-energy side. Their separation of 0.18 eV indicates a vibronic origin. In addition, weak, but distinct, photoinduced absorptions are found in the low-energy region. For T_6 and T_7 , clear shoulders are present on the low-energy edge of the principal PIA band. Additionally, CH_2Cl_2 solutions of T_7 and T_{11} display weak PIA bands in the NIR domain. We have obtained almost identical PIA spectra in a variety of oxygen-free organic solvents. Figure 5(b) shows the PIA spectra of T_6 obtained in *p*-xylene, 2MeTHF, CH_2Cl_2 , and 1,2-dichlorobenzene (ODCB) solutions. The transition energy of the principal PIA band is slightly dependent on the nature of the solvent; shifts are on the order of 0.05 eV, similar to the solvent effect of the linear π – π^* absorption. Noticeable, however, is the increased relative intensity of the weaker absorptions for an ODCB solution. This is evident from Fig. 5(b) for T_6 ; while similar results were observed for the other oligothiophenes as well. Compared to CH_2Cl_2 , an ODCB solution of T_6 shows a new well-defined signal at 0.82 eV and an increased intensity of the shoulder on the low-energy side of the principal PIA band at 1.55 eV (in ODCB).

The importance of rigorously excluding oxygen from the sample solutions is demonstrated by the fact that the strong PIA bands are completely quenched after exposing the solu-

FIG. 5. (a) Normalized PIA spectra of oligothiophenes in CH_2Cl_2 solutions. Concentrations are 10^{-4} M T_6 , T_7 , and T_9 ; 3×10^{-5} M T_{11} . (b) Normalized PIA spectra of 10^{-4} M solutions of T_6 in *p*-xylene, 2MeTHF, CH_2Cl_2 , and ODCB at 295 K. Spectra were recorded by pumping with an argon-ion laser at 2.71 eV with 75 mW and a modulation frequency of 23 Hz. Spectra are offset for clarity of presentation.

tion to air. The weak absorptions observed in CH_2Cl_2 , on the other hand, remain essentially unaffected. Since photoexcitation in the presence of oxygen also results in a considerable degradation of the oligomers, no detailed study has been made of the oxygen quenching mechanism.

We attribute the principal PIA bands shown in Fig. 5 to a metastable triplet excited state (T_1) exhibiting a dipole-allowed $T_1 \rightarrow T_2$ absorption. The fact that a single, vibronically coupled, PIA band is found below the $\pi-\pi^*$ transition, eliminates in our view the possibility that singly charged (polaron) or doubly charged (bipolaron) cations are responsible for this PIA band, since for a cation radical at least two intragap absorptions are expected. Photoexcited triplet states of small oligothiophenes have been studied in relation to the photobiological effects of these compounds.⁴³ The transient triplet absorption spectra of α -terthiophene (T_3) and α -tetrathiophene (T_4) have been observed at 2.70 and 2.21 eV, respectively.⁴³ Linear extrapolation of the data shown in Fig. 3(c), to $n=3$ and $n=4$, yields PIA energies for T_3 at 2.4 eV and T_4 at 2.1 eV.

The fact that introduction of oxygen effectively quenches the PIA band of oligothiophenes in CH_2Cl_2 gives additional support that it originates from a triplet-state excitation. A number of studies have shown that the radical cation of α -terthiophene ($T_3^{\cdot+}$) is not affected by molecular oxygen, in contrast to its triplet excited state, 3T_3 , which is readily quenched by oxygen.⁵⁴⁻⁵⁷

The weaker PIA features, most clearly observed in ODCB, are attributed to the monoradical cations (polarons) of the oligothiophenes, formed in a photo-oxidation reaction. The evidence for this assignment is based on oxidation experiments of nonalkylated small oligothiophenes in dilute CH_2Cl_2 solution with ferric chloride which have revealed two new absorptions below the $\pi-\pi^*$ band.^{30,31} The $T_6^{\cdot+}$ cation, e.g., shows two absorptions at 0.84 and 1.59 eV of comparable intensity, while the T_6 dication T_6^{2+} possesses a single absorption at 1.24 eV. These results have been confirmed for partially methylated end-capped oligothiophenes: $T_6^{\cdot+}$ exhibits bands at 0.79 and 1.59 eV; $T_7^{\cdot+}$ at 0.69 and 1.49 eV.^{37,38} In a recent report on oxidation of a didodecyl sexithiophene, virtually identical to the T_6 oligothiophene in the present investigation, $T_6^{\cdot+}$ absorptions are found at 0.87 and 1.60 eV.³⁵ In addition to $T_6^{\cdot+}$, the dimer of the radical cation $(T_6)_2^{\cdot+}$ was also identified, exhibiting absorptions at 1.14 and 1.81 eV. For the corresponding T_6^{2+} dication, a band at 1.31 eV is found with an associated phonon replica at 1.47 eV. The present photo-oxidation data obtained for T_6 (1.55 and 0.82 eV) and T_7 (1.49 and 0.74 eV) in ODCB, are in excellent agreement with these chemical oxidation experiments and strongly support our assignment of the weak PIA features to a polaronic species (monoradical cation). The fact that these bands are only observed in specific, more polar, solvents suggests a solvent-mediated formation as recently proposed for poly(3-alkylthiophene) and poly(3-alkylthienylene vinylene).^{12,13,53} A more detailed survey of these photoexcited polaronic species is presently being investigated.⁵⁸

The relaxation behavior of the triplet PIA bands shown in Fig. 5 was determined by monitoring their magnitude as a function of the chopping frequency. The results are similar for all four oligothiophenes; the data for T_9 are displayed in Fig. 6 as a typical example. The average decrease in PIA intensity is only 10%–20% over the frequency range from 20–4000 Hz. Initially, the signals decay by a $\omega^{-0.03}$ depen-

dence. The weak rolloff of the intensity at high modulation frequencies is interpreted as due to an onset of a $1/\omega$ dependence characteristic for monomolecular decay, with an associated lifetime of less than 50 μs .

In solution at ambient temperature a number of nonradiative processes can be envisaged for the decay of a triplet-state excitation:

triplet-triplet annihilation; (3)

Intersystem crossing (1) is a monomolecular process. Self-quenching (2) and oxygen quenching via (4) or (5) are bimolecular, but will show pseudo-first-order kinetics (only one excited triplet state is involved). Triplet-triplet annihilation, on the other hand, will follow second-order kinetics because two excited triplet states are involved.

To distinguish between first- and second-order decay kinetics, we studied the effect of the pump intensity on the PIA signals; the PIA increases almost linearly with laser pump intensity (I). This is shown for T_9 in Fig. 7, where $\Delta T \propto I^{0.96}$. This almost linear dependence of the PIA signal on the pump intensity excludes triplet-triplet annihilation as a major decay process.

Although we did not study the oxygen quenching of the triplet-state photoexcitation of the oligomers in detail (be-

cause of sample degradation problems), exploratory experiments indicate that oxygen quenching occurs primarily via energy transfer (4); the strong triplet PIA band is completely quenched upon exposure to oxygen, without a significant enhancement of the weak polaronic PIA bands. Energy transfer to oxygen in contrast to electron transfer has also been found in the case of α -terthiophene.⁵⁴⁻⁵⁷ We therefore conclude that the major nonradiative decay processes in solution are reactions (1), (2), and (4). Although molecular oxygen has been removed from the samples, a small residual concentration cannot be excluded.

D. Photoinduced absorption in frozen solution

In order to gain more insight into the nature of the triplet-state photoexcitation we carry out PIA studies of the oligothiophenes under conditions of matrix isolation. In this way we expect to probe the genuine single molecule behavior. At ambient temperature long-lived (triplet) photoexcitations of oligomers in solution are likely to be affected by other molecules via a variety of processes that ultimately result in their decay to the ground state. Similarly, in solid films intermolecular interactions are expected to participate in nonradiative decay. By using dilute solutions of the oligomers in a rigid 2MeTHF glass at 80 K, however, single-chain behavior can be explored. In order to suppress microcrystallization,⁴⁴ the concentrations used were 10^{-5} M for T_6 , T_7 , and T_9 , but for the least soluble oligomer, T_{11} , we used a concentration of 10^{-6} M. The photoinduced absorption spectra of the T_n oligomers in a 2MeTHF glass at 80 K are shown in Fig. 8. The spectra exhibit a strong signal ($\Delta T/T > 10^{-2}$) similar to that of the CH_2Cl_2 solution at ambient temperature. There is, however, no indication of po-

FIG. 6. The dependence of the principal PIA signals of T_9 on the modulation frequency for three different types of samples. The 1.60 eV PIA signal in CH_2Cl_2 (295 K) is shown as asterisks, the 1.52 eV PIA signal in 2MeTHF (80 K) is shown as open triangles, and the 1.38 eV PIA signal in the film (80 K) is shown as solid triangles.

FIG. 7. The dependence of the intensity of the principal PIA signal of T_9 on the pump intensity at 457.9 nm (2.71 eV). The 1.60 eV PIA signal in CH_2Cl_2 (295 K) is shown as asterisks, the 1.52 eV PIA signal in 2MeTHF (80 K) is shown as open triangles, and the 1.38 eV PIA signal in the film (80 K) is shown as solid triangles. Solid lines are best fits of power-law behavior.

FIG. 8. Normalized PIA spectra of oligothiophenes in 2MeTHF glass. Spectra were recorded at 80 K by pumping with an argon-ion laser at 2.71 eV with 50 mW and a modulation frequency of 275 Hz. Concentrations are 10^{-5} M T_6 , T_7 , and T_9 ; 10^{-6} M T_{11} . Spectra are offset for clarity of presentation.

laronic PIA bands in the 2MeTHF glass. At 80 K, the triplet PIA bands range from 1.74 (T_6) to 1.45 eV (T_{11}) and are shifted to lower energy by about 0.08 eV with respect to the spectra at room temperature. This red shift is smaller than the one observed for the π - π^* absorption (0.25 eV). In addition to this shift, the vibrational structure of the PIA band is better resolved as a result of line narrowing. For T_6 , T_7 , and T_9 two vibronic transitions above the absorption maximum can be distinguished. A noticeable exception is T_{11} , which exhibits an additional feature at 1.36 eV. The nature of this absorption will be discussed in more detail in the following where we will show that it originates from the inception of aggregation of T_{11} , even at very low concentration (10^{-6} M). The presence of weak vibrational bands for T_6 , T_7 , and T_9 next to the strong PIA signal is similar to the $T_1 \rightarrow T_2$ PIA spectra of phenylene vinylene oligomers and highly ordered PPV.^{25,26}

The positions of the triplet PIA signals and their vibronic progression in 2MeTHF are linearly dependent on the reciprocal number of thiophene units [Fig. 3(c)], analogous to their absorption maxima in CH_2Cl_2 solution at 295 K.

The dependence of the intensity of the PIA signals on the modulation frequency may reveal the intrinsic lifetime of the photoexcitations. Especially when the transient photoexcited state decays predominantly via a monomolecular mechanism, as expected under matrix-isolated conditions, an analytical expression can be obtained for the steady-state concentration of photoexcitations as a function of the pump intensity (I) and chopper frequency ω . The rate equation describing the evolution of the density of photoexcitations [$n(t)$] that is generated under a chopped pump beam and

FIG. 9. The dependence of the PIA signals of the oligothiophenes in dilute 2MeTHF glassy solutions at 80 K on the modulation frequency. The 1.74 eV band (T_6 , 10^{-5} M) is shown as circles; the 1.62 eV band (T_7 , 10^{-5} M) as diamonds; the 1.52 eV band (T_9 , 10^{-5} M) as triangles; and the 1.45 eV band (T_{11} , 10^{-6} M) as squares. Solid lines represent best fits of ΔT according to Eq. (4).

decreases with a single monomolecular decay time τ is given by

$$\frac{dn(t)}{dt} = G(t) - \frac{n(t)}{\tau}, \quad (1)$$

where $G(t)$ is given by $G(t) = Ig(1 + \cos \omega t)$, with g the efficiency for the creation of photoexcitation (g actually depends on the number of photons absorbed and the quantum efficiency). The steady-state solution for $t \gg \tau$ is of the form

$$n(t) = Ig\tau \left[1 + \frac{1}{\sqrt{1 + \omega^2 \tau^2}} \cos(\omega t - \phi) \right], \quad (2)$$

where

$$\tan \phi = \omega \tau. \quad (3)$$

As a result, the change in transmission (ΔT) as a function of modulation frequency and pump intensity is given by

$$\Delta T \propto \frac{Ig\tau}{\sqrt{1 + \omega^2 \tau^2}}. \quad (4)$$

Figure 9 shows the dependence of ΔT on chopping frequency for the oligomers in 2MeTHF at 80 K and the best fits to a monomolecular decay described by Eq. (4). Figure 9 indicates that the lifetime of the photoexcitation decreases with increasing oligomer length, from $\tau = 470 \mu\text{s}$ for T_6 to $\tau = 250 \mu\text{s}$ for T_{11} (see Table I).

In our experiment, we detect the photoinduced absorption using a phase-sensitive lock-in technique which monitors both the maximum intensity (ΔT) and its phase angle (ϕ). A plot of $\tan \phi$ vs ω is expected to yield a linear relationship with a slope equal to τ [Eq. (3)]. Hence, in principle,

TABLE I. Calculated lifetimes $\tau(\Delta T)$, $\tau(\phi)$, and τ_s of photoexcitations for monomolecular and bimolecular decay and power-law exponents α of pump intensity dependence of PIA signals.

	2MeTHF			Film		
	$\tau(\Delta T)$ (μ s)	$\tau(\phi)$ (μ s)	α	$\tau(\Delta T)$ (μ s)	τ_s (μ s)	α
T_6	470	380	0.96	180	160	0.60
T_7	350	380	0.90	120	80	0.68
T_9	300	300	0.96	120	70	0.68
T_{11}	250	250	0.98	170	150	0.55

τ can be determined from two independent data sets obtained from a single experiment [Eqs. (3) and (4)]. The plot of $\tan \phi$ vs ω is shown in Fig. 10. The experimental data of $\tan \phi$ vs ω have indicated the necessity to correct the system response in order to obtain a linear relationship between $\tan \phi$ and ω . This was accomplished by measuring the modulation frequency dependence of the luminescence. Since the lifetime of the excited singlet state is very small compared to $1/\omega$ in the frequency range of 20–4000 Hz, the luminescence signal and its phase angle are virtually independent of ω . However, between 20 and 4000 Hz a small phase shift of approximately 10° was measured. All data presented here are corrected for this effect.

The plot of $\tan \phi$ vs ω after correction (Fig. 10) closely follows the expected linear relation. Comparing the lifetimes (Table I) obtained from the best fits of the experimental data using Eqs. (3) [$\tau(\phi)$] and (4) [$\tau(\Delta T)$] the accuracy of this procedure is on the order of 30 μ s, with a noticeable excep-

tion for T_6 where the best-fit values for τ are more than 100 μ s apart.

Furthermore, Eq. (4) reveals that in case of monomolecular decay the PIA signal increases linearly with increasing pump intensity. The data of the PIA bands of the oligomers show an almost linear behavior, $\Delta T \propto I^\alpha$, where $\alpha=0.90$ – 0.98 (Table I). The exponents are identical to the ones obtained in solution at room temperature.

We conclude that in dilute frozen 2MeTHF solutions a truly monomolecular decay takes place as is evident from the dependence of the PIA on modulation frequency and pump intensity. The absence of molecular diffusion in 2MeTHF at 80 K reduces the contribution of reactions (2) and (4) considerably (dilute and essentially oxygen-free solutions). Since no phosphorescence is observed, the triplet excited state decays mainly nonradiatively via intersystem crossing (1).

E. Photoinduced absorption in solid-state films

In a third set of experiments, we studied photoinduced absorption of the oligothiophene films. The films were cast from chloroform solution and studied at 80 K under a vacuum of 10^{-5} Torr. The PIA spectra obtained for the films shown in Fig. 11 are more complex than those obtained from solutions and frozen solutions. The spectrum of T_6 shows three clearly resolved transitions at 1.41, 1.59, and 1.79 eV; where the first PIA band is most intense. For T_7 two distinct PIA signals are observed at 1.28 and 1.48 eV, and a shoulder at approximately 1.64 eV. In contrast to T_6 , the second band (1.48 eV) is the strongest in T_7 . T_9 shows only one dominant PIA signal at 1.38 eV and a second, much less intense, peak at 1.54 eV. Finally for T_{11} the main PIA band is centered at 1.26 eV, superimposed on a weak signal ranging from 1.0–1.7 eV.

The spacing of the various signals in each of the oligomers suggests that it originates from vibrational structure. A plot of the peak energies vs $1/n$ [Fig. 3(c)] supports this supposition. Figure 3(c) suggests that the signals T_6 1.59; T_7 1.48; T_9 1.38; and T_{11} 1.26 eV belong to the same vibronic transition. The appearance of distinct signals for T_6 and T_7 at lower energies than 1.59 and 1.48 eV, shows that the latter absorptions are not due to the 0–0 phonon transition, but are more likely the result of a 0–1 transition. The 0–0 band, on the other hand, is very intense for T_6 but drops dramatically in intensity for T_7 and is very weak for T_9 and T_{11} . It appears that the relative intensity of the different vibronic transitions varies strongly with the oligomer length. It is likely that this effect is due to the degree of crystallinity; a more rigidly packed material may limit the magnitude of allowed structural changes and will therefore influence the potential energy surface of both initial and final state. It has been reported that the crystallinity of the oligomers used in the present study decreases with increasing molecular length, T_{11} exhibits an almost amorphous structure.⁷

Triplet excitons have been tentatively attributed to PIA bands observed for poly(3-dodecylthiophene) at 1.00 eV¹¹ and for purified poly(3-octylthiophene) at 1.05 eV.²¹ These energies are intermediate to the energy of the PIA band for

FIG. 10. The dependence of the phase angle ϕ of the PIA bands of the oligothiophenes in dilute 2MeTHF glassy solutions at 80 K on the modulation frequency. The 1.74 eV band (T_6 , 10^{-5} M) is shown as circles; the 1.62 eV band (T_7 , 10^{-5} M) as diamonds; the 1.52 eV band (T_9 , 10^{-5} M) as triangles; and the 1.45 eV band (T_{11} , 10^{-6} M) as squares. Solid lines represent best fits of $\tan \phi$ according to Eq. (3).

FIG. 11. Normalized PIA spectra of oligothiophene solid-state films. Spectra were recorded at 80 K by pumping with an argon-ion laser at 2.71 eV with 25 mW and a modulation frequency of 275 Hz. Spectra are offset for clarity of presentation.

T_{11} (1.26 eV) and the energy for an infinite number of thiophene units (0.88 eV), obtained by extrapolating the 0–1 transitions shown in Fig. 3(c).

To gain insight in the decay processes in the film, the dependence of the PIA features in the films on the pump intensity has been investigated. All PIA signals for the oligomer films show a sublinear power-law dependence with exponents varying between 0.55 and 0.68. A typical example is shown in Fig. 7 for T_9 . The sublinear dependence on the pump intensity indicates a significant contribution of bimolecular decay processes where two photoexcitations recombine, such as triplet–triplet annihilation. For bimolecular decay the rate equation for $n(t)$ can be expressed as

$$\frac{dn(t)}{dt} = G(t) - \beta n(t)^2. \quad (5)$$

Here the lifetime is dependent on the pump beam intensity.^{53,59} The steady-state solution for ΔT for a symmetric square wave light modulation $G(t)$ is given by

$$\Delta T \propto \sqrt{gI/\beta} \cdot \frac{\alpha \tanh \alpha}{\alpha + \tanh \alpha}, \quad (6)$$

where $\alpha = \pi/(\omega\tau_s)$ and $\tau_s = (gI\beta)^{-0.5}$. The parameter τ_s represents the lifetime under steady-state conditions. Examination of this equation shows that the frequency dependence of ΔT for bimolecular decay is similar to the one for monomolecular decay: $\Delta T \propto \omega^{-1}$ for $\omega\tau_s \gg 1$ and ΔT is independent of ω for $\omega\tau_s \ll 1$.

All PIA signals of the films show a similar relaxation behavior upon increasing the modulation frequency. The relaxation behavior for T_9 is shown in Fig. 6 as a typical ex-

FIG. 12. Normalized PIA spectra of T_{11} oligothiophene at 80 K as a film (dotted line) and incorporated in a 2MeTHF glass at concentrations of 10^{-6} (solid line) and 10^{-5} M (dashed line).

ample, for which a lifetime of 120 μ s is obtained when the data are fitted to Eq. (4) (monomolecular decay). Table I contains the lifetimes inferred from fitting to monomolecular [Eq. (4)] and bimolecular decay [Eq. (6)]. Table I reveals that the photoexcitation lifetime in the film is significantly smaller than the one in the 2MeTHF glass. Since both experiments are performed at 80 K, we believe that the reduced lifetime in the films may be attributed to intermolecular interactions. The sublinear dependence on intensity indicates the contribution of bimolecular decay.

F. Photoinduced absorption of aggregated frozen solutions

Upon cooling, an increased oligothiophene concentration in 2MeTHF induces aggregation which can be monitored by absorption and photoluminescence. Because a different decay mechanism of the triplet-state excitation prevails under matrix-isolated conditions compared to the solid film, it is of interest to study photoinduced absorption in concentrated frozen solutions where aggregation occurs. Figure 12 shows the normalized PIA spectra obtained at 80 K for T_{11} in 10^{-6} and 10^{-5} M concentrations in 2MeTHF and in a film. Comparison of the spectra reveals that the spectrum at 10^{-5} M exhibits the principal absorption features present in both the film (1.26 eV) and the dilute 10^{-6} M solution (1.45 eV). Figure 13 displays the PIA signal intensity as a function of the pump power. The signal at 1.45 eV increases almost linearly with I for both concentrations ($\alpha = 0.98$ –1.00). The fact that the shoulder at 1.62 eV possesses a similar pump intensity dependence ($\alpha = 0.97$) supports its assignment as due to a higher vibronic transition. However, the signals at 1.26 eV, observed in the film and the 10^{-5} M solution, depend less strongly on the pump intensity, with power-law exponents of $\alpha = 0.55$ and $\alpha = 0.49$, respectively. The PIA band at 1.36 eV, observed in the most dilute solution, possesses an intermediate behavior ($\alpha = 0.79$). These results demonstrate that at higher concentrations and low temperatures the oligomer

FIG. 13. The dependence of the PIA bands shown in Fig. 14 on the intensity of the pump beam. The asterisks represent the data of the T_{11} film; the open markers show the 10^{-6} M solid 2MeTHF solution; and the solid markers the 10^{-5} M solid 2MeTHF solution. Solid lines are best fits according to power-law dependence with exponents as indicated in the inset.

chains apparently aggregate to form small clusters or microcrystallites similar to those in solid films. Particularly revealing is the buildup of the band at 1.26 eV as the concentration increases; the position of this band is identical to the PIA feature in the film. In addition, the emergence of bimolecular decay supports the formation of aggregates.

Apparently, freezing T_{11} at 10^{-6} M concentration in 2MeTHF at 80 K gives rise to predominantly isolated chains, whereas at 10^{-5} M appreciable aggregation occurs. We believe that the intermediate PIA signal at 1.36 eV for the most dilute solution can be attributed to the onset of this aggregation effect. Aggregation at higher concentration is also inferred from the luminescence spectra shown in Fig. 4; at 10^{-5} M the spectrum approaches the one of the film (although some solution-like emission at 2.21 eV is still present).

IV. CONCLUSIONS

We have described the results of a comprehensive study of the optical properties of a series of medium-sized α -oligothiophene films and solutions at ambient and cryogenic temperatures. The absorption and luminescence of the oligomers were studied in relation to their conjugation length in solutions, frozen solutions, and films. The luminescence spectra indicate that a considerable conformational change to a more rigid planar structure occurs in the singlet excited state, prior to radiative decay. Furthermore, all oligothiophenes exhibit a strong, vibronically coupled, PIA band attributed to a metastable triplet-state photoexcitation. We find that the absorption maximum of the PIA band is proportional to the reciprocal number of thiophene units, analogous to the behavior of linear absorption and luminescence. The

triplet-state photoexcitation was characterized by monitoring the modulation frequency and intensity dependencies, and all PIA data are consistent with the formation of a metastable triplet excited state (T_1). These photoexcitations are formed via intersystem crossing from the photoexcited singlet state. The relatively large spin-orbit coupling constant of sulfur ($\xi = -184 \text{ cm}^{-1}$) enhances the quantum yield for triplet formation. The narrow bandwidth of the PIA band ($<0.2 \text{ eV}$) in solution compared to the linear $S_0 \rightarrow S_1$ absorption band ($\pm 0.7 \text{ eV}$) indicates the absence of inhomogeneous broadening and a well-defined geometry for the photoexcited triplet state (T_1), which can be explained by an increased contribution of a more rigid quinoid structure to the electronic configuration of the excited molecule in the triplet state. In addition to a triplet excited state, photoexcitation of the oligothiophenes in specific solvents at ambient temperature, reveals the presence of radical cations created in a solvent-mediated photo-oxidation reaction.^{12,13,59}

We have shown that both the energies of the triplet PIA bands and the nature of the decay process of the photoexcitation depend on the degree of aggregation. There is a significant red shift of the PIA band when the oligothiophenes aggregate, either in a solid film or upon freezing a concentrated solution. Distinct monomolecular decay has been observed under matrix-isolated (single chain) conditions in a dilute 2MeTHF glass. At ambient temperature, however, the significant molecular mobility in solution gives rise to additional intermolecular energy transfer processes. In the solid-state films, on the other hand, or in concentrated frozen solutions where aggregation of oligothiophenes occurs, we find a significant contribution of bimolecular decay.

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