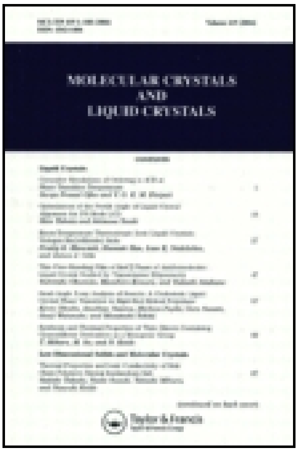

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TRIPLET STATE PHOTOEXCITATIONS IN FROZEN SOLUTIONS OF OLIGOTHIOPHENES

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Abstract We present studies of near-steady-state photoinduced absorption (PIA) spectroscopy of well-defined α-oligothiophenes (T_n, n = 6,7,9, and 11) in frozen 2MeTHF solution. The PIA spectra and the excited state lifetimes are consistent with the signatures of a photoexcited triplet state. The triplet photoexcitation is created via an intrachain mechanism and decays nonradiatively with monomolecular kinetics.

INTRODUCTION

The uniform degree of polymerization and their well-defined chemical structure make oligomers instrumental to access properties of π-conjugated systems that critically depend on the conjugation length. Several of the basic features of π-conjugated materials can be explained by the molecular characteristics of small subunits. In this paper we focus on near-steady-state photoinduced absorption (PIA) studies of four well-defined substituted α-oligothiophenes, with respectively 6, 7, 9, and 11 thiophene units (Figure 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.[1-3] We present the PIA in frozen solution at 80 K under conditions of matrix isolation. In this way we expect to probe the genuine single molecule behavior. In solution at ambient temperature long-lived photo-excitations of oligomers 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.

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Using this method strong PIA spectra exhibiting a single vibronically resolved transition are observed for the oligothiophenes 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. We find that under matrix-isolated (single chain) conditions the photoexcitation decays with monomolecular kinetics. Having a series of well-defined oligomers, we explore the effect of increasing conjugation length.

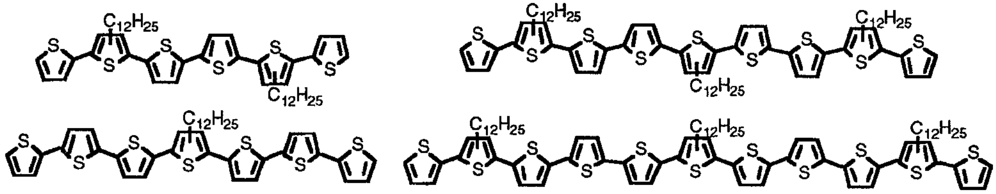

FIGURE 1 Molecular structures of the T_6, T_7, T_9 and T_{11} oligothiophenes.

EXPERIMENT

The synthesis of the oligothiophenes has been described previously.[1-3] Samples were prepared under oxygen-free argon atmosphere and placed in sealed 3mm cuvettes. 2-Methyltetrahydrofuran (2MeTHF) has been used, since it forms a clear transparent glass at 80 K. The cuvette containing the glassy 2MeTHF matrix is cooled by placing it in a transparent double walled dewar vessel filled with liquid nitrogen. To suppress chain aggregation and microcrystallization at 80 K,[4] the concentration of the oligothiophenes is on the order of 10^{-5}-10^{-6} M . Linear absorption and photoluminescence indicate the presence of single chains under these conditions. Near-steady-state PIA spectroscopy was performed with a mechanically modulated pump-and-probe technique, which has been described in more detail in previous publications.[5,6] Excitation was provided by the 457.9 line of an Ar-ion laser at 50 mW, chopped at 275 Hz.

RESULTS AND DISCUSSION

The photoinduced absorption spectra of the T_n oligomers in a 2MeTHF glass at 80 K are shown in Figure 2. The spectra exhibit a strong signal ($\Delta T/T > 10^{-2}$). The most prominent band in the PIA spectra shifts gradually to lower energy for the longer oligomers: 1.74 eV

(T_6), 1.62 (T_7), 1.52 (T_9) and 1.45 eV (T_{11}) The PIA bands exhibit vibrational structure on the high-energy side. 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. Increasing the concentration of T_{11} reveals, however, that the PIA band at 1.36 eV originates from the inception of aggregation of T_{11}, even at very low concentration (10^{-6} M). The positions of the triplet PIA signals and their vibronic progression in 2MeTHF are linearly dependent on the reciprocal number of thiophene units (Figure 3).

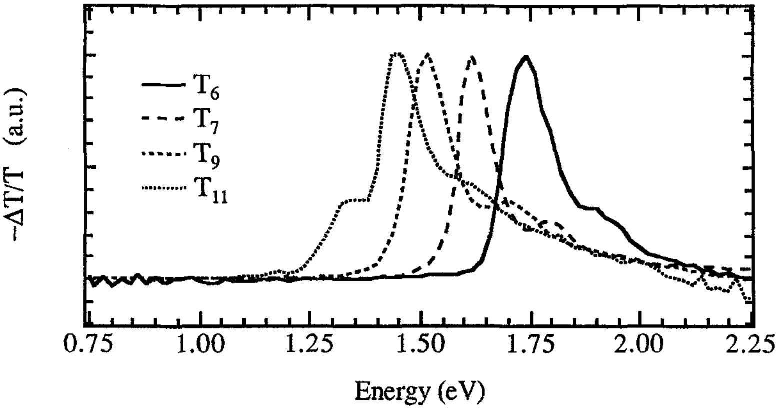

FIGURE 2 Normalized PIA spectra of oligothiophenes in 2MeTHF glass.

We attribute the PIA bands to a metastable triplet 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 π-π* transition eliminates in our view the possibility that single charged (polaron) or doubly charged (bipolaron) cations are responsible for this PIA band, since for a polaron/bipolaron at least two intragap absorptions are expected.[7-8] Transient triplet absorption spectra have been observed for α-terthiophene (2.70 eV), α-tetrathiophene (2.21 eV), and recently for α-sexithiophene (1.80 eV) in solution at ambient temperature.[9-11] These $T_1 \rightarrow T_2$ absorption energies support our assignment for T_n. The presence of weak vibrational bands for 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.[12,13]

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

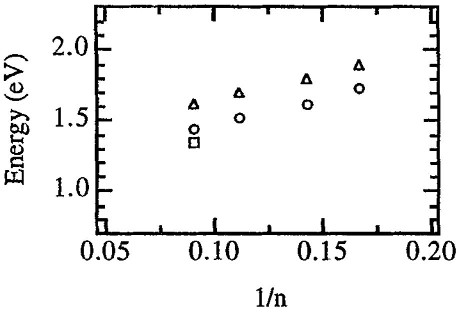

FIGURE 3 Energies of PIA bands of oligothiophenes in 2MeTHF glass at 80 K. Two vibronic transitions are included in the graph.

frequency ω. The rate equation describing the evolution of the density of photoexcitations ($n(t)$) that is generated under a chopped pump beam and decreases with a single monomolecular decay time τ is given by[14]

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

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

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

where $\tan \phi = \omega\tau$. As a result, the change in transmission (ΔT) as a function of modulation frequency and pump intensity is given by

$$\Delta T \propto \frac{Ig\tau}{\sqrt{1+\omega^2\tau^2}} \tag{3}$$

Figure 4 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. 3. Figure 4 indicates that the lifetime of the photoexcitation decreases with increasing oligomer length: τ=470 μs (T_6), τ=350 μs (T_7), τ=300 μs (T_9) and τ=250 μs (T_{11}).

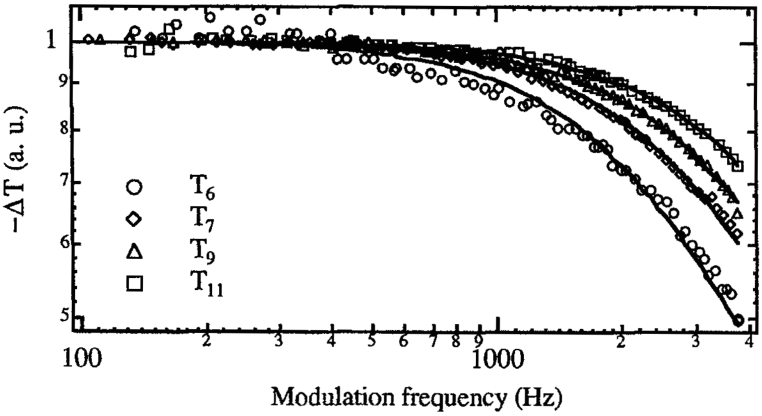

FIGURE 4 PIA signals of the oligothiophenes in dilute 2MeTHF solutions at 80 K vs. modulation frequency. Solid lines are best fits of ΔT according to Eq.3.

Eq. 3 reveals furthermore 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. We are prompted to 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 self-quenching and triplet-triplet annihilation reactions considerably (dilute and essentially oxygen-free conditions). Since no phosphorescence is observed, the triplet excited state decays mainly nonradiatively via intersystem crossing.

CONCLUSION

All oligothiophenes exhibit a strong, vibronically coupled, PIA band attributed to a metastable triplet-state photoexcitation. 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).Distinct monomolecular decay has been observed under matrix-isolated (single chain) conditions in a dilute 2MeTHF glass.

These photoexcitations are formed via intersystem crossing from the photoexcited singlet state. The relatively large spin orbit coupling constant of sulfur (ζ=-184 cm^{-1}) enhances the quantum yield for triplet formation. The narrow band width of the PIA band (< 0.2 eV) in solution compared to the linear $S_0 \rightarrow S_1$ absorption band (± 0.7 eV) indicates the absence of inhomogeneous broadening and a well-defined geometry for the photoexcited triplet state (T_1). This suggests an increased contribution of a more rigid quinoid structure to the electronic configuration of the excited molecule in the triplet state.

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