

Spectral diffusion in poly(*para*-phenylene)-type polymers with different energetic disorderSebastian T. Hoffmann,¹ Heinz Bässler,² Jan-Moritz Koenen,³ Michael Forster,³ Ullrich Scherf,³ Esther Scheler,⁴ Peter Strohriegl,⁴ and Anna Köhler^{1,*}¹*Experimental Physics II, Department of Physics, University of Bayreuth, 95440 Bayreuth, Germany*²*Physical Chemistry, Philipps-Universität Marburg, 35032 Marburg, Germany*³*Macromolecular Chemistry, Bergische Universität Wuppertal, 42097 Wuppertal, Germany*⁴*Macromolecular Chemistry I, Department of Chemistry, University of Bayreuth, Bayreuth 95440, Germany*

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We have employed quasicontinuous fluorescence and phosphorescence spectroscopy within a temperature range between 10 and 500 K to monitor the spectral diffusion of singlet and triplet excitons in a series of π -conjugated polymers. We investigated (i) how spectral diffusion is controlled by the degree of energetic disorder present in the amorphous film (that is reflected by the inhomogeneous broadening of the photoluminescence spectra) and (ii) how this process depends on the range of the electronic coupling (by comparing singlet exciton diffusion via long-range Förster transfer against triplet exciton diffusion by short-range Dexter transfer). For singlets, we find that the fluorescence spectra bear out a bathochromic shift upon cooling the sample down to a critical temperature below which the shift saturates. This bathochromic shift is a signature of spectral relaxation. Random-walk theory applied to excitation transport within a Gaussian density-of-states distribution is both necessary and sufficient to rationalize the experimental results in a quantitative fashion. The same behavior is observed for triplets in weakly disordered systems, such as in a polymer containing platinum in the main chain and a ladder-type polyphenylene. In contrast we observe a hypsochromic shift of the phosphorescence spectra below a characteristic temperature for triplets in systems with at least moderate energetic disorder. The hypsochromic shift proves that triplet exciton relaxation becomes frustrated because thermally activated exciton jumps that otherwise promote spectral diffusion become progressively frozen out. The frustration effect is controlled by the jump distance and thus it is specific for triplet excitations that migrate via short-range coupling among strongly localized states as compared to singlet excitons.

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I. INTRODUCTION

In modern electronic devices such as organic light emitting diodes, field effect transistors, and organic solar cells the active elements are often organic layers prepared by either vapor phase deposition or spin coating.¹⁻⁶ This facilitates the manufacturing process but gives rise to disorder effects. When abandoning the translational symmetry in a crystal, valence and conduction bands as well as transport bands of neutral excitons are split into a distribution of localized states [density-of-states (DOS) distribution].^{7,8} A manifestation of this effect is the inhomogeneous broadening of absorption and photoluminescence (PL) spectra of organic bulk films and chromophors embedded in a glassy matrix.⁹

Disorder has an important bearing on the transport of electronic excitations such as charge carriers or neutral excitons. In a crystalline molecular solid they usually migrate incoherently at the bottom of the respective transport bands.¹⁰ If the bands are split into a distribution of states, an excitation generated randomly at a transport site such as a luminescent chromophore will, while migrating, tend to occupy tails states of the DOS.⁷ This process is referred to as electronic relaxation via spectral diffusion. In the case of singlet excitons in a film of organic chromophors, such as a conjugated polymer, this phenomenon is reflected in the finite Stokes shift between the origins of absorption and emission. Being a time-dependent process this relaxation can be assessed by monitoring the evolution of the photoluminescence spectrum in a time-resolved fashion by employing gated detection.¹¹

Hopping theory predicts that an excitation generated at an arbitrary energy within a Gaussian DOS distribution will relax by transfer to a neighboring site with lower energy. Eventually it will approach quasiequilibrium at an energy $-\sigma^2/kT$ below the center of a DOS with variance σ , provided that the time needed to reach that equilibrium energy is shorter than the intrinsic lifetime of the exciton, or, in the case of charge carriers, shorter than the time required for a charge carrier to reach the exit electrode.¹² At finite temperature the establishment of quasiequilibrium requires a balance between thermally activated upward jumps of the excitation and relaxing downward jumps. At lower temperatures, this balance may not longer be achieved and two phenomena should become important.

(i) When the jump rate is temperature activated, a lower temperature leads to an increase in the time required for an excitation to jump. As a result, the excitation may decay before relaxation is completed. In other words, energetic relaxation and the associated spectral diffusion are terminated.

(ii) For an excitation to reach a very low energy site, a thermally activated detour via a higher energy site may be required. At low temperatures, this process is no longer feasible implying that spectral diffusion becomes kinetically frozen. It should give rise to frustration implying that in the $T \rightarrow 0$ limit excitons will end their lives at higher energies within the DOS that they would at intermediate temperatures. This predicts that there should be a hypsochromic shift of the luminescence spectrum at low temperatures. The effect of frustration regarding the relaxation of excitons within a Gaussian DOS has been treated theoretically in the $T \rightarrow 0$

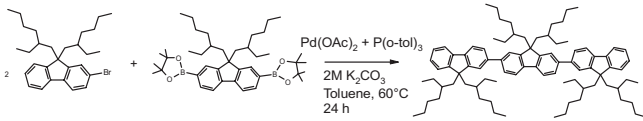


FIG. 1. Suzuki cross coupling leading to a fluorene trimer.

limit¹³ and verified by time-dependent phosphorescence spectroscopy on a benzophenone glass at either 80 and 6 K, respectively.¹⁴

This paper deals with the fundamental phenomenon of spectral diffusion of neutral spin singlet and spin triplet excitations in amorphous films of organic semiconductors. The material system considered are mostly *para*-phenylene-type conjugated polymers that emit both fluorescence and phosphorescence.^{15–17} From the temperature-dependent shift of the fluorescence and phosphorescence spectra we experimentally identify the spectral diffusion in singlet and triplet excitons and analyze the temperature dependence quantitatively in terms of random-walk theory. An essential part of the work is devoted to the effect of kinetic frustration that we observe for the triplet excitons. The freezing out of energetic relaxation is characteristic for a random system in which the excitations are strongly localized. This phenomenon has been recognized before yet has received little attention in the literature. It is hoped that the new experimental results will stimulate theoretical advances to understand how the effect of frustration evolves upon lowering the temperature.

II. EXPERIMENTAL METHODS

The PF2/6 (poly(2,7-(9,9-bis(2-ethylhexyl)fluorene))) was received from American Dye Sources Ltd. (ADS), Canada, and has a molecular weight (M_w) of about 70 kg/mol. The fluorene trimer was synthesized following the palladium catalyzed Suzuki cross coupling with palladium (II) acetate as catalytic species (Fig. 1). For the synthesis of the trimer one mole of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-9,9-di(2-ethylhexyl)fluorene and two moles of 2-bromo-9,9-di(2-ethylhexyl)fluorene were applied. A detailed description of the synthetic conditions leading to the fluorene monomers and oligomers is found in Refs. 18 and 19. Polyindenofluorene (poly-2,8-indenofluorene) (PIF) has been synthesized according to Merlet *et al.*²⁰ with a weight-average molecular weight M_w of 400 kg/mol (number average molecular weight $M_n=154$ kg/mol, polydispersity index PDI=2.60). The polymer was extracted by an Soxhlet-extraction one after another by methanol, hexane, ethylacetate, dichloromethane, and chloroform. DOOPPP [dioctyloxy-poly(*p*-phenylene)] has been synthesized according to Huang *et al.*²¹ and has a molecular weight of about 24.5 kg/mol ($M_n=14.5$ kg/mol, PDI=1.69). The polymer was extracted by an Soxhlet-extraction one after another by methanol, hexane, acetone, and ethylacetate. Methyl-substituted ladder-type poly(*p*-phenylene) (MeLPPP) has been synthesized according to Scherf and Müllen²² with M_w of 66 kg/mol ($M_n=27$ kg/mol, PDI=2.44). The data for the Pt-containing polymer displayed in Fig. 2 are replotted from Ref. 24.

For optical measurements, thin films were spun cast from toluene solutions with concentrations of 20 mg/ml onto quartz (Spectrosil B) substrates. Films were typically of 100–130 nm thickness as measured using a Dektak 150 Systems profilometer from Veeco. A Cary5000 UV-Vis-NIR spectrometer was used to take the absorption spectra of the thin films. The PL spectra were taken with the samples mounted in a continuous flow helium cryostat. The temperature was controlled with an Oxford Intelligent Temperature Controller-4 (ITC-502). For the purely organic compounds, excitation was provided by a pulsed, frequency-tripled NdYAG 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 1 Hz by a self-made electronic delay generator. The light emitted by the sample was dispersed and subsequently detected by a time gated intensified charge-coupled-device camera (Andor iStar DH734-18F-9AM). The phosphorescence measurements were taken with a delay time of 10 ms and a gate width of 80 ms which corresponds to a near cw situation. The measurements were carried out at an excitation density of about $250 \mu\text{J cm}^{-2} \text{ pulse}^{-1}$. To increase the signal-to-noise ratio, all spectra were obtained by averaging over 200 laser shots at a particular delay time. For fluorescence measurements, a delay time and a gate width of 50 ns were employed.

III. RESULTS

Figure 2 shows the chemical structures and abbreviations of the material system investigated along with their fluorescence and phosphorescence spectra and the room-temperature absorption spectra. Our choice of materials comprises two different polymers with a low degree of disorder that are Pt-polymer and MeLPPP. In addition we investigated a series of poly(*p*-phenylene)-type polymers with increasing structural freedom to allow for ring torsions, namely, MeLPPP, PIF, PF2/6, and DOOPPP. Finally, to enable a comparison between polymers and short chain oligomers, the PF2/6 trimer is included. The fluorescence and phosphorescence spectra were recorded at a range of temperatures between 10 K and up to 500 K, dependent on the material. Except for DOOPPP the emission spectra bear out vibrational structure. For clarity, spectra are only displayed for a few selected temperatures. A representative set of fluorescence and phosphorescence spectra taken at a range of temperatures between 10 and 300 K are plotted in Figs. 2(b) and 2(c) for PIF on an extended energy scale.

Figure 2 demonstrates that, for all compounds investigated, the fluorescence spectra experience a continuous bathochromic shift (i.e., to lower energies) as the temperature is lowered until they become spectrally stationary at a certain characteristic temperature T_c that will be defined in the discussion. For the phosphorescence spectra, some bathochromic shift occurs for the Pt-polymer and MeLPPP while the remaining polymers and the PF2/6 trimer exhibit a hypsochromic shift (i.e., a shift to higher energies). Unfortunately, triplet quenching due to impurities precludes recording phosphorescence spectra significantly above T_c .

The shifts of the 0-0 peaks in fluorescence and phosphorescence, relative to the position at 10 K, are displayed in

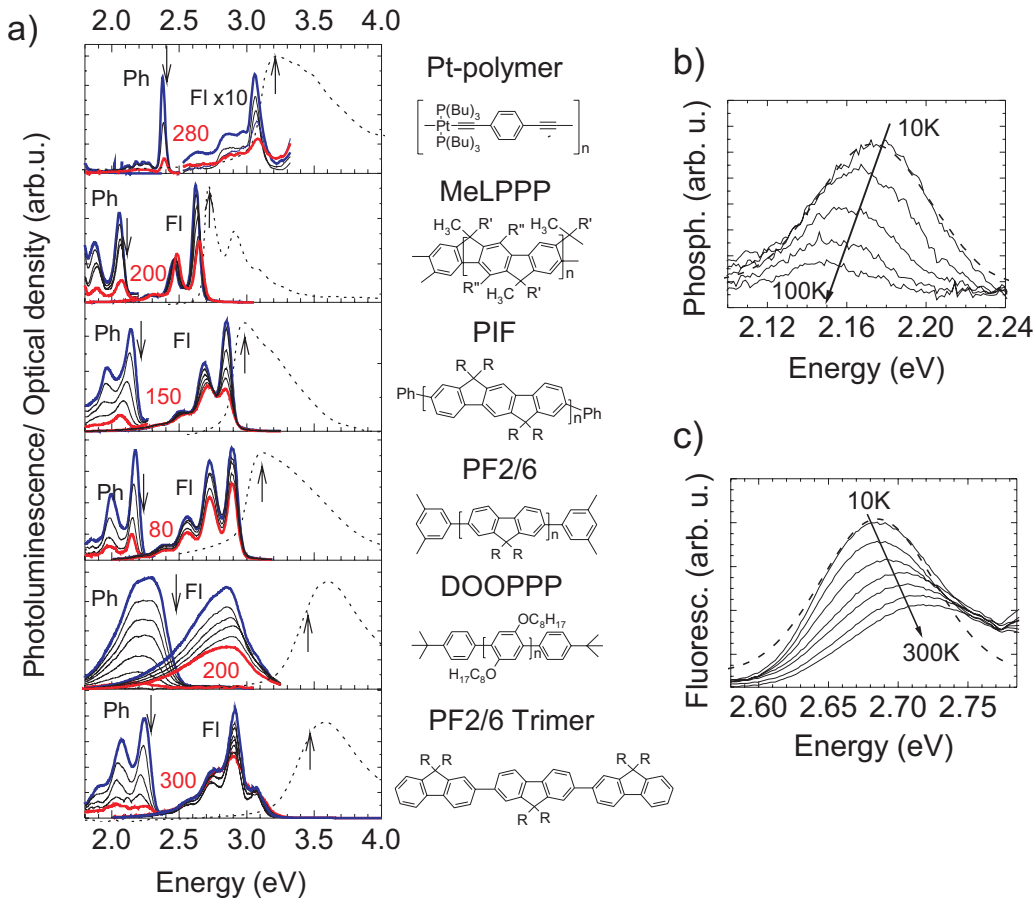


FIG. 2. (Color online) (a) Fluorescence (FI) and phosphorescence (Ph) spectra (solid lines) at selected temperatures for Pt-polymer, MeLPPP, PIF, PF2/6, DOOPPP, and PF2/6 Trimer (top to bottom) along with the absorption spectra at 300 K (dotted line). The data for the Pt-polymer are replotted for ease of comparison from Sudha Devi *et al.* (Ref. 23). The smoothed emission spectra are shown from 10 K (blue upper thick line) onwards until the signal disappears (red lower thick line) at the temperature indicated in the figure. The arrow indicates the center of the DOS. The chemical structures and abbreviations for the materials are shown on the side of the respective spectra with $R=2$ -ethylhexyl, $R'=1,4$ - C_6H_4 - n - $C_{10}H_{21}$, and $R''=n$ - C_6H_{13} . (b) Phosphorescence spectra of PIF between 10 and 100 K in steps of 20 K. A Gaussian curve is fitted through the curve at 10 K for comparison. (c) Fluorescence spectra of PIF between 10 and 300 K in steps of 50 K. A Gaussian curve is fitted through the curve at 10 K for comparison.

Fig. 3. For the phosphorescence, the 0-0 position was read directly off the spectra. If necessary, a Gaussian curve was fitted through the peak such as to better define the center of the peak. In contrast, for fluorescence, the energy was taken from the 0-1 vibrational peak and the energetic separation between the 0-0 and the 0-1 transition at 10 K was added as a constant offset. This correction is necessary since the 0-0 emission can be distorted by reabsorption effects, which become particularly prominent at elevated temperatures due to inhomogeneous broadening of the absorption band. Such reabsorption effects are especially strong for materials with a small Stokes' shift such as MeLPPP and PIF.

We note that the characteristic temperature T_c below which the phosphorescence bears out a hypsochromic shift is lower for systems in which the inhomogeneous width of the $T_1 \rightarrow S_0$ 0-0 emission is smaller. Since this bandwidth is a measure of the degree of disorder, this observation is an indication that both the absolute spectral shift as well as the temperature range over which it occurs are controlled by disorder. As an assessment of degree of disorder the $S_1 \rightarrow S_0$ and the $T_1 \rightarrow S_0$ spectra were fitted to Franck-

Condon progressions to give variances σ_S and σ_T for singlet and triplet states, respectively, over a broad temperature range. The temperature dependence of σ is displayed in Fig. 4. There is only a minor temperature dependence, in particular, for the triplet state. We note that the present value of σ_T for PF2/6 (37 meV) is close to the value of 41 meV deduced earlier from delayed fluorescence studies.^{15,25} It is particularly gratifying that this value of σ_T for PF2/6 is also in agreement with the value inferred from the temperature dependence of the exciton diffusion.²⁶

IV. DISCUSSION

Over the past decade, a good qualitative understanding of spectral diffusion has been obtained.²⁷ A basic assumption of the model is that excitations, i.e., excitons or charge carriers, execute random walks within a manifold of localized states with a Gaussian-shaped DOS. The Gaussian shape has been verified spectroscopically and via an analytic theory.⁹ The dynamics of a packet of noninteracting excitations generated at arbitrary start energies has been modeled consistently in

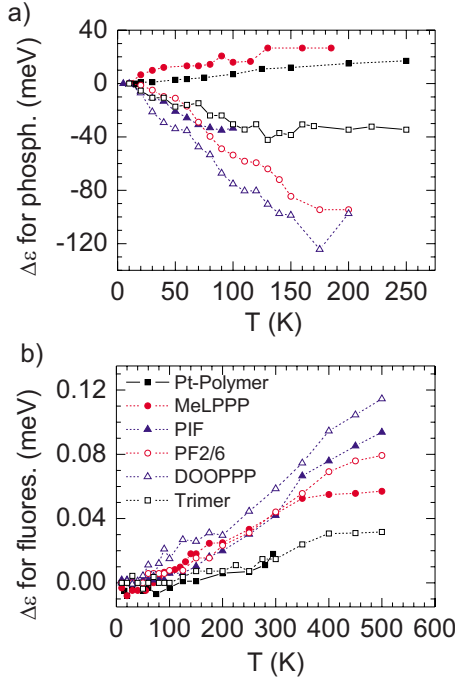


FIG. 3. (Color online) Energies of the 0-0 peak position of (a) the phosphorescence spectra and (b) the fluorescence spectra for the Pt-polymer, MeLPPP, PIF, PF2/6, DOOPPP, and PF2/6 Trimer. The energies are given relative to the 0-0 position at 10 K. The dotted lines serve as a guide to the eye.

terms of effective-medium methods,¹² Monte Carlo simulation,¹² and stochastic hopping theory.^{27,28} In these works it was shown that an excitation, be it a charge carrier or an exciton of either singlet or triplet character, executes a random walk in which it tends to relax toward the tail states of the DOS. Charge carriers and triplet excitons migrate usually via short-range orbital overlap interactions such as Dexter-type exchange coupling. Of course, the jump rate for triplets excitons is much lower than that of charge carriers because in triplet exciton motion two charges have to be exchanged simultaneously. Singlet excitons, in contrast, migrate via (long-range) Förster-type dipole coupling.²⁹⁻³¹ The absolute timescale of the energetic relaxation depends on the coupling strength between the sites and on the starting energy of an excitation within the DOS but, remarkably, the functional dependence of the excitation energy on time and temperature, $\varepsilon(t, T)$, is independent of the type of coupling.¹² The general functional dependence is shown as schematic in Fig. 5 and will be discussed below.

Let us first note that the relaxation pattern is independent on whether or not the excitations are dressed with lattice distortion (polaron). This has been verified by comparing the time-resolved shift of fluorescence spectra of poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) and an analogous polymer in which the phenylene groups have been replaced by biphenylene group. In the latter, the torsional motion in the biphenylene group gives rise to a significant polaronic contribution to exciton transfer, yet the time dependence of the relaxation pattern is independent of the presence of the polaronic contribution, except for a scaling factor regarding the minimum jump

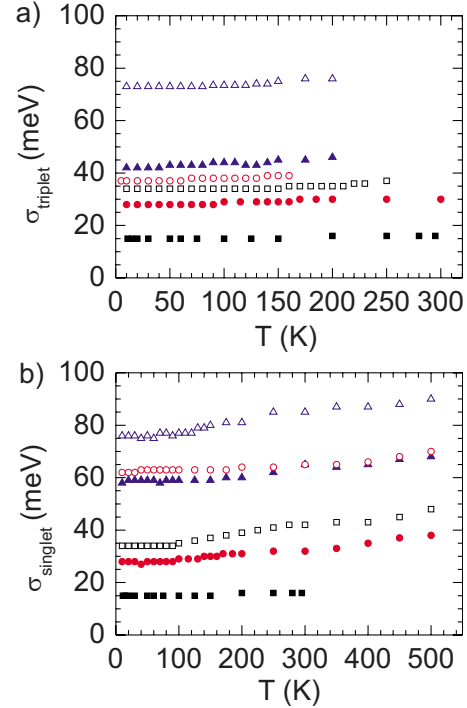


FIG. 4. (Color online) The temperature dependence of the disorder parameter σ for Pt-polymer, MeLPPP, PIF, PF2/6, DOOPPP, and PF2/6 Trimer for (a) phosphorescence and (b) fluorescence as shown in Fig. 3(b).

time.³² In the case of polaronic excitations this jump time is temperature activated and both polaron effects and disorder contribute to the temperature dependence.

As mentioned in the introduction to this paper, there are two processes that become relevant at lower temperatures, that is, first the termination of spectral diffusion when the jump time exceeds the lifetime of the excitation and second the kinetic frustration of the relaxation. We shall now consider in greater detail the first process. The minimum jump time an excitation needs is given by the reciprocal jump rate (ν_0) between two isoenergetic sites in the center of the DOS, as this is the fastest possible jump. As time proceeds the excitations relax energetically featuring approximately a $\Delta\varepsilon/\sigma \propto \log \nu_0 t$ law. This time dependence of the relaxation arises since the number of target sites decreases as the relaxation process proceeds. Concomitantly, the diffusivity of the excitations also decreases. In the course of a relaxation process at intermediate temperatures an excitation may find it easier to make a thermally activated upward jump in order to continue its relaxation path rather than executing an exothermic long-distance jump. Eventually quasiequilibrium between upward and downward jumps will be attained at an energy $\varepsilon_\infty = -\sigma^2/kT$ relative to the center of a DOS with variance σ . In passing, we note that thermally activated upward jumps are necessary for an excitation to diffuse. This is reflected for instance in the temperature dependence of charge-carrier mobility. It should also manifest itself in temperature-activated exciton diffusion.

Figure 5 depicts the course of relaxation in a schematic way. During relaxation the mean energy, i.e., the center of the occupational DOS, features a $\Delta\varepsilon/\sigma$ vs $\log \nu_0 t$ law inde-

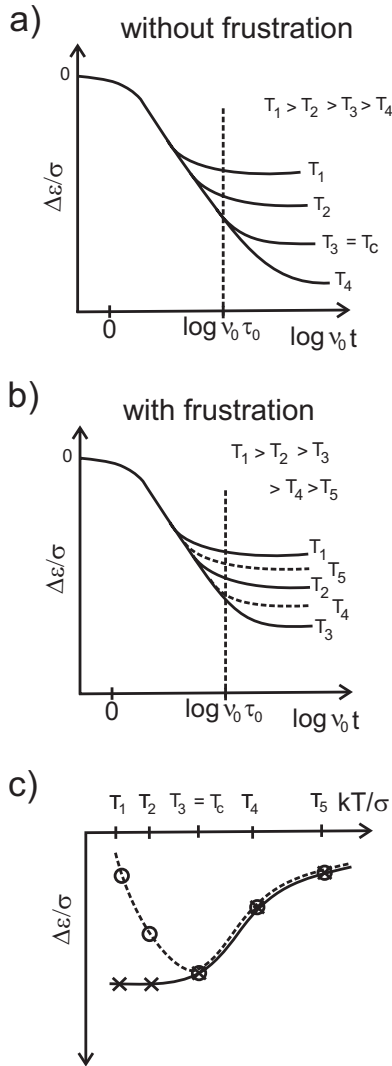


FIG. 5. Schematic illustration of $\Delta\varepsilon/\sigma$ vs $\log \nu_0 t$ for excitations with finite lifetime, drawn for different temperatures T (a) without frustration and (b) in presence of frustration. At the exciton lifetime τ_0 the relaxation of excitons is stopped. Without frustration, the normalized mean energy $\Delta\varepsilon/\sigma$ becomes temperature independent, yet in the presence of frustration, $\Delta\varepsilon/\sigma$ raises with decreasing temperature. (c) The dependence of $\Delta\varepsilon/\sigma$ vs σ/kT in the absence of frustration (solid line, crosses) and in the presence of frustration (dotted line, circles).

pendent of σ . Quasiequilibrium will be attained at a characteristic time that increases upon lowering the temperature [Fig. 5(a)]. Since the lifetime of the excitons is finite, the relaxation process is terminated at the exciton lifetime. This has an important bearing on the temperature dependence of the mean energy of the packet of excitons. Figure 5(a) indicates that at higher temperatures excitons can relax to quasiequilibrium and a plot of $\Delta\varepsilon(T)/\sigma(T)$ should obey $\Delta\varepsilon(T)/\sigma(T) = -\sigma(T)/kT$ law because $\Delta\varepsilon(T) = -\sigma(T)^2/kT$ [Fig. 5(c)]. Below a demarcation temperature (T_c) the relaxation of excitons is terminated at the exciton lifetime. This implies that the normalized mean energy $\Delta\varepsilon(T)/\sigma(T)$ must become temperature independent for $T < T_c$. So far, we have tacitly assumed that diffusional relaxation of excitations is not kinetically blocked.

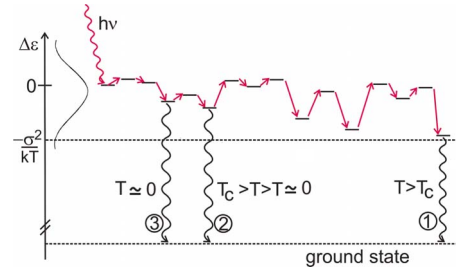


FIG. 6. (Color online) Schematic illustrating the appearance of frustrated spectral diffusion at different temperatures as described in the text.

The second process, that can become relevant at low temperatures, is a frustration of the relaxation process. This is illustrated in Figs. 5(b) and 6. Recall that an excitation tends to follow the fastest decay route in order to reach low lying tail states of the DOS [case (1) in Fig. 6]. As already mentioned, this can and often does involve intermediate thermal activation toward a higher lying transport site. Upon lowering the temperature the number of acceptor sites with still lower energy decreases and the need for intermediate activation increases. As a result the relaxation process and, concomitantly, the diffusivity is slowed down. At $T < T_c$, some intermediate thermal activation required for subsequent relaxation still occurs, yet it is insufficient for attaining quasiequilibrium. Therefore, excitons will emit before they reach quasiequilibrium and concomitantly the emission will be hypsochromically shifted [case (2) in Fig. 6 and T4 in Fig. 5(b)]. In the $T \rightarrow 0$ limit thermal activation is completely frozen and a detour involving a higher lying site is blocked. Therefore excitons can relax within the DOS only via energy-dissipative jumps and eventually long-distance jumps [case (3)]. Mean-field theories fail to account for this effect which was borne out, however, in Monte Carlo simulations.¹³ Meanwhile it has been explained in terms of analytically solved Master-equation dynamics¹³ in the $T \rightarrow 0$ limit. Since this freezing effect of relaxation at very low temperatures is associated with isolated sites from which nonactivated jumps to lower lying target sites are unavailable during their lifetime, it should only be observable for charge carriers and triplet excitons that migrate via short-ranged exchange coupling yet not for singlet excitons that diffuse via long ranged dipole coupling.

The freezing effect on triplet excitons has previously been observed in a benzophenone glass.¹⁴ Gated phosphorescence spectra were measured at 6 and 80 K. At 6 K the spectral relaxation was significantly slowed as compared to 80 K and followed the $\Delta\varepsilon/\sigma \propto \sqrt{\log \nu_0 t}$ predicted by Movaghar *et al.*'s¹³ theory in the limit of $T \rightarrow 0$ while at 80 K, $\Delta\varepsilon/\sigma$ followed the conventional $\Delta\varepsilon/\sigma \propto \log \nu_0 t$ law. The work of Rothe and Monkman¹⁶ on PF2/6 used this theory to analyze the results on the time-dependent phosphorescence of PF2/6 at 15 K. However, the complete temperature dependence of the spectral diffusion of both singlet and triplet excitons has, to our knowledge, not been reported so far.

We shall first analyze the experimental results on spectral diffusion of *singlet* excitons in our systems in terms of the concept of random walks within a Gaussian DOS. We iden-

TABLE I. Estimated center of the DOS employed for Fig. 7.

	$S_1 \leftarrow S_0$ (eV)	$T_1 \leftarrow S_0$ (eV)
Pt-Polymer	3.21	2.40
MeLPPP	2.72	2.12
PIF	3.01	2.21
PF2/6	3.10	2.22
DOOPPP	3.41	2.47
PF2/6 Trimer	3.45	2.28

tify the center of the DOS with the peak of the 300 K $S_1 \leftarrow S_0$ 0-0 absorption and we infer its width $\sigma(T)$ from a Franck-Condon fit to the fluorescence spectrum at different temperatures. The values derived in this way for the center energy of the DOS are listed in Table I and are marked by arrows in Fig. 2. Then we plot the energy difference $\Delta\varepsilon(T)$ between the center of the DOS and the center of the $S_1 \rightarrow S_0$ 0-0 fluorescence band normalized to $\sigma(T)$,

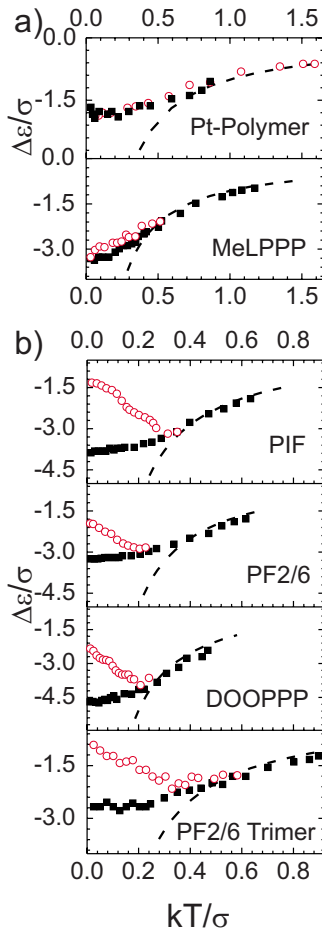


FIG. 7. (Color online) Energy difference $\Delta\varepsilon$ between the center of the DOS and the center of the $S_1 \rightarrow S_0$ 0-0 fluorescence band (black filled squares) or the center of the $T_1 \rightarrow S_0$ 0-0 phosphorescence band (red open circles) normalized to σ versus kT/σ . The dashed curve is the theoretically predicted $\Delta\varepsilon/\sigma(T) = -\sigma(T)/kT$ dependence. (a) For the low-disorder materials Pt-polymer and MeLPPP and (b) for PIF, PF2/6, DOOPPP, and the PF2/6 trimer.

i.e., $\Delta\varepsilon(T)/\sigma(T)$, versus $kT/\sigma(T)$. The result is shown in Fig. 7. The dashed curve is the theoretically predicted $\Delta\varepsilon(T)/\sigma(T) = -\sigma(T)/kT$ dependence.

Figure 7 demonstrates that at moderate temperatures, i.e., $kT/\sigma > 0.2-0.5$, the agreement between experiment and theory is excellent. At lower temperatures $\Delta\varepsilon/\sigma(T)$ saturates. This is a signature of the excitons decaying intrinsically before they can continue their relaxation pathway toward the bottom states of the DOS. Therefore the fluorescence spectrum must become independent of temperature. The saturation values of $\Delta\varepsilon/\sigma$ between -3 and -4 for PF2/6, MeLPPP, PIF, and DOOPPP, and PF2/6 Trimer translates into a critical concentration of acceptors below which energy transfer of singlet excitons is blocked. The fraction of these acceptor sites is given by the value of the integral over the density of states, i.e., $\int_{-\infty}^{-\Delta\varepsilon/\sigma} \frac{1}{\sqrt{2\pi\sigma^2}} \exp(-\frac{\Delta\varepsilon^2}{2\sigma^2}) d\Delta\varepsilon$. The saturation value of $\Delta\varepsilon/\sigma$ is less for the Pt-polymer (~ -1.5). The likely reason is the short lifetime of the S_1 state due to efficient intersystem crossing to the triplet manifold. The quantitative agreement between experiment and theory proves that (i) spectral diffusion of singlets is terminated at low temperatures, yet it is not frustrated and that (ii) the Stokes shift between absorption and fluorescence including its temperature dependence is essentially determined by spectral diffusion rather than by conformational site relaxation.

We shall now discuss the temperature dependence of the phosphorescence spectra in our systems. Except for MeLPPP and the Pt-polymer the temperature induced shift of the phosphorescence spectra is fundamentally different from that of the fluorescence spectra. Unfortunately triplet quenching at higher temperatures precludes collecting phosphorescence data above 100 K in case of PF2/6 and around 200 K for the other materials. Figure 2 demonstrates that the 0-0 peak position of the $T_1 \rightarrow S_0$ transition features a hypsochromic shift upon further cooling. For analyzing the data we take the disorder parameter $\sigma_T(T)$ of triplet excitons from the $T_1 \rightarrow S_0$ emission and choose the center of the DOS of triplet states freely under consideration of the mirror symmetry between emission and absorption and of the width of the triplet DOS. The values derived are listed in Table I. This allows plotting the energetic shift as a function of temperature on a $\Delta\varepsilon(T)/\sigma_T(T)$ vs $kT/\sigma(T)$ scale. The result is included in Fig. 7. While the two low-disorder compounds Pt-polymer and MeLPPP show a behavior like that of the singlets, all of the other compounds show a shallow minimum for the $\Delta\varepsilon/\sigma_T$ data at a normalized temperature of $kT/\sigma \sim 0.2-0.3$. At lower temperatures $\Delta\varepsilon/\sigma$ increases. Overall, the increase from the minimum value to the $T \rightarrow 0$ value exceeds 1σ . This is consistent with Movaghar *et al.*'s¹³ theory of frustrated diffusion in the $T \rightarrow 0$ limit. The results thus document (i) the occurrence of frustrated diffusion below a critical temperature T_c of less than about $(0.2-0.3) \sigma/k$ and (ii) that the degree of frustration, inferred from the hypsochromic shift of the phosphorescence spectra at low temperatures, increases as the $T \rightarrow 0$ limit is approached. Interestingly, this effect is not observed with MeLPPP and the Pt-polymer that are the least disordered systems in the series of compounds investigated.

To summarize our analysis of the experimental data, above T_c we observe a bathochromic shift upon lowering the

temperature for the singlet state in all materials we investigated. The bathochromic shift also occurs for the triplet state in the two compounds where data could be collected in this range, that is, the Pt-polymer and the PF2/6 trimer. Below T_c , we observe a *termination* of the relaxation process for the singlet state in all compounds and for the triplet state in the two more ordered polymers MeLPPP and Pt-polymer. In contrast, relaxation is *frustrated* for the triplet states in the remaining polymers and in the PF2/6 trimer. One may ask what causes the difference in relaxation behavior. The variation observed for the triplets between MeLPPP and the Pt-polymer on the one side, and PIF, PF2/6, DOOPPP, and PF2/6 trimer on the other side indicate that the spin state by itself or oligomer length are not sufficient to explain the results. Similarly, polaronic effects cannot be invoked to explain the occurrence of termination or frustration behavior. One might argue that the temperature-dependent shifts of fluorescence and phosphorescence be a consequence of a temperature-dependent geometric distortion, i.e., a temperature-dependent (true) Stokes' shift. The geometric relaxation energy is given by the product of vibration energy times Huang-Rhys factor. Any change in the relaxation energy and, in particular, any effect of temperature should therefore be manifested in a change in the Huang-Rhys factor. If we consider PF2/6 as an example, we observe shifts in the phosphorescence spectra (from 10 to 80 K) and the fluorescence spectra (from 10 to 150 K) of about -30 and 20 meV, respectively (Fig. 3). However, if we normalize the associated emission spectra displayed in Fig. 2 to the 0-0 peak we find no difference in the ratio of 0-1 to 0-0 peak, i.e., the Huang-Rhys factor is constant. From this it follows that the shifts observed cannot be explained by geometric relaxation effects. Similarly, we note that the intensity of the vibrational side peaks in MeLPPP is comparable to that of PIF and PF2/6 while that in the Pt-polymer is much lower, so the appearance or lack of frustration does not correlate with the geometric relaxation energy.

The appearance of frustration can also not be assigned to the degree of disorder present in a compound. First, the variance of the occupational DOS in a singlet state is equal or larger than that in the triplet state and second, the lack of frustration in MeLPPP and the Pt-polymer cannot be due to their lower variance of the DOS since this is taken care of by normalizing the data to units of σ . It is worthwhile recalling that the frustration event is caused by the need for an activation energy in order to reach a far away lower energy site via a higher energy detour over nearby sites. From this it follows that the appearance of frustration is associated with the distance over which the coupling between sites occurs. Singlet states diffuse mainly via dipole-dipole coupling (Förster-type energy transfer) that, by nature of its R^{-6} dependence, allows for transfer between sites at considerable distance such as a few nanometers. Within a Förster radius of a few nanometers, the existence of a site with lower energy is likely and so energetic relaxation via diffusion can proceed without the need for an activation energy for a large number of jumps. Triplet transfer, in contrast, requires orbital overlap and so relaxation requires either a lower energy nearest neighbor or, alternatively, a phonon mode that allows for thermal activation to a higher energy neighboring site. This short range of

the coupling results in the frustration process outlined above and this is observed for the PIF, PF2/6, DOOPPP polymers, and the PF2/6 trimer. The two polymers MeLPPP and Pt-polymer where termination of spectral diffusion is observed are characterized by a low degree of disorder in the occupational DOS. We repeat and stress that the small variance of the DOS, and the associated lower activation energy required for triplet state diffusion, cannot account for the absence of frustration, as is evident from considering data normalized to units of σ . Rather, it is a different phenomenon often associated with weak disorder that causes the lack of frustration. Weak disorder implies that the exciton is spread out over a larger effective conjugation length. As a consequence, the exciton can sample a larger number of neighbor chains that can act as target sites for nonactivated triplet exciton transfer. Thus, the reason for frustrated diffusion is suspended. We therefore come to the conclusion that the long-range interaction, characteristic for singlets, causes the termination behavior of their spectral diffusion while the short-range coupling for triplets in at least moderately disordered materials gives rise to frustration. An interesting case to study in future will be charge carriers that, like triplets, rely on orbital overlap for transfer, yet that also, like triplets in MeLPPP, can delocalize over a large part of the chain.

Since there is currently no theory available to calculate the temperature dependence of frustrated spectral diffusion, the experimental data cannot be compared with theory. One can only compare the $\Delta\varepsilon/\sigma_T$ values in the $T \rightarrow 0$ limit with the prediction of Movaghar *et al.*'s theory¹³ for a realistic choice for the ratio between the minimum exciton jump time in a hypothetically ordered hopping system and the intrinsic exciton lifetime. It predicts $\Delta\varepsilon/\sigma_T \sim -2$ at $T \rightarrow 0$, consistent with experiment. One may go one step further and identify elements for a future theoretical concept that rests upon the description of the phenomenon of frustrated spectral diffusion outlined in the beginning of this discussion. The essential idea is the following: Once a packet of excitons in a hopping system with short-range coupling has relaxed to a critical energy within the DOS, further relaxation requires thermal activation to an exciton mobility edge ε_{mob} . The mobility edge denotes the energy within the DOS at which an exciton can execute jumps without requiring thermal activation. The probability to reach that mobility edge ε_{mob} is controlled by a Boltzmann factor, $\nu_\infty \exp\{-[\varepsilon_{mob} - \varepsilon(T)]/kT\}$. Activation to the mobility edge has to compete with intrinsic exciton decay, i.e., $\nu_\infty \exp\{-[\varepsilon_{mob} - \varepsilon(T)]/kT\} \geq \tau^{-1}$. (τ is the lifetime of the exciton) Since both τ^{-1} and ν_∞ are essentially temperature independent in the low-temperature range where frustration occurs, the Boltzmann factor has also to be temperature independent implying that $[\varepsilon_{mob} - \varepsilon(T)]/\sigma \sim kT/\sigma$, i.e., the energy of packets of excitons should increase linearly with decreasing temperature toward ε_{mob} in the $T \rightarrow 0$ limit. It is obvious that mapping this process into a two level system is a serious oversimplification because it ignores the stochastic character of this highly complicated process but this outline can be considered as a zero-order approach to treat triplet relaxation under the condition of frustration.

V. CONCLUSIONS

The present work provides a spectroscopic assessment of relaxation of excitations migrating incoherently in a disor-

dered organic solid featuring a Gaussian-type density-of-states distribution. Test systems investigated are a series of conjugated polymers and a trimer employing fluorescence and phosphorescence spectroscopy within a temperature range between 10 and 500 K. In order to rationalize the temperature dependence of the Stokes' shift between absorption and fluorescence in a quantitative fashion it is both necessary and sufficient to invoke Movaghar *et al.*'s hopping theory for excitations that couple by long-range dipole interactions.¹² In contrast, the phosphorescence spectra of the majority of compounds feature a hypsochromic shift below a certain critical temperature, i.e., the spectra shift toward to the blue spectral range upon lowering the temperature. This is a signature of the occurrence of frustrated relaxation/

diffusion. The reason is that triplet excitons couple by short-range orbital overlap interaction. This leads to localization within the exciton lifetime. A critical test of this concept is provided by the observation that the frustration effect is suspended in systems with weak disorder and, accordingly, longer effective conjugation length that allows excitons to explore a larger number of acceptor sites.

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