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Evidence for temperature-independent triplet diffusion in a ladder-type conjugated polymer

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We study the temperature dependence of triplet formation and decay by considering the phosphorescence dynamics in a prototypical conjugated polymer matrix. The dynamics of triplet formation as a function of temperature are unraveled by applying an electric field during optical singlet generation and recording the phosphorescence quenching. The diffusivity of triplet excitons in conjugated polymers is shown to be independent of temperature up to 200 K. We propose a diffusion model that describes the relaxation dynamics of triplet excitons at all times through triplet-triplet annihilation and spin orbit coupling at static heavy atom sites.

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Molecular semiconductors are characterized by large exchange splittings and weak spin orbit coupling. In optoelectronic devices, such as organic light-emitting diodes (OLEDs), this results in the formation of two distinct excited state species of singlet and triplet spin configuration. Whereas great progress has been made over the past decade in understanding the kinetics of singlet excitations in organic materials as diverse as molecular semiconductors,[1,2] carbon nanotubes,[3] and artificial or natural light-harvesting complexes,[4] little attention has been paid to the dynamics of triplet excitations. As triplets constitute the dominant species in OLEDs (Ref. 5) and offer considerable potential for long-range energy transfer in molecular solids due to their long lifetime,[6] a microscopic picture of the dynamics of triplet excitons in disordered molecular solids and in particular in conjugated polymers is urgently required. Unfortunately, the radiative transition of the triplet to the ground state is generally spin forbidden, impeding a direct spectroscopic observation. Photoinduced absorption can yield some insight into triplet dynamics,[7,8] but is often complicated by the presence of charged excited state species, which can only be separated using spin resonance techniques.[9] Most time resolved studies of triplet kinetics to date have relied on the detection of delayed fluorescence (DF). As this signal is always a mixture of geminate carrier recombination and triplet-triplet annihilation (TTA), only a *nonlinear* measure of the triplet population can be reached, which requires further interpretation. Some conjugated polymers exhibit extremely weak phosphorescence at low temperatures, which provides a direct *linear* measure of the triplet density.[10] However, in most cases phosphorescence occurs on very long time scales from thermalized triplet excitons trapped in the tail of an often broad density of states.[11] We recently demonstrated a powerful technique for visualizing nonthermalized triplets in conjugated polymers at room temperature. Inclusion of trace concentrations of heavy metal atoms on the polymer backbone barely modifies triplet generation but opens a highly efficient radiative decay channel for migrating triplet excitons through highly local spin-orbit coupling.[12] This method opens a window to the *nonthermalized* migrating triplets, which are directly relevant to devices such as OLEDs.

Whereas singlet exciton migration in molecular solids can be adequately described in the framework of Förster-type dipole-dipole coupling, the kinetics of the triplet excitons are driven by nearest neighbor exchange interactions.[6] Under certain circumstances, the theory of nonradiative energy transfer predicts a temperature independent exciton migration. Here we show that the migration of nonthermalized triplet excitons is temperature independent, as is the case for a pure dipole-dipole coupling process,[13] and we demonstrate a comprehensive diffusion model that accounts for the observed triplet kinetics over a wide range of temperatures and times. Field quenching experiments confirm that it is the triplet *generation* which is temperature dependent due to heterogeneous intersystem crossing (ISC) efficiencies at different sites in the polymer matrix.

The polymeric material system used in this study is a diaryl (diphenyl)-substituted ladder-type poly(paraphenylene) (PhLPPP, inset in Fig. 1) containing a trace concentration of covalently bound Pd atoms (~100 ppm), as

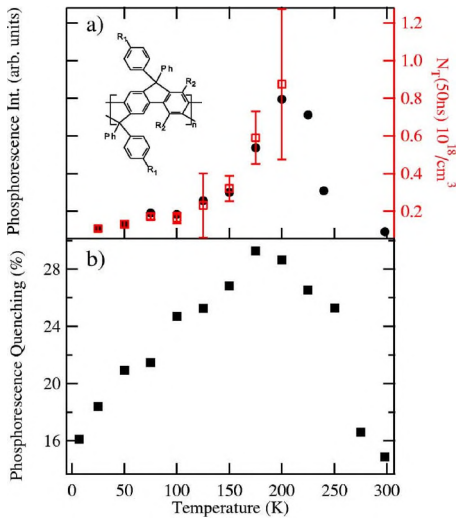

FIG. 1. (Color online) (a) Phosphorescence intensity (filled circles) at 50 ns measured with a 10 ns gate versus temperature. The triplet population at 50 ns as estimated for optimal convergence is also shown (open squares, see text). Inset: chemical structure of PhLPPP (*R*1: decyl; *R*2: hexyl). (b) Quenching efficiency of the phosphorescence (50 ns delay; 10 ns gate) as a function of temperature under application of an electric field of 1 MV/cm.

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confirmed by inductively coupled plasma optical emission spectroscopy. For the temperature dependence of triplet decay dynamics a 100 nm thin film of PhLPPP was spin-coated on an indium tin oxide (ITO) substrate mounted in a wide-field view cold-finger He cryostat. Electric fields were applied using a typical light emitting diode configuration with ITO and Al electrodes addressed in reverse bias. Carrier-pair dissociation at the electrodes was minimized by using 10-nm-thick SiO_x insulating layers. Time resolved photoluminescence spectroscopy was performed using 150 fs pulses of 1 kHz repetition rate to excite the polymer in the second vibronic progression at 400 nm. Upon excitation, a variable electronic time delay (10 ns resolution) with a variable integration time adjusted to 20% of the delay provided by an intensified gated charge coupled device spectrometer was used to resolve the transient emission.

Under optical excitation triplet generation in LPPP at excitation energies below 3 eV relies mostly on ISC of singlets ($S_1 \rightarrow T_1$).[14] Subsequently, highly localized triplet spin-orbit coupling at the Pd sites enables efficient otherwise forbidden radiative recombination over a wide range of temperatures. Since the phosphorescence band of PhLPPP is spectrally almost identical to that of the metal-free analogous polymers, such as the methyl substituted LPPP,[10] it is implied that triplet harvesting occurs adiabatically. In contrast, in polymers with heteromolecular triplet sensitizers triplet harvesting usually occurs through carrier or exciton trapping involving energy dissipation.[15–18] The absence of an energy gradient to the Pd sites thus renders PhLPPP ideal for noninvasive measurements of the true triplet kinetics in polymeric matrices.

It is often assumed that DF originates mostly from TTA ($T_1+T_1 \rightarrow S_1+\text{phonons}$) and there have been several attempts to describe triplet migration in hydrocarbon polymer films from the decay dynamics of DF.[19,20] Electric fields allow a much stronger modulation of DF than of prompt fluorescence, which demonstrates that—certainly in the ladder-type polymers—DF must arise from species more weakly bound than the singlets.[21] These species are generally attributed to polaron pairs generated upon photoexcitation ($PP_S \rightarrow S_1$). In contrast, triplets are more tightly bound, which is readily seen in the fact that the phosphorescence intensity cannot be modulated by an electric field applied *after* laser excitation.[22]

For a quantitative understanding of triplet migration kinetics it is essential to understand the temperature dependence of the dynamics responsible for the generation of the initial triplet population. The dependence of the phosphorescence intensity at 50 ns on temperature is shown in Fig. 1(a) (solid circles). An initial delay of 50 ns is chosen to remove prompt fluorescence. The observed nonmonotonic dependence that peaks at 200 K shows that either the triplet radiative/nonradiative decay rates or the triplet density depend substantially on temperature. In order to reveal the correlation between the dynamics of photogenerated singlets and triplet formation an electric field (1 MV/cm) is applied to the polymer film throughout optical excitation and detection. The phosphorescence intensity between 50 and 100 ns after optical excitation is recorded with and without the electric field for a temperature range between 10 and 280 K. The electric field phosphorescence quenching efficiency [Fig. 1(b)] exhibits a similar dependence on temperature as the

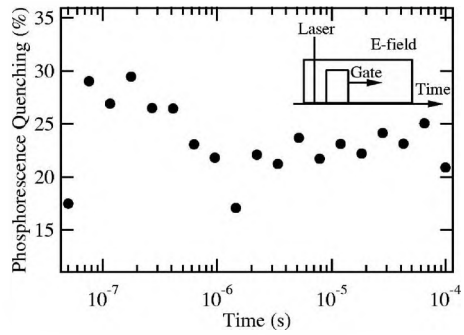

FIG. 2. Time resolved phosphorescence quenching efficiency at 75 K. The electric field is applied throughout the measurement. The inset shows the pulse sequence applied in the measurement.

initial phosphorescence at 50 ns. The phosphorescence quenching originates from the field quenching of optically excited singlets, whereas triplets themselves are not quenched. This is confirmed by the virtually time-independent phosphorescence quenching efficiency shown in Fig. 2. The increase of both the initial phosphorescence intensity and of the quenching efficiency up to 200 K can therefore only be due to enhanced triplet formation. A reasonable interpretation is that singlet diffusion within the polymer film increases with increased thermal energy due to the possibility of uphill migration steps in the disordered energetic environment.[23] This increases the probability of a singlet reaching a site in the polymer matrix of enhanced ISC. Although the Pd atoms constitute obvious candidates for such diffusion driven ISC sites, we stress that other chemical defects such as oxygen will also enhance ISC (Ref. 6) with increasing temperature.

The change of the slope at 200 K in the two plots in Fig. 1 could be attributed to the onset of an efficient nonradiative mechanism for singlets, which would lead to a lower triplet generation rate. We were recently able to demonstrate that collective intramolecular interchromophoric effects manifested in single molecule blinking become relevant in ladder-type polymers at a similar temperature.[24] We therefore propose that for $T \gtrsim 200$ K singlets incoherently couple with most of the chromophoric sites within one polymer molecule, which dramatically increases the sensitivity to quenching sites on the chain. This effect raises the probability of quenching during singlet diffusion in the polymer film. The dependence of the triplet density on temperature is therefore dominated by nonradiative effects for $T \gtrsim 200$ K.

Temporally and spectrally resolved phosphorescence is performed so as to gain insight into the triplet kinetics post-triplet formation. Figure 3 shows the phosphorescence decay curves of a PhLPPP film between 50 ns and 150 μs measured in a temperature range between 25 and 298 K (the temperature increases towards the bottom of the graph and the decay curves are shifted for clarity). In all cases the actual emission spectra were recorded. In contrast to trapped, thermalized triplets, which give rise to a blueshift of the phosphorescence upon heating,[11] the nonthermalized triplets studied here display a slight ($\sim$2 meV) spectral shift to the red upon heating.[25] The presence of Pd atoms in the polymer matrix increases the overall phosphorescence intensity com-

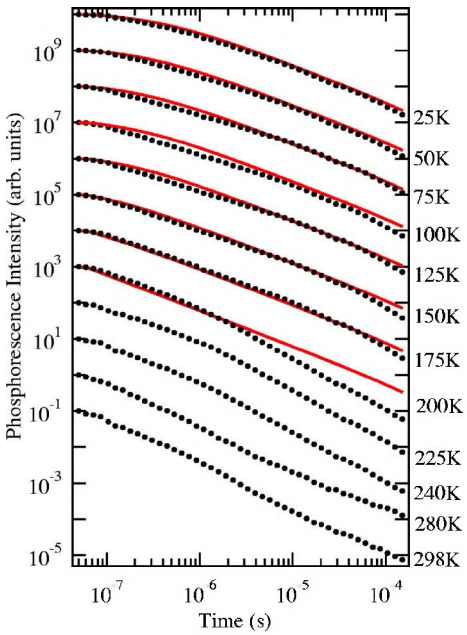

FIG. 3. (Color online) Phosphorescence decay curves of a PhLPPP matrix between 50 ns and 150 μs (measured in gate lengths of 20% of the delay) for different temperatures. The decay curves are shifted vertically for clarity. Solid lines correspond to the theoretical results.

pared to measurements on other polymers exhibiting triplet emission.[10] Whereas qualitatively the phosphorescence decay curves mirror the migration dynamics of triplets to Pd sites, it is important to note that the migration dynamics depend both on the initial triplet density and triplet diffusivity, as well as on the presence of nonradiative quenching mechanisms. Thus in order to develop a quantitative understanding of the triplet kinetics it is necessary to resort to the dynamic approach of diffusion theory.

We assume that triplet migration can be described in configuration space in terms of time-dependent Smoluchowski theory in the limit of very low triplet concentrations. This approach is one of the basic methods used to describe kinetics of diffusion-controlled reactions.[26] In our case, we account for both TTA and reverse ISC at the Pd sites leading to phosphorescence via spin-orbit coupling. Considering these effects, the time evolution of the triplet density is given by

$$\frac{dN_T}{dt} = -k_1 N_{\mathrm{Pd}} N_T - k_2 N_T^2, \tag{1}$$

where N_T is the triplet density and N_{Pd} is the effective palladium concentration. The kinetics are expressed in terms of the time-dependent rates given by[26,27]

$$k_1 = 4\pi D_T R_{\mathrm{Pd}}\left(1 + \frac{R_{\mathrm{Pd}}}{\sqrt{\pi D_T t}}\right),$$

$$k_2 = 8\pi D_T R_{\mathrm{TTA}}\left(1 + \frac{R_{TTA}}{\sqrt{2\pi D_T t}}\right), \tag{2}$$

where D_T is the triplet diffusivity, and R_{Pd}, R_{TTA} are the triplet-Pd spin orbit coupling radius and the scattering length of TTA, respectively. In order to reduce the number of parameters, we approximate both R_{Pd} and R_{TTA} to 5 Å and we note here that this approximation does not affect the temperature dependence of the derived diffusivity. The concentration of effective Pd sites in the film is estimated as 3×10^{16} cm^{-3}.[12] The initial condition of the triplet population at the lowest temperature under consideration (25 K) is derived from the optimal convergence between theory and experiment as 1×10^{17} cm^{-3}. The initial conditions for the higher temperatures are scaled according to the measured phosphorescence intensity at 50 ns (Fig. 1) and are allowed to vary by ±10% to optimize the convergence [Fig. 1(a), open squares; the error bars correspond to the fitting error]. The diffusivity D_T therefore constitutes the only free fitting parameter. The results of the calculation for temperatures between 25 and 200 K are shown in Fig. 3 (solid curves). Surprisingly, the calculated diffusivity is virtually independent of temperature, as summarized in Fig. 4. An average value of $(19.69 \pm 1.42) \times 10^{-6}$ cm^2/s is obtained, in agreement with prior estimates of triplet migration in anthracene crystals.[28] Interestingly, temperature independent energy transfer has been previously observed in some photosynthetic light-harvesting processes, e.g., between the two types of bacteriochlorophyll *a* (from B800 to B850) contained in peripheral light-harvesting complexes (LH2).[29]

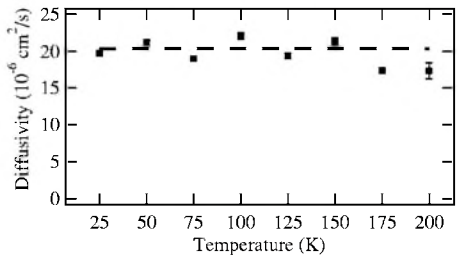

FIG. 4. Dependence of diffusivity on temperature as derived from the phosphorescence decay curves using the diffusion model described in the text. The error bars correspond to the fitting error and the dashed line is a guide to the eye.

For low temperatures measurement and theory are in excellent agreement over three orders of magnitude in time and intensity. Here we should note that in our model we have assumed a uniform probability of triplet generation within the polymer matrix. With increasing temperature a deviation appears for times after 50 μs. This deviation is understood to originate from the increased role of nonradiative effects with increasing temperature that set in around 200 K and constitute an additional quenching channel for triplets. As the nature of the triplet quenching channel for $T \gtrsim 200$ K is not entirely clear its inclusion in the diffusion model is not attempted here.

Intuitively, one would expect the diffusivity of a "freely" migrating neutral species to increase with temperature. However, the triplet excitons in the isotropic polymer matrix cannot be viewed within the framework of kinetic gas theory. Instead, the motion of a triplet from one site to another constitutes a correlated two-particle (electron and hole) motion, where the increased kinetic (thermal) energy of the two excitonic constituents cannot be transferred to a center of mass

motion of the exciton. A quantitative explanation of the surprising *independence* of diffusivity on temperature should be sought in the microscopic mechanism of triplet exchange energy transfer between near-resonant neighboring sites. In this case, the transfer probability depends on the exchange integral, the energetic overlap between excited and unoccupied triplet states, and the exponential dependence on the reciprocal absolute temperature. Since the exchange integral is independent of temperature, triplet energy transfer becomes independent of temperature for nearly degenerate excited and unoccupied triplet states. However, very little information on these quantities can be drawn from experiment since direct radiative triplet transitions are dipole forbidden. Therefore, our experimental findings provide an indirect way of gaining insight into the microscopic triplet dynamics, on which future microscopic theoretical studies may rely.

In conclusion, we have resolved the temperature dependence of triplet formation and migration in a triplet sensitized π-conjugated polymer matrix. Both TTA and local spin-orbit coupling lead to triplet depletion with time. Whereas the diffusion of nonthermalized triplets is principally temperature independent, a thermal activation mechanism in the singlet diffusivity has to be invoked to explain the substantial ISC rates found in conjugated polymers. Our results have important implications for the fundamental understanding of the spatial dynamics of the primary electronic excitations in polymer matrices. In particular, the high diffusivity of triplets illustrates how to optimize triplet harvesting in OLEDs.[16] High levels of phosphorescence dopants will modify the film quality and potentially reduce the triplet diffusivity. Efficient triplet harvesting in heterostructures is best achieved with very low levels of short-lived phosphorescence dopants, as in the present case of trace metal atom impurities.

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