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Triplet energy transfer in conjugated polymers. III. An experimental assessment regarding the influence of disorder on polaronic transport

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It is a general notion that, in organic semiconductors, the transport of electronic excitations, such as neutral excitons of singlet or triplet type and charge carriers, is controlled by both, polaron and disorder effects. For compounds with low energetic disorder triplet exciton diffusion can be described in the framework of Marcus-theory [see Sudha Devi *et al.*,Phys. Rev. B **78**, 045210 (2008)], and a theoretical model for diffusion in more disordered compounds has been developed [see Fishchuk *et al.*, Phys. Rev. B **78**, 045211 (2008)]. Here we experimentally demonstrate that such a modified Marcus-type model is suitable to describe triplet exciton transport in commonly used poly(*p*-phenylene)-type polymers and oligomers. In particular, we provide a *quantitative spectroscopic* assessment of the polaronic and the disorder contribution to triplet exciton transport as a function of conjugation length. Franck-Condon analyses of the phosphorescence spectra and temperature-dependent triplet diffusion combined with analytic transport theory demonstrate that, in contrast to charge carriers, Marcus-type jump rates with dominantly polaronic activation energies control the motion of triplet excitons above a transition temperature.

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I. INTRODUCTION

Organic semiconductors are by now used commercially in various electronic devices such as solar cells, transistors, or light-emitting diodes (LEDs). In organic LEDs, a large fraction of the excited states are formed in a triplet spin state.[1,2] The diffusion of such triplet excitons to other phosphorescent emitters, to defect sites, or to other triplets (giving rise to triplet-triplet annihilation) therefore controls the efficiency of displays or lighting devices based on organic light emitting diodes.[3,4] Yet despite the prominent role of triplet exciton diffusion in organic semiconductor devices there are only few reports dedicated to the fundamental mechanism that control triplet transport in solid amorphous films.[4–11]

For excited states to transfer their energy from one site to another requires (i) some electronic coupling, (ii) sufficient (thermal) energy to overcome possible differences between the initial and final site energies that may arise due to energetic disorder in the amorphous film and, (iii), it requires a change in the configuration of the molecular backbone at the initial and final sites. While the electronic coupling between spin-singlet electrons is dominated by a dipole-dipole interaction (Förster-type transfer),[12] an orbital overlap mechanism such as exchange coupling (Dexter-type transfer) (Ref. 13) is required to provide the electronic coupling for triplet transfer.[14] The electronic coupling for both, singlets and triplets, has been investigated in some detail.[12–15] Extensive studies are also available on the effect of energetic disorder on triplet exciton diffusion. A theoretical description of time-dependent transport for both charged and neutral electronic excitations in random systems has been developed by Movaghar *et al.*[16,17] Subsequent gated phosphorescence studies in a benzophenone glass confirmed the notion that, in a disordered density of states, triplet exciton transport is a dispersive hopping process.[18] Later on, Rothe and Monkman[7] applied that concept to triplet motion in polyfluorene films. These works were, however, only concerned with the disorder contribution to triplet diffusion. They did not consider the effects caused by the associated change in molecular geometry. This change in molecular configuration upon energy transfer represents a polaronic effect. It implies that the exciton drags the conformational distortion with it when it moves, i.e., that the excitation is a polaron exciton. Some authors have pointed out that the polaronic nature of the excitation should cause energy transfer to require an activation energy and thus to be temperature dependent,[9,19–21] yet we are not aware of detailed systematic experimental studies on this issue. In charge transport studies, there have been *theoretical* advances to incorporate both effects.[22] However, for charges it is notoriously difficult to experimentally distinguish disorder and polaron contributions to the temperature dependence of charge mobility because of the lack of independent information on the geometric reorganization energy associated with a charge.[23] Such complementary information can, however, be extracted from spectroscopic studies of triplet excitons that also couple via exchange interaction as charged carriers do. The intention of the present work is (i) to show that a theory for polaron transport in the presence of disorder is applicable to treat triplet transport in random systems, (ii) to quantitatively discriminate between polaron and disorder effects based upon phosphorescence spectroscopy, and (iii) to identify guiding principles for materials design regarding optimizing polaron or disorder contributions.

We have recently presented an experimental study on triplet diffusion in a Pt polymer that is characterized by a very low degree of energetic disorder in an amorphous film, and we were able to show that a Holstein small polaron model can be used to quantitatively account for the temperature dependence of the diffusion (paper I).[24] In this model, energy transfer is considered to occur via a multiphonon hopping process down to a transition temperature below which the necessary thermal activation energy is no longer available so that tunneling prevails. The key point of the study is that the geometric reorganization energy λ deduced from the optical spectra can quantitatively account for the activation energy E_a of the triplet transport by $E_a=\lambda/4$, thus confirming the general approach of applying a polaron model. We note that above the transition temperature, the Holstein Small polaron model is mathematically identical to Marcus theory. In a subsequent work we presented an extended theoretical treatment in which the effects of energetic disorder are taken into account (paper II).[25] The thin films used in organic semiconductor devices are usually amorphous, and the associated spatial fluctuation of the dielectric polarization in the film causes the energy levels of the chromophores to vary statistically, leading to a Gaussian distribution of chromophore energies that is referred to as energetic disorder. Variations in the length of conjugated segments in polymer films can further add to the width of the variance σ of this distribution. While the theoretical expression was corroborated for the low-disorder Pt polymer, a *systematic experimental study* on a range of organic semiconductors, confirming the predicted effects of disorder on the triplet transport, has not yet been carried out.

In this work, we investigate the effect of energetic disorder and geometric relaxation on triplet state diffusion for two series of model compounds in which the conjugation length is varied systematically (Fig. 1). First, we compare four poly(*p*-phenylene)-based polymers (series I), where increasing possibilities for torsions along the chain increase the energetic disorder along the series (and concomitantly reduce the conjugation length), and second we compare polymer, trimer and dimer of a polyfluorene (series II) to establish the oligomer length dependence of the polaronic and disorder contributions. By doing so we provide experimental evidence for the applicability of a small polaron model that includes the effects of disorder to describe triplet exciton diffusion. In particular, we quantitatively compare the contribution of polaronic effects and disorders effects to triplet transfer.

We note that the model we employ does not specify on the nature of the electronic coupling, except that the coupling be weak enough for the transport be nonadiabatic. The results presented here are therefore applicable and of general importance for nonadiabatic transfer of any electronic excitation, be it a triplet state, singlet state or a charge carrier. The parameter that will change when extending the model to singlets or charges is the ratio of the polaronic and disorder contribution, as this is dependent on the details of the exciton-bath interaction for each relevant electronic state.[26–30]

II. EXPERIMENTAL METHODS

The PF2/6 was received from American Dye Sources Ltd. (ADS), Canada, and has a molecular weight M_w of about 70 kg/mol. MeLPPP, PIF and DOOPPP were synthesized as described in Refs. 31–33, with molecular weights M_w (and polydispersity index PDI) of 66 kg/mol (PDI=2.44), 400 kg/mol (PDI=2.60), and 24.5 kg/mol (PDI=1.69), respectively. The fluorene dimer and trimer were synthesized following a palladium catalyzed Suzuki cross coupling as detailed in Refs. 34 and 35. Optical measurements are taken on thin films of about 115 ± 15 nm thickness, which were prepared by spin coating from toluene solutions (20 mg/ml) onto quartz (Spectrosil B) substrates. A Cary5000 ultraviolet-visible spectrometer was used to take the absorption spectra. Temperature-dependent luminescence spectra were taken as detailed in Ref. 36 with the sample placed in a continuous flow cryostat. In brief, 6 ns pulses at 355 nm (3.49 eV) with an excitation density of about 280 μJ cm^{-2} pulse^{-1} (60 μJ cm^{-2} pulse^{-1} for MeLPPP) were used for excitation, and detection occurred with a time gated intensified charge coupled device (iCCD) camera at a delay time of 10 ms and a gate width of 80 ms. We note that the gate width and excitation density correspond to near steady-state conditions in the bimolecular regime. Franck-Condon progressions were carried out as described in detail by Khan *et al.*[37] for a polyfluorene polymer using the same Raman frequencies and the same refractive index. For the dimer and the trimer, the refractive index was shifted in energy to account for the higher optical gap.

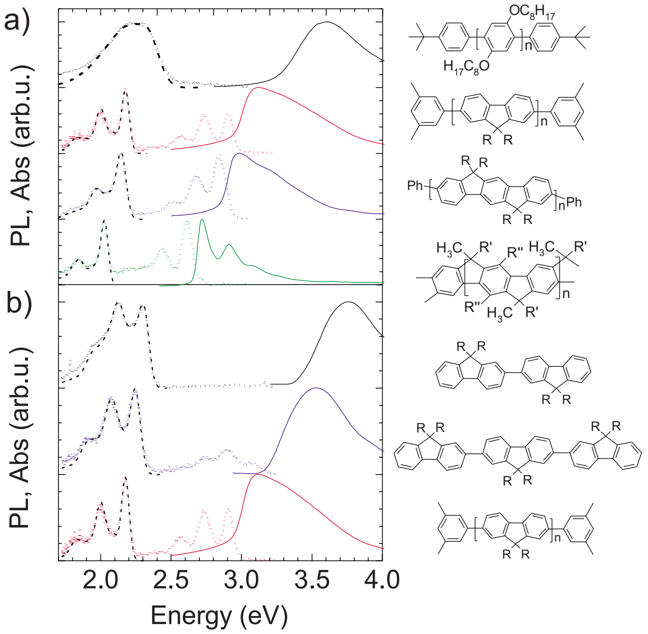

FIG. 1. (Color online) Absorption (solid line), photoluminescence (dotted line), and chemical structures (a) of DOOPPP, PF2/6, PIF, and MeLPPP (from top to bottom) and (b) of PF2/6 dimer, trimer, and polymer (from top to bottom) with R=2-ethylhexyl, $R'=1,4\text{-}C_6H_4\text{-}n\text{-}C_{10}H_{21}$, and $R''=\text{-}n\text{-}C_6H_{13}$. Franck-Condon fits (dashed line) to the phosphorescence spectra are also included.

III. RESULTS

The mathematical derivation of our model is outlined in Ref. 25. Essentially, an expression for Holstein's small po-

TABLE I. Comparison of the disorder parameter σ and the activation energy E_a derived from a Franck-Condon analysis to the 10 K phosphorescence spectra (Fig. 1) and derived by fitting Eq. (1) to the temperature dependence of the triplet diffusion rate (Fig. 3). For 300 K, the contribution of disorder $\sigma^2/4k_BT$ to the total effective activation energy E_{eff} are listed. For reference, the Huang-Rhys parameter S and the electronic coupling J are also included. The value for J is calculated on the premise that $W_e=k_D$ and $c=1$.

	From optical data (Fig. 1)			From diffusion data (Fig. 2)				
	S	σ (meV)	E_a (meV)	σ (meV)	E_a (meV)	$\sigma^2/4k_BT$ (meV)	E_{eff} (meV)	J (meV)
MeLPPP	0.93	29 ± 5	65 ± 4	36 ± 8	74 ± 8	13 ± 6	87 ± 10	27 ± 6
PIF	0.97	43 ± 6	67 ± 4	38 ± 8	79 ± 8	14 ± 6	93 ± 10	24 ± 5
PF2/6	1.05	39 ± 4	78 ± 5	40 ± 9	80 ± 8	15 ± 7	96 ± 11	19 ± 3
DOOPPP	1.13	70 ± 5	81 ± 5	69 ± 9	86 ± 9	46 ± 12	131 ± 15	8 ± 1
PF2/6	1.05	39 ± 4	78 ± 5	40 ± 9	80 ± 8	15 ± 7	96 ± 11	19 ± 3
Trimer	1.38	36 ± 3	101 ± 7	31 ± 10	118 ± 9	9 ± 6	127 ± 11	4.5 ± 0.5
Dimer	1.62	34 ± 3	118 ± 8	26 ± 8	165 ± 13	7 ± 4	172 ± 14	2.0 ± 0.2

laron model is taken as derived by Emin,[38] where energetic differences between the initial and final site are explicitly taken into account. A high- and a low-temperature regime, divided by a transition temperature T_T, are considered separately. The low-temperature equation corresponds to a Miller-Abrahams model while the high-temperature expression is of a Marcus type. By applying an effective-medium approach, the energetic variations are expressed through the variance σ of the Gaussian density of states. The triplet transfer rate is then given by

$$W_e=\frac{J_0^2}{\hbar}\exp\left(-2\frac{a}{L}\right)\sqrt{\frac{\pi}{4E_a k_B T}}\exp\left[-\frac{E_a}{k_B T}-\frac{1}{8}\left(\frac{\sigma}{k_B T}\right)^2\right],\quad T \gg T_T, \tag{1}$$

$$W_e=\nu_0\exp\left(-2\frac{a}{L}\right)\exp\left[-\frac{1}{2}\left(\frac{\sigma}{k_B T}\right)^2\right],\quad T \ll T_T, \tag{2}$$

where a is an average distance between neighboring localized states, L is the effective triplet localization radius, ν_0 can be considered as an attempt-to-jump frequency, and J_0 is a constant that relates to the electronic coupling. E_a is the activation energy in the absence of energetic disorder, i.e., it includes only polaronic contributions, and it is related to the geometric reorganization energy λ by $E_a=\lambda/4$.[24] According to Eqs. (1) and (2), the temperature dependence of triplet transfer is entirely determined through the parameters σ and λ that characterize the degrees of energetic disorder and geometric relaxation. In contrast to charges, for excitons, both parameters can be inferred from an analysis of the optical spectra. We shall now first derive σ and λ from the phosphorescence spectra and then compare this with the values we obtain by fitting Eqs. (1) and (2) to the temperature dependence of the triplet diffusion rate.

Figure 1 shows the chemical structures of the compounds, their thin-film absorption spectra and the emission spectra along with a Franck-Condon fit to the phosphorescence. The absorption spectra are broad and show the expected bathochromic shifts due to an increase in conjugation length (series I) or oligomer length (series II). The emission spectra consist of two bands that are assigned to delayed fluorescence (centered around about 2.8 eV) and phosphorescence (at about 2.1 eV), respectively. This assignment is based on the fact that the high-energy band is identical to the prompt fluorescence except for the longer lifetime, and the low-energy band has similar vibrational spacing than the fluorescence, is separated by 0.7 eV from the fluorescence, has a lifetime exceeding 1 s at 10 K and resembles the phosphorescence spectra of closely related compounds.[7,39] The geometric reorganization energy λ simply corresponds to the vibrational relaxation energy, E_{rel}, that is connected with one excitation and one deexcitation process, i.e., $\lambda=2E_{rel}$ (see paper I).[24] We can therefore derive the reorganization energy λ and the energetic disorder parameter σ by fitting a Franck-Condon progression to the 10 K phosphorescence spectra. E_{rel} is given by $E_{rel}=\Sigma_i S_i \hbar\omega_i$, where S_i is the Huang-Rhys parameter for the vibrational mode i with frequency $\hbar\omega_i$. The Franck-Condon fit and the experimental data agree well as can be seen in Fig. 1. The resulting values for the total Huang-Rhys parameter $S=\Sigma_i S_i$, the activation energy E_a and the disorder parameter σ are summarized in Table I. Along series I, i.e., from MeLPPP to DOOPPP, we observe an increase in both, the degree of energetic disorder as manifested in σ and the amount of geometric relaxation parameterized through $E_a(=\lambda/4)$. Qualitatively, this is already evident when merely considering the linewidth of the 0-0 phosphorescence peak (for σ) and the relative intensity of the 0-1/0-0 peak (for λ). Both effects are well understood and relate to the increase in the torsional degree of freedom along the series. In series II, we observe a decrease in the reorganization energy and an increase in the degree of energetic disorder with increasing oligomer length. The former reflects the larger delocalization of the excited-state wave function while the latter arises from a higher conformational variation for longer oligomers. The two sets allow us therefore to investigate compounds where the polaronic and disorder parameters λ and σ vary system-

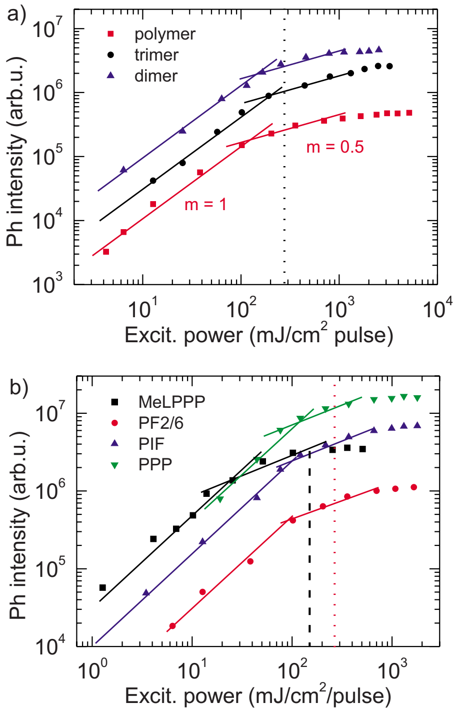

FIG. 2. (Color online) The dependence of the phosphorescence on the excitation power (a) PF2/6 dimer, trimer, and polymer and (b) for DOOPPP, PF2/6, PIF, and MeLPPP. The symbols correspond to experimentally measured data. The solid lines indicate slopes of 1 (monomolecular regime) and 0.5 (bimolecular regime). They serve as a guide to the eye. The dotted vertical line indicates the excitation power used for the data presented in the paper, except for MeLPPP where the excitation power used is indicated by a dashed line.

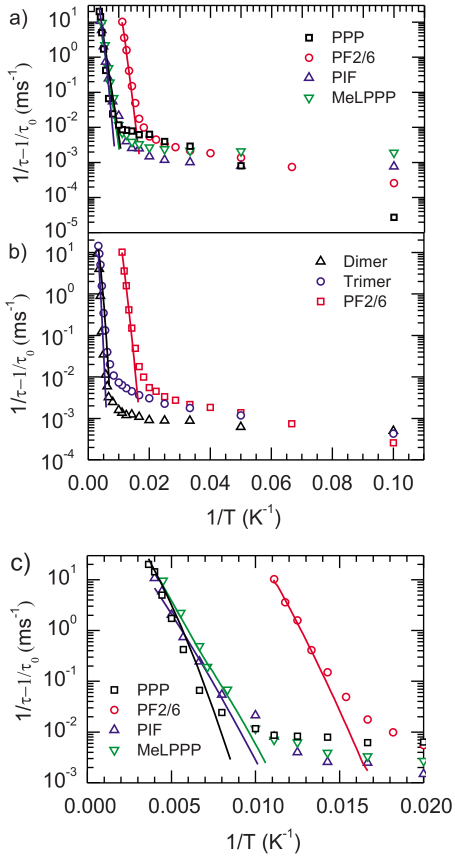

FIG. 3. (Color online) Arrhenius plot of the phosphorescence decay rate $\frac{1}{\tau}-\frac{1}{\tau_0}$ against inverse temperature (a) for the MeLPPP, PIF, PF2/6, and DOOPPP and (b) for the PF2/6 dimer, trimer, and polymer. Solid lines indicate fits of Eq. (1) to the high-temperature part yielding the parameters listed in Table I. A closeup of (a) is shown in (c), focusing on the $1/T$ range of 0.0–0.02 1/K.

atically (in phase for set I and in opposite directions for set II) while the molecular backbone does not change its chemical nature.

We now require the temperature dependence of the triplet diffusion rate k_D, which can be inferred from the measurement of the phosphorescence lifetime in the bimolecular regime. Figure 2 shows the phosphorescence intensity as a function of the excitation power. The measurements presented in Fig. 1 and Fig. 3 were carried out with the excitation energies indicated in Fig. 2. This corresponds to the intensity where bimolecular recombination is already present, yet the concentration of triplets is not altered significantly by the recombination. In this regime, a triplet exciton may decay radiatively with a rate k_r or nonradiatively by internal conversion with a rate k_{ic}. We consider k_r and k_{ic} to be independent of temperature.[40–43] Furthermore, the triplet may decay nonradiatively through diffusion with a temperature-dependent rate $k_D(T)$ to sites where it is quenched, such as sites with other triplets giving rise to triplet-triplet annihilation or defect sites. We consider the quenching rate to be fast compared to the diffusion process so that the rate of triplet quenching is limited by the temperature-dependent triplet diffusion rate k_D. Consequently, the lifetime τ is a function of temperature, and it is given by $\tau(T)=[k_r+k_{ic}+ck_D(T)]^{-1}$, where c is a proportionality constant that depends on the concentration of triplets and quenchers. If we presume there is no triplet diffusion at 5 K, we obtain $\tau(5\ \mathrm{K})=[k_r+k_{ic}]^{-1}=\tau_0$, so that the temperature dependence of $k_D(T)$ can be determined experimentally according to $k_D(T)=c[\tau(T)^{-1}-\tau_0^{-1}]$. This is displayed in Fig. 3 as a function of inverse temperature and on a semilogarithmic scale. For all compounds we observe a low-temperature regime, where the triplet diffusion is only weakly temperature dependent, and a high-temperature regime that is characterized by a large activation energy. The transition between the two regimes is around 100 ± 50 K with the higher temperatures for the more disordered compounds. From a fit of Eq. (1) to the high-temperature branch values for σ and E_a can be derived as well as for the pre-exponential factor $J=J_0\exp(-a/L)$ (Table I), except for multiplication by a constant.

IV. DISCUSSION

If we compare the σ and E_a values we obtained from the Franck-Condon analysis of the phosphorescence spectra with those inferred from fitting the temperature dependence of the triplet diffusion rate, we find excellent agreement for all the polymers. For the oligomers, the match is of a slightly lower quality due to a less exact Franck-Condon fit,[44] yet it is still good. We take this result to be an experimental verification of the interplay between activated energy-transfer processes and static disorder, quantitatively consistent with the disorder-modified polaron model suggested in our paper II.[25] As already pointed out in Sec. I, these findings demonstrate that a theory for polaron transport in the presence of disorder, as first derived to describe charge-carrier mobility, is applicable to treat triplet exciton transport in amorphous organic semiconductors. This is consistent with a report by Closs *et al.*[11] who found that triplet transfer rates in polyphenyl systems could be correlated with the corresponding electron transfer rates. Moreover, for triplet excitons, information on the energy associated with the geometric rearrangement is available through Franck-Condon analysis of the phosphorescence spectra. It is therefore possible to assess the contribution of both, polaron and disorder effect in a quantitative fashion. This is in contrast to charge carriers where the polaron energy is spectroscopically elusive. As a side comment, we remark that in contrast to our results on amorphous films, for molecular crystals such as anthracene a Holstein small polaron model is not sufficient to account for the temperature dependence of triplet transport. Munn and Siebrand[9] report that a quadratic electron-phonon coupling needs to be taken into account.

We remind the reader that our model does not consider the nature of the electronic coupling between an initial and final transfer site. Rather is concerned with the change in molecular geometry that is associated with the transfer. Equations (1) and (2) should therefore also be applicable to singlet exciton diffusion (suitably adapted).[45] Singlet diffusion is usually treated in the framework of Förster-type resonance energy transfer, where the effects of disorder and coupling to low-energy phonons are usually implicitly included through the spectral overlap integral.[26–30] Equations (1) and (2) have been applied to and are in fact originally derived to describe the charge-carrier mobility at zero electrical field (with E_a in that case corresponding to half the polaron binding energy).[46] For charge carriers, however, E_a and σ are only accessible from the transport data, while for excitons, both transport and optical data can be taken as two independent ways to derive these parameters. In addition to confirming the theoretical approach, this is of some practical value, since it implies that a measurement of the phosphorescence spectrum readily provides the activation energy for triplet diffusion.

In order to further assess the relative contribution of polaronic effects and disorder effects to the triplet dynamics, it is useful to define an effective activation energy according to[46]

$$E_{eff} = -k_B \left\{ \frac{d[\ln(W_e)]}{d\left(\frac{1}{T}\right)} \right\} = E_a + \frac{1}{4}\frac{\sigma^2}{k_B T}. \qquad (3)$$

E_{eff} is the sum of the temperature-independent polaronic contribution E_a and a temperature-dependent disorder contribution. Table I includes the disorder contribution and total activation energy for $T = 300$ K, where most devices are operated.

When comparing the polaronic and disorder contributions we are able to identify guiding principles for materials design. First we note that for short oligomers such as the PF2/6 dimer and trimer, disorder adds less than 10% to the total activation energy and is thus negligible. Second, σ becomes largest and E_a smallest in the polymer limit. Yet even for DOOPPP, the most disordered polymer we investigated, transport is dominated by the polaronic effects as is evident from an E_a of 86 meV compared to a disorder contribution of 46 meV. The lattice distortion associated with an excited state takes its smallest possible value for the case of a well-conjugated polymer such as MeLPPP, while it is highest for a short oligomer like the PF2/6 dimer. The dominant polaronic nature of the triplet exciton diffusion we find implies therefore that well-conjugated polymers are best suited as triplet-transporting materials for energy-transfer purposes. In contrast short oligomers or highly disordered polymers are the material of choice when the triplet is intended to stay put, for example, to obtain a high radiative decay rate.

The dominant influence of the geometric distortion on the temperature dependence of the diffusion process is specific to the excitations being triplets. For example, charge carriers, by nature of being more delocalized, tend to have a much higher disorder and lower geometric relaxation energy associated with them, and that alters the relative contribution of both effects. We now briefly comment on the size of the electronic coupling J we obtain. The electronic coupling increases by a factor of 3 from the PF2/6 dimer to polymer, and by a factor of 5 from the most disordered polymer, DOOPPP; to the highly conjugated MeLPPP. This emphasizes the need for orbital overlap in the transfer of triplet excitons which is best along a well-conjugated polymer chain.

Finally we consider triplet diffusion in the range below the transition temperature T_T. We first note that approaching T_T from high temperatures, the disorder contribution increases strongly. At temperatures below T_T, triplet diffusion can no longer be considered as the polaronic multiphonon hopping transport expressed in Eq. (1) above. Rather, it needs to be described as the single-phonon-assisted tunneling process between the initial and final site given in Eq. (2) [for detail, see paper II (Ref. 25)]. While very good qualitative agreement can be obtained with the trend predicted by Eq. (2), the absolute values of the slope are too low to be consistent with the disorder parameter derived from the optical spectra. The reason for this is given by the fact that our model is based on the establishment of quasiequilibrium. Below T_T, in the tunneling regime, quasiequilibrium will not be reached for triplets in disordered compounds, since spectral diffusion becomes frustrated.[36] This is essentially a result of the short range of the triplet electronic coupling. Paradoxically, the frustrated spectral diffusion, i.e., frustrated diffusion in energy space, accelerates the diffusion in real physical space. Kinetically frustrated excitons are located in the density of states (DOS) at an energy that is higher than that in thermal equilibrium. This enables them to move (at that energy) with only little or no activation energy over a large number of sites without relaxing to tail states of the DOS.

Consequently, the experimentally measured diffusion rate is higher than what is expected for excitations in thermal equilibrium. Future theoretical work would be required to model diffusion in the low-temperature regime in the presence of frustration.

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