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Citation: The Journal of Chemical Physics 144, 074904 (2016); doi: 10.1063/1.4941700
View online: http://dx.doi.org/10.1063/1.4941700
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/144/7?ver=pdfcov
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The effect of intermolecular interaction on excited states in p-DTS(FBTTH)₂

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(Received 26 November 2015; accepted 28 January 2016; published online 18 February 2016)

Using optical spectroscopy in solution and thin film, and supported by quantum chemical calculations, we investigated the aggregation process of the donor-acceptor type molecule p-DTS(FBTTH)₂. We demonstrate that cooling a solution induces a disorder-order phase transition that proceeds in three stages analogous to the steps observed in semi-rigid conjugated polymers. By analyzing the spectra, we are able to identify the spectral signature of monomer and aggregate in absorption and emission. From this we find that in films, the fraction of aggregates is near 100% which is in contrast to films made from semi-rigid conjugated polymers. © 2016 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4941700]

INTRODUCTION

During the last two decades, organic bulk heterojunction (BHJ) solar cells have mostly been made using a conjugated polymer as electron donor and a fullerene derivative as electron acceptor material, as these components are well soluble, blend well, and form smooth films with suitable morphologies.¹ In the last few years, highly efficient organic BHJ solar cells have also been prepared which use soluble small molecules as the semiconducting donor component.²–⁹ Power conversion efficiencies exceeding 10% have even been reported when soluble small molecules are used in ternary blends.¹⁰ Soluble small molecules are well-defined in terms of their molecular weight. Compared to conjugated polymers, they can be prepared, characterized, and purified easily with a low batch-to-batch variation, which is of advantage for large-scale industrial applications.

A molecular donor that has proven to be particularly suitable for efficient solar cell applications is 7,7′-[4,4-bis(2-ethylhexyl)-4H-silolo[3,2-b:4,5-b′]dithiophene-2,6-diyl][bis(6-fluoro-4-(5′-hexyl-2,2′-bithiophene)-5-yl]benzo[c][1, 2,5]thiadiazole] (p-DTS(FBTTH)₂) (Figure 1(a)).¹¹ The performance of BHJ solar cells made with p-DTS(FBTTH)₂ as donor, however, depends strongly on the film processing conditions. Love et al. demonstrated that different processing methods, such as thermal annealing or using diaryldiimide as acceptor, can improve the power conversion efficiency of the solar cell.¹² Using electron microscopy and X-ray measurements, they could show that the high power conversion efficiencies were associated with an existing network of crystalline grains, where high π-π* overlap ensures good charge transport between adjacent molecules. The π-stacking, however, also manifested itself in the absorption spectra of the BHJ films. In highly efficient solar cells made with a fullerene-derivative as acceptor, the absorption spectra showed a prominent 0-0 peak of the p-DTS(FBTTH)₂, whereas this peak is reduced in less efficient cells. This is also the case when the fullerene is replaced by a perylene diimide as acceptor.¹² While electron microscopy and X-ray measurements are expensive and time-consuming techniques, absorption measurements do not require much time and are widely available in laboratories for sample characterization. Moreover, absorption and photoluminescence measurements are also sensitive to short-range order and interactions, which is relevant for the process of exciton dissociation, while many structural techniques are more suitable for long-range order that controls transport properties.

A prerequisite to using optical spectroscopy for sample analysis is that the absorption and emission spectra pertaining to aggregated p-DTS(FBTTH)₂ are identified clearly and that they are sufficiently distinct from the spectra of the non-interacting molecules. A clear identification requires in particular a spectral deconvolution of monomer and aggregate spectra. To this end, we have investigated the absorption and emission spectra of p-DTS(FBTTH)₂ in dilute solution, more concentrated solution and in the thin film as a function of temperature. We identify the spectra pertaining to non-interacting molecules (“monomers”) and those pertaining to ordered, interacting molecules (“aggregates”). The disorder-order transition that we observe upon cooling occurs in three stages, in the same way as for semi-crystalline conjugated polymers. However, owing to the monodispersity of the small molecule sample, the transition is very sharp, in contrast to that observed in polydisperse semi-crystalline...
polymer samples. Moreover, p-DTS(FBTTH)$_2$ films can be prepared to contain essentially only aggregates, in contrast to thin films made from semi-crystalline polymers that contain typically only up to 60% of aggregated phase.\textsuperscript{13,14}

EXPERIMENTAL METHODS

Sample preparation

7,7’-[4,4-bis(2-ethylhexyl)-4H-silolo[3,2-b:4,5-b’]dithiophene-2,6-diyl]bis[6-fluoro-4-(5’-hexyl-2,2'-bithiophene)-5-yl]benzo[c][1,2,5]thiadiazole, p-DTS(FBTTH)$_2$, was prepared as reported in Ref. 11. For spectroscopic studies, solutions in 2-methyl-tetrahydrofurane (MTHF) were prepared at two concentrations, that is, $4.1 \times 10^{-5}$M (“dilute solution,” 0.05 g/l) and $1.6 \times 10^{-4}$M (“more concentrated solution,” 0.2 g/l), by stirring overnight at about 50°C and 500 rpm, to ensure that all of the materials were completely dissolved. Solutions for spin-casting thin films were made at a concentration of $6.6 \times 10^{-3}$M (8 g/l). To prepare solutions in ethanol and hexane, both at $1.0 \times 10^{-3}$M (0.12 g/l) and $4.1 \times 10^{-5}$M (0.05 g/l), we first dissolved the p-DTS(FBTTH)$_2$ in a very small amount of MTHF before adding ethanol or hexane. The amount of MTHF was about 1% of the total final solution. These solutions were always measured immediately after preparation, where all the material seemed to be dissolved and the solution was clear. Over time, e.g., after 1 h, solids precipitated out of the ethanol and hexane solution. For measurements, solutions were filled into a 1 mm fused silica cuvette or films were prepared on Spectrosl B quartz substrates by spin-coating out of a 80°C hot solution at 800 rpm for 60 s.

FIG. 1. (a) Chemical structure of p-DTS(FBTTH)$_2$, along with photoluminescence and absorption spectra (b) taken in a $4.1 \times 10^{-5}$M MTHF solution (“dil.”) at four different temperatures (at 300 K, the emission taken in hexane solution is also indicated (dotted black line)), (c) taken from a thin film, spun-cast from a MTHF solution, at room temperature, and (d) taken in a $1.6 \times 10^{-4}$M MTHF solution (“conc.”) at four different temperatures. The vertical grey lines at 1.9 eV are a guide for the eye.
Absorption and photoluminescence measurements

Absorption and emission spectra for MTHF solutions and films were recorded with a home-built setup in a temperature range between 300 K and 5 K. The samples were placed under helium in a temperature controlled continuous flow helium cryostat from Oxford Instruments. The light source for absorption measurements was a xenon-lamp. To achieve minimum light intensity striking the sample, two correlated monochromators were used, one for incident and the other for transmitted light. As detection unit, there was a silicon diode connected to a lock-in-amplifier. The emission spectra were corrected for the transmission of the setup.

Photoluminescence measurements were carried out in situ with excitation by a continuous-wave diode laser from Coherent at 405 nm (3.06 eV) and with detection as for the absorption measurements. Absorption and emission spectra were recorded successively at the same temperature and sample spot. The sample cooling was done in steps with a waiting time of 20 min after each temperature was reached. The spectra are corrected for changes in absorption or scattering upon lowering the temperature.

Site-selective photoluminescence measurements with the sample in a temperature controlled continuous flow helium cryostat were carried out using the 355 nm pulsed emission from a Nd:YAG laser as input for a computer controlled UV/Vis optical parametric oscillator to obtain a tunable excitation pulse with a duration of 4–5 ns at 10 Hz. The detection system was a charge-coupled device camera from Andor coupled to a MS125 spectograph.

Absorption and emission spectra in ethanol and hexane solution at room temperature were taken with commercial setups: a Cary 5000 UV/Vis spectrometer from Varian for absorption measurements and a FP-8600 spectral photometer from Jasco for emission measurements.

Quantum chemical calculations

Ground state geometry optimization was performed using density functional theory (DFT), while the vertical excitations and the optimization of the geometry of the first excited state were performed using time-dependent density functional theory (TD DFT). All calculations were performed with Gaussian09 revision C.01 program. The long-range corrected functional CAM-B3LYP was used, together with 6-31G** basis set, as the previous studies demonstrated that it accurately describes properties of similar molecules.

In all calculations, the alkyl chains were replaced by methyl groups. No symmetry constraints were imposed on the ground state nor on the excited state geometry. Influence of the solvent (tetrahydrofuran) was modelled using polarizable continuum media model using the integral equation formalism (IEFPCM). For geometry optimizations, the equilibrium solvation was used, while for the vertical excitations from the ground state, a state-specific non-equilibrium solvation was used, where the slow (rotational) component of the solvent response was calculated for the ground state, and only the fast (electronic) contribution was calculated for the excited state. The character of the excited states was investigated using natural transition orbitals (NTOs).

RESULTS

Figure 1 shows measurements of photoluminescence and absorption of p-DTS(FBTTH2)2 in dilute MTHF solution, more concentrated MTHF solution, and in the thin film. These spectra serve as a starting point to assess the impact of intermolecular interactions on excited states in p-DTS(FBTTH2)2. In dilute solution (Figure 1(b)), the absorption and emission spectra at room temperature are both broad and show little structure. Upon cooling from 300 K, the absorption spectra slightly shift to lower energies and continuously acquire a more distinct vibrational structure with increasing weight in the 0-0 transition (centred at 2.00–1.95 eV in the temperature range 300–70 K). In contrast, the emission spectra merely show a minor bathochromic shift and remain broad until 150 K. At lower temperatures, the emission is well structured so that it resembles the mirror image of absorption, and it is shifted further to the blue spectral range. Measurements in steps of about 20 K (see Figure S1 in the supplementary material) indicate that this change in the spectrum occurs discontinuously between 150 K and 130 K.

Quantum chemical calculations show that the ground state geometry of p-DTS(FBTTH2)2 is fairly planar, with no torsion between the central dithienosilole (DTS) donor and the fluorobenzothiadiazole acceptor, about 12° of torsion angle between the fluorobenzothiadiazole acceptor and the dithiophene donor, and about 18° of torsion angle between the two thiophenes (Figure 2(a)). The energy for rotations is in the range of 1 kcal/mol (about 40 meV per molecule), implying that there may be a distribution of angles at room temperature. We therefore attribute the spectral changes in absorption which are observed upon cooling to a gradual freezing out of the rotational dynamics. The relaxed excited state geometry of p-DTS(FBTTH2)2 in tetrahydrofuran (THF) is calculated to be entirely flat (Figure 2(b)). Thus, at least for lower temperatures such as 210 K and 150 K, where the absorption spectra are already structured, a structured emission with a clear 0-0 transition could be expected. This is in contrast to the broad emission that is observed. A well-structured emission spectrum is, however, observed even at room temperature when p-DTS(FBTTH2)2 is dissolved in the non-polar solvent hexane. This is shown as dotted line in Figure 1(b). An analysis of the natural transition orbitals of p-DTS(FBTTH2)2 indicates that the first excited state has some charge-transfer character, with the electron density being transferred from the central and outer donor units, DTS and dithiophene, to the fluorobenzothiadiazole acceptor (Figure 2(c)). Associated with this charge transfer is the increase in dipole moment. The dipole moment for the molecule in THF is calculated to be 0.64 D in the ground state. Upon vertical excitation, a dipole moment of 1.77 D is calculated which reduces slightly to 1.64 D in the relaxed excited state geometry in THF. Evidently, the bathochromic shift and the lack of vibrational structure in the emission spectra taken in the moderately polar solvent MTHF—in contrast to the non-polar solvent hexane—can be
attributed to interaction between the excited p-DTS(FBTTH)$_2$ and the polar solvent. Upon excitation of p-DTS(FBTTH)$_2$, the MTHF molecules rearrange their position and orientation to optimize their electrostatic interaction with the solute, such as to minimize the overall energy. The broadening arises from a distribution of polarization energies since the positions and orientations of the solvent molecules fluctuate in the liquid phase. Below the glass transition temperature of MTHF, which is at 137 K, a rearrangement of solvent molecules is no longer possible. As a result, the emission energy is only lowered due to the electronic polarization of the MTHF molecules, while the structure is retained.

When a four times more concentrated MTHF solution is investigated (Figure 1(d)), no differences arise compared to the dilute solution for temperatures down to 205 K. At lower temperatures, an additional absorption peak arises centered at about 1.8 eV. While the onset of emission at 150 K still occurs at the same energy as for the dilute solution, i.e., at about 1.9 eV, the peak of emission shifts to lower energies and an additional shoulder near 1.4 eV emerges. The spectrum is better resolved at 70 K, so that three features are clearly discernible at about 1.42 eV, 1.65 eV, and 1.85 eV. At 70 K, the striking observation of an emission peak (at 1.85 eV) at higher energy than the lowest-energy absorption peak (at 1.80 eV) of the same material gives an indication that two different species may be giving rise to these spectra.

It is noteworthy that the absorption and emission spectra measured in concentrated solution are still distinct from thin film room temperature spectra (Figure 1(c)). The position of the lowest-energy absorption peak at about 1.80 eV matches that of the more concentrated solution, yet the weight in the vibrational peaks differs. The emission is broad and unstructured with a center energy of 1.55 eV.

The additional contribution to the spectra, which emerges in the more concentrated solution, can be identified by subtracting the spectra taken at the same temperature yet at two different concentrations from each other. This is displayed in Figure 3. To allow for the subtraction, the low-concentration spectrum needs to be normalized in overall intensity such as to match the high energy part of the spectrum. It is also necessary to shift the low-concentration spectrum by 40 meV to the blue spectral range in order to account for the concentration-dependent solvent-shift on the transition energy. Very similar spectra result when using alternative approaches to separate the two contributions, i.e., by subtracting the spectrum just above the transition temperature from the spectrum just below the transition temperature, with both spectra having the same concentration, or by modelling the spectrum as a sum of two Franck-Condon progressions. These approaches are detailed in the supplementary material (Figures S2 and S3).

We attribute the additional absorption and emission in the more concentrated solution to interacting p-DTS(FBTTH)$_2$ such as dimers or larger aggregates. The relative amount of monomers and aggregates can be deduced from the spectra when the change in oscillator strength $\epsilon$ upon aggregation is taken into account. For this, we compare the absorption spectrum at 205 K containing only monomer absorption with the absorption spectrum at 198 K that contains monomer absorption and aggregate absorption. The spectra and the deconvolution in monomer and aggregate absorption are shown in Figure S4 in the supplementary material.

Upon lowering the temperature from 205 K to 198 K, the absorption from the aggregates appears. Upon aggregation, the monomer absorption reduces by $\int \Delta I_M(\lambda) \, d\lambda$, where $\Delta I_M$ is the difference in the monomeric absorption prevailing at 205 K and 198 K. At the same time, an aggregate absorption of $\int \Delta I_A(\lambda) \, d\lambda$ appears. Here, $\Delta I_A$ is the aggregate absorption prevailing at 198 K. Since the absorption by the monomer (aggregate) is proportional to the oscillator strength of the monomer, $\epsilon_M$ (of the aggregate, $\epsilon_A$), it follows that the ratio $F$ between the oscillator strength of the two species can therefore be deduced by

$$F = \frac{\int \Delta I_A(\lambda) \, d\lambda}{\int \Delta I_M(\lambda) \, d\lambda} = \frac{\epsilon_A}{\epsilon_M}$$

As detailed by Clark et al. and in the associated supplementary material, this approach is only valid when an isosbestic point is formed upon the transition, which is the case here (see Figure S11 in the supplementary material). We find that the area ratio $F$ from the aggregate-induced absorption compared to the reduction in monomeric absorption is $F = 0.64$. Thus, the oscillator strength in the aggregates is only about two thirds of that in the monomer.

FIG. 2. (a) Ground state geometry, with $\varphi_1 = 11.9^\circ$ and $\varphi_2 = 17.5^\circ$, and (b) relaxed first excited state geometry, with $\varphi_1 = 0.4^\circ$ and $\varphi_2 = 3.1^\circ$, of p-DTS(FBTTH)$_2$ in a THF solution, in side and top views, as obtained from quantum-chemical calculations. (c) Natural transition orbitals (NTOs) for the first singlet excited state of p-DTS(FBTTH)$_2$ in THF, hole orbitals depicted on the left, with corresponding electron orbitals on the right side of the figure. Values denote the contribution of a given pair of NTOs to the excitation. The arrows serve to highlight the changes in electron density.
FIG. 3. Spectral deconvolution of (a) photoluminescence and (b) absorption spectra of p-DTS(FBTTH)$_2$ (red and blue line) taken in a $1.6 \times 10^{-4}$M MTHF solution at 190 K into a spectral contribution attributed to monomer (black filled line) and to aggregates (green filled line). Respectively, upon cooling, (c) the photoluminescence spectrum at 70 K. (d) Fraction of aggregates of p-DTS(FBTTH)$_2$ in a $1.6 \times 10^{-4}$M MTHF solution as a function of temperature.

Using this result, we derive a maximum fraction of about 0.45 of aggregates in the more concentrated solution. The evolution of the fraction of aggregates with temperature, shown in Figure 3(d), shows a very steep onset at 200 K, and only shallow evolution below 150 K.

The appearance of aggregation upon cooling a solution has been reported before for some π-conjugated polymers, such as P3HT, MEH-PPV, and PCPDTBT$^{13,14,24–26}$ For these polymers, the process of aggregation upon cooling was found to proceed in three distinct phases, i.e., (i) a swelling up and planarization upon cooling, (ii) a transition with an isosbestic point, and (iii) a further planarization of the aggregates formed. The detailed display of the temperature-dependent absorption spectra in Figure 4(b) indicates that even though p-DTS(FBTTH)$_2$ is not a polymer, aggregation seems to take place in the same fashion. Of course, the red-shift of absorption in the range from 300 K to 205 K does not indicate a swelling up of the molecular structure but rather an increasing conjugation and planarity due to a reduction in torsional dynamics, as mentioned above. Yet, the isosbestic point in the transition range (204–170 K) and the ongoing planarization at lower temperatures are evident in the absorption spectra in the same manner as for the polymers mentioned above.

The evolution of the emission spectra (Figure 4(a)), in contrast, is more unusual. In the range from 300 K to 205 K, the photoluminescence intensity reduces in contrast to the absorption. In the range from 204 K to 170 K, where aggregate absorption appears, the photoluminescence intensity reduces further. The overall emission increases, however, from 150 K on to lower temperatures. The reduction in photoluminescence intensity upon cooling in the temperature range above 150 K also occurs for the more dilute solution, yet to a weaker degree. It is accompanied by a concomitant reduction in photoluminescence lifetime (see Figures S5 and S6 in the supplementary material$^{39}$). The origin for this additional decay channel above 150 K is not clear. We speculate that upon cooling, some colliding molecules may form excimer-type states that are non-emissive. Such a phenomenon has been observed previously for pyrene-derivatives in the concentration range preceding the formation of aggregates.$^{27}$ For the more concentrated solution in the 204–170 K range, some reduction in photoluminescence intensity can be attributed to the reduced oscillator strength of the aggregates that has been shown to be 64% of the monomer oscillator strength by the analysis of the absorption spectra. The strong increase in photoluminescence intensity below 150 K at roughly constant absorption strength suggests a freezing out of a non-radiative decay channel. Besides the more special case of possible excimer formation, a significant and typical non-radiative decay mechanism in organic molecules is intersystem crossing from the excited singlet to the triplet state. In the absence of heavy metals, the necessary spin-orbit coupling for this is usually provided by vibrations that mix σ- and π-orbitals, such as ring rotations.$^{28}$ In the glassy matrix that prevails below 150 K,
both translational and rotational motions are impeded, so that not only excimer formation but, moreover, intersystem crossing should be suppressed. We attribute the increase in photoluminescence intensity below 150 K to this mechanism, in particular, for the higher energy emission that is due to the planarized monomer.

Site-selective photoluminescence spectroscopy has been employed to further confirm that the spectra of the higher concentrated solution are composed of two contributions. Figure 5(a) displays the photoluminescence spectra obtained for excitation at different energies. For ease of reference, these energies are indicated by arrows in the associated absorption spectra shown in Figure 5(b). Nearly identical emission spectra result when the more concentrated MTHF solution is excited at different energies between 1.82 eV and 3.06 eV at room temperature. This clearly confirms the absence of any aggregate emission at 295 K. When exciting at a position where only the aggregate absorbs, i.e., at 1.82 eV, the emission features only two clear peaks at about 1.45 eV and 1.60 eV, in good agreement with the peak positions derived from the difference between the emission spectra of more and less dilute solutions (see Figure 3). These two features also remain clearly visible when exciting at the onset of the second absorption band, at 2.81 eV and at 3.06 eV, which was the excitation energy used throughout this study. In addition, peaks at 1.85 eV and 1.70 eV superimpose, which matches the position of the photoluminescence peaks observed at 70 K in the more dilute solution (see Figure 1). The latter two peaks dominate the spectrum when exciting at 2.21 eV, i.e., in the center of the monomer absorption. Thus, the site-selective emission spectra confirm the spectral deconvolution presented in Figure 3.

A 1.0 \times 10^{-4} M solution of the very polar solvent ethanol was investigated at room temperature, in order to obtain insight into the spectra resulting from only aggregates (Figure 5(a), bottom panel and Figure 5(b), dotted line). We repeated the measurements using a 4.1 \times 10^{-5} M solution and obtained identical absorption and emission spectra. In a 4.1 \times 10^{-5} M solution, energy transfer from individual molecules dissolved in solution to aggregates can be excluded. Thus, the lack of monomeric emission, i.e., emission above 1.8 eV in Figure 5(a), bottom panel, for excitation at 2.81 eV or 2.21 eV, testifies in the absence of monomers. This implies that the associated absorption spectrum can be attributed to absorption from aggregates. This aggregate absorption spectrum in Figure 5(b) is in good agreement with the spectrum derived by spectral deconvolution (cf. Figure 3(b)). The emission obtained for excitation at 1.82 eV matches the spectral range where aggregate emission is observed, though the spectral shape differs.

The difference in spectral shape seen in MTHF, ethanol, and film requires clarification. Figure 6 compares the room temperature absorption and emission spectra. From the nearly identical absorption spectra obtained in ethanol and in the thin film, we can conclude that a film spun from MTHF solution contains merely aggregated regions without any significant
amount of amorphous regions. Recall that we use the term “aggregate” to denote electronically interacting molecules with at least short-range order, as opposed to molecules in an amorphous environment that interact merely by van der Waals forces.

In absorption, the spectra obtained in ethanol or thin film differ from those obtained in MTHF by a bathochromic shift of about 200 meV and by being more structured. The peak positions and intensities in ethanol/thin film are consistent with those observed for the aggregates formed in ethanol or thin film than in frozen MTHF. This is plausible considering that only aggregates prevail in ethanol whereas aggregated and monomeric species are present in almost equal ratios in frozen MTHF as shown above. We therefore attribute the difference in relative 0-0 peak intensity between the emission spectra in MTHF on the one hand and ethanol or film on the other hand to differences in the local environment in which the aggregates are embedded, which affects energetic disorder and excited state correlation.

FIG. 5. (a) Photoluminescence spectra of p-DTS(FBTTH)$_2$ for different excitation energies taken in a 1.6 × 10$^{-4}$ M MTHF solution at 295 K (top), at 60 K (middle), and in a 1.0 × 10$^{-4}$ M ethanol solution at 295 K (bottom panel). (b) Absorption spectra of p-DTS(FBTTH)$_2$ taken in a 1.6 × 10$^{-4}$ M MTHF solution at 300 K (dashed line) and 60 K (solid line) and in a 1.0 × 10$^{-4}$ M ethanol solution at 295 K (dotted line). The arrows are indicating the different excitation energies used for (a).

There are two aspects of this study that are of important value. First, the clear identification of the absorption and emission spectra from aggregated p-DTS(FBTTH)$_2$ allows for quick routine evaluation of films intended for solar cells and the processing techniques applied. Second, p-DTS(FBTTH)$_2$ is a low molecular weight compound with a polydispersity of unity. It is enlightening to compare the process of aggregation in this semi-rigid molecule to that observed in semi-rigid polymers. In the same ways as in polymers, we observe that aggregation proceeds in a three-step process, where the actual process of dimer/aggregate formation is preceded by planarization of the molecular backbone, and followed by further optimization of the aggregate geometry. It appears that the process of planarization is required a priori to enable the intermolecular interaction.

For polymers, this is not an obvious requirement since excited state delocalisation along a planarized chain reduces the strength of excitonic coupling between chains. Nevertheless, pre-aggregation planarization is unambiguously material, so that the spectra obtained in ethanol/thin film can be attributed to the aggregates. The additional observation of vibrational structure in the aggregate absorption suggests a more pronounced contribution of π-π transitions compared to the dominant charge-transfer character of the non-aggregated species.

In emission, the difference between the aggregate emissions in ethanol or in the thin film on the one hand and in low-temperature MTHF solution on the other hand is more striking. While the spectral position of the room temperature emission in ethanol/thin film agrees with that observed for the aggregate emission in MTHF as shown in Figure 3, the spectral shape differs. A better resolution can be obtained when considering the thin film photoluminescence spectra at low temperature. Upon cooling, the line width reduces and both absorption and emission shift to lower energy by about 40–60 meV. As a result of the smaller line width, two clear peaks emerge at 1.48 eV and 1.63 eV in the 50 K emission spectra. These peak positions are identical to those observed for the aggregates in MTHF solution (see Figure 3), yet the relative weight between the 0-0 and the 0-1 peak differs.

On the basis of quantum chemical calculations, Spano suggested the relative intensity of the 0-0 peak in aggregate emission to depend on the degree of energetic disorder that is present in the sample. Thus, it appears that there is a higher degree of order in the aggregates formed in ethanol or thin film than in frozen MTHF. This is plausible considering that only aggregates prevail in ethanol/thin film, whereas aggregated and monomeric species are present in almost equal ratios in frozen MTHF as shown above. We therefore attribute the difference in relative 0-0 peak intensity between the emission spectra in MTHF on the one hand and ethanol or film on the other hand to differences in the local environment in which the aggregates are embedded, which affects energetic disorder and excited state correlation.

**DISCUSSION**

There are two aspects of this study that are of important value. First, the clear identification of the absorption and emission spectra from aggregated p-DTS(FBTTH)$_2$ allows for quick routine evaluation of films intended for solar cells and the processing techniques applied.

Second, p-DTS(FBTTH)$_2$ is a low molecular weight compound with a polydispersity of unity. It is enlightening to compare the process of aggregation in this semi-rigid molecule to that observed in semi-rigid polymers. In the same ways as in polymers, we observe that aggregation proceeds in a three-step process, where the actual process of dimer/aggregate formation is preceded by planarization of the molecular backbone, and followed by further optimization of the aggregate geometry. It appears that the process of planarization is required a priori to enable the intermolecular interaction.

For polymers, this is not an obvious requirement since excited state delocalisation along a planarized chain reduces the strength of excitonic coupling between chains. Nevertheless, pre-aggregation planarization is unambiguously
observed, for example, for the polymers MEH-PPV, P3HT, and PCPDTBT. It has been predicted in Monte Carlo simulations for semi-rigid polymers and was also observed in molecular dynamic calculations for MEH-PPV. In a naïve picture, it may be tempting to invoke steric requirements for the aggregation of polymer chains.

The pre-aggregation planarization evidenced in p-DTS(FBTTH)$_2$ by the red-shift in absorption and emission spectra (Figure 4) is consistent with temperature-dependent absorption measurement on poly($p$-phenylene vinylene) oligomers. There, the occurrence of aggregation in solution correlates with the nature of the side chain. In oligomers with alkoxy side chains, ground and excited states are planar and aggregation in MTHF solution is observed. In contrast when the oligomer carries alkyl side chains, aggregation in MTHF solution cannot be induced by reducing temperature, and this is associated with a twisted ground state geometry and a non-planar excited state geometry. The ground state geometry of p-DTS(FBTTH)$_2$ in MTHF is fairly flat (see Figure 2), with planar central units and torsion angles of only 12° and 18° to the outer two thiophene rings. After aggregation, e.g., in a single crystal structure, an entirely planar conformation is observed by X-ray studies. In view of the weak torsions in the ground state conformation in MTHF, it is remarkable that planarization necessarily precedes aggregation and is not simply induced as geometric reorganization after aggregation. Arguments based on steric requirements that one may invoke for polymers are certainly not convincing in the case of this molecule. A more compelling explanation is that an increasing planarization, resulting from the freezing out of torsional dynamics, reduces the solubility of the molecule in the solvent, so that a reduced solvation dynamics assists the formation of aggregates.

A further illuminating aspect in this comparison of the disorder-order transition between $\pi$-conjugated polymers and molecules consists in the remarkable sharpness of the transition observed in Figure 3(d). For commercial MEH-PPV or P3HT samples with polydispersity indices (PDIs) exceeding 2, the disorder-order transition is smeared out over a large temperature range, so that their temperature dependence resembles a second order phase transition. In contrast, well-defined P3HT polymer samples with different molecular weights, yet low polydispersity index of PDI <1.2, have a more narrow transition range that results in a steeper appearance of the transition. The transition temperature itself, defined as the point of inflexion when the fraction of aggregates is displayed versus temperature, reduces with molecular weight, in agreement with the theoretical description of Sanchez for a disorder-order transition.

It was suggested that the broadness of the transition observed for polydisperse polymer samples may result from a superposition of different transition temperatures for the different molecular weight fractions contained in the polydisperse sample.
The width of the transition can be quantified by considering the Full Width at Half Maximum (FWHM) of the first derivative to the temperature dependence of the aggregate fraction, as shown in Figure S7 (supplementary material). By this measure, the p-DTS(FTTHT)$_2$ sample with a PDI = 1 has a FWHM of 6 K, P3HT with PDI = 1.2 has a FWHM of 14 K, and commercial P3HT with PDI = 2 has a FWHM of 35 K. Both P3HT have a comparable molecular weight of 19 ± 1 kD.

In summary, the spectroscopic investigation of aggregation in p-DTS(FTTHT)$_2$ in dilute solution, more concentrated solution, and in the thin film has allowed us to identify the aggregate signature. With this tool, the absorption spectra of solar cells comprising p-DTS(FTTHT)$_2$ can be analysed to infer the fraction of aggregates in the solar cell without need for expensive and time-consuming structural techniques. The latter will only be required when information on long-range order is desired. Moreover, the comparison of the aggregate formation in this stiff molecule to that in π-conjugated polymers has highlighted the importance of torsional dynamics in the aggregation process.

ACKNOWLEDGMENTS

We gratefully acknowledge support from the Hans-Seidel-Stiftung through a stipend to M.R. by funds from the German Federal Ministry of Education and Research (BMBF), support from the German Science Foundation through the Research Training Group GRK 1640 “Photophysics of Synthetic and Biological Multichromophoric Systems,” and from the State of Bavaria through the Research Network “Solar Technologies go Hybrid.” J.A.L., G.C.B., and T.Q.N. thank the Department of the Navy, Office of Naval Research (Award No. N00014-14-1-0580) for support. T.Q.N. thanks the Camille Dreyfus Teacher Scholar Award.


39. See supplementary material at http://dx.doi.org/10.1063/1.4941700 for the following: Figures S1–S7 contain the photoluminescence and absorption spectra taken in $4.1 \times 10^{-5}$ M MTHF solution at different temperatures; spectral separation of photoluminescence and absorption in a $1.6 \times 10^{-5}$ M MTHF solution at different temperatures into a spectral contribution attributed to monomer and to aggregates; Franck-Condon fits to the photoluminescence and absorption spectra of monomer and aggregates; the Raman spectrum; comparison of the absorption in $1.6 \times 10^{-6}$ M MTHF solution at 205 K and at 198 K; photoluminescence and absorption spectra in a $4.1 \times 10^{-5}$ M MTHF solution at different temperatures; the fluorescence decay curves in a $4.1 \times 10^{-5}$ M MTHF solution at different temperatures; and the first derivative of the fraction of aggregates plotted against relative temperature. For ease of reference, Figures S8–S11 give absorption and photoluminescence spectra in a $1.6 \times 10^{-5}$ M MTHF solution at different temperatures, measured in fine temperature steps and over a broad energy range, photoluminescence and absorption spectra in $4.1 \times 10^{-5}$ M MTHF solution at different temperatures, photoluminescence spectra in a thin film at different temperatures, and absorption spectra in $1.6 \times 10^{-5}$ M MTHF solution at temperatures between 205 K and 150 K forming an isosbestic point at 1.94 eV.