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# Triplet energy transfer in conjugated polymers. I. Experimental investigation of a weakly disordered compound

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Efficient triplet exciton emission has allowed improved operation of organic light-emitting diodes (LEDs). To enhance the device performance, it is necessary to understand what governs the motion of triplet excitons through the organic semiconductor. Here, we have investigated triplet diffusion using a model compound that has weak energetic disorder. The Dexter-type triplet energy transfer is found to be thermally activated down to a transition temperature $T_T$, below which the transfer rate is only weakly temperature dependent. We show that above the transition temperature, Dexter energy transfer can be described within the framework of Marcus theory. We suggest that below $T_T$, the nature of the transfer changes from phonon-assisted hopping to quantum-mechanical tunneling. The lower electron-phonon coupling and higher electronic coupling in the polymer compared to the monomer results in an enhanced triplet diffusion rate.

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## I. INTRODUCTION

The photophysics of triplet excitons is receiving more attention as a result of the success of phosphorescent organic light emitting diodes (OLEDs) that are now employed for display and lighting applications.[1] Triplets are the main emissive species in such OLEDs so that the diffusion of triplet excitons to either quenching sites or emissive dopant sites can prove crucial for the efficiency of the OLED. A detailed understanding of what governs triplet diffusion (triplet energy transfer) is therefore essential to make significant progress with phosphorescent host-guest systems.[2–12] Furthermore, the understanding of triplet transfer plays an important role not only in the field of organic LEDs, but also in photovoltaic[13–16] and biological applications.[17,18]

After a decade of intensive scientific research, we have a reasonable understanding of the *energetics* of the triplet excited state,[19–27] though a picture for the triplet *dynamics* is only currently being developed.[28–31] A key issue to be discussed is the microscopic mechanism of triplet diffusion. At present, little is known at an experimental or theoretical level about the motion of triplet excitons in disordered molecular or polymeric solids. The mechanism of exciton migration has already been debated in the late 1960s for molecular crystals.[32,33] Singh *et al.*[34] suggested a bandlike character for the triplet motion. In contrast, Jortner *et al.*[35] argued a hopping-type transport for a localized exciton whose motion is followed by the lattice distortion. The experimental evidence for the arguments was usually sought in the temperature dependence of phosphorescence and delayed fluorescence (with temperature dependence suggesting hopping and temperature independence pointing to bandlike transport), yet the interpretation of the data was complicated by the presence of traps in the molecular crystals and hence the issue was not clarified satisfactorily.[33,36] For the disordered conjugated polymers used for semiconductor applications today such as polyparaphenylenes or polyfluorenes, evidence has been presented for both, temperature independent and temperature activated triplet diffusion mechanisms, and a more detailed understanding is therefore highly desirable.[29,30]

Triplet energy transfer is usually described by the Dexter-mechanism.[37,38] It can be considered as simultaneous exchange of the electrons in highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) between the donor and the acceptor molecules.[39,40] Electron transfer in various molecular systems has been successfully modeled with Marcus[41,42] theory. In this paper, we demonstrate that, above a transition temperature, Marcus theory can also provide a suitable model for triplet energy transfer in a semiconducting polymer. A major feature of Marcus theory is that the transfer rate is exponentially related to the reorganization energy associated with the presence of an electronic charge. Here, we demonstrate that, in a similar fashion, triplet energy transfer can be expressed as a phonon-assisted hopping process that depends exponentially on the geometric relaxation energy associated with the transfer.

For conjugated polymers, there is the added complication that charge transfer can be dominated by the effects of energetic disorder,[43,44] and this may also apply to triplet diffusion since it is associated with a transfer of two charges. In this paper, we aim to investigate the "intrinsic" properties of triplet diffusion without disorder-induced effects, so we have chosen a model compound that exhibits very little energetic disorder. How the nature of triplet diffusion is affected by the disorder present in many commonly used polymers is the concern of the next paper.[45]

The model compound we use is a well-characterized platinum poly-yne[19–21,46,47] shown as inset in Fig. 1. As will be discussed in detail below, its well-structured narrow phosphorescence spectrum is a manifestation of narrow density of states with little energetic disorder. The inclusion of the

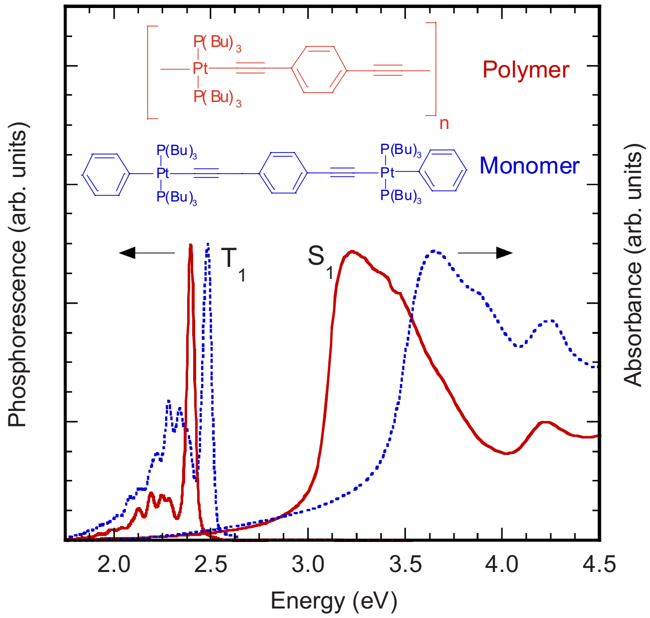

FIG. 1. (Color online) The normalized phosphorescence spectra at 10 K and absorption spectra at 300 K of the polymer (solid line) and the monomer (dotted line). The chemical structures of the polymer and the monomer are shown as inset. Excitation for luminescence was provided by a continuous-wave argon-ion laser at 3.49 eV.

heavy metal platinum in the chain makes phosphorescence easy to detect. At the same time, the emission originates from conjugated linker between the platinum sites as can be seen from comparison with the analogous all-organic compound.[19] The materials used in phosphorescent OLEDs may be small molecules or polymeric materials and the photophysical properties of triplet excitons such as energetics, formation, and decay have been demonstrated to depend on chain length.[21,24,25,48–50] We therefore consider it appropriate to explore how the chain length may affect the diffusion of triplet excitons as well. To this end, we compare our model polymer with its corresponding monomer.

## II. EXPERIMENTAL METHODS

The polymer and monomer were synthesized and characterized as described elsewhere.[51,52] The average molecular weight of the polymer is 96 000 g/mol, corresponding to about 130 repeat units in the chain. The molecular weight was determined by gel permeation chromatography and was found consistent with values reported earlier.[52] The nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 300 MHz spectrometer at 124.44 MHz. The $^{31}$P spectra were referenced to external $H_3PO_4$. The solvent used for NMR was $CD_2Cl_2$.

For optical measurements, thin films were spun cast from dichloromethane solutions of concentrations 10 and 20 mg/ml, respectively, of the polymer and the monomer on quartz (Spectrosil B) substrates using a conventional photoresist spin coater. Films were typically of 100 nm thickness as measured using a Dektak Systems profilometer. A Hewlett-Packard ultraviolet-visible spectrometer was used to take the absorption spectra of the thin films. The photoluminescence (PL) spectra were taken with the samples mounted in a continuous flow helium cryostat. The temperature was controlled with an Oxford Intelligent Temperature Controller (ITC-4). The excitation was provided by the UV lines of a continuous-wave (cw) argon-ion laser (3.49 eV) with typical intensities of 0.25 $\text{mW/mm}^2$. The PL spectra were recorded using a spectrograph with an optical fiber input coupled to a cooled charge coupled device (CCD) detection system (Oriel IntraspecIV).

For excitation density dependent phosphorescence measurements and triplet lifetime measurements, the samples were mounted in a helium cryostat and they were excited using a pulsed, frequency-tripled neodymium YAG laser at 355 nm (3.49 eV) (Spectron SL401). The duration of the laser pulses was 6 ns and the laser was operated at a repetition rate of 10 Hz. The light emitted by the sample was dispersed and subsequently detected by a time gated/intensified CCD camera (Andor iStar DH734–18F-9AM). The measurements were taken with a delay time of 200 ns and a gate width of 1 ms. The lifetime measurements at all temperatures were carried out at an excitation density of 25 $\mu\text{J/cm}^2\text{/pulse}$. To increase the signal-to-noise ratio, all spectra were obtained by averaging over 100 laser shots. The number of excitons formed per repeat unit of the compounds studied here was found out by assuming that the excitation energy is homogeneously absorbed and intersystem crossing rate is 1 and hence the number of excitons formed per chain is same as that of the number of photons absorbed. The chain density in the film is calculated by comparing optical densities of solutions with known concentration and optical densities of the film. At temperatures exceeding 325 K, differential scanning calorimetry indicates a possible phase transition to occur in the monomer film, so the phosphorescence lifetime was measured only up to 325 K.

## III. RESULTS

Figure 1 shows the thin-film absorption and phosphorescence spectra of the polymer and the monomer studied. Following absorption into the singlet $S_1$ excited state, heavy-metal induced spin-orbit coupling causes a high intersystem crossing into the triplet $T_1$ excited state from which the strong phosphorescence displayed in Fig. 1 occurs.[21] The polymer and monomer differ mainly in their degree of conjugation. The increased conjugation in the polymer is evident primarily through the redshift in absorption when going from the monomer to the polymer. Furthermore, the intensity of the vibrational sidebands in the polymer triplet emission is reduced compared to the monomer. This indicates a reduced lattice distortion due to an increased delocalization of the electronic wave function in the polymer. Such a lower geometric relaxation energy in longer oligomers is well established for conjugated systems.[53]

Despite their chemical similarity, the polymer and the monomer differ in the evolution of the overall phosphorescence intensity with temperature [Fig. 2(a)]. While the phosphorescence is strongly temperature dependent in the poly-

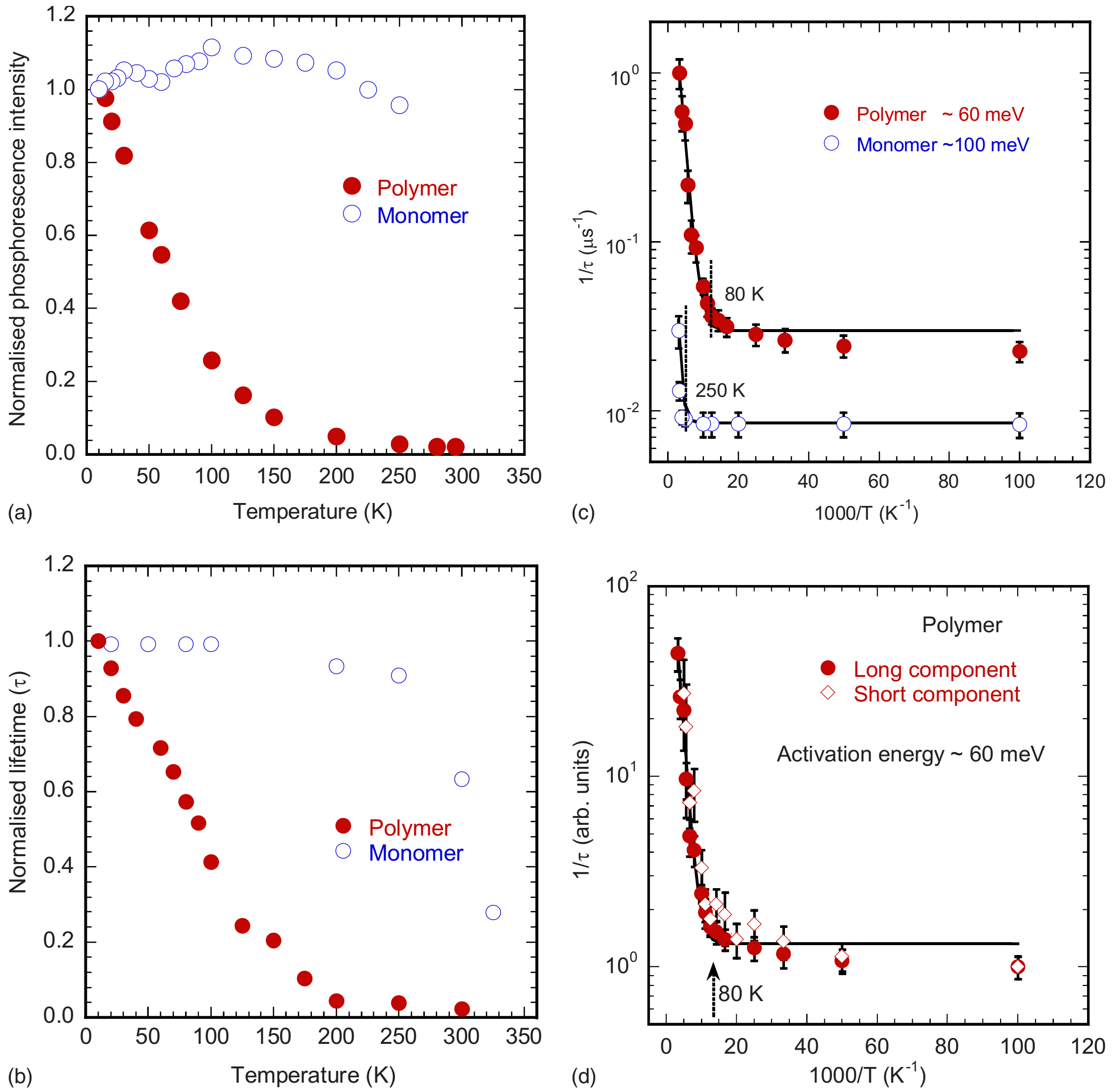

FIG. 2. (Color online) (a) The dependence of normalized integrated phosphorescence intensity on temperature for the polymer and the monomer. (b) The triplet lifetimes ($\tau$) plotted against temperature for the polymer and the monomer as described in the text. The lifetimes at 10 K for the polymer (45 $\mu$s) and the monomer (120 $\mu$s) are normalized to unity for comparison. (c) Arrhenius plot of the phosphorescence decay rate ($1/\tau$) against inverse temperature (1000/T). The black curves correspond to the equation $1/\tau = a \times \sqrt{1/T}\exp[-E_a/k_BT]+b$ with an activation energy ($E_a$) of 60 meV for the polymer and 100 meV for the monomer. The dotted lines indicate the transition temperatures 80 and 250 K. (d) Arrhenius plot of the phosphorescence decay rate ($1/\tau$) in the polymer. Both the long lived and short-lived components of the triplet lifetimes are shown as filled circles and crosses, respectively. The lifetimes at 10 K are normalized to unity to allow for comparison. A fit corresponding to the equation $1/\tau = a \times \sqrt{1/T}\exp[-E_a/k_BT]+b$ is also shown, yielding an activation energy ($E_a$) of approximately 60 meV for both components.

mer, there is little temperature dependence in the monomer up to around 200 K above which it starts to reduce. This cannot be due to a difference in the internal-conversion process in the two compounds. Internal conversion follows the "energy-gap law,"[21,38] for which the nonradiative decay rate of a triplet state is determined by the highest-energy vibrational mode associated. For both, the polymer and the monomer, the highest-energy vibrational mode is the same, namely, $C\equiv C$ stretching mode.[21,46,54] We therefore attribute the reduction of phosphorescence intensity with increasing temperature to a thermally activated diffusion of the excited state to quenching sites such as chemical defects. In fact, nuclear magnetic resonance data (see Sec. II) indicate an average of about four missing terbutylphosphine ligands per polymer chain. This corresponds to two defect sites per chain. For the more stable monomer, the defect density is below the detection threshold, i.e., less than one missing phosphine in 100 Pt monomers.

A quenching effect should manifest itself in form of a reduced lifetime of the triplets. For the polymer, the phosphorescence can be fitted with a biexponential decay response at all temperatures from 10 to 300 K, whereas for the monomer the decay is monoexponential, with a lifetime of around 120 $\mu$s up to 200 K. A deviation from monoexponential decay is consistent with diffusion to a spatial distribution of quenching sites. The lifetimes of polymer and

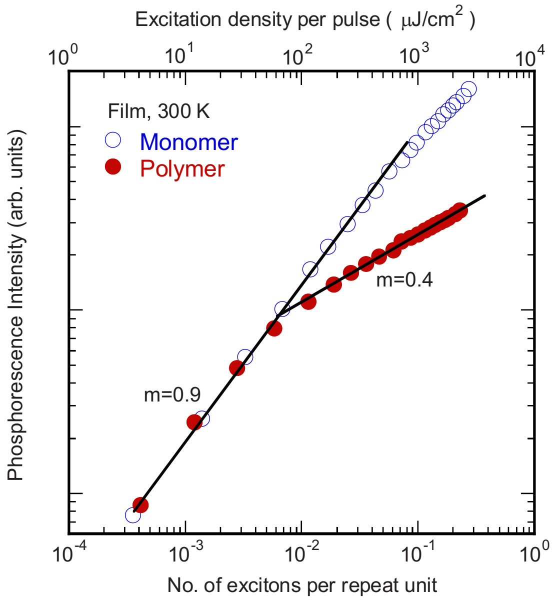

FIG. 3. (Color online) The integrated phosphorescence intensity is plotted against the number of excitons created per repeat unit (bottom $X$ axis) for the polymer (closed circles) and the monomer (open circles). The corresponding excitation density per pulse is shown on the top $X$ axis. Also shown are lines corresponding to the slopes of $m=0.9$ and $m=0.4$ on the double-logarithmic scale. Excitation was provided by pulsed YAG laser at 3.49 eV.

monomer show a similar dependence on temperature as the phosphorescence intensity. This is displayed in Fig. 2(b). For a clear presentation, we chose to plot only the longer lived components of the triplet lifetimes ($t$) obtained from the biexponential fits as both components have the same temperature dependence [see Fig. 2(d)].

The associated phosphorescence decay rate $1/\tau$ for both the polymer and the monomer can be displayed as an Arrhenius plot as shown in Fig. 2(c). Above a "transition temperature" (80 K for the polymer and 250 K for the monomer), a strong temperature dependence of the decay rate occurs. We observe, (i) the transition temperature is much lower for the polymer compared to the monomer, (ii) the thermal activation energy in the polymer is much lower than in the monomer (see below), and (iii) below the transition temperature, the decay rate is constant for the monomer, but weakly temperature dependent for the polymer.

The display of just the long lifetime component for the polymer can be justified by comparing the Arrhenius plots corresponding to the "long-lived" and "short-lived" components of biexponential fit for the polymer in Fig. 2(d). The lifetimes of both components are normalized to unity at 10 K, but not scaled in any other way. The parallel evolution of both components of the triplet lifetimes with temperature yields the same activation energy for triplet energy transfer ($\sim$60 meV).

In order to further explore these differences between polymer and monomer in the excited-state decay, we measured the dependence of the phosphorescence intensity on incident laser power (Fig. 3) at 300 K. For the monomer, this dependence is almost linear up to high powers, suggesting a monomolecular decay of the triplet excitons. In contrast, for the polymer, a nearly linear dependence on excitation densities is followed by an approximately square-root dependence at high excitation densities. The former indicates monomolecular decay of the triplets, while the latter is characteristic of bimolecular processes such as triplet-triplet annihilation. The onset of bimolecular recombination occurs when there is about one exciton per 100 repeat units. As an average chain consists of about 130 repeat units, this implies that bimolecular decay sets on at the excitation density for which more than one exciton per polymer chain is generated. Figure 3 therefore suggests that triplet excitons annihilate each other efficiently on a single polymer chain[28] while this process is not as efficient in a film of monomers.

For an interpretation of these experimental findings, it is important to be aware that the energetic disorder present in our model compounds is relatively low. Energetic disorder can be assessed, for example, through the bathochromic shift of the luminescence spectra that typically occurs in disordered organic semiconductors when going from 300 to 10 K. This shift arises usually due to the spectral diffusion of the excited state in the density of states (DOS) and so it is related to the width of the DOS.[55] As shown in Fig. 4, the 0–0 peak of the phosphorescence in the polymer shifts to the red by about 20 meV between 300 and 10 K. In the monomer, the phosphorescence peak shifts only by 3 meV. These small values point to a very narrow DOS.

The overall qualitative picture that emerges from the experimental data is that triplet excitons diffuse along the polymer chain until they are trapped or annihilated, thus reducing the phosphorescence lifetime. We consider that it is the diffusion process that is thermally activated. There are two points to be noted. First, triplet diffusion seems to occur much more efficiently on the polymer than in the monomer as is evident from Fig. 3. Second, for both polymer and monomer, there is a low-temperature regime with no (for the monomer) or weak temperature dependence (for the polymer) followed by a high-temperature regime characterized by a thermally activated process (Fig. 2). We first discuss the thermally activated regime, i.e., above 80 K for the polymer or above 250 K for the monomer.

## IV. DISCUSSION

Triplet excitons migrate via the Dexter transfer mechanism. Here, we consider Dexter energy transfer to involve the motion of an exciton that strongly interacts with molecular vibrations. This transfer can be considered as a double electron exchange, involving the simultaneous exchange of an electron from the HOMO and the LUMO of neighboring molecules as illustrated in Fig. 5(a).[39,40] Charge transfer and, we propose, therefore also Dexter energy transfer, may be described using Marcus[41,42] theory.[56] Here, we aim in particular to explore the relationship between the activation energy for the diffusion process and the relaxation energy associated with the $T_1 \rightarrow S_0$ transition in the molecule.

In general, the electron transfer rate given by Marcus[41,42] theory is

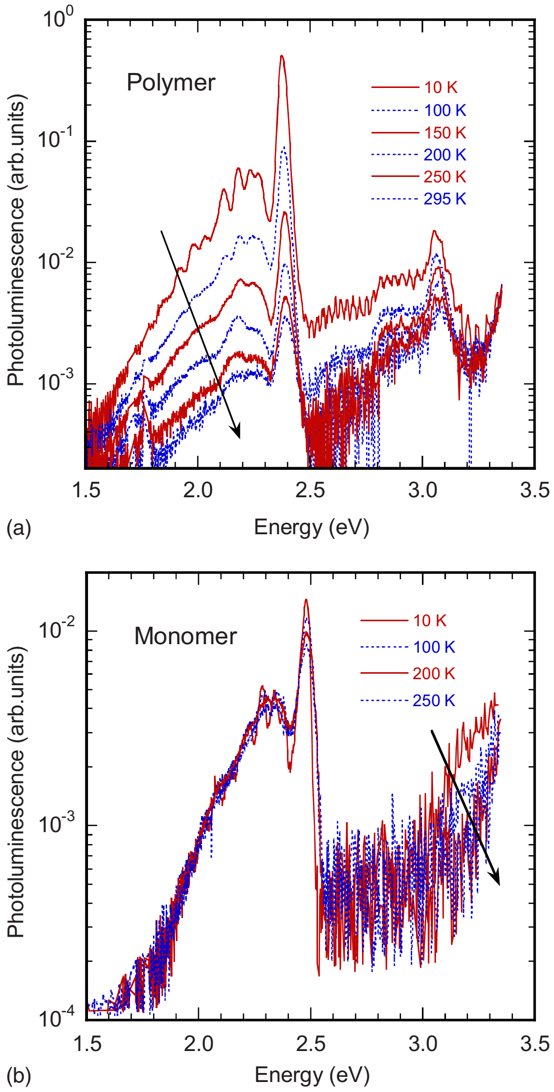

FIG. 4. (Color online) The temperature dependence of the photoluminescence spectra for (a) the polymer and (b) the monomer. The spectra are displayed on a logarithmic scale for clarity. The arrow indicates the direction of increasing temperature.

$$W_{\mathrm{if}} = \frac{2\pi}{\hbar} J_{\mathrm{if}}^2 \sqrt{\frac{1}{4\pi k_B T \lambda}} \exp\left[-\frac{E_a}{k_B T}\right],$$

$$\text{with } E_a = \frac{\lambda}{4}\left[1+\frac{\Delta G^0}{\lambda}\right]^2, \tag{1}$$

where $J_{\mathrm{if}}$ is the electronic coupling between the initial state $i$ and the final state $f$ and $E_a$ is the activation energy for the reaction. $\Delta G^0$ is the variation of Gibb's free energy (or the energy gained) during the reaction. For identical donor and acceptor molecules, $\Delta G^0$ is zero and hence the activation energy depends only on the reorganization energy $\lambda$ required to attain the equilibrium geometry configuration of the acceptor as shown in Fig. 5(b):

$$E_a = \frac{\lambda}{4}. \tag{2}$$

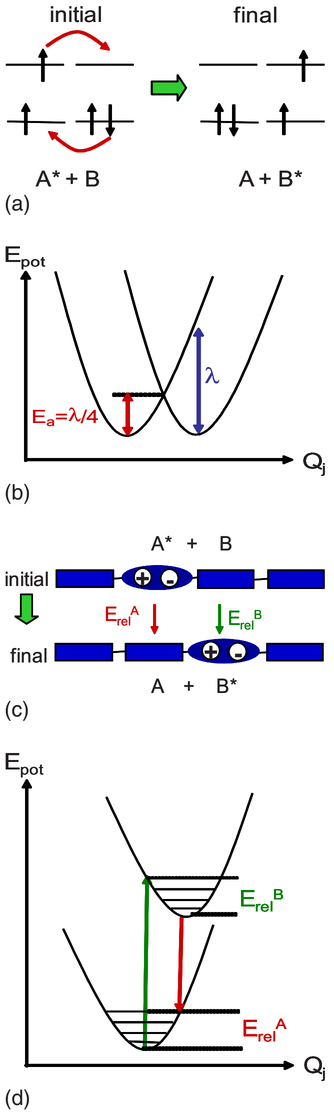

FIG. 5. (Color online) Schematic illustration of Dexter transfer in a Marcus theory description. (a) Frontier orbital representation of the energy-transfer reaction $A^*+B\rightarrow A+B^*$. (b) Marcus electron transfer in the configuration coordinate representation for a self-reaction ($\Delta G^0=0$). The activation energy required for the transfer $E_a$ and the reorganization energy $\lambda$ are shown. (c) Exciton migration from donor $A^*$ to acceptor B along a polymer chain. $E_{\mathrm{rel}}^A$ and $E_{\mathrm{rel}}^B$ represent the relaxation energies of the donor and the acceptor, respectively. (d) The processes of donor de-excitation and acceptor excitation in a configuration coordinate diagram. The associated relaxation energies $E_{\mathrm{rel}}^A$ and $E_{\mathrm{rel}}^B$ are indicated.

Analogous to an electron transfer reaction, energy transfer from a chromophore A to B can be described as a reaction of the type $A^*+B\rightarrow A+B^*$. The reorganization energy $\lambda$ is then the sum of the geometric relaxation energies ($E_{\mathrm{Rel}}$) associated with the transitions $A^*\rightarrow A$ and $B\rightarrow B^*$.[56,57] This is illustrated in Figs. 5(c) and 5(d).

$$\lambda = E_{\mathrm{rel}}^A + E_{\mathrm{rel}}^B = 2E_{\mathrm{rel}} \quad \text{and so} \quad E_a = \frac{E_{\mathrm{rel}}}{2}. \tag{3}$$

This relaxation energy is the energy associated with the geometrical rearrangement after an excitation or de-excitation process. It can therefore be inferred from an analysis of the emission spectra. The relaxation energy associated with a vibrational normal mode $\omega_j$ is given by the energy of the mode times the Huang-Rhys-parameter $S_j$ of that mode.[46,58] The total relaxation energy of an optical transition is obtained by summing up the individual contributions:

$$E_{\mathrm{rel}} = \sum_j \hbar\omega_j S_j. \qquad (4)$$

For the Pt polymer and monomer, the dominant modes are the $C\equiv C$ stretching mode at 260 meV (2100 $\mathrm{cm}^{-1}$), a benzene ring breathing mode at about 200 meV (1600 $\mathrm{cm}^{-1}$), and a number of C-H and C-C modes in the range of 100–150 meV (840–1200 $\mathrm{cm}^{-1}$) that contribute less to the overall relaxation energy.[46,54] An analysis of the phosphorescence spectra for the polymer and monomer give relaxation energies of about 100 and 180 meV, respectively.[46,54] If we relate this geometric relaxation energy to the activation energy according to Eq. (3), we obtain an activation energy $E_a$ of about 50 meV for the polymer and 90 meV for the monomer.

These activation energies, derived on the basis of the spectral response of the phosphorescence, are similar to the activation energies obtained from the temperature dependence of the phosphorescence intensity [Fig. 2(b)]. In Fig. 2(b), the whole data range is fitted with the equation $1/\tau = a\times\sqrt{1/T}\exp[-E_a/k_BT]+b$. The first expression accounts for the temperature dependence of the phosphorescence decay rate due to diffusion to quenching sites [c.f. Equation (1)], while the constant $b$ represents the sum of the temperature-independent nonradiative and radiative decay rates. The fit gives activation energies of about $60\pm 10$ meV and 100–300 meV for the polymer and the monomer, respectively. The larger variation in the monomer is due to the small data range available in the high-temperature regime. This demonstrates that the thermally activated diffusion of triplet excitons in an organic polymer and in a monomer can indeed be described within the framework of Marcus theory, where the reorganization energy $\lambda$ and thus the geometric relaxation energy $E_{\mathrm{rel}}$ controls the temperature dependence of the transfer rate. We point out that in our approach, we have not considered any contributions of the external reorganization energy such as interactions of the triplet exciton with intermolecular phonon modes. This is justified by the fact that the triplets, being nonpolar in nature, interact only little with the external polarization as suggested first by Singh *et al.*[34] in 1965 and later by Closs *et al.*[39]

With our model, we need to be able to account for the difference in the temperature dependence of triplet diffusion in the polymer and in the monomer. We have shown that this triplet diffusion depends exponentially on the geometric relaxation energy of the molecule. The stronger geometric distortion in the monomer therefore results in a higher activation energy for triplet diffusion compared to the polymer. The geometric relaxation energy commonly reduces with chain length as a result of a more delocalized excited-state wave function.[53] Consequently, the activation energy for Dexter transfer will also reduce for more delocalized systems. Thus, a significant inference of our analysis is that triplets should generally diffuse more easily along highly conjugated chains than along systems with short conjugation lengths.

From the pre-exponential factor in the fit to Fig. 2(b), we can also derive the (temperature independent) coupling matrix element $J_{\mathrm{if}}$. We find $J_{\mathrm{if}}$ is 0.14 $\mathrm{cm}^{-1}$ for the polymer and 0.03 $\mathrm{cm}^{-1}$ for the monomer. It is interesting to compare these values to ones found for two ruthenium complexes bridged by a ethynylene-substituted biphenyl bridge.[59] The polymer value is about equal to the coupling one obtains with a torsion angle around 50–60° while couplings as low as the monomer value are only found for torsion angles of 90°. The exchange coupling $J$ depends on the overlap of the excited-state wave functions of the initial and final sites. In the polymer, these wave functions are more delocalized (as evident from the lower vibrational side peaks, see Fig. 1) and can overlap to some degree along the chain. In contrast, for the monomer, such an overlap has to occur between neighboring molecules. The five times larger coupling in the polymer is therefore not surprising. In summary, triplet state diffusion in the polymer is thus enhanced by two factors: first, by a lower activation energy due to less geometric distortion along the chain and second, by a strong intrachain electronic coupling.

We have not found it necessary to consider effects due to energetic disorder for the analysis presented above. This simple approach is justified here through the narrow width of the 0–0 peak in the phosphorescence spectra and the lack of any noticeable spectral shift when going from 300 to 10 K as shown in Figs. 4(a) and 4(b), respectively. The observation of Arrhenius-type temperature dependence of phosphorescence intensity and the good agreement between the experimental and modeled activation energies using Marcus theory indicates that the disorder contribution to the triplet energy transfer is not significant. (A non-Arrhenius type temperature dependence would be expected for a disordered system.[43,60]) Many polymers, however, show a larger degree of disorder due to conformational variation and the resultant distribution of conjugation lengths.[43,60] In such a case, disorder might need to be included explicitly in the form of a distribution of variation of free energies $\Delta G^0$. The corresponding theoretical treatment will be presented in another publication.[45]

We next consider the low-temperature regime, that is, below 80 K for the polymer or below 250 K for the monomer. This regime is characterized by a decay rate $1/\tau$ that is temperature independent for the monomer and only weakly temperature activated (with an activation energy of 5 meV) for the polymer [Fig. 2(c)]. For the case of the monomer, the temperature independent intensity and lifetime are consistent with emission from triplets that are immobile (or where diffusion to quenching sites is too inefficient to contribute to the decay rate). However, for the polymer, the weak temperature dependence [which is very marked in the linear temperature plots for intensity and lifetime in Figs. 2(a) and 2(b)] does indicate that triplet excitons are still mobile. Further evidence for triplet migration at temperatures below the transition temperature in the polymer comes from the observation of bimolecular annihilation at high excitation densities.[61] We propose that this regime is that of transport by tunneling, with the residual weak temperature dependence due to small site-to-site energetic disorder.

We point out that this interpretation of the low and high-temperature regime for the polymer is in accordance with the model for small polaron motion first suggested by Holstein[62] and Friedman[63] and further developed by Emin and coworkers.[64–66] In the small polaron model, charge transport occurs due to two processes, that is phonon-assisted hopping (nondiagonal transitions) and tunneling (diagonal transitions). At high temperatures, the former dominates while at low temperatures the latter takes over. This model was initially developed for a one-dimensional molecular crystal where all sites are identical in energy so that tunneling would lead to the formation of a polaron band (since the wave functions can overlap throughout the crystal). In our noncrystalline compounds, the small variation in site energy suffices to prevent the formation of a band (as wave function overlap only occurs between two adjacent sites, or at best a few), yet the nature of the charge transfer is the same. The model describes the motion of a *small* polaron, i.e., a self-trapped charge carrier with a surrounding lattice deformation. We consider this condition of self-localization due to high electron-phonon coupling is fulfilled for a triplet exciton as evidenced, for example, in the small extent of the geometric distortion associated with the triplet state.[46] Consequently, an interpretation of the experimental data in the framework of a small polaron model is appropriate. In the high-temperature regime, the small polaron model gives the same mathematical description for the charge-transfer rate as the Marcus theory.[57] The small polaron model has been formulated both for large electronic coupling (adiabatic case) and weak electronic coupling (referred to as nonadiabatic or perturbative treatment). As shall be discussed in more detail in the following paper,[45] for the particular compounds used here, the electronic coupling is small so that the nonadiabatic case applies.

Experimental systems where the Holstein polaron model describes charge transport have been hard to find. The predicted transition from tunneling transport to phonon-assisted hopping can only be observed when the relaxation energy is larger than the bandwidth. Yet in highly conjugated systems, it is not always certain that polarons are sufficiently self-localized to form the small polaron required to see this transition. In addition, polarons are charged and thus are susceptible to long-range Coulomb disorder. This can prevent the crossover to the low-temperature tunneling regime and instead the transport becomes disorder controlled. In contrast, *triplets* are nonpolar and are therefore much less susceptible to Coulomb disorder. It should also be noted that the triplets are inherently more localized than polarons and for the particular polymers studied here, this localization and the associated small bandwidth is further enhanced by the weak conjugation through the platinum groups.

## V. CONCLUSIONS

Using a weakly disordered model compound, we have investigated the mechanism of triplet migration in organic semiconductors. Similar to the theoretical predictions for polaron transport made by Holstein and Emin, we are able to distinguish a low-temperature regime that we associate with a tunneling process, and a high-temperature regime where thermally activated hopping occurs that can be described within the framework of Marcus theory. In addition to this, we find a strong dependence of the triplet transfer on chain length, with a higher triplet diffusion rate in the polymer than in the monomer. This is attributed to more delocalized excited-state wave function in the polymer which results in a lower geometric relaxation energy and higher electronic coupling along the polymer chain.

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