Tunable Aggregation and Luminescence of Bis(diarylethene)sexithiophenes

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Diarylethenes with two different side groups (phenyl and chloro) were appended to both α-ends of a sexithiophene unit. The temperature dependent aggregation properties for both compounds were characterized by steady state and transient absorption spectroscopy. The peripheral side groups show an unexpectedly significant influence on the electronic properties of the sexithiophene core. Furthermore, the relative influence of the phenyl and chloro substituents on the aggregation behavior observed is remarkable. The phenyl compound exhibits formation of H-aggregates over a narrow temperature range, between 240 and 200 K, typical of strong intermolecular interactions. In contrast, the chloro compound shows gradual aggregation over a wide temperature range, forming H-aggregates albeit with weaker intermolecular interactions. The results demonstrate that minor changes in the structure lead to tunability of the aggregation and corresponding luminescence properties of sexithiophenes in solution and hold particular relevance to supramolecular and polymer systems based on sexithiophene units.

Introduction

Since the discovery of conducting polymers by Heeger and MacDiarmid in the late 1970s, π-conjugated systems have seen increasing application in areas as diverse as supramolecular chemistry and organic electronics in FETs, OLEDs, molecular wires, photovoltaic cells and electrochromic materials. Oligothiophenes in particular show remarkable optical and electronic properties. Their widespread use is due to their stability toward molecular oxygen and water. From a supramolecular perspective, oligothiophenes are especially attractive as components in molecular devices where they can act as bridging units, i.e., molecular wires, between functional units, as well as active components in their own right. The distinct advantage that oligothiophenes provide over their polymeric analogues is their precisely defined structure. Furthermore, in contrast to conventional semiconducting materials, subtle structural changes can yield dramatic effects in conductivity and luminescence properties. Whereas in polythiophene the material properties are affected by kinks and bends in their structures, oligothiophenes can form rigid, well-ordered structures more easily. The type of order determines the luminescence and electronic properties of oligothiophenes, providing the tunability required for application in optoelectronic devices.

A wide range of substituted oligothiophenes have been reported in solution, as well as in thin films and single crystals, with sexithiophene-based systems receiving the most attention. The properties of oligothiophenes can be tuned via synthetic modification and processing. The impact of strong intermolecular interactions between oligothiophenes on solubility typically requires that long alkyl side chains are employed to improve solubility and/or control aggregation. However, while such an approach improves solubility and processability, the steric interactions introduced by the alkyl side chains at the β positions impact on the photophysical and electronic properties in comparison to nonsubstituted oligothiophenes. An alternative approach is to modify oligothiophenes by end-capping the α,α-positions with functional groups, for instance, to control aggregation. This approach limits the steric hindrance and therefore the effects of functionalization on electronic and spectroscopic properties. A further extension is the introduction of added functionality such as photochromism to change the conjugation path length of oligothiophenes.

Recently, we have reported the synthesis and photochemical and electrochemical properties of two α,α-sexithiophene compounds 1 and 2 (Figure 1). These molecules incorporate two photoresponsive units in the form of photoswitchable dithienylhexafluorocyclopentenes. These molecular photochromic switching units have proven their versatility in optoelectronic memory and display devices due to their fatigue resistance and thermal stability. Surprisingly, despite the fact that the...
n-Hexane, cyclohexane, isopentane (mp 113 K), and ethanol/methanol (4:1, \( T_g \) 115–125 K) were of spectroscopic grade or better and used as received. Hexane was used in room temperature steady state absorption spectra, cyclohexane was employed in the room temperature time-resolved measurements, and isopentane and ethanol/methanol were used in temperature dependent measurements. The synthesis and characterization of compounds 1o and 2o are reported elsewhere.31 UV/vis spectra were recorded using a HP8453 diode array spectrophotometer or a JASCO V570 UV/vis-NIR spectrophotometer equipped with an integrating sphere for solid state measurements (JASCO-ISN470). Thin films, for solid state absorption spectra, were obtained by drop casting a dichloromethane solution of the compounds onto a glass slide. Fluorescence spectra were recorded on a JobinYvon Fluorolog MAX or a JASCO 7200 fluorometer. An Oxford Instruments OptistatDN was used for temperature dependent measurements. For the decomposition of the spectra into Gaussian bands, the nanometer scale was changed to reciprocal centimeters and the intensities of the spectra were corrected according to \( \nu = I(\lambda) \times \lambda^{-2} \).37 Fluorescence lifetime measurements were obtained using an Edinburgh Instruments F900n single photon counting instrument as described elsewhere.38

Time-resolved transient absorption spectroscopy was performed using an amplified Ti:Sapphire system (Clark CPA-2001) producing pulses at a 1 kHz rate. Part of the output was directed into a noncollinear optical parametric amplifier (NOPA) to generate near transform-limited pulses centered at 475 nm with a bandwidth of \( \sim 30 \text{ nm} \). For compound 2o the output of the amplified Ti:sapphire was frequency doubled to 388 nm. These pump pulses were used to excite the sample. Broadband probe pulses (450–750 nm) were obtained from a white light continuum (WLC) by focusing part of the output of the CPA into a 2 mm sapphire crystal. After passing through the sample, the WLC probe was directed into a spectrum analyzer (\( \sim 1 \text{ nm resolution} \) working at a 1 kHz detection rate and locked to the laser system. This fast detection system allowed for monitoring of the transient absorption signal on a shot-to-shot basis. Every other pump pulse was blocked by a chopper, providing a pump and/or probe pulses the pump induced changes in the absorption of the probe are detected as \( \Delta \text{OD} = -\log(I_{\text{pump off}}/I_{\text{pump on}}) \). The time resolution in the transient absorption measurements was...
The system response was linear (15 ps limited to a maximum of 100 nJ for most measurements. The excitation energy was cooled to 150 and 125 K for measurements in ethanol/isopentane, respectively. The excitation energy was limited to a maximum of 100 nJ for most measurements. The system response was linear (15–20% of the molecules are excited at an excitation power of 200 nJ) up to an excitation power of 100 μW (200 nJ per pulse). Kinetics obtained at 30 and 100 μW could be fitted with identical time constants.

Results and Discussion

Steady State Absorption Spectroscopy. The steady state absorption spectrum of I0 in solution and in the solid state as a powder and as a drop cast film at room temperature are shown in Figure 2a. In solution, the absorption spectrum consists of two absorption bands showing little structure. The solid state diffuse reflectance spectrum of a powdered solid sample is red-shifted and significantly more structured than the absorption spectrum in solution, suggesting partial ordering in the solid state. The absorption spectrum of a thin film of I0 is comparable to that of the diffuse reflectance spectrum of the powdered solid. The spectral features in the solid state can be assigned to a vibronic progression as observed in other sexithiophene based systems at room and low temperature. However, it is probable that in the solid state, either as a powder or a drop cast film, there will be a mixture of amorphous and microcrystalline material, the former reducing the resolution of the vibronic progression.

The temperature dependence of the absorption spectrum of I0 in isopentane is shown in Figure 2b. The shape of the absorption spectrum is strongly temperature dependent; the absorption band undergoes a bathochromic shift of ~20 nm and shows resolved spectral features below 220 K. At 120 K, the main absorption band in the visible region, λ_max at ~430–440 nm, shows significant structure. The structure is similar, although considerably more pronounced compared to that observed in the (solid state) absorption and diffuse reflectance spectra.

Furthermore, the better resolution of the vibrational progression, in the absorption spectra of a solution at 120 K, compared with the solid state spectra suggest that the sample is aggregated with a greater degree of intermolecular order. The change in the visible spectrum from a broad unstructured absorption to a red-shifted structured spectrum occurs over a relatively narrow temperature range (180–220 K), well above the onset of the glass transition temperature of the solvent (~115 K) and is independent of concentration between 10^-6 and 10^-4 M (Figure 3 and Figure S2, Supporting Information).

Compound I0 is strongly emissive in solution at room temperature (Φ_fl = 0.2) and the fluorescence spectrum shows a vibrational progression typical of sexithiophenes (Figure 4). The symmetry between the featureless absorption and structured fluorescence spectra for oligothiophenes in solution has been noted previously. The fluorescence spectrum is decomposed into three bands centered at 17,570, 18,690, and 19,980 cm^-1, corresponding to a vibrational progression of ~1100–1200 cm^-1. Comparison with the Raman and IR spectra of I0 indicates that the progression is coupled primarily to a C–C stretching vibration of the thiophene and that the emission originates from the sexithiophene unit. The Stokes shift in hexane is determined, by comparison of the origins of the deconvoluted absorption and fluorescence spectra (21,570 and...
The X-ray single crystal diffraction structure of crystals of 1o (grown from dichloromethane solution) was reported earlier. The molecules are stacked with their long axis parallel making an angle to the horizontal (so-called herringbone structure). Molecules of 1o stack together with an offset of one thiophene ring between the layers; i.e., the first thiophene of layer A lies below the second thiophene of layer B. This specific stacking of chromophores with their transition moments lying along their long axes, parallel to one another, is described as an H-aggregate. In this type of aggregate the transition from the lowest exciton state to the ground state is optically forbidden due to symmetry selection rules. Relaxation therefore occurs mainly via nonradiative processes resulting in a lower fluorescence quantum yield than observed in solution. Intermolecular interactions between the closely spaced molecules in these aggregates will cause splitting of the molecular energy levels into a series of exciton states.

Between 250 and 300 K, the fluorescence of 1o is essentially temperature independent, but the fluorescence spectrum changes considerably between 200 and 250 K. Below 180 K the fluorescence is weak (~1% of the intensity observed at 298 K) and has a distinctly different band shape (Figures 3 and 4). As with the temperature dependence of the absorption spectrum, this effect is still observed after a 30-fold decrease in concentration. The fluorescence spectrum obtained at 120 K is a sum of three bands centered at 19 980 cm\(^{-1}\), 24 670, 27 640, and 30 780 cm\(^{-1}\). This value is less than the typical Stokes shift observed for unsubstituted oligothiophenes of 3000–3500 cm\(^{-1}\). In the solid state, either as a powder or a drop cast film, 1o is essentially nonfluorescent (i.e., the intensity is of the same order of magnitude as the Raman scattering from the sample), in stark contrast to 1o in solution.

At 120 K the fluorescence of 2o is weaker than that of 1o, which is consistent with the 0–0 transition being blue-shifted to a lower energy in 2o. However, 2o shows a gradual red shift and increase in intensity with decreasing temperature and the distinct phase transition observed for 1o is absent. The fluorescence of 2o is less structured than that of 1o. Nevertheless, the fluorescence spectrum can be decomposed into three bands centered at 18 800, 20 415, and 27 840 cm\(^{-1}\). These results would predict a difference in the photoexcited state dynamics at low (125 K) and high (298 K) temperatures. To further elucidate the nature of these systems, their ultrafast dynamics were measured under

Comparison between the Steady State Spectroscopy of 1o and 2o. As for 1o, the lowest energy absorption band of 2o at room temperature is decomposed into three bands, centered at 24 670, 27 640, and 30 780 cm\(^{-1}\). However, the most noticeable difference in the effects of the peripheral chloro and phenyl groups is already visible in the absorption spectra; for 2o, the spectra are blue-shifted compared to 1o (see Figure 5 for comparison, and Supporting Information for a complete set of spectra of 2o). This implies that although the end groups are connected to the sexithiophene unit via an electron deficient alkene bond (by virtue of the electron withdrawing properties of the perfluorocyclopentene), electronic communication is not precluded. The temperature dependence of the integrated absorption spectrum of 2o shows a gradual red shift and increase in intensity with decreasing temperature and the distinct phase transition observed for 1o is absent.

The fluorescence of 2o is less structured than that of 1o. Nevertheless, the fluorescence spectrum can be decomposed into three bands centered at 18 800, 19 040, and 20 415 cm\(^{-1}\), respectively. Again an abrupt temperature dependent phase transition in the fluorescence spectra is absent.

It is apparent that the phenyl substituent plays a key role in driving specific intermolecular interactions. Comparison with 2o shows that aggregation occurs to a lesser extent, i.e., the intermolecular interactions are less strong, or that aggregates, different from those of 1o, are formed. Hence minor changes to the peripheral groups affect aggregation behavior and consequently the temperature dependence of the luminescence properties can be tuned.

Transient Absorption Spectroscopy. Steady state spectroscopy indicated formation of H-aggregates at lower temperatures for 1o, and to a lesser extent for 2o. These results would predict a difference in the photoexcited state dynamics at low (125 K) and high (298 K) temperatures. To further elucidate the nature of these systems, their ultrafast dynamics were measured under
a range of conditions. Transient absorption spectroscopy can provide deeper insight into the effect of the peripheral phenyl and chloro groups on aggregate formation. The steady state spectra assist in the assignment of features in the transient absorption spectra. The steady state spectra show a similar red shift in the SE signal with maxima at 700 nm. Hence the positive signal in the transient spectra is comparable with that observed at 298 K (Figure 2) it is apparent that 1o does not show significant absorption at wavelengths >500 nm; hence within the spectral window examined here (480–760 nm) ground state bleaching will not be observed. A structured negative signal (pump-induced transmission increase) is observed between 480 and 650 nm, while between 650 and 760 nm a positive signal (pump-induced absorption) dominates the spectrum. At longer time delays (>1 ns) the main spectral feature is a relatively narrow positive band centered at 700 nm. The negative signal in the transient spectra is comparable with the inverse of the steady state fluorescence spectrum of 1o at room temperature (Figure 4 and gray shading Figure 6a), indicating that the negative transient signal is due to stimulated emission (SE) from the S1 to S0 state. The positive signal between 650 and 760 nm is assigned to excited state absorption (ESA) from S1 to S0, superimposed on a second signal at around 700 nm, the nature of which cannot be assigned directly on the basis of the steady state spectra. The decay over the whole spectral window can be fitted to a biexponential function with time constants of 35 ps (±6 ps) and 550 ps (±60 ps). The first time constant is tentatively assigned to a vibrational cooling process. The second time constant matches the fluorescence lifetime determined by single photon counting (600 ± 30 ps) and is similar to the lifetime of the lowest excited state in unsubstituted T6 in solution (800 ps) and agrees closely with the lifetime of substituted T5 (300 ps). Both SE and ESA regions can be fitted with identical decay constants, indicating that the ESA at ~750 nm is due to the S1 to S0 transition. The signal at 700 nm grows in with a 550 ps time constant, hence the corresponding state must be populated from the S1 state. The lifetime of the state centered at 700 nm is beyond the resolution of the present system (maximum scan range ~6 ns). However, the absence of a depletion at 700 nm prior to the t0 of the pump–probe scan sets an upper limit for the lifetime of this state to be much less than the inverse of the repetition rate of the laser (500 µs). In assigning the transient absorption band at 700 nm, the formation of the monocationic state of the compound (1o+ absorbs at ~750–800 nm) or formation of 1c, which absorbs at 640 nm, can be excluded. The rate of the process is typical of intersystem crossing (ISC) in oligothiophenes from a singlet to a triplet state. The shape of the band compares closely with the T1 to T0 transition in sexithiophene (T6) in dichloromethane at 680 nm. Hence the positive signal in 1o at 700 nm is assigned to the T1 to T0 transition.

The transient spectra of 1o recorded at 125 K are shown in Figure 7. The transient spectra are similar in certain respects to those observed at 298 K; i.e., negative signals are observed in the region 500–700 nm and a positive signal is seen at wavelengths longer than 700 nm. As at 298 K, the ESA at 700–750 nm is again assigned to the S1–S0 transition. However, there are also distinct differences between the spectra at the two temperatures. The steady state absorption spectrum at 125 K is red-shifted compared to that at 298 K. The lowest energy absorption in the steady state absorption spectra of 1o at 125 K is relatively intense at ~505 nm (Figure 2b) and falls within the spectral window examined (500–750 nm). Hence, in contrast to 298 K, a ground state bleaching signal is expected and indeed a negative signal centered at ~515 nm is observed in the transient spectra of 1o at 125 K that is assigned to ground state bleaching of the S0–S1 transition.

The steady state fluorescence spectrum at 125 K is red-shifted compared with that observed at 298 K (Figure 4b). The transient spectra show a similar red shift in the SE signal with maxima
(i.e., at 1 ps after excitation in Figure 7a) at 544 and 588 nm at 298 and 125 K, respectively. Although the vibrational progression at 125 K differs between the transient SE and the steady state fluorescence spectra, the characteristic vibrational substructure remains recognizable (i.e., maxima at 588 and 631 nm for SE and 546, 588, 628, and 667 nm for the steady state fluorescence). The fact that not all the bands visible in the steady state fluorescence spectra are observed in the transient SE spectra can be explained by overlapping signals; i.e., ESA both at the red and the blue side of the SE can distort the shape compared with the steady state fluorescence spectrum.

The decrease in fluorescence intensity at low temperature (vide supra) was attributed to the formation of H-aggregates. Therefore, it is expected that the dynamics, observed at 125 and 298 K are different. The dynamics are considerably faster at 125 K with components of 650 fs ($\pm 170$ fs) and 5.7 ps ($\pm 1.7$ ps), Figure 7b. Additionally longer-lived signals are observed that have a smaller amplitude (by a factor of 4–40) than the fast components. These long-lived signals can be fitted with two components, i.e., 390 ps ($\pm 140$ ps) and a time constant that is beyond the maximum scan range of the system, but with an upper limit of $\approx 500$ $\mu$s. The sharp decrease in the transient signal that is observed especially at 515 nm (Figure 7b) is not assigned to ultrafast kinetics in the system but instead to a coherent artifact. The presence of two distinct species, one in the aggregated state and a small amount as isolated molecules, is based on the assignment of the several decay time constants at 125 K. The latter, as seen at 298 K, give rise to the $\approx 400$ ps and $\approx 500$ $\mu$s decay times. Therefore, the faster time constants are characteristic of the aggregated species with efficient nonradiative deactivation expected due to the intermolecular interactions present. The fastest time constant of 650 fs is assigned to rapid relaxation to the lowest vibrational state in $S_1$. The nature of the state that decays with the 5.7 ps time constant is unclear. Lanzani et al. tentatively attributed a similar picosecond time constant to charge separation. It is perhaps more probable that there are local defects and impurities in the H-aggregates that cause the trapping of the excited excitons after rapid intermolecular energy transfer. Figure 8 shows tentative energy diagrams for the molecules and the aggregates.

Comparison between the Transient Absorption Spectroscopy of 1o and 2o. Table 1 shows the results of the fitting of the transients in 1o and 2o. At room temperature the different bands in the transient spectra agree well with those observed for 1o. As expected, the spectral features mirror the steady state spectra, and therefore, the SE in 2o shows few spectral features (Figure S6, Supporting Information). The three time constants that are needed to fit the transients in 2o are similar and have the same physical origin as those of 1o. The excited state lifetime in 2o is considerably longer than in 1o. A possible explanation is a difference in the destabilization of the planar configuration of the molecules by the substituent. Along these lines, the
are not. As for 125 K are coincidently similar; however, the amplitudes of the data are less clear for 125 K transients appears to be coincident; however, the quality of the data precludes identification of a similar subpicosecond time constant as in 1o. The separate datasets for 1o and 2o at 125 K are of poorer quality, due to the low concentrations achievable in solution. However, it is clear that a short time constant dominates the dynamics. The presence of an 8 ps time constant in both the 298 and the 125 K transients appears to be coincident; however, the quality of the data precludes identification of a similar subpicosecond time constant as in 1o.

The results from steady state spectroscopy could not discriminate between the formation of aggregates showing smaller intermolecular interactions or different types of aggregates in 1o and 2o. The decrease in fluorescence intensity in 2o indicated the formation of H-aggregates. Moreover, no additional spectral features typical for different arrangements such as J-aggregates, superradiance, and a narrow J-aggregate peak, were observed. However, the time-resolved data provide a definite answer. While for 1o the temperature dependence of the transient absorption decay time constants is indicative of aggregation, the data are less clear for 2o. The decay time constants at 298 and 125 K are coincidently similar; however, the amplitudes are not. As for 1o, the amplitude of the fast component at 125 K in 2o exceeds the amplitude of the long component. On the basis of this similarity, we conclude that H-aggregates are formed by both compounds. Nevertheless, the intermolecular interactions are stronger for 1o, indicating that the phenyl group in 1o contributes considerably to the intermolecular interactions by additional π–π interactions.

Conclusion

We have studied two α-substituted sexithiophene compounds with two peripheral side groups (i.e., phenyl and chloro) in solution under several different conditions by steady state and time-resolved spectroscopies. The absorption, fluorescence, and transient spectra of 1o and their respective temperature dependence manifest the formation of aggregates upon decreasing temperature. While at 298 K the system consists of isolated molecules, below 180 K specific intermolecular interactions drive the system to form H-aggregates. Likewise, H-aggregates have also been observed in solid state samples of 1o as revealed by absorption and X-ray spectroscopy. Analogue measurements of 2o indicate a markedly different aggregation behavior; quenching of the fluorescence was not complete and occurred gradually over the whole temperature range. The transient spectral data for 1o and 2o at 125 K provides strong evidence that both compounds form H-aggregates. Nevertheless, the interactions between the molecules of 2o are weaker and lack the potential for π–π stacking of the peripheral phenyl rings of 1o. This result leads to the conclusion that there is a pronounced effect of the peripheral substituent (i.e., phenyl vs chloro) on both the electronic and aggregative properties of these systems. The hexafluorocyclopentene groups facilitate communication between the sexithiophene and the chloro and phenyl-substituted monothiophene unit. These results demonstrate that well-structured intermolecular aggregation can be achieved in the absence of more traditional functional units such as amides and ureas. Furthermore, these data provide an understanding of the electronic properties of these compounds essential to their application in multicompartment molecular systems.

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**TABLE 1: Transient Absorption Kinetics from Exponential Fits for 1o and 2o**

<table>
<thead>
<tr>
<th>T (K)</th>
<th>decay constant (ps)</th>
<th>T (K)</th>
<th>decay constant (ps)</th>
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<tbody>
<tr>
<td>1o 298</td>
<td>35 60</td>
<td>2o 298</td>
<td>8.3 1.3</td>
</tr>
<tr>
<td>&lt;500 µs</td>
<td>6 ps</td>
<td>&lt;500 µs</td>
<td>3.2 ps</td>
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<tr>
<td>1o 125</td>
<td>650 5.7</td>
<td>2o 125</td>
<td>8.6 1.5</td>
</tr>
<tr>
<td>390 ps</td>
<td>170 fs</td>
<td>390 ps</td>
<td>1.7 ps</td>
</tr>
<tr>
<td>&lt;500 µs</td>
<td>140 ps</td>
<td>&lt;500 µs</td>
<td>0.3 ns</td>
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</tbody>
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The uncertainties in the decay constants are determined by fitting ~20 transients per experiment. The standard deviation of the fits was taken as the uncertainty.
Supporting Information Available: Temperature dependent absorption and fluorescence spectra of 1o and 2o. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes
