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Enhanced Triplet Formation by Twisted Intramolecular Charge-Transfer Excited States in Conjugated Oligomers and Polymers

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The triplet yield and intersystem crossing rate of a set of conjugated oligomers and polymers that, in polar solvents, form a charge-transfer state with a twisted conformation has been investigated. It was observed that in these dibenzothiophene-fluorene oligomers a greater than 10-fold increase on the triplet yield is achieved by simply changing the medium polarity to favor the formation of the twisted charge-transfer state, while the fluorescence lifetime is only slightly increased. The increase in the intersystem crossing rate is attributed to the improved mixing between the singlet and triplet states in the twisted excited state. In analogous polymers, the intersystem crossing rate does not show the same increase, most likely because of the greater energetic and conformational disorder increasing the intersystem crossing rate at all times, regardless of the formation of the twisted charge-transfer state or not.

Introduction

In many conjugated molecules, particularly the families of conjugated polymers successfully developed for display applications, only a small fraction of photoexcitations undergo intersystem crossing (ISC) and contribute to the triplet population. Consequently fluorescence quantum yields of conjugated polymers are normally high.[1] The fraction of singlets that undergo ISC to the triplet manifold can be increased if dopants with appropriate energy levels to sensitize the polymer triplet state through sequential energy transfer are used. Alternatively, high triplet populations can be created if spin−orbit coupling in the molecule is increased by the presence of heavy atoms.[2,3]

In light emitting devices, emission is the result of exciton formation from electron−hole recombination, which potentially proceeds via a charge-separated intermediate state.[4] Thus, the triplet population can reach far higher values than during optical excitation, and this represents an important limit on the device efficiency. From simple quantum mechanical spin statistics, 75% of the total recombination events are predicted to result in triplet excitons. However, much lower values for the triplet fraction have been reported, suggesting that the triplet exciton formation mechanism through a charge-separated state does not entirely preserve the spin statistics and could be dependent on the emissive material.[5–8]

Conjugated co-oligomers and copolymers have represented a step change in the development of materials for polymer-based organic light emitting diodes, and the incorporation of moieties with specific properties can be used to tailor the polymer for a specific application, such as improved charge transport or emission tuning.[9–13] Systems containing moieties with different electron affinity result in the molecule having a strong ground-state dipole. The resultant excited-state is often of charge-transfer (CT) character; the concomitant broad emission can be utilized to great effect in white light emitting devices.[14] Additionally one might expect the high electron affinity segments to act as charge traps directly forming the CT excited-state during optical excitation, thus reducing the prob-
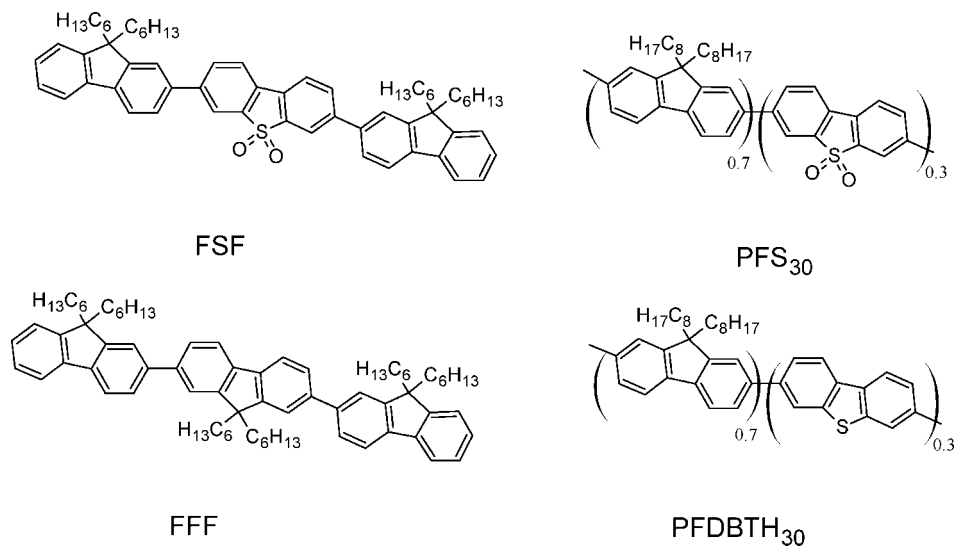
ability of charge trapping at undesirable defect states. In CT states, there is potential for increased mixing between singlet and triplet states due partly to the much lower singlet−triplet energy gap in CT states compared to locally excited (LE) states,[15] as well as the often accompanying structural relaxation that plays an important part in determining the photophysics of the molecule. Thus, given the importance of the relationship between singlets and triplets for device physics, it is of paramount importance to understand the effects of such CT states on triplet formation rates. One such class of CT state forming copolymers are the efficient, broad spectrum emitting fluorene(dibenzothiophene-*s*,*s*-dioxide) co-oligomers and co-polymers.[16]

In this article, the triplet population on fluorene(dibenzothiophene-*s*,*s*-dioxide)fluorene oligomers (Chart 1) and their analogous polymers is followed by femtosecond photoinduced absorption and ground-state recovery (GSR), in methylcyclohexane (MCH) and ethanol solution. The two solvents with different polarity induce different stabilization of the emissive intramolecular CT state of FSF.[16] In polar solvents, the CT state is stabilized by the solvent cage and accompanied by large amplitude motions to adapt the molecular structure to the new charge distribution; comparison with model compounds suggests that this takes the form of a level conformational twisting between the dibenzothiophene-*s*,*s*-dioxide unit and one of the fluorenes. This twisted CT state[17] is similar to the more formally defined twisted interconnected CT (TICT) state excited state. In such a case, the electron and hole reside on different parts of the molecule, which are stabilized by a twist in the molecule of up to 90°. Conversely, in nonpolar environments, the excited-state behaves like that of a fluorene oligomer, known as the LE state. Additionally, two copolymers with similar structures (PFDBTH$_{30}$) and (PFS$_{30}$) are included in the study, the former with purely excitonic behavior in solution and solid state and the latter behaving like the FSF oligomer in solutions of different polarity and showing characteristics of the twisted CT state in the solid state.[18]

The photophysics of TICT states and other intramolecular CT states has been studied extensively in the past, with many

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Triplet Formation by Conjugated Polymers

J. Phys. Chem. B, Vol. 112, No. 27, 2008 **8011**

CHART 1: Structures of the Polymers and Oligomers under Study

FSF

PFS$_{30}$

FFF

PFDBTH$_{30}$

investigations made into the nature of the CT and the rate of the molecular rearrangements. The compounds are generally well characterized in terms of their fluorescent properties and the activation of the dual fluorescence from the LE and CT states.[17,19] Previously, only a few attempts have been made to study the triplet properties of such intramolecular CT states; in some flash photolysis studies, the existence of two triplets has been reported,[20] whereas in other work, no evidence of the existence of a triplet CT state is found.[21] The commonly held position in the literature is that the lowest triplet state of the molecule is that of the LE state, in agreement with the notion that CT excited states generally have a smaller S_1-T_1 splitting than exciton states. In conjugated polymers $E(S_1-T_1)$ is known to be >0.7 eV.[22,23] In the past, the rate of ISC has been predicted to increase in TICT states and other twisted conformation excited states.[21] This has been suggested by drawing comparison with the case of intermolecular CT exciplexes, which can relax by a charge recombination mechanism yielding the singlet ground-state or the triplet excited state. This phenomenon has been observed in both small-molecule[24] and polymer blend-based[25] intermolecular charge-separated states. However, the increase in ISC rate has not been thus far observed for intramolecular CT state-forming molecules.[21,26]

Experimental Section

Triplet yield measurements were made using the GSR technique developed in our previous work.[27,28] The principal of the experiment is to create an excited-state population with a pump pulse and to probe the recovery of the ground-state as the excitons decay, thus probing the total number of excited states rather than just the singlets. The signal recorded is the same as other photoinduced absorption experiments; dT/T is the change in transmission of the sample when excited, normalized by the mean transmission of the sample, the only difference being that because the photobeaching is being probed, the signal is positive rather than negative. Two regimes are observed: the recovery of the singlet states manifests itself as a fast recovery of the ground-state absorption, and the slower decay of the triplets appears as a plateau in the short time regime, offsetting the singlet decay from the baseline. When the GSR is observed on a slow (microsecond to millisecond) time scale, the recovery originates from the decay of the triplet states. The correlation of the fast recovery with the lifetime of the singlet and the slow

component with the triplet lifetime provides an additional check that the two states observed in the recovery of the ground-state are the singlet and triplet exciton. The kinetic scheme is given in eqs 1 and 2. From the ratio of the two components, it is possible to calculate the proportion of triplets formed optically, i.e., the ISC ratio, from eq 3. To improve the accuracy of the fitting of the singlet decay, global analysis can be used to analyze the decays of the GSR and the excited-state absorption.

$$\frac{dN}{dt} = \frac{dN_S}{dt} + \frac{dN_T}{dt} = -N_s k_s - N_s k_{nr} - N_T k_T \quad (1)$$

$$N = Ae^{-k_s t} + Be^{-k_{nr} t} + Ce^{-k_T t} \quad (2)$$

$$\varphi_T = \frac{B}{A + B + C} \quad (3)$$

where, N is the total number of excited states, N_s is the number of singlets, N_T is the number of triplet states, and k_s, k_{nr}, and k_T are the rates of singlet decay, non-radiative decay, and triplet decay, respectively. In the integrated rate equation (eq 2), A, B, and C are the preexponential factors for the decay components, and φ_T is the ISC yield.

In the fast time regime, the system to measure the GSR is a conventional single wavelength pump−probe experiment based on a 100 kHz amplified mode locked Ti:Sapphire laser system. The pump and probe pulses are the second harmonic of the laser at 390nm, and an optical delay stage is used to provide a relative delay of the probe beam of up to 4 ns. In the long time regime, kinetics are measured with a pulsed Nd:YAG laser as the pump and a continuous wave (cw) diode laser as the probe, either at 405 nm to probe the GSR or in the photoinduced absorption of the triplet to measure the lifetime to the triplet.[2,27]

Additionally, excited-state absorption spectra are measured with the ultrafast system using a white light supercontinuum as the probe for the short-lived singlet excited states.[29] For the long-lived triplet states, the triplet excited-state absorption is measured with a conventional quasi-cw photoinduced absorption spectrometer.[30] Singlet lifetimes measured by time-correlated single photon counting are also used to calculate the ISC rate; in most cases, the lifetimes are taken from the literature.[16,18,31] It is important to note that the quantitative determination of the triplet yield from the GSR relies on the absence of any photoinduced absorptions in the region where the photobleaching is probed. Figure 2 shows the spectra of the excited-state
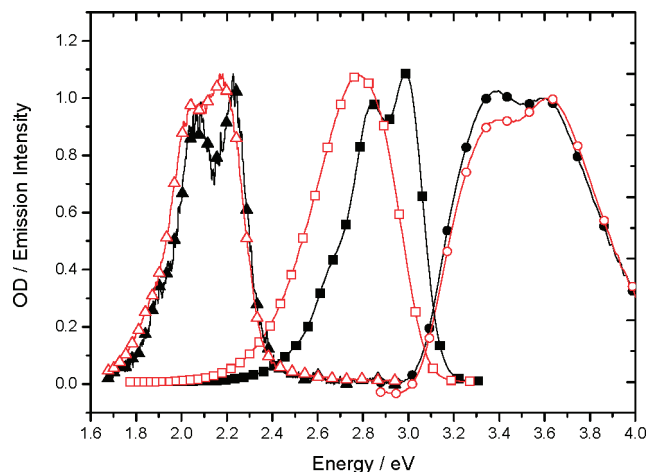
Figure 1. Compendium of spectra (absorption (●,○), fluorescence (■,□), phosphorescence (▲,△) for the FSF oligomer in MCH (filled symbols) and ethanol (open symbols).
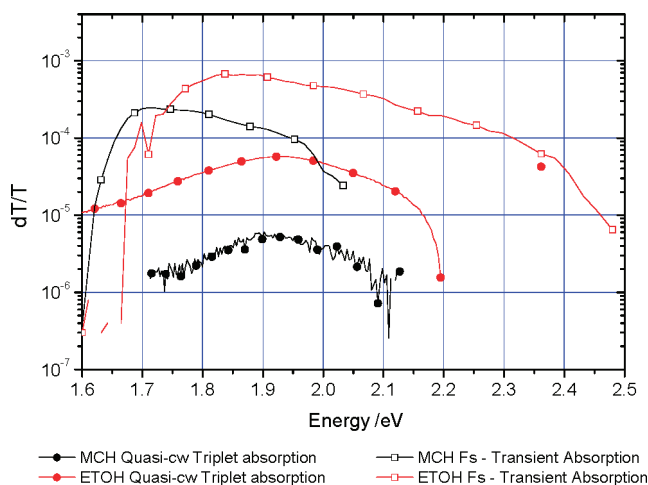

Figure 2. Compendium of photoinduced absorption spectra for the FSF oligomer in MCH and ethanol.

absorptions in the FSF molecule. It can be estimated that, at the probe wavelength for the GSR (3.2 eV), the strength of the absorption features is less than 1% of that at the peak, thus the influence on the large photobleaching signal observed is negligible.

Results

The fluorescence spectra in Figure 1 show the change in fluorescence with solvent; there is significant loss of vibronic structure and shift in the peak position of about 200 meV in the more polar ethanol compared to the MCH. The change is consistent with a change of the character of the excited-state from the LE state to an excited-state with strong CT character. The nature of the CT state has been characterized further in the previous work by Dias et al., and a CT state with some degree of conformational twisting is believed to be formed;[16] this is similar to the more formally defined TICT state. Excited-state absorption of the singlet/CT state is shown in Figure 2, in which the spectra show similar effects to the fluorescence. In MCH, the photoinduced absorption of the oligomer peaks at 1.71 eV, which is consistent with the absorption of the singlet excited-state in a polyfluorene trimer previously measured.[32] In the more polar solvent ethanol, there is a significant shift of the peak to 1.87 eV and an energy change of 160 meV. Broad, high-energy, excited-state absorption features in conjugated polymers and
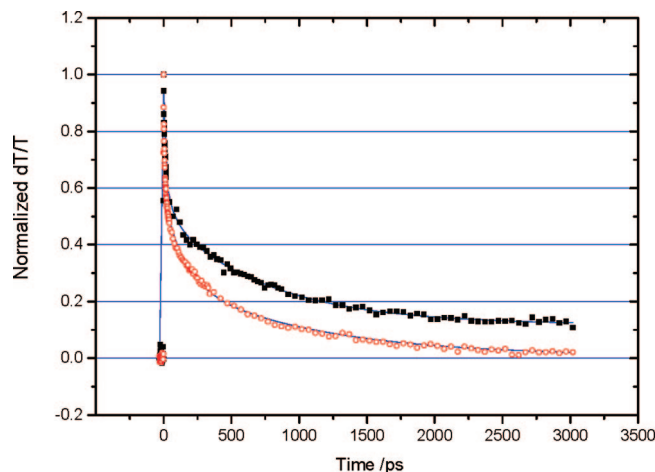

Figure 3. GSR for the FSF oligomer in MCH (red) and ethanol (black).

oligomers usually characterize charged states, either CT states, individually charged species (free polarons), or self-trapped CT excitons.[33–35] The solvatochromic effect in the excited-state absorption is in the opposite sense to that of the fluorescence: the fluorescence moves to lower energy in a polar solvent, whereas the excited-state absorption shifts to higher energy in the more polar solvent. The different effect of the polar solvent on the first excited-state and higher excited states is a strong indicator of the change of character of the state from an excitonic state to a CT state in a polar environment.

GSR decays in Figure 3 for the FSF oligomer show that there is a significant difference in the kinetics for the two media; in the MCH solution, almost all of the excited states decay in the 4 ns time window of the experiment, leaving few long-lived triplet states. In the polar environment of the ethanol solution, there is a large offset at long times from the triplet excited states. The lifetimes of the fluorescence measured previously with time correlated single photon counting (TCSPC) are 1.0 ns and 1.8 ns for the MCH solution and ethanol, respectively. The GSR kinetics are fitted with biexponential decays incorporating the lifetimes of the fluorescence as well as an offset for the triplet states, which do not significantly decay within the time window of the experiment; this is in place of the triplet term in eq 3. An additional fast component is present in the GSR; this is attributed to the non-radiative decay processes of the states and is the second exponential in the fit to eq 2. From the ratio of the offset due to the triplets and the maximum absorption, the yield of ISC is calculated using eq 3; for the FSF oligomer in MCH and ethanol, $\Phi_T = 0.007 \pm 0.005$ and $\Phi_T = 0.10 \pm 0.02$, respectively. As a check, one can calculate the proportion of the states that recover with the fluorescence lifetime and compare this with the fluorescence quantum yield of the oligomers. There is excellent agreement in both cases: for MCH, 0.83 ± 0.05 of the states decay with 1.0 ns lifetime, and the photoluminescence quantum yield (PLQY) is 0.82 ± 0.05; for ethanol, 0.69 ± 0.05 of the states decay with a fluorescence lifetime of 1.8 ns compared to a PLQY of 0.66 ± 0.05. The low triplet yield of the FSF oligomer in MCH compares well with the triplet yield measured by GSR for a fluorene-only trimer (FFF) where $\Phi_T = 0.004 \pm 0.005$ is measured.

Quasi-cw photoinduced absorption spectra of the oligomers in the two different degassed solvents show a similar trend to the GSR; the transient triplet absorptions in Figure 2 show the same spectra but with the intensity of the absorption in ethanol being approximately 11 times that of the absorption in MCH.

Triplet Formation by Conjugated Polymers

J. Phys. Chem. B, Vol. 112, No. 27, 2008 **8013**

TABLE 1: Triplet Yields, Singlet Lifetimes, and ISC Rates for a Number of Different Polyfluorene Copolymers and Oligomers

	solvent	emission	$\tau_f{}^a$	Φ_T	$E(S_1-T_1)^b$	$K_{isc}/10^6 S^{-1}$
FSF	MCH	415nm/3.00 eV	1.0	0.007	0.77	8.5
FSF	ethanol	448nm/2.77 eV	1.8	0.1	0.60	56
FFF	toluene	400nm/3.10 eV	0.66	0.004	0.90	5.3
FFSFF	toluene	430nm/2.88 eV	0.6	0.006	0.78	9.0
FFSFF	ethanol	453nm/2.74 eV	1.0	0.025	0.64	25
FFFFF	toluene	407nm/3.05 eV	0.55	0.005	0.80	13
PFDBTH$_{30}$	toluene	415nm/3.00 eV	0.35	0.065		185
PFDBTH$_{30}$	cyclohexanone	415nm/3.00 eV	0.38	0.060		158
PFS$_{30}$	toluene	430nm/2.88 eV	0.55	0.072	0.81	130
PFS$_{30}$	chloroform	450nm/2.76 eV	0.85	0.11	0.69	129
PFS$_{30}$	cyclohexanone	465nm/2.67 eV	1.1	0.14	0.60	127
PFDBTH$_{30}$	film	431nm/2.88 eV	0.26^c	0.03		113
PFS$_{30}$	film	469nm/2.64 eV	0.67^c	0.13		195
PFO	film	420nm/2.95 eV	0.32^c	0.033		100
PF2/6 (35mer)	toluene	413nm/3.00 eV	0.41	0.013	0.82	31
PFO (long)	toluene	413nm/3.00 eV	0.4	0.04	0.82	100

^{a} Fluorescence lifetimes taken from single photon counting[16,18,31] and the calculated rates of ISC. ^{b} Triplet energy gaps determined form triplet energies measured by phosphorescence spectroscopy and extracted form the literature.[31] ^{c} Decay lifetimes calculated from the weighted average of the singlet decay components in the pump probe data, and the ISC rates calculated from these.

This represents a similar increase in the triplet yield as the GSR indicates. Verification of the induced absorption as the triplet exciton can be made first by comparing with the literature value for the position of the transient triplet absorption of the fluorene trimer,[32] as well as the strong quenching effect of dissolved oxygen on the absorption peak. Additionally, the absence of any solvatochromic effect on the triplet absorption confirms this as an excitonic (LE) species rather than one of CT character.

The triplet yield for the oligomers FFSFF and FFFFF has also been measured; the results are presented in Table 1. As before, there is a significant increase in the triplet yield going from the two exciton-like species FFFFF and FFSFF in toluene to the twisted CT species FFSFF forms in ethanol. However, in this case, the increase in triplet yield is considerably smaller: only 4 times compared to the 14-fold increase in the smaller oligomers.

The conjugated polymers polyfluorene-*co*-dibenzothiophene (PFDBTH$_{30}$) and polyfluorene-*co*-dibenzothiophene-*s,s*-dioxide (PFS$_{30}$) show similar behavior with respect to the formation of a CT state as the oligomeric species FSF.[18] In polar solvents, PFS$_{30}$ has the broad fluorescence associated with the stabilized CT state and more structured LE emission in nonpolar solvents. In contrast, PFDBTH$_{30}$ does not readily form the CT state in either solvent, thus the two materials can be used as a model system for CT state formation without the need to change solvent. The same observation is made in the solid state: thin films of PFS$_{30}$ show broad CT emission, whereas the PFDBTH$_{30}$ shows only structured exciton emission. Effectively, the strong intrinsic dipole moment of the PFS$_{30}$ polymer means that the individual chains feel a polar environment, which stabilizes the formation of the CT state. It is likely that, in the solid state, the polymer chains occupy a variety of different conformations, with some being more planar, which favor the formation of an LE like species, and some that are twisted, which favor the formation of the CT state. The high efficiency of exciton diffusion and the lower energy of the CT state means that all the excited states end up in the twisted CT form as a result of migration, regardless of whether the chains are able to undergo conformational change after excitation or not.

The GSR data in Table 1 show the triplet yields for the two polymers. In the polymer PFDBTH$_{30}$ where there is never a CT state formed, there is little difference in the GSR in either the polar or unpolar solvent. Using the same fitting procedure
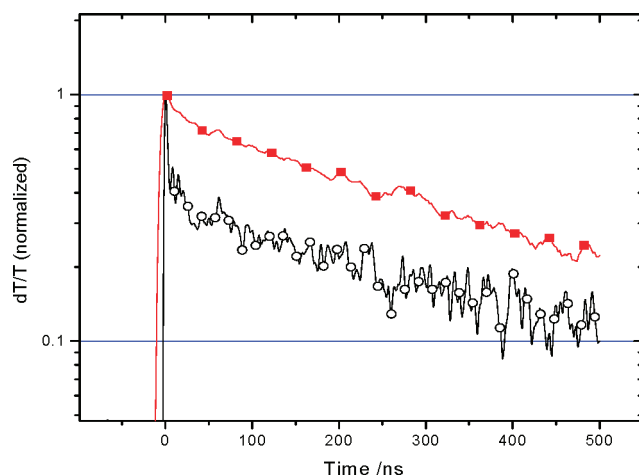

Figure 4. The long time recovery of the ground-state at 405 nm (○) and the decay of the triplet photoinduced absorption at 780 nm (■) for the polymer PFS$_{30}$ in chloroform.

as for the oligomers, one estimates a triplet yield (toluene) of $\Phi_T = 0.07 \pm 0.02$. For the polymer PFS$_{30}$ in the nonpolar toluene, a triplet yield of $\Phi_T = 0.07 \pm 0.02$ is also measured; the favorable comparison between the two materials in nonpolar solvents provides assurance that the LE states of the two polymers are similar. In contrast to PFDBTH$_{30}$ in the polar solvents where little change in the triplet yield is observed, PFS$_{30}$ shows significant increase in the triplet yield up to $\Phi_T = 0.14 \pm 0.02$ in cyclohexanone.

To verify that there are no other long-lived states such as excimers or defect states present in the solution that would falsely become attributed to the triplet yield, the GSR has been measured on a nanosecond time scale. This is compared to the triplet lifetime in Figure 4; for the polymer PFS$_{30}$ in chloroform, the GSR at 405 nm shows a fast recovery with a lifetime of a few nanoseconds (limited by a detector time resolution of 5 ns) from the singlet decay and a slow recovery with a lifetime of ~300 ns from the decay of the triplet. The decay of the triplet in the GSR compares well with the triplet decay measured at the transient triplet photoinduced absorption (1.6 eV). Similar results are obtained for the other materials and solvents measured. Thus the assumption that the only long-lived state present in the polymer is the triplet exciton can be maintained.

In the solid state, thin films of the polymers PFS_{30} and $PFDBTH_{30}$ show similar behavior; the PFS_{30} has a higher triplet yield than the $PFDBTH_{30}$. The CT state in PFS_{30} is stabilized by the interactions between neighboring chains, which results in a larger triplet yield. Conversely, in the polymer $PFDBTH_{30}$ where the excited-state is always of LE character, the interchain interaction does not lead to a higher triplet yield. The situation does of course become more complicated in the solid state, as one must account for the accelerated decay rate for the singlets attributed to the diffusion-controlled bimolecular annihilation of the excitons.[29,36] Effort has been made to minimize this effect by using low temperature and very low excitation density (<1 μJ cm^{-2}). Global analysis of the data at the wavelengths of the GSR and the singlet excited-state absorption leads to a triplet yield of $\Phi_T = 0.03 \pm 0.01$ for the non-CT-forming $PFDBTH_{30}$ and $\Phi_T = 0.13 \pm 0.02$ for the CT-state-forming PFS_{30}.

Phosphorescence of the oligomer FSF (Figure 1) in low-temperature glasses of ethanol and MCH shows a sharp phosphorescence peak at 2.2 eV (550nm) with a vibronic replica at 660 nm. This is comparable to the phosphorescence of polyfluorene oligomers and homopolymers such as the prototypical PFO; this is in agreement with the findings of previous studies that the lowest triplet excited-state is of LE character.[37]

Discussion

It is clear from the data in Table 1 that, in the FSF family of oligomers, the population of an intramolecular CT state increases the number of triplets formed; if the increases in triplet yield were comparable to the increase in lifetime of the singlet state then this would be an unremarkable discovery. For a system with a constant ISC rate, the increase in singlet lifetime would result in a concomitant increase in the triplet yield. In order to quantify the effect of the environment on the ISC in the conjugated oligomers and polymers, one must calculate the ISC rate, thus removing the effect of the singlet lifetime changes that the environment also induces. The ISC rate is given by eq 4, where k_s is the singlet decay rate, k_{isc} is the ISC rate, and Φ_T is the ISC yield. In the cases where nonsingle exponential fluorescence lifetimes are found, k_s is derived from a weighted average of the lifetimes.

$$k_{isc} = \Phi_T k_s \tag{4}$$

To understand the changes in ISC rates, it is helpful to remind oneself that the requirements for ISC are twofold.[15,38] From the golden-rule for radiationless transitions, an expression for the rate of intersystem crossing[39] can be derived:

$$k_{isc} = \frac{2\pi}{\hbar} \langle {}^1\Psi^0 | H_{SO} | {}^3\Psi^0 \rangle^2 [FCWD] \tag{5}$$

The two requirements are clear: first, the isoenergetic nature of the spin flip from the singlet to the triplet state means there must be an accepting triplet state, either a purely electronic or a vibrational sublevel of an electronic transition, close in energy to the singlet. This manifests itself in the Franck–Condon weighted density of states (FCWD), which is essentially an overlap integral between the initial and final states in the nonradiative transition. A small overlap between the donor singlet and accepting triplet results in a low ISC rate. The other requirement for ISC is some perturbation to the singlet to allow S–T mixing to facilitate the normally spin-forbidden triplet formation. This perturbation generally originates from the spin–orbit interaction (H_{SO}) between the donating singlet and accepting triplet ($^1\Psi^0$ and $^3\Psi^0$, respectively), although spin-vibronic and vibrational mixing is also possible. In the fluorene

oligomers, the triplet is predominantly out of the plane of the molecule; this is a general condition for planar polyacenes.[40] This is because the mixing of two $\pi\pi$ states (as the singlet and triplet both are) is only allowed by the out-of-plane components of the spin–orbit operator (H_{SO}), as both H_{SO} and the π states are symmetric to in-plane rotation.[15,38] In the literature it is generally accepted that the out-of-plane C–H vibrational modes mediate the mixing between the singlet and triplet states.[38] Conversely, when nonbonding electrons are involved, the in-plane components of H_{SO} are able to mix $\pi\pi-n\pi$, and, consequentially, the (three-center) spin–orbit integral is greater, with a concomitant increase in the ISC rate. For transitions with a large S_1-T_1 gap, there is the possibility of ISC to higher triplet (T_n) levels; the differing symmetry of these states could allow a larger mixing between the singlet and triplet states and a higher ISC rate.

Returning to the FCWD factor, which describes the vibrational overlap of the states required for the nonradiative transition, one must consider the energy gap between the excited singlet and triplet states. It is well-known that the probability of a nonradiative transition is increased as the energy gap is decreased, as a result of the more favorable overlap of the potential energy surfaces.[41] Once again the presence of higher (vibrational and electronic) triplet states than the phosphorescent T_1 could contribute to an increase in the ISC rate. Following the crossing to the triplet manifold, the state rapidly relaxes to the lowest triplet (T_1) state, so the reverse ISC to the S_1 state is not possible.

The oligomer FSF shows an almost 7-fold increase in the ISC rate when the twisted CT state is present in the polar environment compared with being in the LE state formed in a nonpolar environment. However, going to the longer oligomer FFSFF, the effect is diminished to approximately 3 times, and for the polymers, there is little change in the ISC rate; the increase in triplet yield in $PFSF_{30}$ appears only because of the increase in singlet lifetime. In order to reconcile this apparent difference in the mechanism of the ISC on going from the oligomers to the polymers, the rate of ISC in each case is compared to its analogous fluorene oligomer, i.e., one must compare FSF with an FFF trimer. It is apparent that the fluorene–dibenzothiophene oligomers in nonpolar solvents, i.e., in the LE excited-state, behave exactly like their analogous fluorene oligomers; the same observation is made in fluorescence studies. It is valuable to note the apparent weakness of the effect of the sulfur atom, contrasting the oligothiophenes where the triplet yield is high. This is due to the functionalization of the thiophene to thiophene-*s,s*-dioxide, removing the sulfur lone pair from interacting with the excited state.[42]

In the oligomers FSF and FFSFF in their CT state, there is a clear reduction in the k_{isc} on going to the longer oligomer, but both show a significantly greater number of triplets than in the planar LE state. This phenomenon has been observed previously in both the oligothiophenes and phenylalkenes, where experiment has shown a reduction in the ISC rate with increasing oligomer length.[43,44] Calculations have suggested that this is due to the geometry of the excited state: the more twisted bi- and terthiophenes have a higher ISC rate due to greater possibility of spin–orbit coupling mediated singlet–triplet mixing than in the more planar longer oligomers.[39] Further, ultrafast studies of terthiophene have shown a reduction of the ISC rate as the molecule relaxes from a twisted geometry to a more planar conformation.[45,46] These results provide the answer to understanding the high triplet yield in the twisted CT state; the ISC rate is greater because of the twisting of the molecule in its CT

Triplet Formation by Conjugated Polymers

J. Phys. Chem. B, Vol. 112, No. 27, 2008 **8015**

state rather than the CT character of the state itself. Indeed a general survey of the ISC rates in purely aromatic molecules reveals that the more planar, rigid molecules generally have a lower ISC rate than nonplanar molecules.[47] Taking the oligothiophenes and phenyl-alkenes as a guide and the [48]fact that the formation of twisted excited states is generally less favorable in large molecules, one can suggest that the lower ISC rate observed in the larger FFSFF oligomer is due to the less twisted nature of the excited state. To rationalize the increase in ISC rate in a twisted molecule, one must remember the out-of-plane nature of the triplet compared to the in-plane nature of the singlet in the planar polyacenes. In a twisted analogue of such a molecule, the potential for mixing in-plane singlet and an out-of-plane triplet states is greatly increased as a result of a reduction in the symmetry of the molecule. The increase in the twisted nature of the stabilized CT state for the FSF oligomer compared to the FFSFF in the polar solvent can also be drawn from the fluorescence lifetimes; one would expect a more twisted excited-state to have less coupling to the predominantly planar ground-state and lower fluorescence decay rate. The effect of a change in the orbital nature of the state on the ISC rate is not relevant for this system, as the similarity of the absorption spectrum in the two solvents confirms the $\pi\pi^*$ nature of the excited-state for both the LE and stabilized twisted CT state.

It is possible that the reduction in the S_1–T_1 energy gap could be partly responsible for the increase in ISC upon forming the lower energy CT state, in common with the well-established energy gap law for nonradiative transitions mentioned above. However, previous studies of the energy gap law for S_1–T_1 ISC have suggested that, for similar increases in the ISC rate to those observed in these molecules, an energy gap change of ~1 eV is required.[49] this is substantially greater than the change in energy gap between the FSF in MCH and ethanol of <0.2 eV; therefore it is very likely that there is another mechanism dominating the observed changes in the ISC rate. In addition to this, most papers[15,39] suggest that direct ISC to the T_1 level is very inefficient compared to crossing to higher electronic or vibronic excited states; the energy gaps between the S_1 and these higher triplet states are difficult to determine experimentally.

In the polymer analogues of the FSF system, there is no noticeable increase in the ISC rate associated with the change form the LE to the CT excited state. There is also no great change in the ISC rate between the CT-forming polymer (PFS$_{30}$) to the non-CT-forming PFDBT. In reality, there is a slight reduction in k_{isc} in PFS$_{30}$ due to the interaction of the sulfur lone pair with the excited-state in PFDBT. From this, one conclusion that can be drawn is that the CT state is less twisted in the polymers compared to the oligomers, and so the increase in ISC upon forming the CT state is very small. This suggestion of a lower level of conformational twisting upon forming the CT state in the polymer is as expected. The large bulky polymer molecules are expected to be less able to undergo conformational relaxation of any type because of their size, and this is supported by the observation that, although similar magnitudes of energetic relaxation are observed for conjugated oligofluorenes and polyfluorenes, the spectral shift of the polymer contains a significant contribution from energy migration as well as conformational relaxation.[50] In addition, other studies indicate a reduction in Stokes shift in conjugated polymers upon increasing chain length,[48] which is supportive of a reduced conformational relaxation for long-chain conjugated polymers.

One cannot fail to notice that all the polymer ISC rates are significantly higher than the ISC rates for the oligomers, even for the polyfluorene homopolymers. Generally, when considering the move from oligomers to polymers, a consideration for the energetic and conformational disorder must be made; this is particularly important in random copolymers such as these. The random arrangement of the co-oligomers in the chain leads to segments with more or less of the dibenzothiophene(-dioxide) units, leading to changes in the energy of the state. Hence, the random oligomers have a much broader distribution of states (DOS), confirmed by the broader absorption spectrum. The random nature of the units could also lead to segments favoring different excited states (LE or CT), which lead to different levels of twisting in the excited state, all of which affect the spin–orbit coupling and hence ISC rate. The broader DOS that polymers possess compared to their oligomeric analogues can have a dramatic effect the ISC. For example, in a system where the S_1–T overlap integral is small, an increase in the width of the DOS can increase the FCWD overlap integral between the singlet and accepting triplet and, hence, the ISC rate. Additionally, one can consider the change in the energetic position of the higher excited triplet states; generally, as the oligomer length increases, the triplets become more closely packed in energy terms with a trend to decreased singlet–triplet splitting as the chain length increases.[51,52] Thus, there may be more possibilities for energetically favorable accepting triplet states close to the singlet energy in the polymers compared to oligomers. Finally, the variety of different torsion angles between the neighboring chromaphores on a polymer chain[53,54] could lead to many possibilities for different degrees of mixing of singlet and triplet states and an increase in the ISC rate over the predominantly planar conformation of the smaller (non-CT-forming) oligomers.

Thus one can suggest that the ISC rate is higher in the polymers compared to the oligomers because of the generally increased disorder and better singlet–triplet energy mixing in the polymer due to better energy overlap and conformational disorder compared to well-defined oligomers. In the solid state in the conjugated polymers there is an increase in the ISC rate upon stabilization of the CT state. It seems that the effect of the CT formation on the ISC rate is once again significant; it is most likely that, because of the ease of migration in the solid state, the excitons are able to find the most twisted, lowest energy sites with the greatest CT state stabilization that are accompanied by the highest ISC rate.

The nature of the accepting triplet state is of interest to the mechanism of ISC; one would expect that in every case the lowest triplet state is the LE state, and indeed all the evidence (phosphorescence, transient triplet absorption) points to this being the case. This leads to two possibilities: the accepting triplet could be of LE character, with the ISC directly between the LE or CT singlet and the LE triplet; alternatively, there could be ISC from the CT singlet to a CT triplet in the polar media followed by relaxation to the LE triplet. The difference between these two mechanisms is very difficult to distinguish, as the singlet–triplet splitting in pure CT states is generally smaller than that of LE states, thus the energetic relaxation of the triplet to the lower LE triplet is expected to be rapid. While it is clear that, in the oligomers, the presence of a CT state with some degree of twisting does sensitize the triplets, whether this is through a triplet CT state intermediate or directly to the LE triplet is difficult to determine.

Conclusion

In summary, a higher triplet yield has been found in conjugated oligomers forming a CT singlet state compared to an LE singlet state; the higher triplet yield of the former can be attributed to increased torsional motions in the CT state

8016 *J. Phys. Chem. B, Vol. 112, No. 27, 2008*

King et al.

compared to the predominantly planar LE state. The mechanism of the increase is due to the twisted nature of the excited-state increasing the spin−orbit coupling mediated mixing between the singlet and triplet states, thus a twisted CT state is more likely to have a higher ISC rate than that of a planar LE state. The effect of this enhancement becomes diminished as the level of torsional change in the excited-state is reduced as the oligomer size increases. The effect of the CT formation on the ISC rate in large conjugated polymers is negligible because of the reduction in the twisting of the state and the generally greater ISC rate in polymers compared to the oligomers. An increase in the triplet yield in the CT excited state in polymer analogues is observed purely as a result of an increase in the singlet lifetime with a relatively constant ISC rate.

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