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Study of the energy transfer processes in polyfluorene doped with tetraphenyl porphyrin

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The energy transfer processes between polyfluorene and tetraphenyl porphyrin have been investigated through steady state and time resolved measurements. Radiative transfer is found to be negligible and so the results are analyzed in terms of Förster resonance energy transfer. Rate equations are fitted to the experimental data to obtain values for the concentration dependent energy transfer rate. From this, we calculate a value of 38 Å for the energy transfer distance. This compares well with the value for the Förster radius we calculate from the spectral overlap, even though Förster theory is not strictly valid for this system. *© 2003 American Institute of Physics.*
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INTRODUCTION

Polyfluorene has emerged as the most promising conjugated polymer for use in organic light emitting diodes (oLEDs).[1,2] It emits in the blue part of the spectrum, with a progression of vibronic peaks, and has a high fluorescence quantum yield. It is easily processed into thin films through spin coating onto substrates from solution.[3] The luminescent properties of a thin film may be altered by doping with a suitable dye.[4–7] Energy may be efficiently transferred from the polymer to the dye, with the result that the emission is redshifted. Energy transfer can be radiative or nonradiative.[8] Radiative transfer involves the emission of a photon by the polymer and subsequent reabsorption by the dopant, and is a relatively slow and inefficient process. Nonradiative transfer occurs via a dipole–dipole interaction between the initial and final states, and is a very fast process. Both radiative and nonradiative transfer depend on the overlap between the emission spectra of the polymer and the absorption spectra of the dopant, so their contributions can be difficult to distinguish.

We have carried out experiments to investigate the energy transfer processes between polyfluorene and the dye tetraphenyl porphyrin. Nonradiative transfer is shown to dominate, and we analyze this process in terms of resonant energy transfer. A rate equation model for this process is derived and used to fit the experimental results. A value for the energy transfer distance is calculated, and we compare this to the value predicted for the Förster radius from spectral overlap calculations, including a strongly dispersive refractive index term, and a value derived at the equivalent emission point for the donor and acceptor. Good agreement is found, showing that the simple dipole–dipole approximation of Förster theory works well even for systems where the point dipole approximation would seem to break down.[9]

BACKGROUND

In polyfluorene, absorption of a photon causes an electron to be promoted from the $\pi-\pi^*$ band. A hole is left behind, and the electron and hole interact to form a quasiparticle called an exciton. The excited molecule can then relax through radiative or nonradiative recombination of the electron and hole. In nonradiative recombination, the energy is dissipated in the film in the form of phonons. In radiative recombination, the energy is released through emission of a photon. There is a change in the equilibrium configuration of the polymer upon excitation, and excitons also migrate to lower energy segments of longer conjugation, such that the emission spectra is redshifted and displays vibronic character. These processes occur on a rapid time scale, i.e., rapid energy migration within 1 ps, then a slower redshift due to excitation hopping during the next 100 ps after excitation.

In studying energy transfer from a polymer to a dopant in a solid film, two processes must be considered—radiative and nonradiative transfer. Radiative transfer involves the emission of a photon by the polymer and subsequent reabsorption by the dopant. It is a slow process, limited by the polymer's natural fluorescence lifetime. On the other hand, nonradiative transfer is an extremely efficient process, resulting from the resonance between an initial configuration of an excited molecule *m* and unexcited molecule *n*, and a final state of an excited molecule *n* and unexcited molecule *m*. This resonance integral can be expanded into a multipole–multipole series, the first term of which is a dipole–dipole

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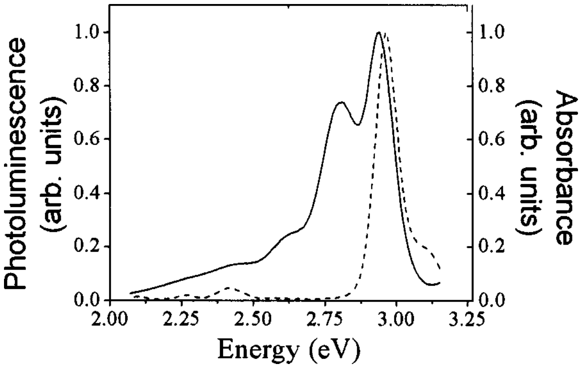

FIG. 1. The overlap between polyfluorene emission (solid line) and TPP absorption (dashed line).

interaction. The effect of this interaction was first calculated by Förster.[10] He defined the Förster radius R_0 as being the distance at which the probability of resonant energy transfer between two isolated molecules is equal to the probability of relaxation by all other processes,

$$R_0^6=\frac{9000\kappa^2\ln 10}{128\pi^5 n^4 N_{\mathrm{AV}}}\varphi_{\mathrm{FL}}\int_0^\infty \frac{f_{\mathrm{D}}(\nu)\varepsilon_{\mathrm{A}}(\nu)}{\nu^4}\,d\nu. \tag{1a}$$

Here, φ_{FL} is the quantum yield of fluorescence of the donor, n is the refractive index of the medium, $f_{\mathrm{D}}(\nu)$ is the normalized emission spectra of the donor, $\varepsilon_{\mathrm{A}}(\nu)$ is the molar absorption coefficient of the acceptor. κ^2 is a configurational term to take into account the relative orientation of the transition dipole moments of the donor and acceptor. It can take a value between 0 and 4. For a large distribution of donor–acceptor pairs, the mean value is 2/3. The overlap between polyfluorene emission and tetraphenyl porphyrin (TPP) absorption is shown in Fig. 1.

Note that in Eq. (1a), the refractive index appears outside the integral. In Förster's original calculations, the two isolated molecules were considered to be in a medium of constant refractive index. In solution, or in an inert polymer host, this is valid. However, here the polyfluorene itself is the host, with a strongly dependent refractive index over its emission region. Since an excitation may be transferred across several polymer chains, we propose that a frequency dependent refractive index should be used. This would be evaluated as part of the overlap integral. The polyfluorene refractive index is shown in Fig. 2,

$$R_0^6=\frac{9000k^2\ln 10}{128\pi^5 N_{\mathrm{AV}}}\varphi_{\mathrm{FL}}\int_0^\infty \frac{f_{\mathrm{D}}(\nu)\varepsilon_{\mathrm{A}}(\nu)}{[n(\nu)]^4\nu^4}\,d\nu. \tag{1b}$$

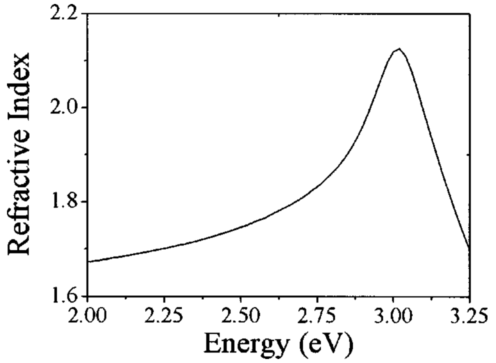

FIG. 2. The measured refractive index of polyfluorene.

In our analysis, both Eqs. (1a) and (1b) are used and the resulting values compared. We also note that higher order terms of the resonance integral might be important. However, as shown by Dexter,[11] these higher order processes are strongly dependent on donor–acceptor separation and so we have ignored them as the acceptor is not chemically attached to the donor and should be of order 5–10 Å away from each other.

In our system, when a polymer molecule and a dopant molecule are separated by R_0, the rate of resonance energy transfer is equal to the combined rate of radiative and nonradiative decay,

$$k_T=k_{\mathrm{R}}+k_{\mathrm{NR}}. \tag{2}$$

In the steady state, the rate equations for the populations of the ground and excited states of the polymer and dopant are as follows:

$$\frac{d[\mathrm{D}^*]}{dt}=G-(k_{\mathrm{DR}}+k_{\mathrm{DNR}}+k_T[\mathrm{A}])[\mathrm{D}^*], \tag{3a}$$

$$\frac{d[\mathrm{D}]}{dt}=-G+(k_{\mathrm{DR}}+k_{\mathrm{DNR}}+k_T[\mathrm{A}])[\mathrm{D}^*], \tag{3b}$$

$$\frac{d[\mathrm{A}^*]}{dt}=(k_T+\alpha\cdot k_{\mathrm{DR}})[\mathrm{D}^*][\mathrm{A}]-(k_{\mathrm{AR}}+k_{\mathrm{ANR}})[\mathrm{A}^*], \tag{3c}$$

$$\frac{\mathrm{d}[\mathrm{A}]}{dt}=-(k_T+\alpha\cdot k_{\mathrm{DR}})[\mathrm{D}^*][\mathrm{A}]+(k_{\mathrm{AR}}+k_{\mathrm{ANR}})[\mathrm{A}^*], \tag{3d}$$

where G is the generation rate of excitons in the polymer, [D], $[\mathrm{D}^*]$ are the numbers of donors (polymers) in the ground and excited states, [A], $[\mathrm{A}^*]$ are the numbers of acceptors (dopants) in the ground and excited states. k_{DR}, k_{DNR} are the radiative and nonradiative decay rates of the donor, and k_{AR}, k_{ANR} are the radiative and nonradiative decay rates of the acceptor (in ps^{-1}). k_T is the nonradiative energy transfer rate (per dopant ps^{-1}). α is a constant to take into account the TPP's absorption of the polyfluorene emission (radiative transfer).

The intensity of the emission from the polymer (in photons per units time) is

$$I_{\mathrm{D}}=\left(\frac{d[\mathrm{D}^*]}{dt}\right)_{\mathrm{emission}}=k_{\mathrm{DR}}[\mathrm{D}^*] \tag{4a}$$

and from the dopant

$$I_{\mathrm{A}}=\left(\frac{d[\mathrm{A}]}{dt}\right)_{\mathrm{emission}}=k_{\mathrm{AR}}[\mathrm{A}^*]. \tag{4b}$$

These intensities were the two quantities that could be directly measured in this experiment. In the steady state, Eq. (3) can be solved to give

$$\frac{I_{\mathrm{A}}}{I_{\mathrm{D}}}=\frac{k_T[\mathrm{A}]\cdot\varphi_{QY}^{\mathrm{TPP}}}{k_{\mathrm{DR}}}. \tag{5}$$

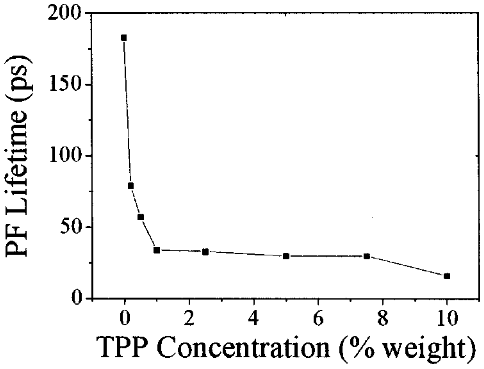

FIG. 3. The effect of TPP concentration on the fluorescence lifetime of polyfluorene.

Here, we have neglected radiative transfer and so set $\alpha = 0$. The only unknown in this equation is $k_T[\mathrm{A}]$. We fit our results to this equation to find $k_T[\mathrm{A}]$ as a function of dopant concentration.

EXPERIMENT

The polyfluorene used was poly(9,9-diethylhexylfluorene) PF2/6. Its synthesis is described elsewhere.[2,12] Tetraphenyl porphyrin was obtained from Porphyrin Products, Inc., and used without further purification. PF2/6 and varying amounts of TPP were first separately dissolved in toluene. These PF2/6 and TPP solutions were then mixed together to obtain final solutions of 10 mg/ml PF2/6, doped with 0%, 0.1%, 0.2%, 0.4%, 0.8%, and 1.6% TPP by weight. Doped and undoped PF2/6 films were obtained by spincoating these solutions onto Spectrosil disks, at 1500 rpm. This gave films of 75±3 nm thickness, as measured on a Tencor AlphaStep profilometer. Film thickness showed no systematic variation with dopant concentration.

Steady state emission spectra were measured using an integrating sphere inside a Fluoromax-3 spectrometer. The films were excited at 350 nm, as PF2/6 absorbs strongly here but we avoid direct excitation of the TPP. The emission spectra were corrected for background and instrument response and then the analysis was carried out.

Time resolved spectra were measured using the second harmonic (360 or 385 nm) from a 120 fs Ti:sapphire laser (Coherent Mira) as an excitation source and a streak camera detection system (Hamamatsu 4334). The system has a temporal response function of 20 ps. Throughout, excitation intensities were kept very low ($<50\ \mu\mathrm{W\,cm^{-2}}$) so as to avoid bimolecular annihilation processes.

RESULTS AND ANALYSIS

Figure 3 contains the polyfluorene fluorescence decay constant as a function of TPP concentration, calculated from the time resolved emission spectra. The polyfluorene lifetime decreases very sharply with increasing dopant concentration up to 1% by weight, then remains constant at about 35 ps. At 10% doping, the lifetime drops dramatically to the limit of the apparatus. We have yet to investigate this sudden decrease, but believe it may be due to the onset of Dexter transfer or the formation of TPP aggregates.

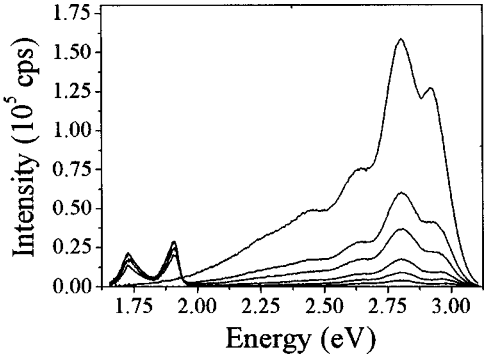

FIG. 4. The emission spectra of polyfluorene doped with varying amounts of TPP. The polyfluorene emission is greatest for the pure sample, and decreases with increasing levels of doping (0%, 0.1%, 0.2%, 0.4%, 0.8%, 1.6%).

Figure 4 shows the emission spectra without normalization. Figures 5 and 6 show the PF2/6 emission and TPP emission, respectively, normalized to the peak of the polyfluorene emission. As stated earlier, any radiative transfer is expected to be small. Its effects may be seen in the emission spectra of the polyfluorene. If radiative transfer is significant, the 0–0 transition peak in the doped samples should be reduced relative to the pure sample, as this peak overlaps most strongly with the TPP absorption. Some quenching can be observed in Fig. 5; however, the effect is small and so we are justified in neglecting radiative transfer. Figure 7 shows the energy transfer rate found by fitting these ratios to the rate equations model. A value of 183 ps was taken for the fluorescence decay lifetime of PF2/6, as found from time-resolved measurements. In the analysis, a value of 0.3 was used for the PF2/6 quantum yield. For the TPP, a quantum yield of 0.12 was taken.

To find the Förster radius, the absolute rate of resonant transfer must be calculated and compared with the natural decay rate of the polyfluorene. The natural decay rate of the polyfluorene is $k_\mathrm{R} + k_\mathrm{NR} = 5.46\ \mathrm{ns}^{-1}$. From Fig. 7, it can be seen that this rate of resonant energy transfer would occur at a concentration of 0.37% by weight. We make the approximation that the TPP molecules are evenly distributed in a "cubic lattice" inside the polymer, and take the density of the film to be $1\ \mathrm{g\,cm^{-3}}$. At this concentration, the molecules

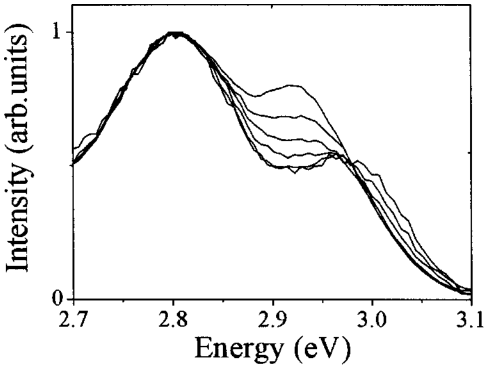

FIG. 5. The normalized polyfluorene emission. The height of the higher energy peak decreases with increasing levels of doping due to polyfluorene self-absorption.

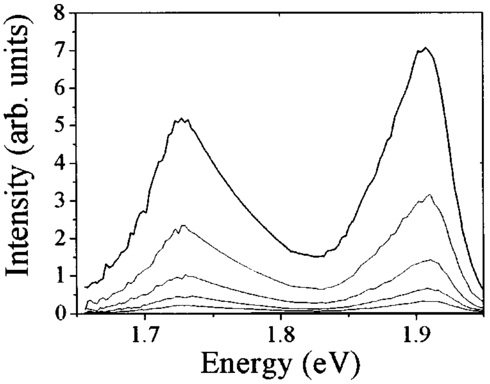

FIG. 6. The TPP emission, normalized to the polyfluorene emission. The TPP emission increases with concentration.

would have a separation of 67 Å. It is important to realize that this separation is not, as some have claimed, the Förster radius.[5] At most, a polymer molecule could be $a_0/\sqrt{3}$ away from a dopant. In fact, the mean distance between a randomly placed excitation and a dopant turns out to be just over half the lattice constant, or in this case, 38 Å.

This experimental value was compared against the theoretical predictions of the spectral overlap Eqs. (1a) and (1b). A value of 2/3 was taken for κ^2. For the frequency independent refractive index, a value of 1.6 was used. This resulted in a Förster radius of 44 Å. The frequency dependent refractive index in Fig. 2 was used in Eq. (1b). A Förster radius of 37 Å was found.

It has been suggested that excitation hopping may play a part in the energy transfer process, i.e., transport may increase the "effective" energy transfer distance.[13,14] With increasing levels of doping one would expect to see a blueshift in the spectra, as excitations have less time to travel to segments of longer conjugation length and lower energy. To investigate this further, we fit Gaussian peaks to the emission modes of the samples in this experiment. The fitting process was performed using the Levenberg–Marquardt algorithm. The only constraint was that the width of the peaks were set equal—with the exception of the first peak since this may be affected by self-absorption and radiative transfer. Figure 8 shows the variation in the spectral positions of the three highest energy peaks with doping level. We estimate the fitted parameters to be accurate to within 0.02 eV at low doping levels, and to within 0.04 eV at high doping levels. Though some blueshift may be observed for the first and third highest energy peaks, these peaks are not so intense and the highest energy one may be affected by self-absorption as previously mentioned. The most reliable analysis should come from the intense peak at 2.81 eV. Here, no systematic blueshift is observed, confirming what is seen in Fig. 5. Either intrachain transport is negligible, or cannot be observed from these steady state spectra.

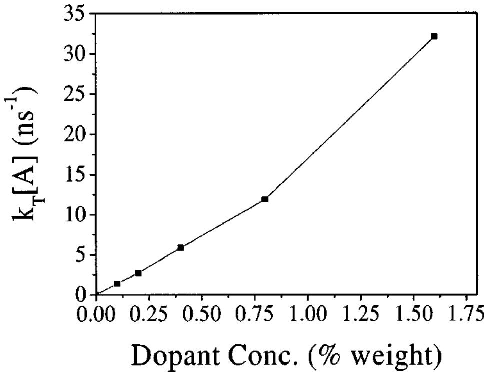

FIG. 7. The resonant energy transfer rate as a function of dopant concentration, calculated using the rate equations model.

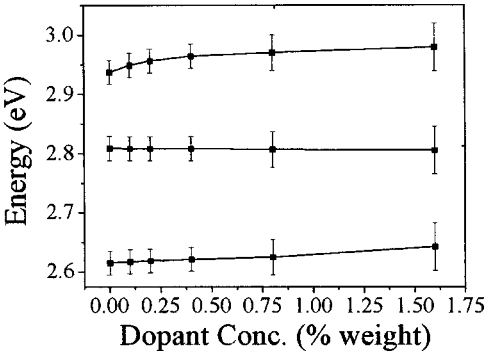

FIG. 8. The variation in spectral position of the polyfluorene vibronic modes with dopant concentration. Each line represents the center of a Gaussian fitted to one of the peaks in the photoluminescence spectra. At 1.6% TPP doping, the polyfluorene emission was very weak and so the lowest energy peak could not be fitted.

We are currently performing low-temperature experiments to investigate further whether or not intrachain transport contributes significantly to the energy transfer process, and we will report our findings soon. For the moment, we identify 38 Å as the room-temperature energy transfer distance between polyfluorene and TPP, rather than as the Förster radius.

CONCLUSIONS

We have calculated the energy transfer distance between PF2/6 and TPP by fitting steady state photoluminescence measurements to a rate equation model neglecting radiative transfer. The value of 38 Å we find for the energy transfer distance lies between the values of 37 and 44 Å predicted for the Förster radius from the spectral overlap, using a dispersive and nondispersive refractive index, respectively. Therefore, we believe that we are justified in neglecting radiative energy transfer. We also note that the Förster model appears to work well here even though it is based on a point dipole approximation. For our system, where a conjugated polymer is the donor and also the host, this would not seem to be valid. From our measurements, there is no evidence of a spectral blueshift on increasing the doping level, which would signify the presence of exciton hopping. Further investigations must be undertaken to determine the role, if any, of hopping in the transfer process. The validity of Förster theory in this system can then be properly tested.

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[1] D. Neher, Macromol. Rapid Commun. **22**, 1365 (2001).

[2] M. Grell, W. Knoll, D. Lupo, A. Meisel, T. Miteva, D. Neher, H. G. Nothofer, U. Scherf, and A. Yasuda, Adv. Mater. **11**, 671 (1999).

[3] Y. Shi, J. Liu, and Y. Yang, J. Appl. Phys. **87**, 4254 (2000).

[4] T. Virgili, D. G. Lidzey, and D. D. C. Bradley, Synth. Met. **111**, 203 (2000).

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

[6] G. Cerullo, S. Stagira, M. Zavelani-Rossi, S. De Silvestri, T. Virgili, D. G. Lidzey, and D. D. C. Bradley, Chem. Phys. Lett. **335**, 27 (2001).

[7] J. Morgado, F. Cacialli, R. Iqbal, S. C. Moratti, A. B. Holmes, G. Yahioglu, L. R. Milgrom, and R. H. Friend, J. Mater. Chem. **11**, 278 (2001).

[8] J. Birks, *Photophysics of Aromatic Molecules* (1970).

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

[10] T. Forster, Discuss. Faraday Soc. **27**, 7 (1959).

[11] D. Dexter, J. Chem. Phys. **21**, 836 (1963).

[12] M. Fukuda, K. Sawada, and K. Yoshino, J. Polym. Sci., Part A: Polym. Chem. **31**, 2465 (1993).

[13] 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).

[14] E. List, C. Creely, G. Leising, N. Schulte, A. Schluter, U. Scherf, K. Mullen, and W. Graupner, Chem. Phys. Lett. **325**, 132 (2000).