

Distance dependence of excitation energy transfer between spacer-separated conjugated polymer films

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We report a systematic study of the scaling with distance of electronic energy transfer between thin films of conjugated polymers separated by a silica spacer. The energy-transfer kinetics were obtained directly from time-resolved photoluminescence measurements and show a $1/z^3$ distance dependence of the transfer rate between the excited donor and the acceptor film for $z \geq 8$ nm. This is consistent with Förster theory; but at shorter separations the energy transfer is slower than predicted and can be explained by the breakdown of the point-dipole approximation at $z \sim 5$ nm. The results are relevant for organic photovoltaics and light-emitting devices, where energy transfer can provide a means of increasing performance.

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I. INTRODUCTION

Resonant energy transfer or Förster transfer is a well-known phenomenon for the transfer of excitation from a donor to an acceptor molecule.¹ It is useful as a means of enhancing the performance of organic light-emitting diodes (OLEDs),² solar cells,³ and polymer lasers.⁴ In the case of white OLEDs (Ref. 5) for lighting, where the simultaneous emission from multiple polymers is required to obtain a broad spectral output, energy transfer plays a critical role. Blending of different materials often does not give a uniform transfer between emitters and it may be better to deposit them as individual layers.⁶

In its originally published form Förster theory applies to the scenario of a random distribution of point dipoles, such as would be found in a solution or dilute blend, and is characterized by a r^{-6} distance dependence. The Förster radius R_0 is the donor-acceptor separation where the rate of energy transfer is half that of the natural decay rate. For a donor with a high photoluminescence (PL) quantum yield (PLQY) and strong spectral overlap with the acceptor's absorbance, R_0 would typically be ~ 5 nm. The r^{-6} roll-off means that transfer efficiency beyond R_0 is expected to be very low. However, it has been shown that the geometry of the system will alter both the distance dependence and the critical transfer distance,^{7,8} where the latter is a generalized form of the Förster radius that takes account of the system's geometry. In some cases this leads to enhanced energy transfer over separations greater than a typical Förster radius.

However, it is still unclear which geometry is best applied when dealing with multilayered polymer structures as these are not point-dipole systems. The point-dipole approximation fails to describe energy transfer between large conjugated molecules at short distances,^{9–11} requiring the use of the line dipole approximation or quantum-mechanical calculations. When this is coupled with the fact that there may be preferential orientation of the polymer chains, particularly when in contact with an interface, the point-dipole approximation to describe layer-to-layer energy transfer appears flawed, but its limitations are not clearly established.

Hill *et al.*¹² reported a $1/x^2$ distance dependence for a layered Langmuir-Blodgett polymer structure, consistent

with energy transfer between extended dipoles in monolayers.⁷ A $1/x^3$ distance dependence for transfer in a donor/acceptor polymer heterojunction was assumed by McGehee and coworkers^{3,13} and proposed as a means of enhancing solar cell performance via either the incorporation of an acceptor polymer film to “harvest” excitons. However as this work used one polymer layer on top of another there was a wide range of distances between the donor and acceptor so that it did not provide a clear test of the scaling of energy transfer with distance.

The purpose of the present work is to investigate systematically the scaling of energy transfer with distance and the limits of the point-dipole approximation in application to conjugated polymers. Using time-resolved PL measurements with a defined system geometry of two polymer films separated by an inert silica spacer layer, we have measured the distance dependence of the energy-transfer rate. The spacer layer ensures that there is no intermixing, eliminating any additional excitation transfer process that would otherwise occur at a polymer-polymer interface. We explore the limits of the point-dipole approximation and discuss how the thicknesses of the donor and acceptor films can modify the apparent power-law dependence on distance, which may account for the range of power-law dependences that have been previously reported.

II. EXPERIMENT

The rate of energy transfer can be maximized by the choice of materials. Crucially the donor should have a high PLQY with strong spectral overlap of its photoluminescence with the absorption spectrum of the acceptor. Poly(3-hexylthiophene) (P3HT) is an efficient photovoltaic material^{14,15} and was chosen as the acceptor. The copolymer poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(1,4-benzo-{2,1',3}-thiadiazole)] (PFOBT), obtained from American Dye Source Inc. (ADS-233YE), was chosen as the donor due to the high spectral overlap between it and P3HT (see Fig. 1). The Förster radius of two point dipoles can be calculated using the following equation:

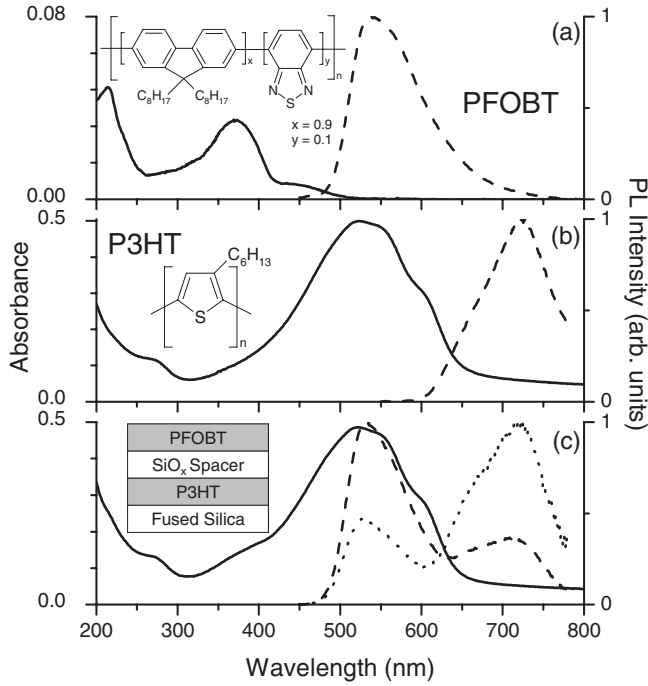


FIG. 1. (a) Absorption (solid line) and normalized PL spectra (dashed line) for PFOBT. (b) Absorption (solid line) and normalized PL spectra (dashed line) for P3HT. (c) Absorption spectrum of a PFOBT-spacer-P3HT sample as shown in the inset. The PL spectra of the samples with 27.2 (dashed line) and 2.1 nm (dotted line) spacers upon 400 nm excitation are also included.

$$R_0 = \frac{9000\kappa^2\eta_D \ln 10}{128\pi^5 n^4 N_A} \int_0^\infty f_D(\lambda)\epsilon_A(\lambda)\lambda^4 d\lambda, \quad (1)$$

where κ^2 is an orientation factor equal to 2/3 for randomly orientated dipoles, $\eta_D=0.81$ is the measured donor PLQY using the method described by Greenham *et al.*,¹⁶ n is the refractive index of the medium, N_A is Avogadro's number, $f_D(\lambda)$ is the fluorescence spectrum of the donor normalized by area, and $\epsilon_A(\lambda)$ is the molar extinction coefficient of the acceptor. The evaluation of the spectral overlap integral is generally performed with the donor fluorescence and acceptor absorption in solution; but these can vary significantly from the corresponding spectra in films. In the case of P3HT the absorption in solution is blueshifted when compared to the film and therefore the overlap is greatly reduced. A further complication arises with the calculation of the molar extinction coefficient as each molecule is assumed to be an acceptor, which is not the case when dealing with polymers. Hence it is necessary to use the chromophore concentration in the calculation of the extinction coefficient. Using a P3HT density of 1.10 g cm^{-3} (Ref. 17) and assuming a chromophore size of 10 repeat units, as deduced from the emission spectra of oligothiophenes,¹⁸ the Förster radius was calculated to be 5.2 nm.

The P3HT was spin coated onto fused silica substrates from a 10 mg/ml chloroform solution at 1600 rpm, and the silica spacer was deposited by electron-beam evaporation at a rate in the range of $0.05\text{--}0.1 \text{ nm s}^{-1}$ on top of the P3HT, providing a surface and a barrier onto which the PFOBT was

spin coated from a 2 mg/ml toluene solution at 4000 rpm. For each thickness of spacer layer two samples were prepared: one with a P3HT acceptor film, as illustrated in Fig. 1(c), and the other without. The latter is a reference that accounts for any impact that the evaporated silica might have on the PFOBT's PL lifetime.

The rate of energy transfer is very sensitive to the donor-acceptor separation and thus it is crucial that the thicknesses of the spacer layers are accurately determined. This was achieved by including a silicon wafer with the samples during the evaporation of the silica. Ellipsometry measurements were performed with a J. A. Woollam M2000DI spectroscopic ellipsometer over the angle range of $45\text{--}75^\circ$ on the wafers both before and after the evaporation. The spacers were found to range from 2.1 to 27.2 nm in thickness. The surface roughness of the evaporated silica films is an important factor to consider as it could result in preferential energy transfer where the spacer is thinnest. Surface roughness measurements performed with an AFM on the reference spacer films revealed these to be smooth and uniform with an average roughness of 0.4 nm. The main source of roughness in the stacked films is at the P3HT film interface, which was measured to have an average surface roughness of 1.2 nm. This roughness of the P3HT would be smoothed by the evaporated silica layer but would still introduce a 0.8 nm error into the spacer thickness values.

The thicknesses of both the PFOBT and P3HT polymer films are also important for defining the dimensions of our system but calculating the film thickness from absorption can be difficult because of reflections from the substrate. To overcome this problem both polymers were characterized using ellipsometry and the resulting models used to generate the absorption as a function of film thickness on fused silica substrates. This was used to calculate the thicknesses of the PFOBT and P3HT films from their absorptions, yielding average values of 4.9 ± 0.2 and 81 ± 2 nm, respectively. Samples were stored under vacuum for the measurements and excited with 400 nm pulses of 100 fs duration at a rate of 80 MHz. The PL emission was detected with a Hamamatsu C6860 streak camera in synchroscan mode over the wavelength range of approximately 460–600 nm, thus excluding any contribution from the P3HT.

III. RESULTS AND DISCUSSION

Figure 2 shows the normalized PL decays for the PFOBT film with the P3HT film present for each spacer thickness. There is a clear trend that the PL decays are faster with decreasing spacer thickness. The reference PL kinetics recorded in the absence of a P3HT layer showed no variation in spacer thickness so these were averaged to obtain a single reference decay. The PL intensity is proportional to the number of excitons in the donor film;

$$I_{\text{PL}}(t) \propto A \int_s^{s+d} N(z,t) dz, \quad (2)$$

where $N(z,t)$ is the exciton concentration at the distance z from the acceptor film, A is the area excited, s is the spacer

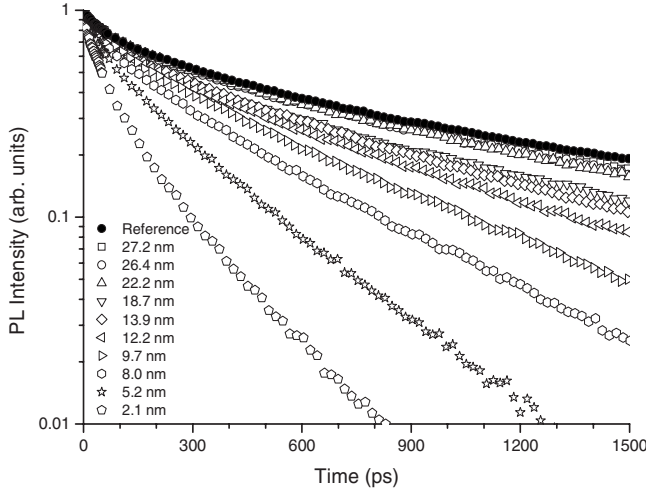


FIG. 2. Normalized PL decays for the PFOBT without an acceptor layer (filled circle) and with the acceptor layer separated by a spacer of varying thickness (open symbols).

thickness, and d is the donor film thickness. With the acceptor present,

$$N(z, t) = N_{\text{ref}}(z, t) e^{-k_{\text{ET}}(z)t}, \quad (3)$$

where $N_{\text{ref}}(z, t)$ describes the exciton distribution in the donor film in the absence of the acceptor film. Following the excitation the excitons will be uniformly distributed throughout the donor film because the absorbance by PFOBT at the excitation wavelength of 400 nm is low [see Fig. 1(a)] and the film is very thin. Therefore $N_{\text{ref}}(t)$ is independent of z . Assuming that the natural decay of the exciton is independent of z , we obtain

$$I_{\text{PL}}(t) \propto N_{\text{ref}}(t) \int_s^{s+d} e^{-k_{\text{ET}}(z)t} dz. \quad (4)$$

It is possible to isolate the decay due solely to energy transfer by dividing the PL decay $I_{\text{PL}}(t)$ by that of the reference $I_{\text{ref}}(t) \propto N_{\text{ref}}(t)$. This ratio for each spacer thickness is shown in Fig. 3. These kinetics exhibit no time dependence except for the two thinnest spacer layers. This is in contrast to the energy transfer in molecular guest-host systems which occurs with a time-dependent¹⁹ rate due to the distribution of donor-acceptor separations. The energy-transfer rate is very sensitive to the donor-acceptor separation with the excitons closest to the acceptor undergoing energy transfer at a much faster rate than those further away. As the donor molecules closest to the acceptor become depleted of excitation, the total energy-transfer rate will decrease as all the remaining excitons will be located further from the acceptor. The reason we do not observe a time-dependent rate for all but the 5.2 and 2.1 nm spacers is that the spacer restricts the donor-acceptor distance, thus preventing the region of the donor film closest to the acceptor from becoming rapidly depleted of excitons. For the 5.2 nm spacer time-dependent energy transfer is observed only for $t > 300$ ps when more than 50% of excitations are transferred. Steady-state PL spectra confirmed a strong decrease in the PFOBT emission with de-

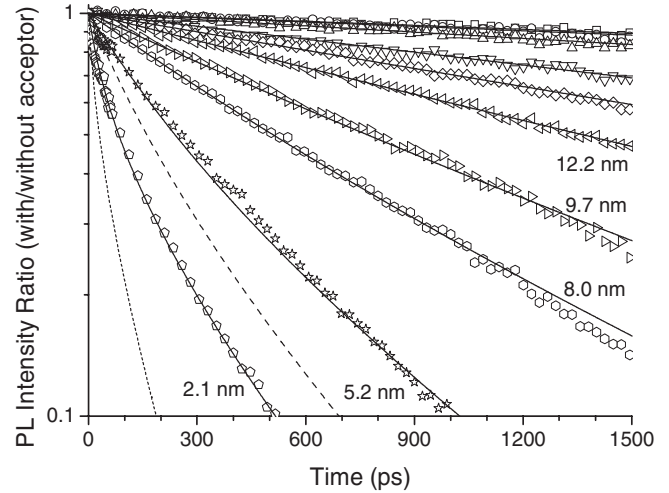


FIG. 3. The ratio of the PL kinetics recorded with and without the acceptor layer. The solid lines represent the fits to the data with Eq. (6) and d_0 values given in Fig. 4. The predicted energy-transfer kinetics for the 2.1 and 5.2 nm spacers using Eq. (6) for $d_0 = 12.2$ nm are shown with short-dashed and long-dashed lines, respectively.

creasing spacer thickness as shown in Fig. 1(c).

For energy transfer between two point dipoles a strong r^{-6} distance dependence was predicted by Förster's theory, where r is the donor-acceptor dipole separation. However, the power dependence of the energy-transfer rate is greatly influenced by the geometry of the system. Replacing the acceptor molecule with a monolayer of acceptor molecules increases the rate of energy transfer and leads to a r^{-4} dependence.⁷ If the acceptor plane is given a thickness then a r^{-3} dependence is predicted.⁸ In each of these scenarios both the donor and acceptor molecules are still considered to be point dipoles. When the length of the donor and acceptor dipoles is much greater than their separation, a weak r^{-2} dependence has been predicted.⁷

Of the aforementioned geometries the point to a thick plane is a logical candidate for describing our system because our samples contain a thick acceptor layer. From Haynes *et al.*⁸ the general equation to describe energy transfer at rate k_{ET} between a point donor and an acceptor film of thickness Δ is

$$k_{\text{ET}}(z) = \frac{d_0^3}{\tau} \left[\frac{1}{z^3} - \frac{1}{(z + \Delta)^3} \right], \quad (5)$$

where z is the distance between the excited donor and the acceptor films, τ is the PL decay time of the donor in the absence of energy transfer, and d_0 is the critical transfer distance. This last parameter corresponds to the donor-acceptor separation at which the energy-transfer rate is half the PL decay rate and is analogous to the Förster radius R_0 . However, by varying the geometry and thus the power dependence of the energy-transfer rate the exact calculation of d_0 also varies. The fit to the energy-transfer kinetics was achieved by substituting Eq. (5) into Eq. (4) and using d_0 as a fitting parameter,

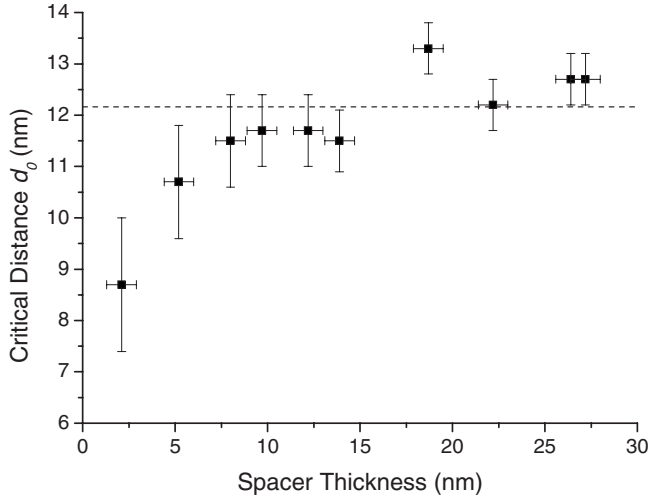


FIG. 4. Value of d_0 for each spacer thickness as obtained by fitting to the energy-transfer kinetics in Fig. 3 with Eq. (6). The uncertainty of ± 0.8 nm in the spacer thickness was used in the fits to evaluate the uncertainty in d_0 values (vertical error bars). The dashed line correspond to $d_0 = 12.2$ nm, which is the average value of d_0 for spacers of 8 nm and thicker.

$$\frac{I_{\text{PL}}(t)}{I_{\text{ref}}(t)} \propto \int_s^{s+d} e^{-d_0^3/\tau(1/(z^3) - 1/(z + \Delta)^3)t} dt, \quad (6)$$

where d is the thickness of the donor film, s is the thickness of the spacer layer, and d_0 is the fitting parameter. The average PL decay time τ was calculated to be 1015 ps from the fit to the reference PL decay with a three-exponential function. We have not included exciton diffusion in our analysis because it is expected to be slow in PFOBT (Ref. 20) as the 9,9-dioctylfluorene-co-benzothiadiazole (F8BT) chromophores are diluted between higher energy poly(9,9-dioctylfluorene) (PFO) segments. Fits to the data using Eq. (6) are shown as solid lines in Fig. 3 and the best-fit values of d_0 for each spacer thickness are displayed in Fig. 4. For spacer thicknesses of 8 nm and greater the best fits were obtained for an average $d_0 = 12.2$ nm, which is much greater than the calculated Förster radius of 5.2 nm. For the 2.1 and 5.2 nm spacers there is a change in the energy-transfer behavior with an apparent reduction in the critical transfer distance. For the thinnest spacer of 2.1 nm the best fit gives $d_0 \sim 9$ nm, which indicates that energy transfer is slower than that predicted by Eq. (6). To further illustrate this point, the kinetics expected for the 2.1 and 5.2 nm spacers with $d_0 = 12.2$ nm are shown as dashed lines in Fig. 3. This discrepancy can be explained by the breakdown of the point-dipole approximation when the spacer thickness is approaching the dimensions of the donor and acceptor chromophores. The PFOBT chromophore is an F8BT unit (emission spectra of F8BT and PFOBT are identical), which has been previously estimated to be approximately 1.5 nm in size.²¹ The chromophore in P3HT is even longer. Additionally, polymers are known to self-orientate when deposited on a surface,²² which would have a significant effect on dipole-dipole interactions and could also account for the $1/z^2$ dependence reported by Hill *et al.*¹²

The inclusion of the acceptor thickness term Δ in Eq. (5) is important as Δ becomes a factor in the calculation of d_0 . This is because the energy-transfer rate is dependent on the acceptor thickness, and if d_0 is defined as the separation at which the energy-transfer rate is half the decay rate then it will vary with the acceptor thickness. This is fundamentally different from the Förster radius, which is purely a property of the materials. However, if a thick acceptor is used the second distance term becomes negligible and Eq. (5) is simplified to

$$k_{\text{ET}} = \frac{1}{\tau} \left(\frac{d_\infty}{z} \right)^3, \quad (7)$$

where d_∞ is the critical transfer distance for an infinite acceptor, which can be calculated⁸ from

$$d_\infty^3 = \frac{3\eta}{2(4\pi n)^4} \int A(\lambda) f(\lambda) \lambda^4 d\lambda, \quad (8)$$

where η is the photoluminescence quantum yield of the donor, n is the refractive index of the medium through which energy transfer occurs, $A(\lambda)$ is the absorbance per unit length of the film, and $f(\lambda)$ is the donor's normalized emission spectrum. For geometries with a thin acceptor the second distance term cannot be ignored and there will be a reduction in the critical transfer distance from d_∞ to d_0 as per the equation below:

$$\frac{1}{d_0^3} = \frac{1}{d_\infty^3} - \frac{1}{(d_0 + \Delta)^3}. \quad (9)$$

Using Eq. (8) we calculate d_∞ to be 18.6 nm for a PFOBT PLQY of 81%, which is larger than the ~ 12 nm value extracted from the fits to the data. This discrepancy may be due to an overestimation of the spectral overlap by Eq. (8), which was derived for homogeneously broadened spectra. Inhomogeneous broadening of the experimental PL and especially absorption spectra lead to the overestimation of the spectral overlap and d_0 in Eq. (8).

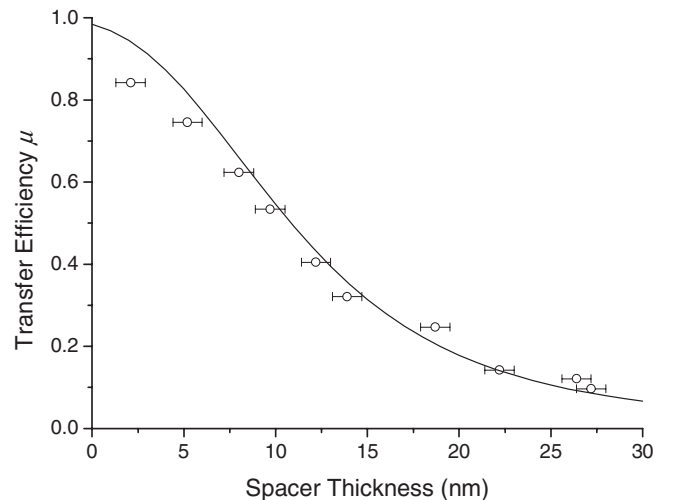


FIG. 5. Transfer efficiency as a function of spacer thickness. Fit to the data with Eq. (10) for $d_0 = 12.2$ nm.

In terms of devices and applications the transfer efficiency is a more useful quantity. This was calculated by integrating the normalized PL decays to obtain the lifetime. For the longer-lived decays the fit to the PL decay was integrated. The transfer efficiency μ is defined as

$$\mu = \frac{\int_0^{\infty} [I_{\text{ref}}(t) - I_{\text{PL}}(t)] dt}{\int_0^{\infty} I_{\text{ref}}(t) dt}, \quad (10)$$

and the experimental values agree with those calculated (shown in Fig. 5) using Eqs. (6) and (10) and $d_0=12.2$ nm for spacer thicknesses of 8 nm and greater. The transfer efficiency is overestimated by 7% for the 5.2 nm and 10% for the 2.1 nm spacer when using the point-dipole approximation. This has to be accounted for when evaluating the transfer efficiency between polymer layers. Transfer efficiency exceeds 50% for a spacer thickness of 10 nm or less, and it is

worth noting that even at large spacer separations there is still noticeable energy transfer.

IV. CONCLUSIONS

We have demonstrated that the energy transfer kinetics between films of conjugated polymers can be described with a z^{-3} dependence of the transfer rate for $z > 5$ nm, where z is the distance between the excited donor segment and the acceptor film. This is consistent with the point-dipole approximation, yielding a value of ~ 12 nm for the critical transfer distance. For $z \leq 5$ nm the point-dipole approximations overestimates the energy-transfer rates and efficiencies. These results highlight the limitations of the point-dipole approximation in describing energy transfer between conjugated polymers on a nanometer scale.

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