Resonance energy transfer from organic chromophores to fullerene molecules

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The mechanism of charge separation in polymeric bulk heterojunction photovoltaic cells is usually described as electron transfer from the absorbing polymer to an electron acceptor material such as (6,6)-phenyl C_{61} butyric acid methyl ester (PCBM). We consider the possibility of energy transfer to PCBM as another potential mechanism for charge separation. We demonstrate resonance energy transfer from a red-emitting organic chromophore (Nile red) to PCBM and measure a Förster radius of 3.1 nm. Using standard Förster energy transfer theory, we calculate a Förster radius (R_0) of around 2.7 nm for this donor-acceptor pair in polystyrene. Nile red has a similar emission spectrum to commonly used conjugated polymers used in polymer/PCBM photovoltaic cells. We consider the implications of an energy transfer mechanism on the design requirements for future photovoltaic cells. © *2006 American Institute of Physics.* [DOI: 10.1063/1.2195890]

INTRODUCTION

Photovoltaic devices based on organic semiconductors have gained the attention of the solar energy community because they can potentially be both efficient and inexpensive.[1–4] Conjugated polymers can act as both the absorbing moiety and charge transporter in heterojunction devices, where an exciton-splitting junction is formed between the absorbing/hole transporting polymer and an electron transporting material. Several electron accepting materials have been used in polymer heterojunction photovoltaic devices, including metal oxides,[5–8] semiconductor nanocrystals,[9,10] and fullerene molecules.[3,11–16] Recent careful measurements of the exciton diffusion length (L_D) in conjugated polymers have shown that it is quite small, with the latest results indicating $L_D \approx 6$ nm in poly(phenylenevinylene)-based polymers.[17] This diffusion length implies a limit to the feature size of the polymer component, because excitons created at a distance beyond L_D from the heterojunction will not be able to diffuse to the interface before decaying. Polymer-fullerene cells easily overcome this limitation using [(6,6)-phenyl C_{61} butyric acid methyl ester] (PCBM), a C_{60} derivative that is soluble and largely miscible with common conjugated polymers, and recent accounts of polymer/PCBM cells have reported efficiencies approaching 5%, the best efficiencies achieved by any organic photovoltaic cells to date.[15,16,18] The intimate mixing of PCBM and polymers in polymer-PCBM cells eliminates exciton diffusion and undoubtedly contributes to the superior performance of these cells compared to other polymer bulk heterojunction photovoltaic cells. The mechanism of charge separation is widely assumed to be ultrafast electron transfer from the polymer to PCBM, based on ultrafast pump-probe

measurements in which the stimulated emission of the polymer vanishes within ∼45 fs of the initial photoexcitation in a 1:3 poly(2-methoxy,5-(3′,7′-dimethyloctyloxy)-*p*-phenylenevinylene) (MDMO-PPV)/PCBM blend.[19] An alternative mechanism for charge separation, which may not be easily distinguishable in a pump-probe experiment, is energy transfer from the polymer to PCBM, followed by hole transfer from the PCBM to the polymer.[20,21] Regardless of the mechanism, experimental evidence suggests near unity charge splitting efficiency; virtually every exciton created in the polymer undergoes geminate charge separation at the polymer/PCBM interface (many geminate pairs eventually recombine, ultimately reducing overall efficiency).[13,22] Although it is clear that no improvement of the charge separation mechanism is needed in polymer/PCBM blends, it is nonetheless important to definitively establish the mechanism(s) involved in charge separation, particularly as new polymers and electron accepting molecules are conceived of to produce increasingly efficient cells. In this letter, we show that efficient energy transfer can and does take place between red-emitting chromophore donors and PCBM over distances of several nanometers. We discuss the implications of our findings on current and future polymer/fullerene-based bulk heterojunction devices.

In nature, solar energy harvesting is performed primarily through a Förster resonance energy transfer mechanism.[23] In a previous paper, we demonstrated that a resonance energy transfer (RET) mechanism can improve exciton harvesting in a flat polymer/titania cell.[24] In Förster's famous formulation of the rate of energy transfer, the overlap between the experimentally measured emission and absorption spectra of the donor and acceptor, respectively, provides an empirical measure of the Coulombic interaction between the oscillating donor and acceptor dipoles and the rate is found to be

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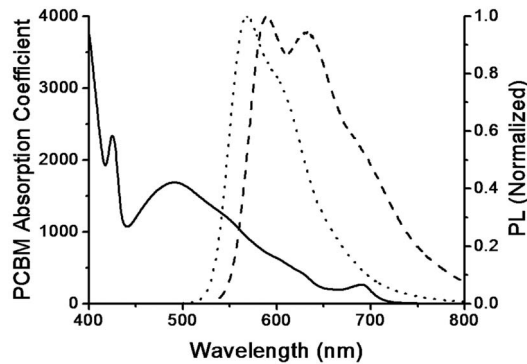
FIG. 1. (Color online) Absorption spectrum of PCBM (solid line), and emission spectra of Nile red (dotted line) and MDMO-PPV (dashed line). The absorption of PCBM was measured with a PCBM solution in toluene. The emission of MDMO-PPV was measured with a pristine film spin cast from chlorobenzene solution.
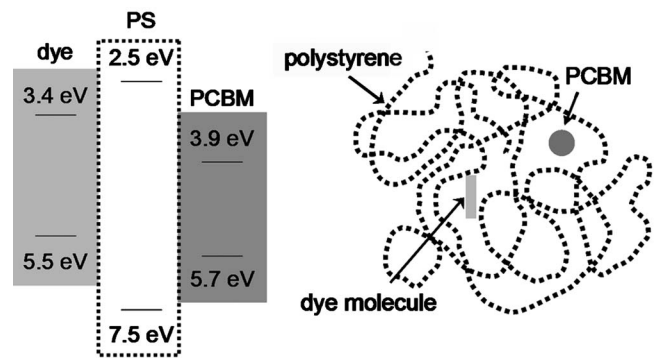

FIG. 2. (Color online) Energy levels with respect to vacuum of Nile red, polystyrene, and PCBM. The polystyrene serves as an insulating spacer layer between the Nile red dye molecules and PCBM.

$$k_{ET} = \frac{1}{\tau_D} \frac{9000 \ln(10) \cdot \kappa^2 \cdot Q_D}{128 \pi^5 N_A n^4 r_{DA}^6} \int_0^\infty F_D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda$$

$$= \frac{1}{\tau_D} \frac{R_0^6}{R^6}, \tag{1}$$

where τ_D is the natural lifetime of the donor in the absence of the acceptor, r_{DA} is the distance between donor and acceptor, κ^2 is a measure of the orientation of the donor and acceptor dipoles (assumed to be 2/3 for randomly oriented dipoles), Q_D is the fluorescence quantum efficiency of the donor, n is the refractive index of the medium the chromophores are embedded in, $F_D(\lambda)$ is the fluorescence intensity of the donor (normalized to have an area of 1 when plotted in wave numbers), $\varepsilon_A(\lambda)$ is the molar absorptivity, and N_A is Avogadro's number. R_0 is the Förster radius, which is the distance at which the rate of energy transfer equals the rate of natural exciton decay. Figure 1 shows the absorption of PCBM and the emission of MDMO-PPV, a conjugated polymer often used in polymer/PCBM cells. Although PCBM exhibits a strongly allowed absorption below ~400 nm, it is interesting to see that a significant overlap is achieved between the MDMO-PPV emission and the often ignored PCBM absorption in the visible portion of the spectrum. Quantum chemical calculations by Shuai and Bredas have shown that, while this portion of the PCBM absorption [corresponding to the highest occupied molecular orbital to lowest unoccupied molecular orbital (HOMO-LUMO) and related transitions] is formally symmetry forbidden, the joint density of states between the HOMO and LUMO is large.[25]

To decouple energy transfer from exciton diffusion in solid films containing fullerene molecules, PCBM and an energy donor were dispersed at very low concentrations in an amorphous, inert polymer matrix, polystyrene (PS). The high glass transition temperature of PS (100 °C) ensured that dopant molecules did not diffuse in the polymer matrix at room temperature. The PS serves as a physical barrier between the fullerene and donor molecules, and its large band gap ensures that it acts as an insulator, incapable of participating in either energy or charge transfer. A low donor concentration discourages donor-donor energy transfer (exciton diffusion). A small, single chromophore dye molecule, Nile red (NR), was chosen to replace the conjugated polymer to eliminate any effects of intramolecular exciton diffusion. Figure 1 shows the electronic spectra of PCBM, NR, and the fluorescence of MDMO-PPV. The NR emission spectrum is similar to MDMO-PPV, ensuring that its spectral overlap with PCBM is similar to that of MDMO-PPV, and its emission spectrum is also similar to that of poly(3-hexylthiophene) (P3HT), another polymer often used in polymer-fullerene bulk heterojunction photovoltaic (PV) cells. Figure 2 shows the energy levels of PCBM, PS, and NR. The average donor-acceptor separation was controlled by the concentration of PCBM in the blend. A low PCBM concentration minimizes both the effects of electron transfer from the dye to PCBM and the possible aggregation of PCBM molecules. In varying the NR loading concentration, evidence of NR aggregation was seen at concentrations above 0.4 wt %. Above 0.4 wt %, the fluorescence spectra appeared to broaden and redshift, consistent with excimer formation. For this reason, 0.2 wt % was the highest concentration used in the films described below. The spectral overlap of the absorption and emission of NR yields a Förster radius R_0 of 2.77 nm for energy transfer from one NR molecule to another, assuming a fluorescence quantum yield of 0.51.[26,27] This corresponds to a concentration threshold of approximately 0.6 wt % (calculated using a quenching sphere with radius R_0 around each chromophore). Therefore, essentially all quenching of the fluorescence of NR in films with NR concentrations much less than 0.6 wt % can be attributed to RET, rather than diffusion followed by electron transfer.

EXPERIMENT

Films of PS/NR and PS/NR/PCBM were prepared by dissolving polystyrene (ACROS, secondary standard, molecular weight 239.7 K, number average molecular weight 119.6 K), Nile red (99%, ACROS), and PCBM in chlorobenzene (anhydrous, 99.8%, Aldrich), and spin casting the resulting solution at 2500 rpm. The concentration of PS was kept constant at 20 mg/ml. Since PS is the dominant component and has a large molecular weight, the viscosity of the solution and hence the thickness of the films (95±2 nm) was fixed by the constant concentration of PS. Photoluminescence (PL) spectra were obtained as described previously,

with an excitation wavelength of 441.9 nm.[24] The excitation intensity was kept below 100 mW/cm² to eliminate any possibility of ground state depletion.

RESULTS AND DISCUSSION

Figure 3 shows the fluorescence quenching of NR as a function of PCBM concentration at five different NR loading concentrations. The substantial fluorescence quenching seen at the low donor and acceptor concentrations in these films is clear evidence of resonance energy transfer from NR to PCBM. The same quenching trend is seen for each NR concentration. If excitons were traveling from one NR molecule to another to get to the quencher a significant fraction of the time, the quenching would have increased with NR concentration. For this study a Förster model is used to calculate the energy transfer efficiency when the donors and acceptors are randomly distributed in a three-dimensional matrix. Because the Förster radius is much smaller than the film thickness (95 nm), the NR/PCMB/PS system can be treated as a quasi-three-dimensional (3D) random mixture. This model predicts that in the absence of molecular diffusion and exciton diffusion, the quenching ratio is given by[28]

$$PL_{DA}/PL_{D} = 1 - \sqrt{\pi}x \exp(x^2)[1 - \text{erf}(x)], \quad (2)$$

where

$$x = (1/2)\sqrt{\pi}C/C_0 \text{ and } C_0 = \frac{1}{(4/3)\pi R_0^3}.$$

Here, the quenching sphere with radius R_0 is given by $1/C_0$. PL_{DA} and PL_{D} are the photoluminescence intensities of the blends containing the donor-acceptor pair and donor, respectively. From the fit to the data using this model in Fig. 3, a RET radius of 3.1 nm is obtained.

Electron transfer is modeled using the Perrin equation, which, in the absence of diffusion of either chromophores or excitons, defines a quenching sphere with radius R_{eff} with the following boundary conditions:

$$k_{ET} = \begin{cases} 0, & \text{when } R > R_{\text{eff}} \\ \infty, & \text{when } R < R_{\text{eff}}. \end{cases} \quad (3)$$

The quenching ratio is then given by[28]

$$PL_{DA}/PL_{D} = \exp(-C/C_0), \quad \text{where } C_0 = \frac{1}{(4/3)\pi R_0^3}. \quad (4)$$

The electron transfer model using $R_{\text{eff}} = 1.5$ nm is shown for comparison and clearly fails to fit the data, as little or no quenching due to electron transfer would be expected at such low donor and acceptor concentrations.

The Förster radius for the NR-PCBM couple was also calculated using the standard Förster equation [Eq. (1)], using 2/3 for κ^2 (random dipole orientation), 1:58 for n (refractive index of PS), and 0.51 for Φ_D (the quantum yield of the donor). Along with the spectral overlap of Nile red and PCBM (Fig. 1), this calculation yields an R_0 of 2.7 nm. The difference between the Förster radius calculated from the spectral overlap versus the experimentally determined value could be explained by the limitations of applying the point-dipole approximation found in Förster's equation[29] to
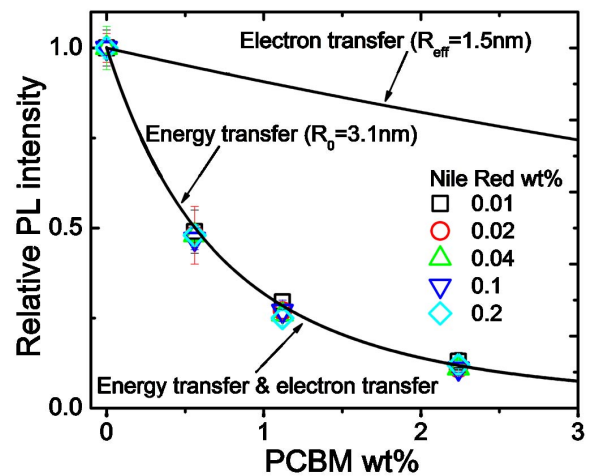

FIG. 3. (Color online) PL quenching vs PCBM wt % for a series of concentrations of Nile red in solid polystyrene films. The upper line is the calculated PL quenching using electron transfer as the only quenching mechanism. The lower line represents the quenching calculated using the Förster energy transfer equation and electron transfer with a Förster radius of 3.1 nm.

PCBM, a large molecule with a symmetry forbidden HOMO-LUMO optical absorption.[30–33] However, some uncertainty in the values of the NR quantum yield and the dipole orientation factor could also contribute to an error in our calculated value. Nevertheless, both R_0 values clearly show that, while PCBM is often thought of as a "large bandgap" material due to its strong absorption in the ultraviolet, its HOMO-LUMO absorption has significant energetic overlap with the emission of most commonly used bulk heterojunction polymers, and therefore RET to PCBM is a mechanism which cannot be overlooked in polymer photovoltaic cells.

While our results and the low PCBM concentration MDMO-PPV/PCBM film results indicate that energy transfer from donor chromophores to C_{60} occurs in some circumstances, it is also important to consider what takes place in the actual photovoltaic devices, where the PCBM loading concentration is very high (45–80 wt % PCBM). At such high loading concentrations, neither long-range Förster-type energy transfer nor exciton diffusion is needed for exciton transport because excitons are created very near PCBM molecules and some degree of wave-function overlap can be assumed. Orbital overlap is required for both an electron transfer mechanism and an "exchange" or Dexter-type energy transfer process. The rigorous *ab initio* calculations needed to differentiate the quantum mechanics of these two mechanisms are well beyond the scope of the present study. Previous studies of C_{60}-energy/electron donor dyad molecules have presented empirical evidence of competition between the processes of energy and electron transfer, with one becoming favorable over the other depending on experimental conditions and orientation of the donor with respect to the fullerene.[34,35]

To date, relatively little attention has been given to the utilization of RET in polymer photovoltaic cells. In a previous study, we showed that directional RET from P3HT to a lower band-gap polymer improves the resulting photocurrent

in PV cells by a factor of three.[24] One major advantage we see to resonance energy transfer for conjugated polymers is that trapping due to low-energy sites in the polymer is minimized; energy transfer should enable faster harvesting of excitons and prevent them from becoming trapped at low-energy sites away from the heterojunction. Energy transfer should also "detrap" excitons from low-energy sites to the acceptor species, thereby potentially relaxing the morphological requirements for efficient exciton transport within a device, and making the use of conjugated polymers with their myriad of energetic states more plausible in photovoltaic devices. These effects may contribute to the outstanding performance of polymer-fullerene PV cells, compared to other bulk heterojunction cells, particularly in cells exhibiting large phase-separated domains, where the long-range RET mechanism can become valuable. In films with well-separated domains, a RET mechanism can be expected to be faster than exciton diffusion; we find it highly relevant that the highest polymer/fullerene efficiencies reported are for P3HT/PCBM cells in which phase separation creates distinct polymer and fullerene domains.[15,16] In these cells, phase separation forms ~10 nm domains, and the P3HT domains are shown to be crystalline, making it unlikely that very many PCBM molecules become incorporated into the P3HT phase. By increasing the spectral overlap between donor and acceptor, the luminescence efficiency of the donor and absorption coefficient of the acceptor, it should be possible to harvest more excitons by resonance energy transfer in cells with increasingly large polymer domains.

Charge separation is clearly fast and efficient in polymer/PCBM blend cells, regardless of the mechanism. However, correctly identifying the mechanism has several important implications for polymer-fullerene cell design. For example, a LUMO offset favorable for electron transfer from the polymer to the PCBM has been a design target for synthesizing new polymers.[36,37] However, in the case of RET followed by hole transfer, the HOMO offset determines if charge separation occurs efficiently. Another consequence of a RET mechanism in polymer photovoltaic cells is that the RET mechanism is not possible for polymers with band gaps lower than ~1.8 eV, due to lack of spectral overlap with PCBM. Thus, low band-gap polymer/PCBM cells cannot take advantage of the RET mechanism and might not perform as well as other polymer/PCBM cells, particularly if large phase separation requires excitons to diffuse to the PCBM interface.

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