Interchain Delocalization of Photoinduced Neutral and Charged States in Nanoaggregates of Lengthy Oligothiophenes

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Abstract: Photoluminescence (PL) and photoinduced absorption (PIA) spectroscopy measurements were performed on two lengthy oligothiophenes, G3-T11-G3 and G3-T17-G3, doubly end-substituted with third generation poly-benzyl ether dendrons. These oligothiophenes form well-defined nanoaggregates in dichloromethane solution upon cooling. The molecularly dissolved and aggregated phases interconvert reversibly in a narrow temperature range. PL and PIA spectroscopy were used to investigate the optical signatures of photoexcited singlet, triplet, and charged states as a function of aggregation. The extent of aggregation could be controlled by varying the temperature. Both the fluorescence and the triplet absorption spectra of the aggregated phase were significantly bathochromically shifted when compared to the spectra of the isolated molecules in solution. These bathochromic shifts indicate that interchain delocalization of the singlet and triplet photoexcitations occurs within the dendritic nanoassemblies. Charged states of G3-T11-G3 and G3-T17-G3 were selectively created by photoexcitation in the presence of an external electron acceptor (tetracyanoethylene). The principal absorption bands of the charged states shift to lower energy upon aggregation. Surprisingly, new high-energy bands are observed in the PIA spectrum of the aggregated phase. These transitions are clear signatures of two-dimensionally delocalized polaronic charge carriers within the nanoaggregates (i.e. intermolecular delocalization over the constituent molecules within the aggregate).

Introduction

Functional properties of organic molecules and polymer materials continue to attract enormous attention in contemporary chemistry and physics. This interest is motivated by the continuing interest for miniaturization of devices to molecular dimensions[1] and by the numerous opportunities that arise for employing molecular electronic and photonic materials in light-emitting diodes, transistors, and photovoltaic devices.[2] Fascinating opportunities arise where molecular and bulk dimensions meet. Especially for inorganic semiconductor nanocrystals and metal quantum clusters, properties begin to differ greatly as one escapes the bulk and begins to examine materials at the nanoscale, thus providing the impetus to miniaturize devices to molecular dimensions.[3,4] However, in the case of organic molecular materials, the electronic and optical properties are fundamentally different from inorganic semiconductors or metals, due to weak intermolecular interactions, and research on semiconducting molecular nanocomposites has been gaining momentum only recently.[5]

Semiconducting molecular nanocomposites can be regarded as a combination of molecular, polymer or inorganic semiconductors that are constructed through self-organizing mechanisms that make use of either mesogenic groups,[6] complementary and antagonistic interactions (e.g. block copolymers),[7] ionic interactions,[8] hydrogen bonding,[9] or π-stacking.[10] In this regard, dendrimers provide a very unique opportunity to study well-

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Chart 1

G3-T11-G3 : n = 1

G3-T17-G3 : n = 2
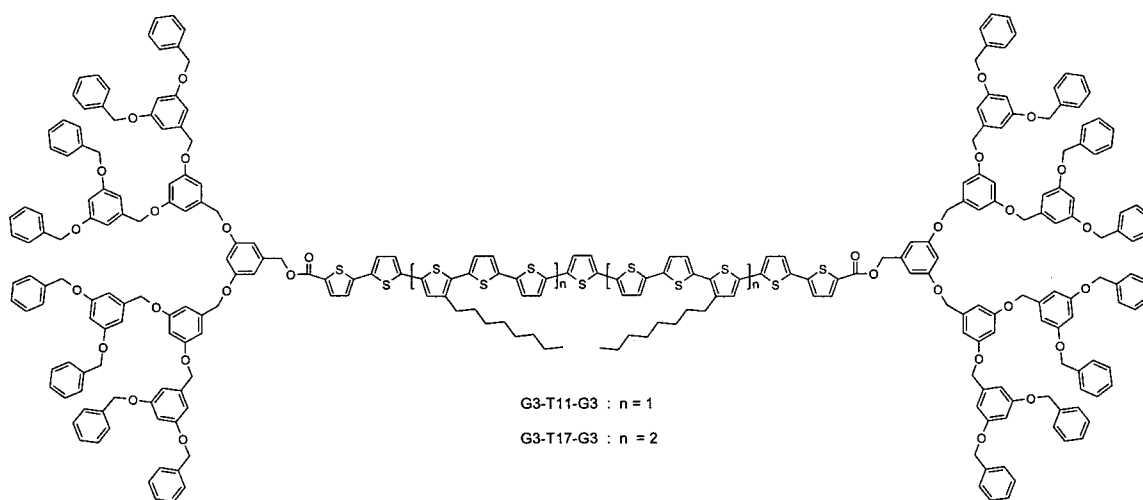
defined molecules having nanoscale dimensions.[11] For instance, dendrimers have been used to apply nature's site-isolation principle from biomimetics to materials science[12] and highly efficient intramolecular light harvesting and energy transfer within a dendritic scaffold has been demonstrated.[13] Both concepts were recently combined in an attempt to prepare color tunable, single layer OLEDs, in which dyes of varying band gaps were isolated within the core of dendrimers bearing peripheral hole-transporting moieties capable of energy transfer.[14]

Self-organization phenomena may represent a novel approach to control intermolecular interactions as well as the size of molecular assemblies, thus resulting in functional materials with new properties and/or enhanced performance in optoelectronic devices. In particular, supramolecular self-organization of π-conjugated polymers has been shown to be of fundamental importance, since the traditional one-dimensional (1D) electronic properties are modified by an increase in interchain coupling.[15,16] These interactions are a crucial parameter that affects the charge carrier mobility in π-conjugated semiconductors, which is currently limited by interchain (2D) hole transport and mesoscale bulk morphology.[15]

A well-known example of the changes that can be expected when interchain interactions occur has been established for substituted polythiophenes. In these conjugated polymers a transition between molecularly disordered polymer chains and aggregated, more ordered, possibly microcrystalline, chains results in a color change. Not surprisingly, the two phases exhibit markedly different absorption spectra.[17] The transition between the two phases and the associated color change that results from a change in temperature is commonly referred to as thermochromism and it can be observed in thin films as well as in solution.[17]

Recently, we described the synthesis of well-defined oligothiophene—dendron triblock copolymers having a dumbbell architecture.[18,19] The thermochromism of these triblock copoly-

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mers based on undeca- and heptadecathiophene cores attached to generation three Fréchet-type poly(benzyl ether) dendrons (G3-T11-G3 and G3-T17-G3, Chart 1) has been studied in solution.[20,21] Self-complexation of G3-T11-G3 and G3-T17-G3 at low temperature in solution was shown to result in the formation of relatively small, but well-defined supramolecular nanoscale assemblies, driven by strong $\pi-\pi$ interactions between the conjugated blocks.[20] The dendritic substituents considerably enhance the solubility of these materials and thus allowed for a wide range of temperatures and concentrations to be examined. The highly branched nature of the dendritic blocks ensures excellent solubility for the ABA triblock copolymers, despite the minimal substitution of the oligothiophene backbone. In these triblock copolymers the oligothiophenes and dendrons provide a subtle balance of rigid and flexible structural elements that is required for the self-assembly in nanoaggregates. The formation of these nanoaggregates is accompanied by dramatic changes in the optical absorption spectra as a result of the intermolecular interactions. The controlled evolution of this self-organization process in solution makes these well-defined oligothiophene derivatives ideal candidates for a detailed investigation of interchain effects on photoexcited states at varying extents of aggregation.

Here we describe the novel spectral signatures observed for photoexcited neutral and charged states that occur in oligothiophene-dendrimer nanoaggregates using variable-temperature photoluminescence (PL) and photoinduced absorption (PIA) spectroscopy. Excitation of aggregates made up of either G3-T11-G3 or G3-T17-G3 results in a significant bathochromic shift of the fluorescence and of the triplet and radical cation (polaron) absorption spectra compared to spectra of molecularly dissolved molecules. Additionally, for the charged state, new high-energy bands are observed in the PIA spectrum of the aggregated phase that are characteristic of two-dimensionally delocalized polaronic charge carriers. These effects demonstrate that a reversible and controlled transformation between typical 1D characteristics of free chains and 2D characteristic of nanoaggregates can be created in molecular semiconductors by self-assembly processes.

Results

Previous thermochromic experiments have verified the formation of nanoaggregates of G3-T11-G3 and G3-T17-G3 in dichloromethane solution and they are summarized in Figure 1.[20] With decreasing temperature the $\pi-\pi*$ transition of G3-T11-G3 (2.59 eV) and G3-T17-G3 (2.57 eV) initially shifts slightly to lower energies because of intramolecular planarization (Figure 1). At a certain temperature, however, depending on the concentration and the length of the conjugated system, a sudden and pronounced transition to a much more resolved spectrum takes place (Figure 1). At this point, a new low-energy aggregation band (2.20 eV for G3-T11-G3 and 2.11 eV for G3-T17-G3) appears in the spectrum. The aggregation process reaches completion within a relatively narrow temperature range (~30 K). The aggregation does not result in a significant increase of viscosity and gelation does not occur. Plotting the normalized absorbance of the aggregation band as a function of the temperature results in a sigmoidal curve (Figure 1). The transition temperature T_m, at which half of the oligomers are in the aggregated phase, shifts to lower temperatures with decreas-

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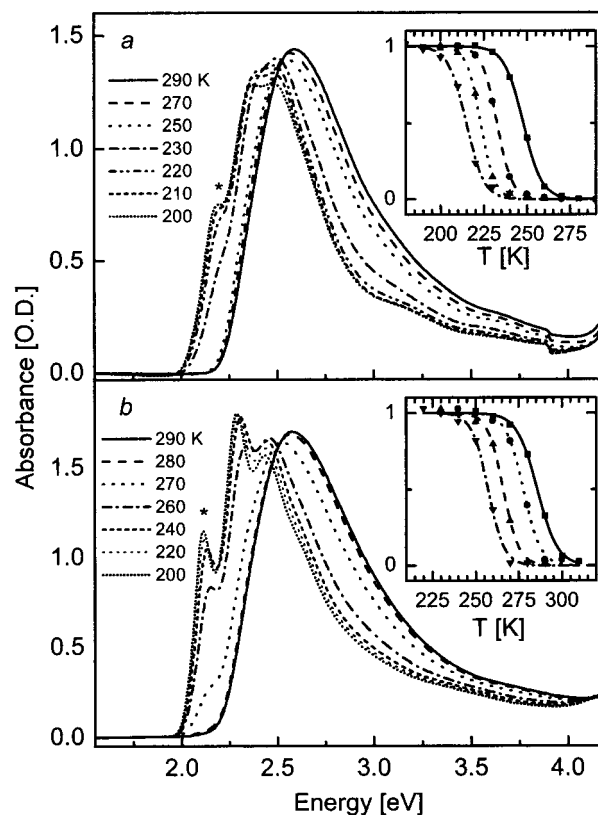

Figure 1. Optical absorption changes upon cooling dichloromethane solutions of (a) G3-T11-G3 and (b) G3-T17-G3. The insets show normalized sigmoidal curves obtained on fitting the intensities of the absorbance at (a) 2.20 eV for G3-T11-G3 (0.3×10^{-6}, 1.0×10^{-6}, 5.2×10^{-6}, and 50×10^{-6} M solutions) and (b) 2.11 eV for G3-T17-G3 (1.0×10^{-6}, 4.5×10^{-6}, 2.0×10^{-5}, and 5.6×10^{-5} M solutions) as a function of the temperature. Down triangles, up triangles, circles, and squares represent increasing concentrations.
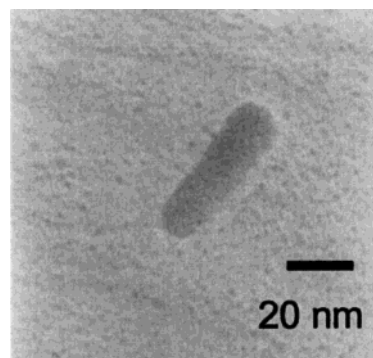

Figure 2. Transmission electron microscopy photograph of an aggregate of G3-T17-G3. The grid was prepared by filtration of a concentrated 273 K dichloromethane solution through the grid.

ing concentration. By combining thermodynamic equations related to both the concentration and the temperature dependence, we have demonstrated that these compounds form well-defined nanosized aggregates upon cooling, containing a limited number (5-6) of molecules.[20] Transmission Electron Microscopy (TEM) photographs (Figure 2) confirm the formation of the well-defined nanoaggregates in dichloromethane. The aggregates exhibit a rather uniform size and rodlike shape with dimensions on the order of 20 nm. The size determined from TEM is larger than expected given the estimated number of constituent oligothiophenes determined from the thermochromic experiments. We tentatively assign this difference in size to the different methods used to generate the nanoaggregates.
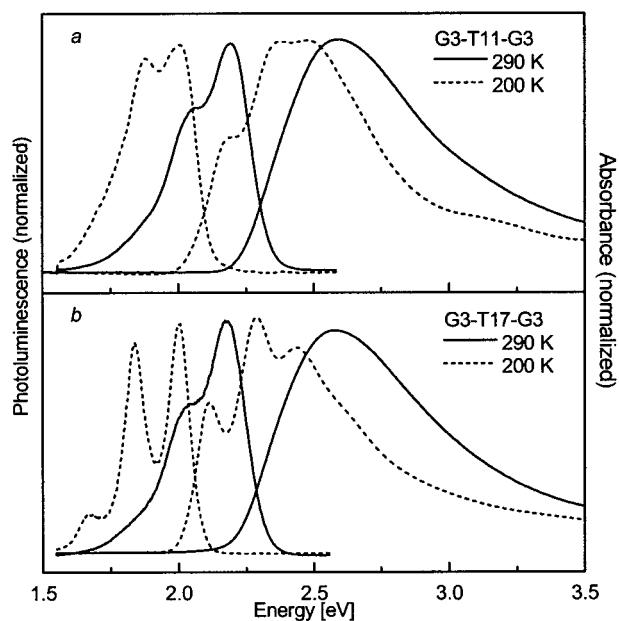
Figure 3. Absorption and emission spectra of (a) molecularly dissolved (PL excited at 2.64 eV, solid lines) and aggregated (PL excited at 2.20 eV, dashed lines) G3-T11-G3 in dichloromethane and (b) molecularly dissolved (PL excited at 2.61 eV, solid lines) and aggregated (PL excited at 2.11 eV, dashed lines) G3-T17-G3 in dichloromethane.

Photoluminescence of Nanoaggregates. The PL spectra of the molecularly dissolved phase (at room temperature) and of the aggregated phase (at low temperature) of G3-T11-G3 and G3-T17-G3 in dichloromethane exhibit considerable differences (Figure 3). The molecularly dissolved phase shows maximum PL intensities at 2.18 and 2.19 eV, with shoulders at 2.05 and 2.03 eV, for G3-T11-G3 and G3-T17-G3, respectively. In contrast, the nanoaggregates show two emission bands of comparable intensity (though much more resolved in the case of G3-T17-G3) at 2.02 and 1.88 eV for G3-T11-G3 and at 2.02 and 1.85 eV for G3-T17-G3. Although Figure 3 shows the normalized spectra it is important to note that the emission of the aggregated phase is quenched by a factor of 2.4 compared to that of molecularly dissolved oligomers. Interestingly, the PL quenching observed for these oligothiophenes is significantly less than that of poly(3-alkylthiophene) aggregates in which a quenching factor of 20 is observed upon going from a good to a poor solvent.[22] While an obvious explanation for the diminished fluorescence intensity is intra-aggregate self-quenching, the lifetime of the singlet-excited state is longer in the aggregate than in the molecularly dissolved state.[22,23] Hence, self-quenching is not the major process and consequently the PL quenching is generally attributed to a decrease of the radiative decay constant in the aggregated phase, while the nonradiative decay constant remains the same or increases slightly.[22] As a result the lifetime of the singlet excited state increases. The increased natural radiative lifetime is a result of interchain interactions that create an excited state that is not radiatively coupled to the ground state. The lower PL quenching for G3-T11-G3 and G3-T17-G3 compared to poly(3-alkylthiophene)s might indicate that, as a result of the bulky dendritic end groups,

Figure 4. PL intensity of (a) G3-T11-G3 in dichloromethane at 2.02 eV (excited at 2.20 eV) (squares) and 2.19 eV (excited at 2.64 eV) (circles) as a function of temperature and (b) G3-T17-G3 in dichloromethane at 2.02 eV (excited at 2.11 eV) (squares) and at 2.18 eV (excited at 2.61 eV) (circles). The concentrations are ∼3 × 10⁻⁶ M.

the molecules pack with an angle between the chain axes in contrast to the linear packing of chains in poly(3-alkylthiophene)s. On the other hand, the optical absorption spectra in the aggregated phase are rather similar for the two systems, suggesting that chain packing is analogous. The regular length of G3-T11-G3 and G3-T17-G3 in comparison to that of poly-(3-alkylthiophene)s probably does not account for the different quenching; e.g. oligo- and poly(*p*-phenylene vinylene) derivatives give a similar increase in excited-state lifetime when going from solution to a thin film.[23]

By recording the PL spectra at different temperatures we confirmed that the aggregate emission emerges at the expense of the free chain emission and goes to completion within a rather narrow temperature range (about 30 K). In this temperature region, molecularly dissolved and aggregated chains coexist. Plotting the normalized intensities of both the free chain fluorescence (at 2.19 eV for G3-T11-G3 and 2.18 eV for G3-T17-G3) and the aggregate fluorescence (at 2.02 eV for G3-T11-G3 and 2.02 eV for G3-T17-G3) as a function of temperature provides sigmoidal curves (Figure 4), whose characteristics display an excellent match to those obtained from the absorption spectra (Figure 1).

Triplet Excited States in Nanoaggregates. To investigate the influence of the different phases and the aggregation phenomenon on photoexcitations other than the singlet excited state we used near-steady state photoinduced absorption (PIA) spectroscopy, which probes the optical spectra of excited states with lifetimes in the micro- and millisecond time domain. It is well established that oligothiophenes readily form triplet (T_1) states via intersystem crossing from the singlet excited (S_1) state (Figure 5). Triplet states of long oligothiophenes and polythiophenes have been identified.[24,25]

The $T_n \leftarrow T_1$ absorption spectra of G3-T11-G3 in dichloromethane at different temperatures obtained by excitation of the $\pi-\pi^*$ transition at 488 nm also show significant differences due to the aggregation process (Figure 6). At 270 K (Figure 6a), where UV/vis and PL spectra indicate that the molecules are molecularly dissolved, the $T_n \leftarrow T_1$ transition is at 1.51 eV.

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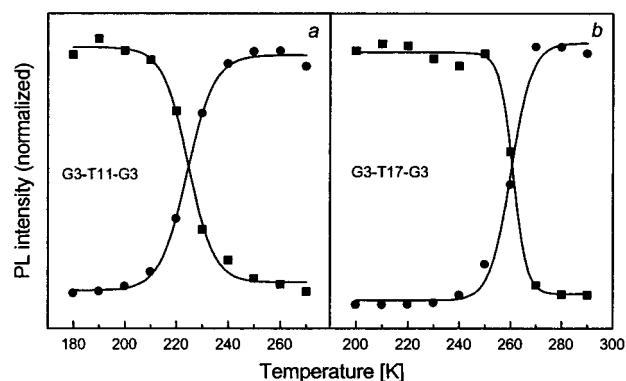
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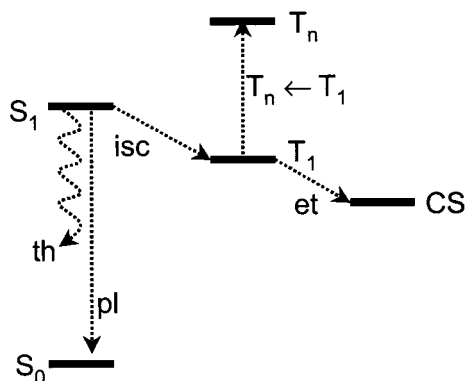
Figure 5. Schematic diagram describing the energy states of the species that are formed via excitation of the oligothiophenes (see text): ground state (S_0); singlet excited state (S_1); triplet state (T_1); charged state (CS); thermal decay (th); photoluminescence (pl); intersystem crossing (isc); and electron transfer (et).
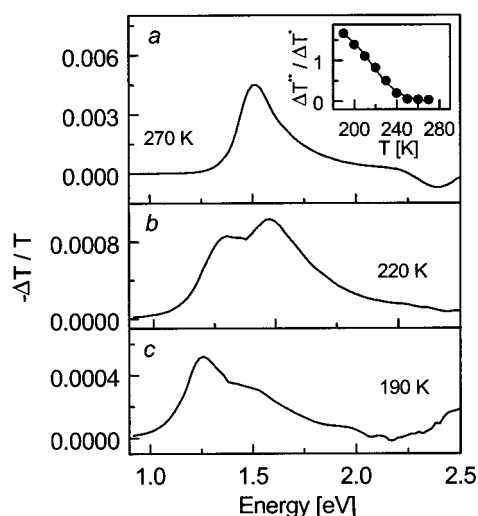

Figure 6. PIA spectra of the triplet state of G3-T11-G3 at (a) 270, (b) 220, and (c) 190 K, where the molecules are in the molecularly dissolved, mixed, and aggregated phases, respectively. The inset of part a shows the ratio between the triplet absorptions at 1.26 and 1.51 eV as a function of the temperature.

At 190 K (Figure 6c), the molecules are completely in the aggregated phase and the $T_n \leftarrow T_1$ transition has red-shifted to 1.26 eV, similar to the red shift of the UV/vis and PL spectra. At intermediate temperatures (220 K, Figure 6b), where UV/vis and PL measurements signify the coexistence of both phases, contributions from both types of triplet absorptions appear in the PIA spectrum. The inset of Figure 6a shows the ratio of the triplet absorptions at 1.26 and 1.51 eV as a function of temperature. The sigmoidal shape confirms the interconversion of triplet states formed via excitation of a dissolved chain at high temperatures into triplet states formed in aggregates at low temperatures. If the red shift would arise from a continuing increase of intrachain order (i.e. planarization) upon cooling, a monotonic red shift would be expected rather than the observed sigmoidal interconversion. The significant red shift at low temperatures suggests that in the triplet manifold, two-dimensional delocalization over several chains occurs (i.e. wave functions that extend intermolecularly). Since the lowest triplet state is known to be rather localized,[26] the delocalization is most likely associated with the higher lying triplet states.
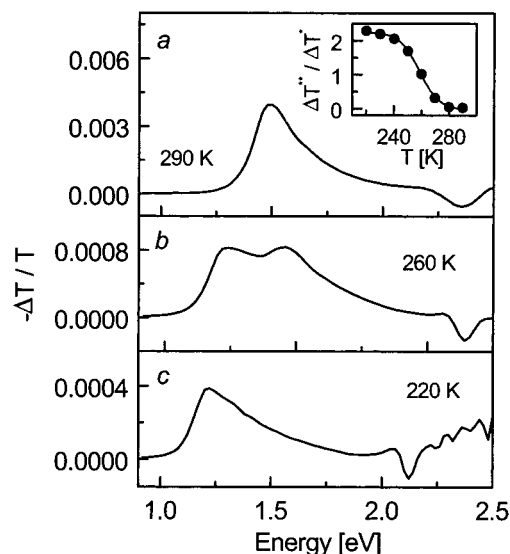

Figure 7. PIA spectra of the triplet state of G3-T17-G3 at (a) 290, (b) 260, and (c) 220 K, where the molecules are in the molecularly dissolved, mixed, and aggregated phases, respectively. The inset of part a shows the ratio between the triplet absorptions at 1.23 and 1.49 eV as a function of the temperature.

The different vertical scales in Figure 6a−c reveal that the PIA intensity is reduced by nearly 1 order of magnitude upon going from 270 to 190 K. Apparently, the decrease of PL intensity observed upon aggregation is accompanied by a decrease of triplet formation via intersystem crossing. The decrease in intersystem crossing could be partly ascribed to a reduction of the spin−orbit coupling, which reduces significantly at small inter-ring torsion angles.[27] Although the quenching of PL and triplet formation could be taken as evidence for an increased thermal decay in the nanoaggregates, it is important to recall that PL studies on poly(3-alkylthiophenes) have shown that the nonradiative lifetime (i.e. the combination of thermal decay and intersystem crossing) is only weakly dependent on the aggregation.[22] On the basis of these results, it is possible to argue that the decrease of intersystem crossing is compensated by an increase of thermal decay in the aggregates compared to isolated molecules.

Similar results were obtained for G3-T17-G3 in dichloromethane (Figure 7). Here, the typical triplet absorptions for both phases appear at slightly lower energies compared to G3-T11-G3 as a consequence of the longer effective conjugation length. For G3-T17-G3, the $T_n \leftarrow T_1$ absorptions interconvert from 1.49 eV for the molecularly dissolved phase to 1.23 eV for the aggregated phase.

The maximum bleaching at 290 K occurs at 2.36 eV, i.e., shifted by about 0.10 eV compared to the value of 2.46 eV in the absorption spectrum of dissolved molecules. At 200 K, the bleaching consists of a single sharp peak located at the position of the first (0−0) vibronic transition of the aggregate absorption (see Figure 1), which suggests that the excitations migrate to the most ordered domains in the aggregates (Figure 7).

By varying the modulation frequency (ω) in the PIA experiment and recording the change in transmission ($-\Delta T$) at the position of the $T_n \leftarrow T_1$ transition, it is possible to determine the lifetime of the triplet state (τ_m) by fitting the data to an analytical expression for monomolecular decay.[28]

(26) Beljonne, D.; Cornil, J.; Friend, R. H.; Janssen, R. A. J.; Brédas, J.-L. *J. Am. Chem. Soc.* **1996**, 118, 6453.

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(28) Dellepiane, G.; Cuniberti, C.; Comoretto, D.; Musso, G. F.; Figari, G.; Piaggi, A.; Borghesi, A. *Phys. Rev. B* **1993**, 48, 7850.
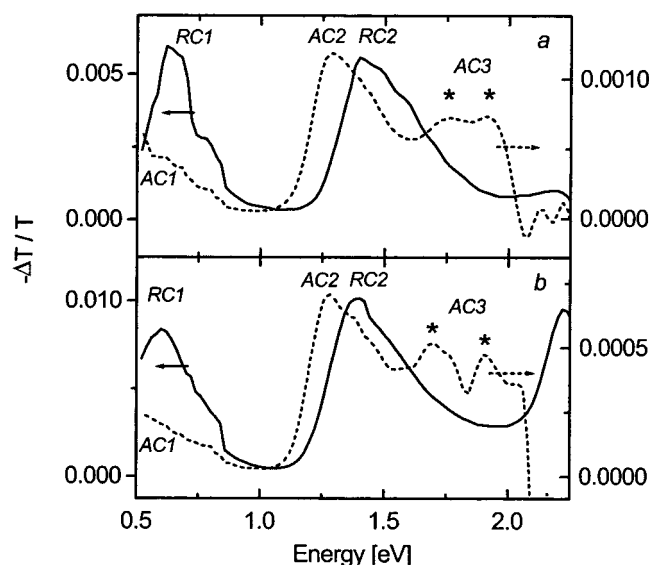
Figure 8. PIA of the radical cations of G3-T11-G3 (a) and G3-T17-G3 (b) generated in the presence of TCNE. The solid lines (left axes) show the radical cation absorption spectra at temperatures where the molecules are molecularly dissolved (290 K) and the dashed lines (right axes) show the low-temperature spectra where the molecules are aggregated (200 K). *RC1, RC2, AC1, AC2, AC3*, and *AC3*' denote specific transitions as indicated in Figure 9. The RC (Radical Cation) transitions are associated with a charge confined to a single chain, whereas the AC (Aggregate Cation) transitions relate to a single charge delocalized over more chains.

$$-\Delta T = \frac{Ig\tau_m}{\sqrt{1 + \omega^2\tau_m^2}} \tag{1}$$

In (1), I is the intensity of the pump beam and g the efficiency of generating the photoinduced species. The frequency-dependent changes of $-\Delta T$ reveal that the photoinduced triplet states have lifetimes on the order of 0.10 ms for a molecularly dissolved oligothiophene and about 0.20 ms for an interchain delocalized triplet state in a nanoaggregate. The slight increase of the triplet-state lifetime in the nanoaggregate compared to the molecularly dissolved state confirms that intra-aggregate self-quenching is not the primary cause for the decrease in the formation of triplet states.

Charged States in Nanoaggregates. Radical cations of oligothiophenes in solution are readily formed via photoexcitation in the presence of an external electron acceptor such as tetracyanoethylene (TCNE).[29] In this reaction the photoexcited S_1 state of the oligothiophene is transformed into a triplet T_1 state via intersystem crossing, which is subsequently oxidized by TCNE via an intermolecular electron transfer reaction to generate the radical cation of the oligothiophene and the TCNE radical anion (Figure 5). Because the electron transfer occurs intermolecularly and the generated radical ions can diffuse freely in solution, the charge-separated state has a long lifetime before the radical ions eventually recombine to the neutral species. The photoinduced absorption spectra of the charged states of G3-T11-G3 (Figure 8a) and G3-T17-G3 (Figure 8b) recorded at 290 and 200 K in the presence of TCNE show that this process is effective for both molecularly dissolved and aggregated oligothiophenes. The solid lines in Figure 8 (left axes) show the radical cation absorptions at 290 K, where the molecules

(29) (a) Scaiano, J. C.; Evans, C.; Arnason, J. T. *J. Photochem. Photobiol. B* **1989**, *3*, 411. (b) Wintgens, V.; Valat, P.; Garnier, F. *J. Chem. Phys.* **1994**, *98*, 228. (c) Janssen, R. A. J.; Moses, D.; Sariciftci, N. S. *J. Chem. Phys.* **1994**, *101*, 9519.
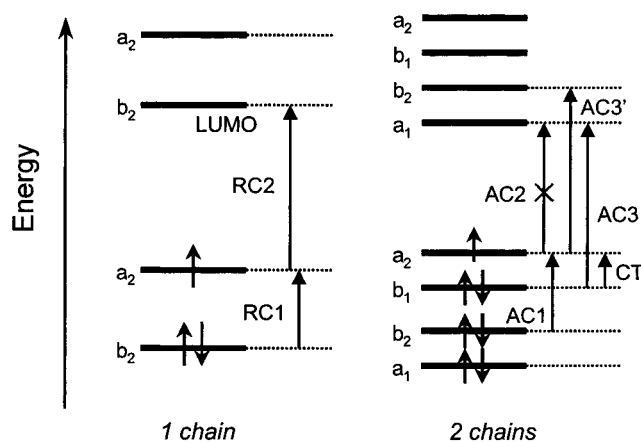

Figure 9. Schematic molecular orbital diagram and symmetry labels of an odd numbered oligothiophene radical cation, localized on a single chain (left) and delocalized over two cofacial chains (right). The principal optical transitions are shown as RC1, RC2, AC1, AC2, AC3, and AC3'.
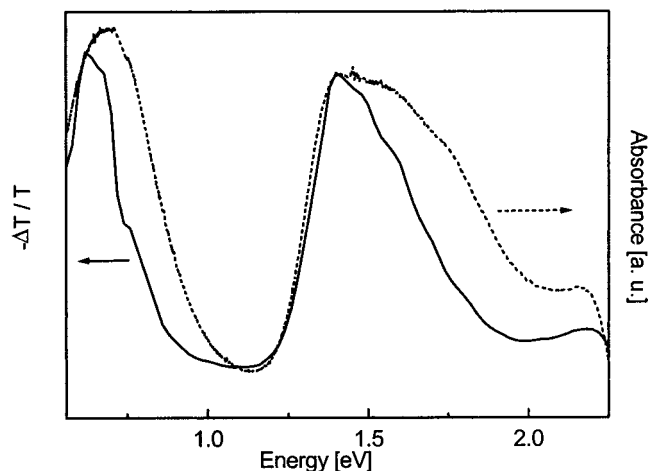

Figure 10. Comparison of the PIA spectrum of G3-T11-G3 radical cations photogenerated in dichloromethane in the presence of TCNE (solid line; left axis) and the formation of radical cations via chemical doping with thianthrenium perchlorate in solution at very low doping levels (~1%) (dashed line; right axis).

are molecularly dissolved, and the dashed lines (right axes) show the spectra at 200 K where the molecules are aggregated.

When the excitation takes place on free chains at 290 K, we find photoinduced absorptions at 0.63 (*RC1*) (*RC* symbolizes Radical Cation) and 1.41 eV (*RC2*) for G3-T11-G3 and at 0.61 (*RC1*) and 1.40 eV (*RC2*) for G3-T17-G3. The *RC1* band is assigned to a transition from the highest doubly occupied level to the singly occupied electronic (polaron) level, while the *RC2* band is assigned to a transition from the singly occupied level to the lowest unoccupied electronic level (Figure 9).[30] Figure 10 illustrates that the absorption spectra of G3-T11-G3 radical cations in solution, obtained by either photoexcitation in the presence of TCNE as electron acceptor or chemical oxidation with thianthrenium perchlorate, are essentially the same and confirm the assignment.[19] Although the onsets of the transitions are very similar in both cases, it can be seen in Figure 10 that the transitions obtained by chemical oxidation are broader. Upon going to higher levels of chemical oxidation, significant shifts to higher energies take place for the *RC1* and *RC2* transitions, being the most distinct for G3-T17-G3. Moreover the width and

(30) Van Haare, J. A. E. H.; Havinga, E. E.; Van Dongen, J. L. J.; Janssen, R. A. J.; Cornil, J.; Bredas, J.-L. *Chem. Eur. J.* **1998**, *4*, 1509.
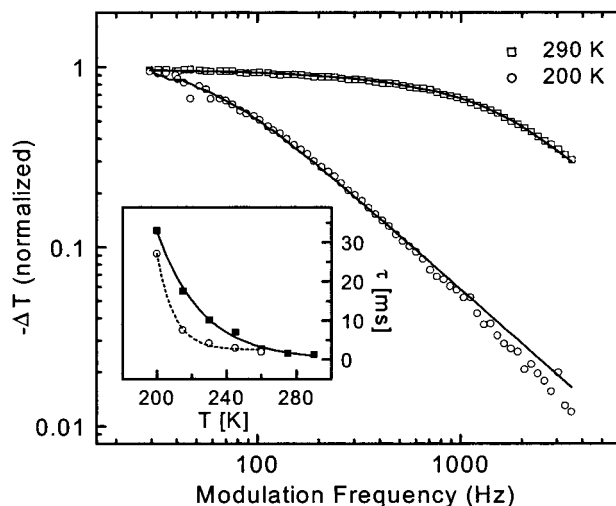
Figure 11. Modulation frequency dependence of the normalized change in transmission at 0.65 eV of the charged state of G3-T17-G3 at 290 K (open squares) and 200 K (open circles). The inset shows the lifetime of radical cations of G3-T11-G3 (open circles) and G3-T17-G3 (solid squares) as a function of temperature.

the shift of the *RC1* and *RC2* transitions show pronounced concentration dependence and are currently under investigation.

When charged oligothiophenes are formed in an aggregated phase at 200 K, the PIA spectrum of the radical cations differs drastically (Figure 8, dashed lines). The initial *RC2* transition has been replaced by a new band, *AC2* (*AC* symbolizes Aggregate Cation), which is red shifted by about 0.12 eV to 1.29 eV for G3-T11-G3 and to 1.28 eV for G3-T17-G3. The *RC1* transition, which was observed for dissolved molecules, apparently has lost a significant part of its intensity, but most likely the *AC1* band, for the aggregated phase, has red-shifted to a position below 0.5 eV, outside our detection range. The red shift of the spectrum is similar to the observed red shifts in the UV/vis absorption, fluorescence, and triplet absorption spectra. Again, the red shift of *AC2* does not occur gradually, but an interconversion between *RC2* and *AC2* takes place in a limited temperature region. Interestingly, additional transitions (marked with an asterisk in Figure 8) at higher energy appear in the spectrum at the onset of aggregation. For G3-T11-G3, these new bands are found at 1.77 and 1.92 eV and for G3-T17-G3 at 1.69 (with a shoulder at 1.75 eV) and 1.91 eV. The possible nature of these new transitions will be discussed in detail below.

The frequency dependence of the normalized photoinduced change in transmission ($-\Delta T$) at 0.65 eV for G3-T17-G3 at 290 (*RC1* open squares) and 200 K (*AC1*, open circles) provides insight into the lifetime of the intermolecular charge-separated state formed by photoexcitation of G3-T17-G3 in the presence of TCNE (Figure 11). At 290 K, where dissolved molecules are excited, $-\Delta T$ changes just half an order of magnitude over the frequency range studied. In contrast, at 200 K, where molecules in an aggregate are excited, $-\Delta T$ decreases by 2 orders of magnitude in the same frequency range. This denotes a significantly longer lifetime of the charge-separated state under these conditions. The charge-separated state decays to the ground state via recombination of the positive charge on molecularly dissolved or aggregated oligothiophene radical cations and the negative charge of the TCNE radical anions. This is a bimolecular recombination reaction and the associated lifetime (τ_b) of the charge-separated states can be obtained from fitting the changes in transmission ($-\Delta T$) at the radical cation bands as a

function of the modulation frequency (2ω) to the expression derived for bimolecular decay:[28]

$$-\Delta T = \sqrt{Ig/\beta}\left(\frac{\alpha \tanh \alpha}{\alpha + \tanh \alpha}\right) \qquad (2)$$

Here, β is the bimolecular decay constant, while $\alpha = \pi/(\omega\tau_b)$, with $\tau_b = (gI\beta)^{-0.5}$ the bimolecular lifetime under steady-state conditions. It is important to note that τ_b depends on the experimental conditions such as concentration and pump-beam intensity.

The lifetime of the photogenerated radical cations of G3-T11-G3 (Figure 11, open circles) and G3-T17-G3 (Figure 11, solid squares), determined using eq 2, increases exponentially from 1 to 2 ms at temperatures where the oligothiophenes are in a molecularly dissolved phase to about 30 ms at temperatures where the molecules are completely aggregated. Hence, the recombination rate is significantly reduced at lower temperatures. The observed decrease of PIA intensity with decreasing temperature (Figure 8) is in part due to the modulation frequency of 275 Hz at which the spectra were recorded (causing overmodulation), and in part due to the reduced formation of the triplet state, which is the precursor to the charged state.

Discussion

The thermochromic changes in the triplet spectra of G3-T11-G3 (Figure 6) and G3-T17-G3 (Figure 7) show that interchain interactions in aggregates not only cause significant changes in the absorption and fluorescence spectra but also affect the excitations in the triplet manifold. In a preliminary account on the thermochromic changes of the triplet excited state of poly-(3-octylthiophene) in 2-methyltetrahydrofuran solution, we previously reported a shift of the $T_n \leftarrow T_1$ transition from 1.50 eV for free chains at 295 K to 1.25 eV for aggregated chains at 190 K, similar to changes observed here.[31] The origin of these spectral changes can now be unambiguously attributed to interchain interactions that occur in the aggregates, but the extent of the interchain delocalization of the T_1 state or the higher-lying triplet states that are involved from these interactions is not directly revealed by these experiments.

The changes in the optical signatures of the charged states upon aggregation are similar to recent experiments on charge carriers in thin films of regioregularly substituted poly(3-hexylthiophene) exhibiting high charge carrier mobilities.[15] Regioregular poly(3-hexylthiophene) self-organizes via interchain stacking in a lamella layer structure with two-dimensional conjugated sheets. Optical charge modulation spectroscopy was used to demonstrate that polaronic charge carriers of poly(3-hexylthiophene) possess a two-dimensional interchain character and exhibit lower relaxation energies than the corresponding radical cations on isolated one-dimensional chains.[15] The two-dimensionally extended polarons in poly(3-hexylthiophene) are characterized by a strong transition just below the optical band gap at a position similar to the *AC3* and *AC3′* transitions observed here for charged aggregates of G3-T11-G3 and G3-T17-G3 (Figure 8).[15,16] On the basis of these similarities, we consider that the wave functions of positive charges in nano-aggregates of G3-T11-G3 and G3-T17-G3 are spread over several chains. The appearance of new optical signatures upon aggregation is corroborated by theoretical calculations, which suggest that new transitions with energies located above *RC2* of the isolated radical cations appear in the presence of interchain

(31) Christiaans, M. P. T.; Langeveld-Voss; B. M. W.; Janssen, R. A. J. *Synth. Met.* **1999**, *101*, 177.

interactions.[32] Recent quantum chemical calculations on the optical signatures of a polaron in a two-chain aggregate of a five-ring oligomer of poly(*p*-phenylene vinylene) confirm these spectral changes.[33] For this aggregate cation (*AC*) with a symmetric cofacial arrangement of chains, both INDO/SDCI and AM1/FC1 quantum chemical calculations reveal that the molecular orbitals are completely delocalized over two conjugated chains, which consequently carry half a unitary charge each. In the dimer configuration the *AC1* transition shifts 0.1−0.2 eV to lower energy (relative to *RC1* for the single molecule), and the *AC2* transition becomes symmetry-forbidden, while a weak charge transfer (*CT*) transition polarized along the packing axis appears in the infrared region (Figure 9).[33] At the same time, the *AC3* and *AC3'* electronic transitions undergo configurational mixing, providing two new transitions of which the higher energy transition is more intense.[33]

These calculations and an analysis of the optical excitations using group theory can be used to interpret the PIA spectra of charged oligothiophene nanoaggregates. In an all-transoid conformation, the long oligothiophenes and a cofacial dimer thereof have C_{2v} symmetry. In the single chain oligomer, the π molecular orbitals therefore possess a_2 and b_2 symmetry and transitions between these molecular orbitals are symmetry-allowed and polarized along the long axis (*x*-axis) of the single chain oligomer. In a cofacial dimer cation, dimer molecular orbitals will form with symmetries as depicted in Figure 9. In the dimer four polaronic levels can be distinguished within the HOMO-LUMO gap (1 doubly occupied, 1 singly occupied, 2 empty). The *AC3* and *AC3'* transitions, which occur among the four polaronic levels of the cofacial dimer, are dipole-allowed and polarized along the long *x*-axis. We assign the new bands observed in Figure 8 (labeled with an asterisk) to states involving these transitions. The same symmetry analysis reveals that the *AC1* transition remains allowed in the cofacial dimer cation. The observed shift of *AC1* to lower energy upon aggregation (Figure 8) is supported by the theoretical calculations.[33] A decrease of *AC2* intensity, which becomes symmetry-forbidden in the dimer cation, however, is not observed experimentally (Figure 8). The same feature was found to remain present in optically excited poly(3-hexylthiophene) films where similar 2D charged excitations were identified.[15] In the present case, this deviation may arise from the fact that the aggregation phenomena in solution result in a more dynamic interaction. Additionally, it can be expected that the actual alignment of G3-T11-G3 and G3-T17-G3 molecules differs from that of a fully symmetric cofacial dimer, which could affect the selection rules for the optical transitions.

Conclusions

Variable-temperature UV/vis absorption spectroscopy has been used to show that G3-T11-G3 and G3-T17-G3 organize into nanoscale aggregates upon cooling in dilute solution. The absorption spectra of both molecularly dissolved and aggregated phases interconvert reversibly with stepwise changes in temperature, instead of shifting gradually. The transition is concentration dependent and occurs in a rather narrow temperature range (about 30 K), where molecularly dissolved and aggregated chains coexist. The well-defined nature of the nanoaggregates of these oligomers was confirmed by TEM.

The presence of two interconverting phases of G3-T11-G3 and G3-T17-G3 in dichloromethane solutions is also reflected by marked differences in the optical signatures of PL and of long-lived photoexcitations recorded using PIA spectroscopy. The emission of the nanoaggregates is shifted to lower energies and exhibits increased vibronic resolution. Likewise, the triplet and radical cation absorption spectra of the nanoaggregates are also bathochromically shifted compared to those of isolated molecules. The shift to lower energy is interpreted as a result of extended delocalization of the excited states in the aggregates. In addition, new high-energy bands appear in the charged aggregate PIA spectra. We propose that these new bands arise from transitions among the polaronic levels, which become allowed in the presence of interchain interactions, similar to results recently obtained for thin films of poly(3-hexylthiophene) and supported by quantum chemical calculations.[15,32,33] The new transitions are clear signatures of charged, interchain delocalized states.

With these experiments we have extended thermochromism in conjugated systems to triplet and charged photoexcitations. We conclude that in well-defined nanoaggregates composed of a limited number of G3-T11-G3 or G3-T17-G3 molecules, a favorable interchain alignment of molecules gives rise to an interchain delocalization of the photoexcited singlet, triplet, and charged states. On the basis of the present results we feel that interesting novel properties may arise when full control over the magnitude of interchain interactions and the size of nanoassemblies can be obtained. The latter can be obtained by carefully engineering the molecular building blocks, i.e. length of the conjugated core and/or the size of the dendrons.

Experimental Section

The synthesis of G3-T11-G3 and G3-T17-G3 has been described in detail elsewhere.[18,19] Dichloromethane was dried and distilled under nitrogen atmosphere and deoxygenated by multiple freeze−pump−thaw cycles before being stored an inert N_2 atmosphere glovebox (<5 ppm H_2O and <5 ppm O_2). UV/vis/near-IR spectra were recorded using a Perkin-Elmer Lambda 900 spectrometer equipped with an Oxford Optistat CF cryostat for variable-temperature experiments and 10 mm or 1 mm near-IR grade suprasil quartz cells. Temperature was kept constant within ±0.3 K. For the temperature-dependent optical absorption experiments the concentration was in the range of 10^{-6} to 10^{-4} M.

Photoluminescence spectra were recorded on a SPEX spectrometer, using a 3 nm bandwidth and optical densities of the solutions of ∼0.1 at the excitation wavelength and an Oxford Optistat DN cryostat for variable-temperature experiments.

Photoinduced absorption (PIA) spectra were recorded between 0.5 and 2.5 eV by exciting with a mechanically modulated continuous wave Ar-ion laser pump beam (488 nm, 25 mW, diameter 2 mm) and monitoring the resulting change in transmission (ΔT) of a tungsten−halogen probe light focused on the sample with a phase-sensitive lock-in amplifier after dispersion by a triple-grating monochromator and detection using Si, InGaAs, and (cooled) InSb detectors. The photoinduced absorption $-\Delta T/T$ is directly calculated from the change in transmission after correction for photoluminescence, which is recorded in a separate experiment. The PIA spectra were recorded with the pump beam in an almost parallel direction to the probe beam. Samples for PIA were prepared in sealed cells in a glovebox (<5 ppm H_2O and <5 ppm O_2) using deoxygenated dichloromethane. The samples were studied at different temperatures, using an Oxford Optistat CF cryostat. Generally, the concentrations used for PIA are on the order of 10^{-5} M. For the measurements in the presence of TCNE, the molar TCNE concentration is 10 times higher than that of the π-conjugated oligomer.

Transmission Electron Microscopy of unstained samples was performed using a JEOL 100 CX operated at 80 kV. A droplet of a 1 mg/mL dichloromethane solution of G3-T17-G3 at 0 °C was placed on a Cu-grid (200 mesh, carbon covered) followed by immediate drainage.

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