The role of exciton diffusion in energy transfer between polyfluorene and tetraphenyl porphyrin

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Singlet exciton migration has been studied in films of the conjugated polymer polyfluorene (PF) by doping the samples with a fluorescent probe molecule, tetraphenyl porphyrin (TPP). Energy transfer in such systems has often been described in terms of Förster transfer, a dipole-dipole mechanism. TPP emission from the films was measured in steady-state, as a function of temperature and dopant concentration. The intensity of the TPP emission was found to be constant up to 150 K, and then to increase with temperature. Therefore, the energy transfer cannot be occurring solely by Förster transfer as that process is temperature-independent. Instead, energy transfer between PF and TPP is considered to take place via thermally-activated exciton diffusion through the polymer followed by Förster transfer between the polymer and dopant. Moreover, TPP emission as a function of dopant concentration could not be described by Förster transfer alone, but could be well fitted at low temperature (15 K) and room temperature by the Yokota-Tanimoto model, which combines diffusion and Förster transfer. Diffusion lengths of 11 ± 2 nm (15 K) and 20 ± 2 nm (room temperature) were found. The nonzero exciton diffusion at low temperature is believed to be due to downhill migration to low energy polymer segments.

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Polyfluorene (PF) is currently the subject of intense research due to the prospect of its use in devices such as polymer light-emitting diodes (PLEDs),[1] organic solar cells,[2,3] and electrically pumped solid-state polymer lasers.[4,5] It is a blue-emitting conjugated polymer with a high photoluminescence quantum yield. The thin films required for applications may be conveniently fabricated by spin-coating the polymer from solution. Optical excitation of PF with UV light causes a π-π^* transition and the creation of a singlet exciton, followed by fluorescence. Electrically exciting PF injects holes and electrons, which may combine to form either singlet or triplet excitons, with subsequent fluorescence and phosphorescence respectively. Besides its applications, PF exhibits a rich variety of physical phenomena, and areas of interest include its morphology,[6–8] alignment properties,[9–12] and excitation migration.[13,14]

The emission color from PF films may be conveniently altered by incorporating suitable dopant molecules.[15–19] Energy transfer from the PF donor to the dopant acceptor followed by radiative decay from the acceptor results in redshifted emission. Efficient nonradiative energy transfer may take place via Förster resonant energy transfer (FRET).[20] This is a dipole-dipole mechanism whose efficiency depends on the overlap between the donor emission spectrum and acceptor absorption spectrum. The efficiency of FRET is usually described in terms of the Förster radius R_0. This is defined as the donor-acceptor separation at which the probability of FRET is equal to the possibility of donor deexcitation by all other pathways, i.e., radiative/nonradiative decay. R_0 can be calculated theoretically from

$$R_0^6 = \frac{9000(\ln 10)\kappa^2 Q_D}{128\pi^5 N_A n^4}\int_0^\infty F_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda, \qquad (1)$$

where κ^2 is an orientation factor, equal to $2/3$ for random donor-acceptor orientation, Q_D is the photoluminescence quantum yield of the pure donor, N_A is Avogadro's number, n is the refractive index of the medium, F_D is the normalized donor fluorescence intensity, and ε_A is the molar absorption coefficient of the acceptor.

In the presence of an acceptor, donor fluorescence decay does not take an exponential form. Rather, due to the dispersive nature of the energy transfer (the mean donor-acceptor separation increases with time, as the donor-acceptor pairs with smallest separations experience FRET first) the decay is predicted to follow a stretched exponential:

$$I_D(t) = I_D^0 \exp\left[\frac{-t}{\tau_D} - 2\gamma\left(\frac{t}{\tau_D}\right)^{1/2}\right] \qquad (2)$$

with $\gamma = C/C_0$, where

$$C_0 = \frac{3000}{2\pi^{3/2} N_A R_0^6} \qquad (3)$$

where τ_D is the donor fluorescence lifetime and C is the acceptor concentration. The critical concentration C_0 is defined as the acceptor concentration at which a sphere of radius R_0 contains one acceptor molecule.

Förster theory has often been used to describe energy transfer in polymer-dopant systems, although its applicability is questionable for several reasons. First, it assumes that the donor and acceptor transition dipole moments are point dipoles. This is hardly the case for a conjugated polymer, where an exciton is delocalized over a segment of several repeat units, several nm in length.[21–23] This is of the same order of magnitude as the Förster radius in these systems. Secondly, it is expected that excitons may migrate some distance through a polymer prior to the final step of FRET to the dopant. This would increase the overall energy transfer distance and result in overestimates for R_0 from experiment if not taken into account.

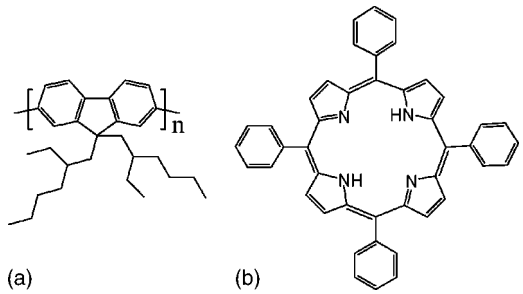

FIG. 1. Chemical structures of (a) poly (9,9-diethylhexyl fluorene) and (b) tetraphenyl porphyrin.

The donor-acceptor system under investigation here is PF doped with tetraphenyl porphyrin (TPP). TPP is a red-emitting planar molecule whose absorption spectrum overlaps strongly with the PF fluorescence, making for efficient energy transfer. PF and TPP chemical structures are shown in Fig. 1. PF emission and TPP absorption and emission spectra are shown in Fig. 2. This system has been the subject of several investigations. R_0 values have been found experimentally, ranging from 4.2 nm to 5.4 nm.[15,17,19] Although the analyses in these experiments did not take energy migration into account, the values tallied well with the value of 4.4 nm predicted from Eq. (1). We have previously suggested[15] that the highly dispersive refractive index of PF should be taken into account in Eq. (1). This leads to a slightly modified value for R_0 of 3.7 nm. The fact that in PF, the exciton cannot strictly be represented by a point dipole has been discussed by Wong, Bagchi, and Rossky,[24] who performed detailed quantum chemical calculations to investigate energy transfer in a PF-TPP system. They found that at small separations, Förster theory fails and the transfer rate varies as R^{-2}. At separations larger than 10 nm, the Förster rate is recovered. With the above definition of Förster radius, they calculated a value for R_0 of 4.0–4.5 nm.

Rather than looking at its application in shifting the colour of PF emission, here we intend to use TPP as a probe to investigate singlet exciton migration through PF films. To this end, a series of PF films doped with a range of concentrations of TPP was fabricated. Steady-state photoluminescence measurements were made on these films at low T and room T. To model the exciton motion, we analyzed the data following the method of Yokota and Tanimoto,[25] who considered the effects of diffusion on resonance energy transfer.

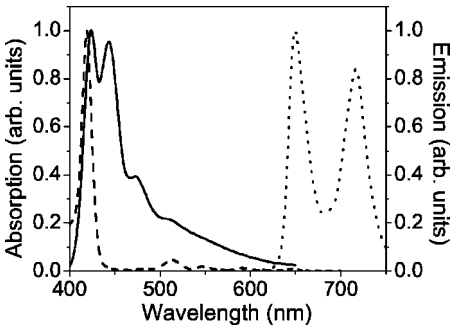

FIG. 2. Emission spectra of PF (solid line); absorption and emission spectra of TPP (dashed line and dotted line respectively).

Using a Padé approximant method,[26] they found the following expression for donor fluorescence decay:

$$I_D(t) = I_D^0 \exp\left[\frac{-t}{\tau_D} - 2B\gamma\left(\frac{t}{\tau_D}\right)^{1/2}\right], \tag{4}$$

$$B = \left(\frac{1 + 10.87x + 15.5x^2}{1 + 8.743x}\right)^{3/4}, \tag{5}$$

$$x = D\alpha^{-1/3}t^{2/3}, \tag{6}$$

$$\alpha = R_0^6/\tau_D, \tag{7}$$

where D is the diffusion coefficient.

Equation (4) predicts the *donor* fluorescence decay in response to a *delta-function* impulse. We wish to predict the *acceptor* fluorescence in *steady-state* as a function of acceptor concentration. To this end, we first find the steady-state donor fluorescence by convoluting Eq. (4) with a step function for each value of C. Then, the energy transferred to an acceptor at concentration C will be proportional to the difference between the donor fluorescence in a pure sample and that in the doped sample,

$$F_{\text{acceptor}} \propto F_{\text{donor}}^{\text{pure}} - F_{\text{donor}}^{\text{doped}}. \tag{8}$$

We would like to comment on this method of convoluting solutions for individual delta functions. The response is actually nonlinear due to the filling up of nearest neighbors, as mentioned earlier. Therefore, one might not expect our approach to be valid. However, we believe it represents a close approximation to the actual solution for the following reasons: there exists an analytical solution for the steady-state donor fluorescence in the absence of diffusion, i.e., for $D=0$. This is given by[27]

$$\frac{F_{\text{donor}}^{\text{doped}}}{F_{\text{donor}}^{\text{pure}}} = 1 - \sqrt{\pi}\gamma \exp(\gamma^2)[1 - \text{erf}(\gamma)]. \tag{9}$$

Comparing the predictions of this equation with those from our model for $D=0$, we find almost identical results (this is shown later in Fig. 4). No similar analytical solution exists predicting steady-state fluorescence in the presence of diffusion. However, diffusion is expected to diminish the effect of the filling up of the nearest neighbors, given that it increases the distance that the excitons can travel: the density of acceptors a distance R from a donor increases as R^2. Therefore since our model gives a good match to the analytical solution in the absence of diffusion it must be expected to yield at least as good matches in the presence of diffusion. It is also noted that Gosele, Hauser, Klein, and Frey[28] investigated exciton diffusion and found similar expressions to Yokota and Tanimoto. In their paper, they noted that the formulas found could be extended to acceptor fluorescence and to any shape of excitation by simple linear convolution.

The critical concentration for this system was calculated as follows. The PF density was taken to be 1 g/cm^3. Dopant concentrations are measured in % w/w, therefore the mass of dopant per volume can be calculated. The molecular weight of TPP is 614, so the dopant concentration in molecules/cm^3 can be found. R_0 is taken as 4.25 nm (from the quantum

chemical calculations of Wong, Bagchi, and Rossky), and the volume of a sphere of this radius calculated. Thus, the critical concentration of one acceptor per "Förster sphere" is found at a weight concentration of 0.57%. From this we can now calculate concentration in units of critical concentration for all the samples.

The PF used in this experiment was poly (9,9-diethylhexyl fluorene). Its synthesis is described elsewhere.[29] TPP was purchased from Porphyrin Products Inc. and used without further purification. Films were prepared by spin-coating PF from a 10 mg/ml solution, with a solvent of three parts toluene to one part chloroform. This mixture was used to prevent crystallization. For making doped samples, solutions were prepared by mixing a PF solution with TPP solutions in appropriate concentrations. Films of the following concentrations were fabricated: 0%, 0.001%, 0.005%, 0.01%, 0.03%, 0.05%, 0.1%, 0.5%, 1%, 1.5%, 2%, and 4% *w*/*w*. For measuring the photoluminescence quantum yield (PLQY) of TPP, a film of TPP in an inert Zeonex matrix was fabricated. TPP and Zeonex were dissolved in chloroform, at a Zeonex concentration of 50 mg/ml, and a TPP:Zeonex weight ratio of 1:2000.

The fluorescence lifetime of a pure PF film was found using a time-correlated single photon counting system. A pulsed diode laser (Picoquant) was used to excite the samples at 390 nm with 75 ps pulses (FWHM). Emission was collected by a first lens and focused by a second lens onto a monochromator slit. The detector was a Peltier-cooled MCP (Hamamatsu). Single photon counting was performed by a Becker and Hickl electronics board and software. Deconvolution of the decays was performed using software provided by Striker.[30] The best fit was achieved with a biexponential decay. It is typical for polymer films to exhibit nonexponential decay due to energy transfer to defects.[31] For the purpose of our analysis however, a single decay time is required. The PF fluorescence decay could be well approximated by a single decay time of 280 ps.

Steady-state photoluminescence measurements were made using a Jobin-Yvon Fluoromax spectrofluorimeter. For the *T*-dependent measurements, samples were mounted in a closed-cycle helium cryostat. Here, samples were excited through the substrate and emission collected from the front-face at an angle of 45°. It was desired to record total luminescence over all angles, and to this end the spectra for all samples were also measured using an integrating sphere. These spectra were compared to those found using the cryostat. A correction factor was found so that spectra measured at any *T* in the cryostat could be rescaled to find the spectra as if they were measured in the integrating sphere.

The room temperature PLQY of TPP was measured by mounting the TPP-Zeonex film in the integrating sphere, following the procedure of Pålsson and Monkman.[32] A value of 0.08 was found. The film was then mounted in the cryostat and emission intensity measured as a function of temperature. The results were then scaled according to the room temperature PLQY to calculate a *T*-dependent PLQY for TPP. This was found to decrease linearly as the temperature was increased.

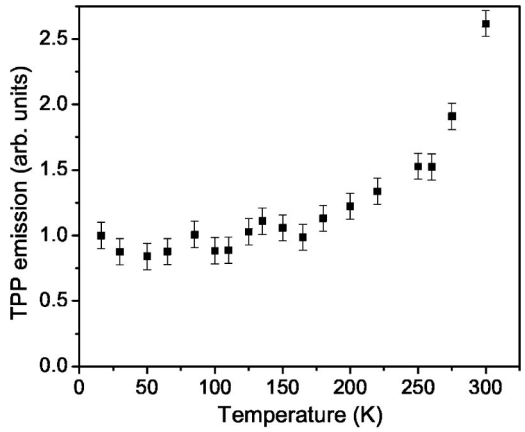

FIG. 3. TPP emission as a function of temperature, for the 0.05% *w*/*w* TPP-doped PF film.

T-dependent measurements on the 0.05% sample were performed. The intensity of the emission from the TPP was recorded and divided by the TPP PLQY at each temperature. Thus, the scaled emission is a measure of the energy transferred between PF and TPP. Results are shown in Fig. 3. The TPP emission appears to be thermally activated, rising quickly with *T* above ~150 K. Below this, it is basically independent of *T*. This implies that at low *T*, the excitons' motion is not thermally assisted.

It should be noted that Eq. (1) states that the Förster radius is proportional to the PLQY of the donor. The PLQY is dependent upon temperature, decreasing as temperature increases. Therefore, one might expect that the Förster radius is also temperature dependent and that this might be responsible for the results observed in Fig. 3. This is not the case for several reasons. First, if PLQY decreases as temperature increases, then so does the Förster radius. This would mean that energy transfer would become *less* efficient at higher temperatures. This is not observed. Also, the origin of the temperature dependence needs to be considered. It is believed to be a result of migration to keto defect sites,[33] where the PL is quenched. The PLQY in Eq. (1) is the intrinsic PLQY, in the absence of energy transfer to acceptors, and is therefore expected to be independent of temperature.

Figure 4 shows the integrated TPP emission at low *T* (15 K) and room *T* (293 K) plotted against average dopant separation. Dopant separation was calculated from concentration by assuming the dopants to be arranged in a simple cubic lattice. The emission is normalized to the emission of the 1.5% *w*/*w* sample. Above this concentration, TPP emission actually decreases, which may be due to aggregation of the dopant molecules. Three lines calculated using Eqs. (4) and (8) are also shown on the plot. Each line was calculated for different values of *D*. The solid line is for $D=0$ nm^2/ps, i.e., pure Förster transfer with no exciton diffusion. This line differs greatly from the experimental data, showing that the transfer process cannot be Förster transfer alone. Also shown (dashed-dotted line) is the prediction for steady-state acceptor fluorescence according to Eq. (9). As mentioned earlier, this is very close to the fit predicted by our model for $D=0$ nm^2/ps. The dotted line and the dashed lines are best fits to the low *T* and room *T* data, with *D* as the only variable

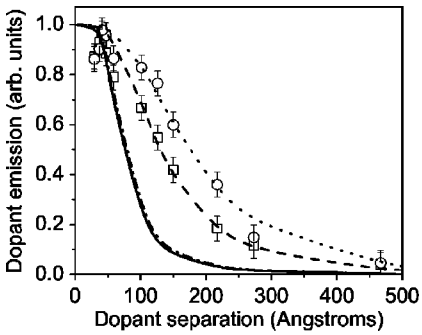

FIG. 4. Dopant emission intensity as a function of dopant separation, at 15 K (open squares) and 293 K (open circles). Lines show fits to the data found using the Yokota-Tanimoto equation, for $D=0$ nm^2/ps (solid line), $D=0.43$ nm^2/ps (dashed line), and $D=1.44$ nm^2/ps (dotted line). Also shown is the prediction for the steady-state acceptor fluorescence according to Eq. (9).

parameter. D values of 0.43 ± 0.15 nm^2/ps and 1.44 ± 0.25 nm^2/ps were found, respectively. The PF fluorescence lifetime was 280 ps, so using the relation $x_{\mathrm{diff}}=(D_0\tau)^{0.5}$ gives us a low T diffusion length of 11 ± 2 nm and a room T diffusion length of 20 ± 2 nm.

This tells us several things. Obviously, it confirms that excitons are more mobile at room T than at low T. However, even at low T, the excitons are not completely immobilized. The nonzero diffusion at low T may be due to the fact that the molecules were excited at 380 nm (3.27 eV), some way above the absorption band edge of the PF. One model of exciton migration describes diffusion taking place in an inhomogeneously-broadened density of states (DOS).[34,35] An exciton is created with an initial energy dependent upon the excitation energy, then undergoes downhill migration through the DOS. This can observed as a redshift in the emission with time. The transport is dispersive, as there are fewer and fewer sites of lower energy for the exciton to migrate to. At elevated temperatures, the phonon bath causes segmental site disorder, promoting uphill hopping and reducing the irreversibility of the migration process. Previously, a localization energy of 2.93 eV (424 nm) has been found in PF[34]—excitation below this energy results in the creation of trapped excitons, as there are no sites of lower energy within range to which they can hop.

In our experiment, one might therefore expect that the excitons were created with excess energy, making hopping to higher energy sites possible even in the absence of phonons. To investigate this, the PF and TPP emission were measured as functions of excitation energy for two of the samples: 0.001% w/w and 0.01% w/w. These samples were excited from 300 nm to 430 nm. The excitation light had a bandwidth of 1.5 nm (FWHM). No differences could be seen for excitation over the entire wavelength range, i.e., no effects due to a localisation energy were observed. There are several possible explanations for this. First, the optical density of the PF is extremely low at wavelengths corresponding to energies below the localization energy. Steady-state experiments performed using a commercial spectrofluorimeter may be unlikely to reveal such effects. Secondly, the absorption of the TPP itself is in the same location as the localization energy of the PF. This could obscure the results here. However, at these doping concentrations direct TPP absorption is highly unlikely.

Another note to make with reference to the migration of excitons through the density of states is that the redshift in the emission will result in a change in the overlap between the PF emission and TPP absorption. This in turn will result in a time-dependent Förster radius. This might be expected to make the use the steady-state PL measurements to resolve the exciton dynamics inaccurate. Meskers *et al.*[34] found that in the most extreme case there is a redshift in the PL spectra of approximately 0.05 eV at low T and 0.04 eV at room T. The effect of this on the theoretical Forster radius was calculated using a redshifted PF photoluminescence spectra in Eq. (1). It was found that at low T, R_0 decreases by less than 4 Å and at room T by less than 3 Å. New diffusion lengths were calculated using these adjusted values in our model, to evaluate the effect of a variable Förster radius. Diffusion lengths of 12.2 nm at low T and 21.6 nm at room T were found.

These values were calculated using the most extreme change in Förster radius and yet they are both still within the error of our previous measurements. Obviously, the effect will not be as large as this—the relaxation takes place over the exciton lifetime and for much of this time the redshift will be smaller. Therefore, relaxation and redshift does not significantly affect the calculated values of diffusion length here.

The nonzero diffusion at low T is therefore attributed to migration to PF segments of lower energy. It is worth noting that the low T diffusion length of 11 nm is not much larger than the persistence length of PF—approximately 7 nm.[36] The nonzero diffusion length may also be a representation of the delocalisation of the exciton.

List *et al.*[37] have also studied energy transfer, between the conjugated polymer ladder type polyparaphenylene vinylene (meLPPP) and a conjugated orange light-emitting macromolecular dye RS19, via T-dependent steady-state photoluminescence measurements. They also found that Förster transfer alone could not explain their results, that the energy transfer process was temperature dependent and concluded that diffusion must play a role. However, the model that they used did not explicitly take diffusion into account. Their model defined a general energy transfer rate without commenting upon the nature of the mechanism. It was assumed that diffusion must be responsible but not shown that a diffusion model would fit the results any better. Moreover, the model did not directly predict a diffusion coefficient or migration length; this was estimated based upon the energy transfer time found and a migration length from other work.

In conclusion, exciton energy transfer from PF to TPP has been investigated by T-dependent steady-state photoluminescence studies. The results were well-fitted by the Yokota-Tanimoto model, which combines exciton diffusion and Förster transfer. It was shown that diffusion must be taken into account to correctly model the energy transfer. At room T, the average migration distance is 20 ± 2 nm. Even at low T, the excitons have a nonzero diffusion coefficient, which is

most likely due to the polymer being excited above the localisation energy. To rigorously test the Yokota-Tanimoto model here, time-resolved measurements should be performed on these samples, so that the expected fluorescence decay can be compared with that predicted. This work is currently in progress.

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