Time-dependent energy transfer rates in a conjugated polymer guest-host system

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We have investigated the energy transfer dynamics in films of a conjugated polyindenofluorene host doped with covalently attached perylene guests. By performing time-resolved measurements of the host luminescence decay under site-selective excitation conditions, we have examined the influence of exciton migration within the host on the temporal evolution of the host-guest energy transfer. We find that highly mobile excitons created at the peak of the host's inhomogeneous density of states transfer to guests considerably faster than more localized excitons created in the low-energy tail, indicating a strong contribution of exciton migration to the overall energy transfer. These effects are significantly more pronounced at low temperature (7 K) than at ambient temperature, suggesting that for the latter, up-hill migration of excitons in the host and a broadening of their homogeneous linewidth may prevent truly site-selective excitation of localized excitons. In the asymptotic long-time limit, the observed dynamics are compatible with long-range single-step Förster energy transfer. However, at early times ($\lesssim 10$ ps) after excitation, the behavior notably deviates from this description, suggesting that diffusion-assisted energy transfer is more important in this regime. The measured changes in excitation transfer rates with temperature and excitation energy correlate well with those observed for the dynamic energy shifts of the vibronic emission peaks from the undoped polymer. Our results therefore indicate that energy-transfer rates in polymeric guest-host systems are strongly time-dependent, owing to a contribution both from exciton relaxation through incoherent hopping within the host's density of states and direct Förster energy transfer.

I. INTRODUCTION

Conjugated polymers are increasingly being used as active materials in solar cells,[1] transistors,[2] and light-emitting displays.[3] These organic semiconductors have significant advantages since they can be easily processed into thin films from solution, permitting adoption of novel techniques of device fabrication such as ink-jet printing.[4] However, one drawback in comparison with their inorganic counterparts is posed by the energetic and positional disorder caused by entanglement of the extended polymer chains and the presence of structural defects. Such disorder results in the formation of potential minima in the energy landscape, leading to strongly dispersive charge carrier motion and exciton diffusion. It has been shown that the creation of photo-excitations in these materials is followed by incoherent hopping processes between localized states on conjugated chain segments.[5–7] Excitons formed near the high-energy end of the inhomogeneous distribution of states (DOS) undergo rapid migration towards longer chain segments until the absence of lower-energy segments in the near surroundings lead to localization. At low temperatures, such exciton migration processes may be suppressed using site-selective excitation, which creates nearly immobile excitons through photoexcitation in the low-energy tail of the DOS.[8–10] Site-selective spectroscopy has therefore emerged as a powerful tool for the investigation of exciton diffusion processes in conjugated polymer films. An additional advantage of polymeric materials for applications in light-emitting devices is the possibility of tuning their emission color by introducing a small amount of a luminescent guest. Efficient excitation transfer from the polymeric host to the guest will then result in an emission spectrum that is largely dominated by the guest luminescence. Theoretical descriptions of energy transfer in these systems are most frequently based on the direct coupling between host and guest dipole moments[11–13] as described by Förster within the point-dipole approximation.[14] However, the results of recent studies have suggested that in addition to direct, single-step excitation transfer from a host to a guest site, exciton migration processes within the host may contribute significantly to the overall transfer process.[15–17] Moreover, the applicability of Förster's theory has been called into question for transfer distances that are small compared to the extent of the exciton wave function along a conjugated segment.[18]

In this paper, we present an investigation into the temporal evolution of energy transfer rates in a dye-doped conjugated polymer. By performing site-selective measurements over a range of temperatures, we exercise control over the amount of exciton migration following excitation. As a result, we are able to examine the relative contribution of energy migration within the polymer host, to the overall energy transfer from the host to the dye guests. Our results indicate that the initial transfer dynamics are governed by fast, diffusion-assisted transfer processes. However, as excitons relax through the host's DOS and their diffusivity decreases, single-step Förster excitation transfer processes become the dominant mechanism.

II. EXPERIMENT

All measurements were performed on films comprising blends of poly(6,6′,12,12′-tetra-2-ethylhexyl-
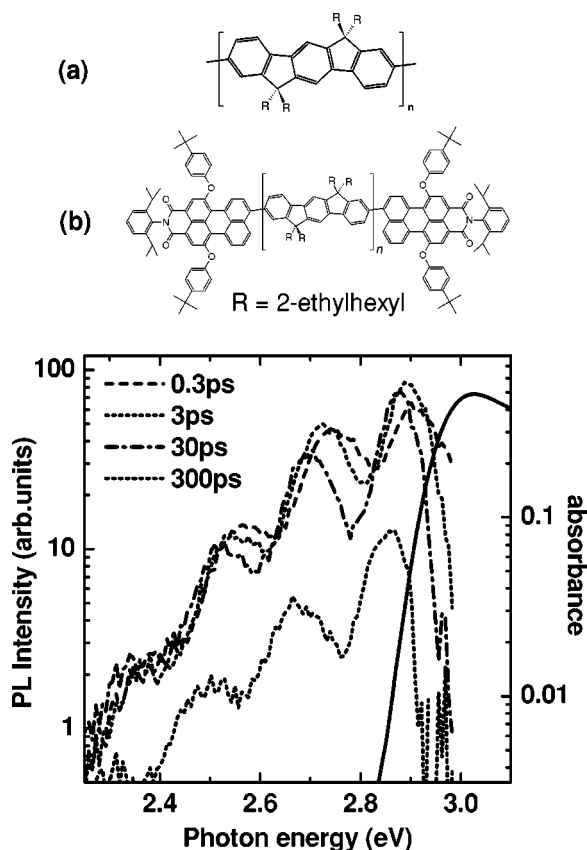
FIG. 1. Top: (a) Chemical structure of PIFTEH. (b) Chemical structure of PEC-PIFTEH. Bottom: Photoluminescence UC spectra of a drop-cast PIFTEH film at various times after excitation (Excitation energy: 3.062 eV, sample temperature: 7 K) together with the absorption spectrum of PIFTEH dissolved in *p*-xylene (solid line, taken at ambient temperature).

2,8-indenofluorene) (PIFTEH) and PIFTEH end capped with a perylene derivative (PEC-PIFTEH). The chemical structures of both polymers are given in Fig. 1. This particular blend system was chosen for a number of reasons. Firstly, the covalent attachment of the perylene guests ensures the absence of phase segregation or aggregation of the guest.[19] Secondly, blending two polymers with identical backbone will result in an even mixture of the two systems, so that the guest concentration can easily and accurately be diluted by adding a chosen relative amount of PIFTEH to PEC-PIFTEH. The maximum guest concentration was limited by that of PEC-PIFTEH (5.5% of the total monomer and dye units) while the smallest concentration investigated (0.34%) was chosen to maintain the average distance between adjacent dyes in the blend sufficiently large compared to the average chain length of PEC-PIFTEH. The latter condition was required to ensure that even though a significant fraction of PEC-PIFTEH chains contain guest molecules on both ends, the guests can nevertheless be considered to be randomly situated in the film. Thirdly, it was recently shown that on-chain transfer of excitations in these systems is slower than interchain transfer by approximately two orders of magnitude.[18] The fact that the dye guests are covalently attached to the polymer chains thus has no impact on the

nature of the investigated photoexcitation transfer. This system is therefore an ideal representative of a polymeric host incorporating randomly distributed dye guests.

Samples were fabricated by drop-casting blend solutions of polymer in *p*-xylene onto Spectrosil B substrates. The resulting films were sufficiently thick ($\approx$ a few microns) to allow site-selective excitation at the low-energy tail of the absorption spectrum. All samples and solutions were prepared and stored in an inert atmosphere to prevent sample degradation.

To investigate the excitation-transfer dynamics in the guest-host systems we performed time-resolved photoluminescence (PL) experiments, using the PL up-conversion (PLUC) technique for the time range of 0.1–100 ps after excitation, and time-correlated single-photon counting (TCSPC) measurements for the range 100–3000 ps. For the PLUC measurements, the samples were excited with the frequency-doubled output from a tunable, mode-locked Ti:sapphire laser supplying 200-fs pulses with photon energy in the near UV, an energy bandwidth of $\approx$20 meV and a repetition rate of 76 MHz. To set the polarization of the exciting beam, it was passed through a $\lambda/2$-plate and a Glan-Thompson polarizing prism. At the excitation power of 0.1 mW on a 100-μm spot no sample degradation effects were observed and all measurements were fully reproducible. The photoluminescence emerging from the sample was collected with a pair of off-axis paraboloidal mirrors, and up-converted in a β-barium-borate crystal using the fundamental laser beam as a gate. Sum-frequency photons were dispersed in a monochromator, and detected by a cooled photomultiplier tube using photon counting techniques. The overall resolution of the system was approximately 350 fs and the spectral resolution was $\approx$50 meV at a detected PL energy of 2.7 eV. Only vertically polarized light could be up converted, and the excitation polarization was chosen to measure the luminescence component polarized parallel to the polarization of the exciting light. For the measurement of time-integrated photoluminescence spectra the PL was dispersed in a double-grating spectrometer (Spectramate 1680) and detected with a Si photodiode using a lock-in technique. Both parallel and perpendicular polarization components were taken using a second Glan-Thompson polarizing prism. The total spectrum was then calculated by adding twice the perpendicular component to the parallel component. Time-resolved and time-integrated spectra were corrected for spectral response using a standard W-filament lamp. For TSCPC measurements, samples were excited at a photon energy of 3.046 eV using a pulsed diode laser with repetition rate of 20 MHz (Picoquant), and photoluminesence was detected with a microchannel plate photomultiplier (Hamamatsu) coupled to a monochromator and TCSPC electronics (Lifespec-ps and VTC900 PC card, Edinburgh Instruments). During measurements, the samples were held in a helium cryostat (Oxford Instruments "Optistat") allowing temperature variation between 6 K and ambient temperature. Absorption spectra of dilute polymer blend solutions in *p*-xylene were taken using an HP8453 ultraviolet-visible spectrophotometer.

III. DISCUSSION

Polyindenofluorenes are blue-light emitters taking an intermediate place between the rigid and planar ladder-type ploy(*para*phenylenes) (LPPP) (Ref. 20) and the more twisted polyfluorenes (PF).[21] The absorption and emission maxima of PIFTEH in solution are located energetically between those of LPPP and PF, with a small Stokes shift of 20 nm (14 meV) indicating a relatively planar structure.[22] Figure 1 shows the time-resolved photoluminescence spectra of a PIFTEH film for various times after excitation. For these measurements, the sample was excited near the peak of the absorption at a photon energy of 3.062 eV and held at a temperature of 7 K. Soon (0.3 ps) after excitation, a strong emission peak at 2.91 eV is observed, followed by vibronic progressions at 2.745, 2.57, and 2.38 eV. The energetic separation of adjacent peaks is compatible with electronic coupling to a range of on-ring and inter-ring C-C stretching modes, as previously identified in the related polyflourenes[23,24] at energies around 200 meV and 136–180 meV, respectively. The spectral resolution in our measurements is too low to permit the observation of individual vibrational modes in this range and we will refer to these emission peaks as (0-0), (0-1), (0-2), and (0-3) in the following. The small Stokes shift observed in solution between the (0-0) peaks of absorption and emission suggests that low-energy torsional motion between phenyl rings[25,26] may also contribute to the vibrational relaxation to a minor extent. When examining the changes of the PL spectra with time, a number of observations can be made. First, the spectrally integrated PL intensity decreases with time due to radiative or non-radiative recombination of excitons. Secondly, all emission peaks shift to lower energy accompanied by a change in the ratio of the intensity of the (0-1) peak to that of the (0-0) peak. This ratio is generally referred to as the Huang-Rhys parameter S and is a direct measure of the geometric relaxation or change in molecular structure following excitation.[8] Similar changes are also found for the peak ratios of the (0-2) and (0-1) transition, indicating that these effects are not simply related to self-absorption. Instead it appears that as time progresses, recombination of excitons occurs increasingly from sites with a more planar ground-state geometry featuring smaller conformational changes upon excitation. Comparable observations have been made previously for a range of other conjugated polymers[5,9,10,27,28] and have generally been attributed to exciton migration within an inhomogeneously broadened density of energy states in the polymeric material. Conformational or structural disorder may interrupt the conjugation along a chain, which may then more adequately be described as a string of conjugated subunits or oligomers of varying lengths and thus exciton confinement or energy. Creation of an exciton somewhere high in the absorption band will be followed by rapid relaxation through this density of states until the exciton becomes localized on a segment longer than those in its closer surroundings. Since longer conjugated segments are associated with less geometric distortion upon excitation,[29,30] the Huang-Rhys factor is found to decrease in unison with the excitonic emission energy.[10] In order to assess and control the amount of exciton migration in PIFTEH, we have per-
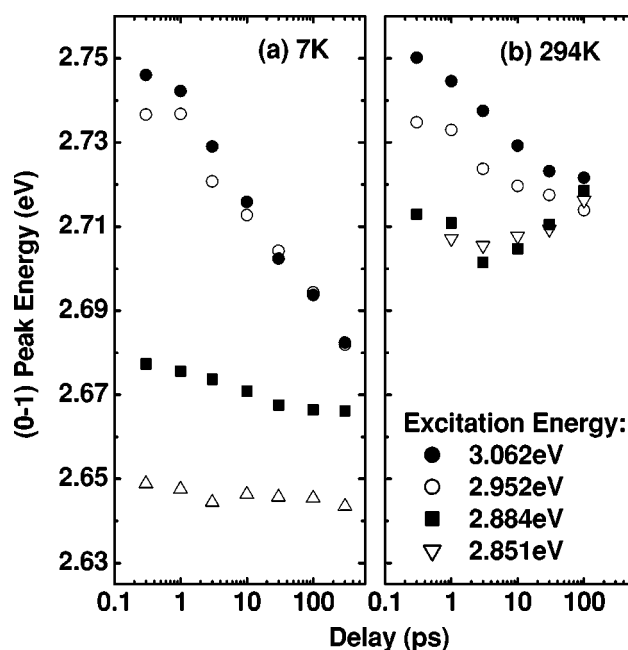

FIG. 2. Energy of the (0-1) PL emission peak from drop-cast PIFTEH as a function of time, taken for various excitation energies and sample temperatures.

formed time-resolved, site-selective measurements on the films. For this purpose, the samples were excited at energies ranging from the maximum of the absorption to the far end of its low-energy tail (see absorption spectrum in Fig. 1). The exciton migration was subsequently monitored by measuring the average energy of the PL emission peaks as a function of time after excitation.[9,10] Figure 2 displays the (0-1) peak energy as a function of time for various excitation energies both at ambient temperature (right) and at 7 K (left). These values were obtained by fitting the sum of four Gaussians to the measured time-resolved spectra. At low temperature (7 K) the peak shifts are compatible with exciton migration through a Gaussian density of states: excitation high in the absorption band is followed by a decrease in the average energy of the exciton, which depends linearly on the logarithm of time.[6] As the excitation energy is reduced below the "localization edge" the average exciton energy immediately after excitation follows the excitation energy and the subsequent red-shifts are suppressed. This is the case for excitation at an energy of 2.851 eV, for which the (0-1) emission peak occurs irrespective of time at an energy of 2.647 eV, i.e., downshifted with respect to the emission energy by approximately an average C-C stretch vibrational energy of 200 meV. At this excitation energy, excitons are therefore created on long segments on which they are highly likely to remain during their lifetime. These low-temperature results are very similar to those obtained for polyfluorene by Meskers *et al.*[9] who were able to model their data successfully using a Monte Carlo simulation based the assumption of incoherent hopping between localized energy states, mediated by dipole-dipole interactions. When increasing the temperature to 294 K (Fig. 2) we find that the relaxation behaviour changes significantly. While excitation high in the absorption band is still followed by rapid energy relaxation,
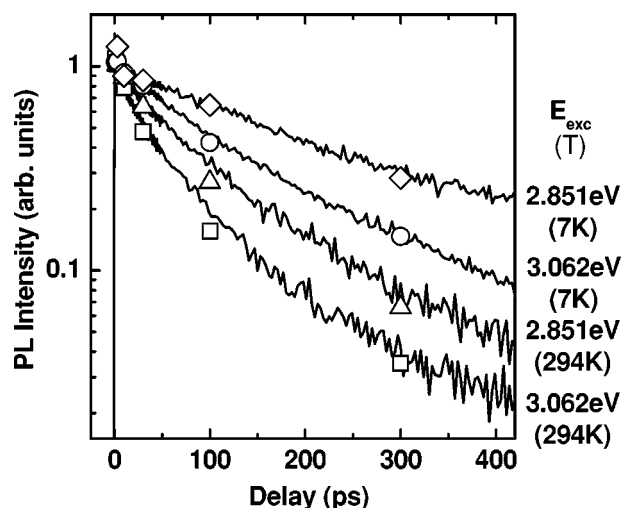
FIG. 3. Solid lines: Photoluminescence UC decay from a PIFTEH film for an excitation energy of either 2.851 or 3.062 eV, and a temperature of either 7 K (detection energy 2.71 eV) or 294 K (detection energy 2.74 eV). Open symbols: spectrally integrated Photoluminescence at various times after excitation for the corresponding excitation and temperature conditions.

FIG. 4. Time-integrated photoluminescence spectra of perylene-doped polyindenofluorene films for various concentrations of the perylene guest, taken at sample temperatures of (a) 294 and (b) 7 K. The films were excited at an energy of 3.062 eV.

the amount by which the energy shifts towards the red within the first 100 ps is now much smaller. This should to some extent be expected, as the increased temperature means that "up-hill" migration processes are now playing a more dominant role. These processes may also be responsible for the slight increase observed in the (0-1) peak energy after ≈ 10 ps for low excitation energies, which has been predicted by recent Monte Carlo simulations.[9] A second effect of increasing the temperature is that for low excitation energies the (0-1) peak energy immediately after excitation is now at significantly higher energy than at 7 K (by over 50 meV for the lowest excitation energy of 2.851 eV). This can be understood considering recent single-molecule studies of LPPP by Müller *et al.*[33] who demonstrated an increase with temperature of the homogeneous linewidth from 2.5 meV at 5 K (in agreement with a decoherence time of a few hundred femtoseconds[34]) to approximately 40 meV at ambient temperature. Choosing an excitation energy in resonance with a few, long segments at ambient temperature will therefore result in the creation of excitons predominantly on shorter segments, which may be out of resonance by a homogeneous line width or so, but are present in significantly larger quantity than the long segments. We conclude that at ambient temperature, up-hill migration and the broadening of the homogeneous linewidth inhibit truly site-selective excitation so that the creation of fully localized excitons is highly unlikely.

Figure 3 shows the time-resolved PL decay from a PIFTEH film measured near the (0-1) emission peak for combinations of two different excitation energies and two temperatures. The excitation energies were chosen to be either 3.062 eV (i.e., near the peak of the PIFTEH absorption) or 2.851 eV (i.e., at an energy for which localized excitons are created at low temperature). The temperatures were set to either 294 K (detection at 2.74 eV) or 7 K (detection at
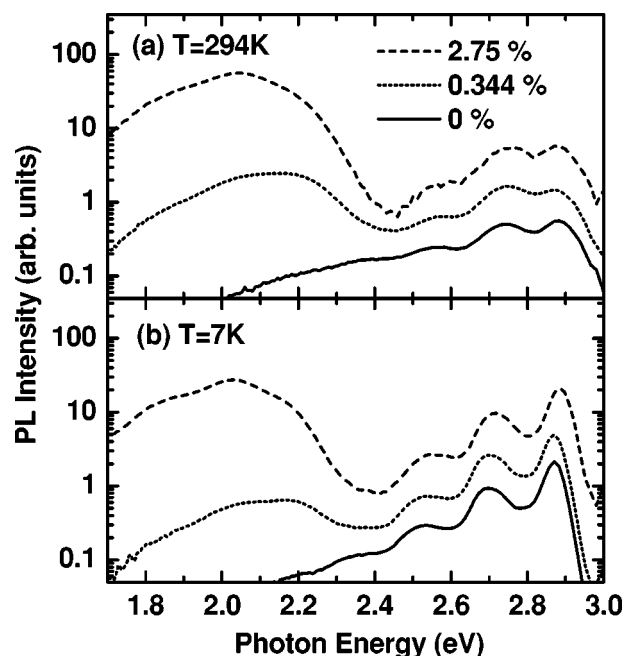
2.71 eV). Superimposed on the curves are the spectrally integrated PL intensities extracted from the time-resolved PL spectra at various times after excitation. At the high-energy end of the (0-0) transition, where rapid exciton relaxation dominates the PL transients, the shape of the PL decay was found to vary strongly with detection energy (not shown) similar to what has previously been observed for a range of conjugated polymers.[5,27] However, from the results displayed in Fig. 3 we deduce, in agreement with previous studies,[7] that at the lower-energy end of the inhomogeneously broadened transitions the PL transients largely reflect the decay of the total exciton population. We observed no significant variation in the shape of the decay curves when varying the detection energy by a few tens of meV, partly as a result of the relatively low spectral resolution (50 meV). The changes in the PL lifetime with excitation energy and temperature shown in Fig. 3 suggest that a certain fraction of nonradiative traps may be present in the PIFTEH films. Changes in the excitation energy and/or temperature will result in a different exciton migration rate, which will in turn affect an exciton's probability of being trapped.[7] In order for us to examine systematically the effect of excitation energy and temperature on the energy transfer in these systems, we now turn to the measurements performed on perylene-doped polyindenofluorene films.

Figure 4 shows the time-integrated PL spectra of blend films for various dye concentrations at ambient (top) and low (bottom) temperature. The excitation energy was set to 3.062 eV thereby ensuring that almost all excitons are created on the PIFTEH host polymer. With increasing dye concentration, the blue emission from PIFTEH in the spectral region 2.3–3 eV decreases with respect to the red emission from the dye guest (1.7–2.3 eV) indicating increasing trans-

fer of excitons from the host to the guest. In the spectral region of the dye emission the PL polarization anisotropy is found to be zero, indicating that PEC-PIFTEH aggregation observed previously for spun-cast films[35] is absent in the drop-cast films used for the present investigation. From the PL spectra displayed in Fig. 4 it is evident that the time-integrated transfer efficiency in the guest-host system is reduced with decreasing temperature. While at ambient temperature, for a sample with dye concentration of 2.75%, the emission is dominated by that of the guest, approximately equal magnitudes are observed for guest and host emission for the same film at 7 K.

Energy transfer in π-conjugated guest-host systems generally relies on a coupling between the dipole moments of the host and the guest chromophore. Within the point-dipole approximation, the rate of transfer k between a host and a guest chromophore was calculated by Förster[14] to be inversely proportional to the sixth power of the guest-host separation R, that is,

$$k = \tau \left(\frac{R_0}{R} \right)^6, \tag{1}$$

where τ is the lifetime of the host excitation in the absence of the guest. The Förster radius R_0 depends on the spectral overlap between the host emission and the guest absorption reflecting the necessity of energetic resonance during the transfer.

As shown previously, the emission of the PIFTEH host overlaps broadly with the absorption of the perylene guest.[35] Small changes, which may occur in the transition energy or bandwidth of the host or guest with temperature, will therefore not affect the Förster energy transfer rate significantly. Consequently, the dependence of transfer efficiency on temperature must be due to a different mechanism.

List *et al.* have observed similar effects in the temperature-dependent transfer efficiencies for a guest host system comprising LPPP and an orange-light-emitting π-conjugated macromolecule.[15] They have interpreted their observations in terms of a thermally activated exciton migration process assisting the direct Förster transfer of excitation from the host to the guest, with an activation energy of 16.5 meV. Using a model based on temperature-dependent (but time-independent) transfer rates they were able to describe the observed changes in the time-integrated transfer efficiencies. In the following, we will establish the time-dependence of this transfer process, and in particular, examine how its dynamics are affected by the presence of exciton diffusion within the host. The decay of the exciton population f in the undoped PIFTEH films can be described by the following rate equation:

$$\frac{d}{dt}f = -\left(\frac{1}{\tau} + r(t) \right)f(t), \tag{2}$$

where τ is the natural exciton lifetime and $r(t)$ a decay rate associated with time-dependent processes such as exciton diffusion to traps and energy relaxation processes. In a PIFTEH host doped with dye guest molecules, the exciton population g suffers an additional loss due to energy transfer to the guest, i.e.,

$$\frac{d}{dt}g = -\left(\frac{1}{\tau} + r(t) \right)g(t) - k(t)g(t), \tag{3}$$

where k is the time-dependent energy transfer rate, which may (amongst other factors) depend on the excitation energy, temperature and guest concentration. If both $f(t)$ and $g(t)$ are known, the transfer rate can be determined from Eqs. (2) and (3) to be

$$k(t) = -\frac{d}{dt} \ln I(t), \quad \text{where } I(t) = \frac{g(t)}{f(t)}. \tag{4}$$

The ratio $I(t)$ thus directly relates to the time-dependent transfer rate of excitons from the host to the guest sites. Recently, Buckley *et al.*[16] have demonstrated that in a guest-host blend based on two conjugated polymers, the PL decay rate of the host polymer is reduced when the excitation energy is tuned from the absorption peak to the absorption edge of the host while simultaneously lowering the temperature from 275 to 12 K. While this effect may reasonably be attributed to a reduction of the energy transfer rate to the guest, some care needs to be taken, as a change in temperature or excitation energy may also alter the PL dynamics $f(t)$ of the undoped host (as observed, e.g., for PIFTEH—see Fig. 3). In order to deconvolve these effects it is therefore essential that one determines the ratio $I(t)$. For this purpose, we measured the PIFTEH host decay $g(t)$ in dye-doped samples for the same four combinations of excitation energy and temperature as those displayed in Fig. 3. These curves were then divided by the PL decay of the undoped host (as given in Fig. 3) to yield the ratio $I(t)$, which is displayed in Fig. 5 for a range of dye concentrations. For further illustration, the times taken for $I(t)$ to decay to $1/e$ of its original value were extracted from the curves and are displayed in Fig. 6 as a function of guest concentration. From these results we can make the following observations. First, shifting the excitation energy from near the host absorption peak (3.062 eV) into the low-energy tail (2.851 eV) results in a reduction of the transfer rate both at ambient (294 K) and low (7 K) temperature. However, this effect is much more pronounced at low temperature than at ambient temperature. At 7 K, tuning the excitation energy into the absorption tail causes an increase of the $1/e$-transfer times on average by a factor of 2.7 over the concentration range 0.69–5.5 %, while the same process at ambient temperature results only in an increase by a factor of 1.2. These observations are in agreement with our interpretation of time-dependent energy relaxation processes displayed in Fig. 2, that is, at ambient temperature exciton migration cannot be suppressed fully and migration-assisted energy transfer will thus also be of importance even for host excitation in the absorption tail. Secondly, we find that a reduction of the temperature from 294 to 7 K strongly reduces the transfer rates for both excitation conditions. This should be expected, as at low temperature, excitons visit significantly fewer sites and take longer to diffuse than at ambient temperature.[9] The changes in the transfer rate with temperature are most significant in the case of excitation in the
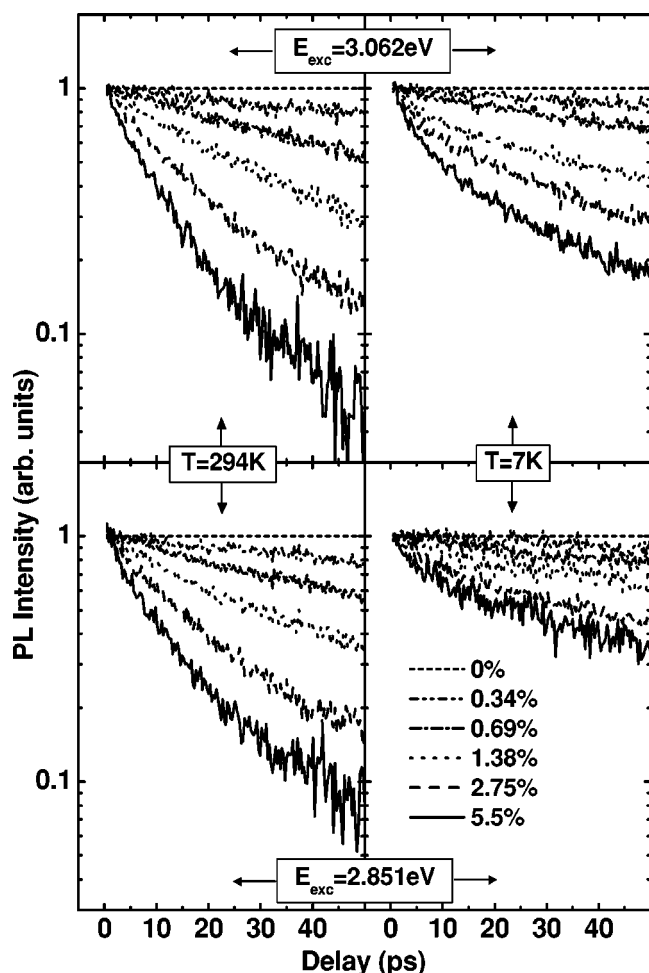
FIG. 5. Excitation transfer dynamics for perylene-doped PIFTEH films with guest concentrations varying between 0.34 and 5.5 %. The curves were obtained by dividing the PLUC decay for perylene-doped PIFTEH by that of undoped PIFTEH. The excitation energy was set to either 2.851 or 3.062 eV, and the sample temperature to either 7 K (detection energy 2.71 eV) or 294 K (detection energy 2.74 eV).

low-energy absorption band (2.851 eV) since excitons created at this energy will be fully localized at low temperature, thereby having only the option of undertaking direct host-guest transfer. Thirdly, the observed changes in the transfer rates with temperature and excitation energy appear to be the stronger the lower the concentration of the guest. For example, at a dye concentration of 0.69% the $1/e$-decay time decreases by approximately an order of magnitude when moving from excitation high in the absorption band to site-selective excitation at low temperature. This trend confirms that exciton diffusion is particularly important for the energy transfer process when the excitations are on average created far away from the nearest guest.

While the $1/e$-transfer times have so far proved useful as a rough indication of the transfer efficiencies, there is no actual reason why the transfer should follow a simple exponential behavior, i.e., occur at a time-independent rate. In fact, both the diffusion-assisted energy transfer and a single-step host-guest Förster transfer within an ensemble of host
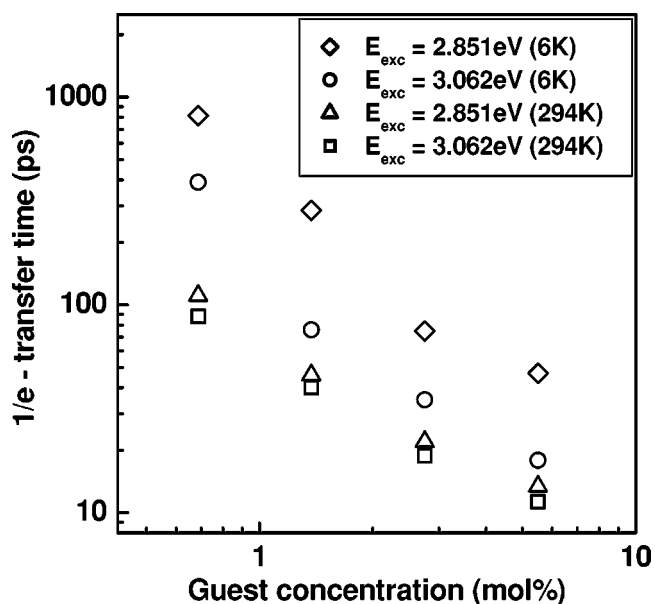

FIG. 6. Times for which the transfer transient displayed in Fig. 5 have decayed to $1/e$ of their initial value, plotted as a function of perylene guest concentration.

excitations would be expected to contain an explicit dependence on time. For excitons migrating through states inhomogeneously distributed in energy, the number of neighbors with energy suitable for a transfer to occur decreases rapidly with time after excitation.[6,36] The exciton diffusion is thus a strong function of time, and so should be its relative contribution to the host-guest excitation transfer rate.

In addition, direct, single-step Förster transfer from a host to randomly distributed guests will in itself result in a time-dependent transfer rate for the ensemble of excitons.[37] This is because excitons located close to a guest will undertake transfer with a faster rate than those located further away, such that the *ensemble-averaged* rate appears to slow with time. Photoexcitation will initially create a population of excitons that are randomly distributed in the host, however, as time progresses this distribution becomes increasingly non-random as only those excitons survive that are located far from guests.[38] For a three-dimensional system with randomly distributed guests, Förster thus found the ensemble-averaged transfer rate to be given by

$$k(t) = \frac{\beta}{\sqrt{t}} \quad \text{with } \beta = \frac{2}{3}\pi^{3/2}\frac{c_A R_0^3}{\sqrt{\tau}}, \quad (5)$$

where c_A is the guest concentration.[37,39]

Theoretical models for the complex exciton diffusion and transfer dynamics in disordered media often yield solutions following stretched-exponential behavior,[7,36,40] that is, the surviving exciton population can be described by

$$I(t) = I_0 \exp\left(-\left[\frac{t}{t_0}\right]^\alpha\right) \quad (6)$$
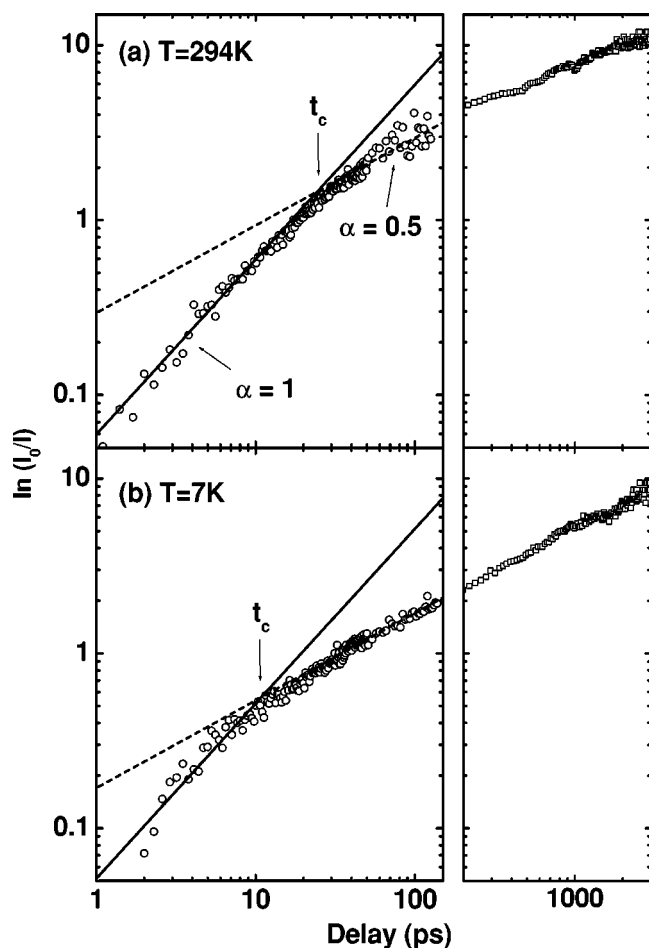
corresponding to a transfer rate

FIG. 7. Left: KWW representation of the excitation transfer transients for a PIFTEH film containing 2.75% perylene guests. The film was excited at an energy of 3.062 eV (detection as stated in Fig. 5) and held at temperature of (a) 294 or (b) 7 K. The solid (dashed) lines represent stretched exponential fits to the short-time (long-time) assymptotic part of the data with exponent $\alpha=1$ ($\alpha=0.5$). The arrows indicate the times t_c at which cross-over occurs between the two regimes. Right: KWW representation of the excitation transfer transients at longer times, as measured for the same sample using TCSPC (excitation at 3.046 eV, detection at 2.70 eV).

$$k(t) = \alpha t_0^{-\alpha} t^{\alpha-1}. \tag{7}$$

A time-independent rate is then characterized by $\alpha=1$ while direct Förster transfer is governed by $\alpha=0.5$ in a three-dimensional system. It is therefore convenient to display our data in Kohlrausch-Williams-Watts (KWW) representation[7] where the logarithm of $\ln(I_0/I)$ is plotted against the logarithm of time after excitation. Examining the slope α of the data in this representation will then allow us to investigate the nature of the excitation transfer processes. Figure 7 shows a KWW plot of the excitation transfer dynamics $I(t)$ at low (7 K) and ambient temperatures (294 K) for a film with a guest concentration of 2.75% after excitation near the peak of the absorption spectrum. The left panels display the early-time dynamics taken by PLUC while the right show the behavior in the range 200–3000 ps after excitation, as mea-

sured using TCSPC under very similar excitation and detection conditions. It can be seen that the dynamics at very early times are characterized by a nearly exponential decay ($\alpha=1$) but gradually merge into a gradient of $\alpha=0.5$ in the asymptotic long-time limit. This behavior is qualitatively observed for all guest concentrations, excitation energies and sample temperatures investigated, albeit over differing time domains. The gradient of $\alpha=0.5$ observed in the long-time limit (≈ 50–3000 ps) strongly suggests that single-step Förster processes dominate the transfer dynamics in this range. We therefore conclude that as excitons undertake energy relaxation processes and become increasingly localized, exciton diffusion within the host contributes decreasingly to the overall excitation transfer to the guest. This interpretation is underlined by our examination of the transfer transient for site-selective excitation at low temperature, for which predominantly localized excitons are generated (not shown). Here, the transfer dynamics follow a stretched-exponential behaviour with $\alpha=0.5$ over most of the decay, indicating that exciton migration has little significance for the overall energy transfer. The general deviation from $\alpha=0.5$ at early times after excitation signals a departure from the single-step Förster model in this regime. One possible explanation could be based on the fact that the early-time dynamics are governed by those excitons that are located close to guests, and which undertake rapid transfer. As for these transfer processes the guest-host separations can be of the order of the exciton extent along the host chain, the point-dipole approximation taken in the Förster model may no longer be valid. Recent calculations by Beljonne *et al.* have contrasted the Förster point-dipole model with a distributed monopole approach, which takes into account the spatial extent of the wave function along conjugated oligomers. Significant differences were found for rates calculated using the two descriptions for conditions of nearest-neighbor transfer, indicating that at those guest-host separations simple models based on Förster's theory are no longer fully applicable.[18] Another possible explanation for the shape of the early-time dynamics is that they may be governed by diffusion-assisted exciton transfer to guests. Exciton diffusion will result in a re-randomization of the spatial exciton distribution in the host with time. While excitons located at host sites near to guests will still transfer that those located further away, exciton diffusion will now repopulate the former sites. The results should be a lifting of the time dependence of the ensemble transfer rate, or a tendency towards $0.5 \lesssim \alpha \lesssim 1$, as is indeed observed.

In order to provide a rough estimate over what range the two identified time regimes extend, we have fitted Eq. (6) to the PLUC data displayed in Fig. 7 (left), first, assuming an exponent $\alpha=1$ and extending the fit only over the first 10 ps, with I_0 left as a fitting parameter. Secondly, the fits were repeated using the same value of I_0 but taking $\alpha=0.5$ to fit only those last points of the data sets, for which a fit with freely variable α resulted in $0.45 < \alpha < 0.55$. Examples of such fits are displayed with the data sets given in Fig. 7 (left). By calculating the point at which the two asymptotic solutions intercept, we can determine a time t_c indicative of the point of crossover between the two regimes. We find that within the concentration range 1.38–5.5 % this cross-over

time shifts from values in the range 20–30 ps at ambient temperature to shorter times of 10–20 ps at low temperature. These trends indicate that the early time behaviour may indeed be dominated by fast exciton migration assisting the transfer of host excitations to guest molecules. As the temperature is reduced, migration of excitons is impeded, so that direct Förster transfer processes appear to be dominating from an earlier time onwards. The cross-over times determined are all in the range of a few tens of picoseconds, which is compatible with most of the redshift occurring within this time scale (see Fig. 2). However, it should be noted that the above analysis only allows a qualitative discussion of the results. Our fitting procedure is somewhat sensitive to the fitting ranges chosen, and both direct Förster transfer and migration-assisted transfer should be operative at all times, albeit to a different extent. Our results show that the transfer rates in π-conjugated guest-host systems depend on time in a complex way, suggesting that simplified models based on time-independent rates have a limited validity. For a more realistic description, the development of microscopic models are required, which take into account the spatial and energetic distribution of sites, and in particular, the delocalization of the exciton wave function.[41]

Our results demonstrate that the redshift observed in the vibronic PL emission peaks as a function of time can indeed be well correlated with the time dependence of exciton diffusivity, in accordance with energy migration models developed by Bässler *et al.*[6,8] In recent work it has been suggested that such redshifts might instead be largely caused by intramolecular relaxation mechanisms, e.g., a planarization of the molecular units following vibrational cooling.[31,32] One argument for this theory relied on the fact that no PL depolarization was observed to accompany the PL redshifts, suggesting the absence of exciton migration within the first 50 ps after excitation.[31] However, depolarization ratios have been shown to depend sensitively on the local order and chain arrangement[42,43] and are therefore often difficult to correlate with actual exciton diffusivity. Our measurement of exciton survival rates in guest-doped polymers may thus prove to be a more reliable way of addressing these issues.

Finally, we should address how general our observations are for the case of conjugated polymers containing (intentionally or unintentionally introduced) guests. The importance of direct, single-step excitation transfer versus diffusion-assisted transfer to the guests will depend on the coupling-strengths associated with either of the two processes. For the PIFTEH-perylene host-guest system used for this study, spectral overlap calculations have suggested a Förster radius of ≈ 3.3 nm (with respect to competition with radiative decay only). The case presented here is therefore intermediate between that for traps whose direct coupling to the host dipole moment is very weak (e.g., carbonyl defects[44]) and for which migration is likely to dominate the energy transfer, and guest-host systems highly optimized for direct Förster transfer through large spectral overlap between host emission and guest absorption.

IV. CONCLUSION

We have presented a detailed study of the dynamics of energy transfer in films of polyindenofluorene emitting blue light, doped with varying amounts of perylene guests. Our results demonstrate that variations in excitation energy or sample temperature have a significant influence on the shape of the transfer transients. Excitons created at the peak of the inhomogeneous density of states were found to transfer noticeably faster than those created in its low-energy tail, indicating that exciton diffusion within the host pays a significant contribution to the overall energy transfer. These effects were considerably more pronounced at low temperature (7 K) than at ambient temperature, suggesting that for the latter, up-hill migration of excitons in the host and a broadened homogeneous linewidth may prevent truly site-selective excitation of localized excitons. In the asymptotic long-time limit, the observed decay dynamics were found to be compatible with long-range single-step Förster transfer. However, at early times ($\lesssim 10$ ps) after excitation, the behaviour notably deviates from this description, suggesting that diffusion-assisted energy transfer makes a strong contribution in this regime. These results indicate that while both diffusion-assisted and single-step Förster transfer of an ensemble of host excitations are expected to slow with time, the former will decrease in relative importance faster than the latter. As a result, the transfer dynamics are governed at early times by diffusion-assisted processes, while at later times the dominant mechanism is transfer of relatively localized excitons from host to guest in a single step. The measured changes in excitation transfer rates with temperature and excitation energy correlate well with those observed for the dynamic energy shifts of the vibronic emission peaks from the undoped polymer. Our study therefore confirms that the time-dependent redshift of the emission from conjugated polymer films can indeed be a sensitive indicator of exciton diffusivity.

[1] J. J. M. Halls, A. A. C, J. D. MacKenzie, W. Wu, M. Inbasekaran, E. P. Woo, and R. H. Friend, Adv. Mater. (Weinheim, Ger.) **12**, 498 (2000).

[2] N. Stutzmann, R. H. Friend, and H. Sirringhaus, Science **299**, 1881 (2003).

[3] R. H. Friend *et al.*, Nature (London) **397**, 121 (1999).

[4] H. Sirringhaus, T. Kawase, R. H. Friend, T. Shimoda, M. Inbasekaran, W. Wu, and E. P. Woo, Science **290**, 212 (2000).

[5] R. Kersting, U. Lemmer, R. F. Mahrt, K. Leo, H. Kurz, H. BÄssler, and E. O. Göbel, Phys. Rev. Lett. **70**, 3820 (1993).

[6] H. BÄssler, in *Hopping and Related Phenomena*, edited by H. Fritzsche and M. Pollak (World Scientific, Singapore, 1990).

[7] B. Mollay, U. Lemmer, R. Kersting, R. F. Mahrt, H. Kurz, H. F. Kauffmann, and H. Bässler, Phys. Rev. B **50**, 10 769 (1994).

[8] H. BÄssler and B. Schweitzer, Acc. Chem. Res. **32**, 173 (1999).

[9] S. C. J. Meskers, J. Hübner, M. Oestreich, and H. Bässler, J. Phys. Chem. B **105**, 9139 (2001).

[10] S. P. Kennedy, N. Garro, and R. T. Phillips, Phys. Rev. B **64**, 115206 (2001).

[11] U. Lemmer, A. Ochse, M. Deussen, R. F. Mahrt, E. O. Göbel, H. Bässler, P. H. Bolivar, G. Wegmann, and H. Kurz, Synth. Met. **78**, 289 (1996).

[12] T. Virgili, D. G. Lidzey, and D. D. C. Bradley, Adv. Mater. (Weinheim, Ger.) **12**, 58 (2000).

[13] G. Cerullo, M. Nisoli, S. Stagira, S. D. Silvestri, G. Lanzani, W. Graupner, E. List, and G. Leising, Chem. Phys. Lett. **288**, 561 (1998).

[14] T. Förster, Ann. Phys. (Leipzig) **2**, 55 (1948).

[15] E. J. W. List, C. Creely, G. Leising, N. Schulte, A. D. Schlüter, U. Scherf, K. Müllen, and W. Graupner, Chem. Phys. Lett. **325**, 132 (2000).

[16] A. R. Buckley, M. D. Rahn, J. Hill, J. Cabanillas-Gonzalez, A. M. Fox, and D. D. C. Bradley, Chem. Phys. Lett. **339**, 331 (2001).

[17] U. Giovanella, C. Botta, M. Gurioli, A. Papagni, R. Tubino, S. Maiorana, P. Del Buttero, D. Alderighi, and J. Kudrna, J. Appl. Phys. **91**, 6511 (2002).

[18] D. Beljonne, G. Pourtois, C. Silva, E. Hennebicq, L. M. Herz, R. H. Friend, G. D. Scholes, S. Setayesh, K. Müllen, and J. L. Brédas, Proc. Natl. Acad. Sci. U.S.A. **99**, 10982 (2002).

[19] C. Ego, D. Marsitzky, S. Becker, J. Zhang, A. C. Grimsdale, K. Müllen, J. D. Mackenzie, C. Silva, and R. H. Friend, J. Am. Chem. Soc. **125**, 437 (2003).

[20] U. Scherf and K. Müllen, Macromolecules **25**, 3546 (1992).

[21] M. Kreyenschmidt, G. Klaerner, T. Fuhrer, J. Ashenhurst, S. Karg, W. D. Chen, V. Y. Lee, J. C. Scott, and R. D. Miller, Macromolecules **31**, 1099 (1998).

[22] S. Setayesh, D. Marsitzky, and K. Müllen, Macromolecules **33**, 2016 (2000).

[23] M. Ariu, D. G. Lidzey, and D. D. C. Bradley, Synth. Met. **111**, 607 (2000).

[24] A. L. T. Khan, P. Sreearunothai, L. M. Herz, M. J. Banach, and A. Köhler, Phys. Rev. B **69**, 085201 (2004).

[25] S. Karabunarliev, E. R. Bittner, and M. Baumgarten, J. Chem. Phys. **114**, 5863 (2001).

[26] M. B. Johnston, L. M. Herz, A. L. T. Khan, A. Köhler, A. G. Davies, and E. H. Linfield, Chem. Phys. Lett. **377**, 256 (2003).

[27] L. M. Herz and R. T. Phillips, Phys. Rev. B **61**, 13 691 (2000).

[28] G. R. Hayes, I. D. W. Samuel, and R. T. Phillips, Phys. Rev. B **52**, R11 569 (1995).

[29] Z. Shuai, J. L. Bredas, and W. P. Su, Chem. Phys. Lett. **228**, 301 (1994).

[30] J. Yu, M. Hayashi, S. H. Lin, K.-K. Liang, J. H. Hsu, W. S. Fann, C. I. Chao, K. R. Chuang, and S. A. Chen, Synth. Met. **82**, 159 (1996).

[31] S. H. Lim, T. G. Bjorklund, and C. J. Bardeen, Chem. Phys. Lett. **342**, 555 (2001).

[32] M. I. Sluch, A. Godt, U. H. F. Bunz, and M. A. Berg, J. Am. Chem. Soc. **123**, 6447 (2001).

[33] J. G. Müller, U. Lemmer, G. Raschke, M. Anni, U. Scherf, J. M. Lupton, and J. Feldmann, Phys. Rev. Lett. **91**, 267403 (2003).

[34] S. P. Kennedy, N. Garro, and R. T. Phillips, Phys. Rev. Lett. **86**, 4148 (2001).

[35] L. M. Herz, C. Silva, R. H. Friend, R. T. Phillips, S. Setayesh, B. Becker, D. Marsitzki, and K. Müllen, Phys. Rev. B **64**, 195203 (2001).

[36] B. Movaghar, M. Grünewald, B. Ries, H. Bässler, and D. Würtz, Phys. Rev. B **33**, 5545 (1986).

[37] T. Förster, Z. Naturforsch. A **4**, 321 (1949).

[38] R. C. Powell, J. Lumin. **11**, 1 (1975).

[39] R. C. Powell, Phys. Rev. B **2**, 2090 (1970).

[40] K. Brunner, A. Tortschanoff, C. Warmuth, H. Bässler, and H. F. Kauffmann, J. Phys. Chem. B **104**, 3781 (2000).

[41] P. Watkins, E. Hennebicq, A. Walker, and D. Beljonne (unpublished).

[42] M. M.-L. Grage, P. W. Wood, R. Ruseckas, T. Pullerits, W. Mitchell, P. L. Burn, I. D. W. Samuel, and V. Sundström, J. Chem. Phys. **118**, 7644 (2003).

[43] J. G. Müller, J. M. Lupton, J. Feldmann, U. Lemmer, and U. Scherf, Appl. Phys. Lett. **84**, 1183 (2004).

[44] M. Yan, L. J. Rothberg, F. Papadimitrakopoulos, M. E. Galvin, and T. M. Miller, Phys. Rev. Lett. **73**, 744 (1994).