

The Impact of Driving Force on Electron Transfer Rates in Photovoltaic Donor–Acceptor Blends

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Organic semiconductors have great potential for the development of large-scale, flexible, and semitransparent solar panels. The primary excitations in organic materials are strongly bound excitons therefore for efficient charge carrier generation it is necessary to use a heterojunction of two materials, one an electron donor and the other an electron acceptor. The free energy difference between the initial (exciton) and final (electron–hole pair) states is known as the “driving force” for electron transfer (ET). Photoinduced ET is a critical process for a wide range of biological, chemical, and physical systems, including natural^[1] and artificial photosynthesis,^[2] photocatalysis and excitonic photovoltaic devices.^[3] A key issue in solar cells is that to generate a high power conversion efficiency, it is desirable to have the smallest driving force necessary to generate free charges, as any excess will lead to increased thermalization losses and consequently a reduced open circuit voltage. A recent study has shown that the photocurrent generation efficiency at short circuit conditions is independent of the excess vibrational energy, suggesting that it is possible to develop efficient blends with a minimal driving force and consequently with almost no energy loss at the interface between donor and acceptor.^[4] Another recent study showed the existence of an optimal driving force for the highest relative efficiency of the mobile charge generation.^[5] Time-resolved spectroscopies have shown that ET

between the donor and acceptor in bulk heterojunctions formed by blending donor and acceptor molecules, depends on blend morphology and occurs on timescales less than 100 fs to tens of picoseconds with longer times representing diffusion-assisted ET.^[3b–m] In organic semiconductors, it is of great interest to separate ET from exciton diffusion to get better understanding of the influence of driving force on the critical process of charge generation. This will allow the optimization of the blend materials’ electrical properties based on a complete understanding of the photophysics, potentially leading to a break-through in the power conversion efficiencies attainable in organic photovoltaic (OPV) solar cells.

In this communication we address this issue by measuring ET rates from thermally relaxed excitons in a high photovoltaic efficiency conjugated polymer, to an assortment of acceptors with a range of electron affinities (EA). Very low loadings of acceptor are used to ensure that the acceptor sites are spread throughout the film so that the blend morphology has no influence on the rate of quenching. Comparably low concentrations of similar quenchers have been shown to remain intimately mixed in the blend^[3,6,7] and a plot demonstrating that acceptor 4 remains intimately mixed well above the concentration used of 0.005 nm⁻³ is shown in the Supporting Information. The donor polymer used was poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]] (PTB7), a highly efficient photovoltaic material,^[8] chosen to be as relevant as possible to the study of OPV optimization. The influence of quenching by Förster resonance energy transfer (FRET) was minimized and the effect of exciton diffusion was determined independently and taken into account. Fast ET in <2 ps is determined for excitons at a distance of <1 nm to an acceptor for driving force between 0.2 and 0.6 eV. Higher and lower driving forces give slower rates of ET. This dependence is well described by Marcus theory and a reorganization energy of ≈0.4 eV. Our results show that ET from a thermally relaxed exciton can be very efficient for transitions occurring at the optimal driving force, and that the energy loss at the donor–acceptor interface can be reduced by reducing the reorganization energy while maintaining the optimum electron affinity or ionization potential offset.

Figure 1a shows the chemical structures and the EA of the acceptors used in this study. EA values were measured by square wave voltammetry in solution and the details are given in Figure S1, Supporting Information. There is some discussion in the literature regarding the measurement of electrochemical potentials of organic semiconductors,^[9] but in this communication, these concerns are mitigated because only the

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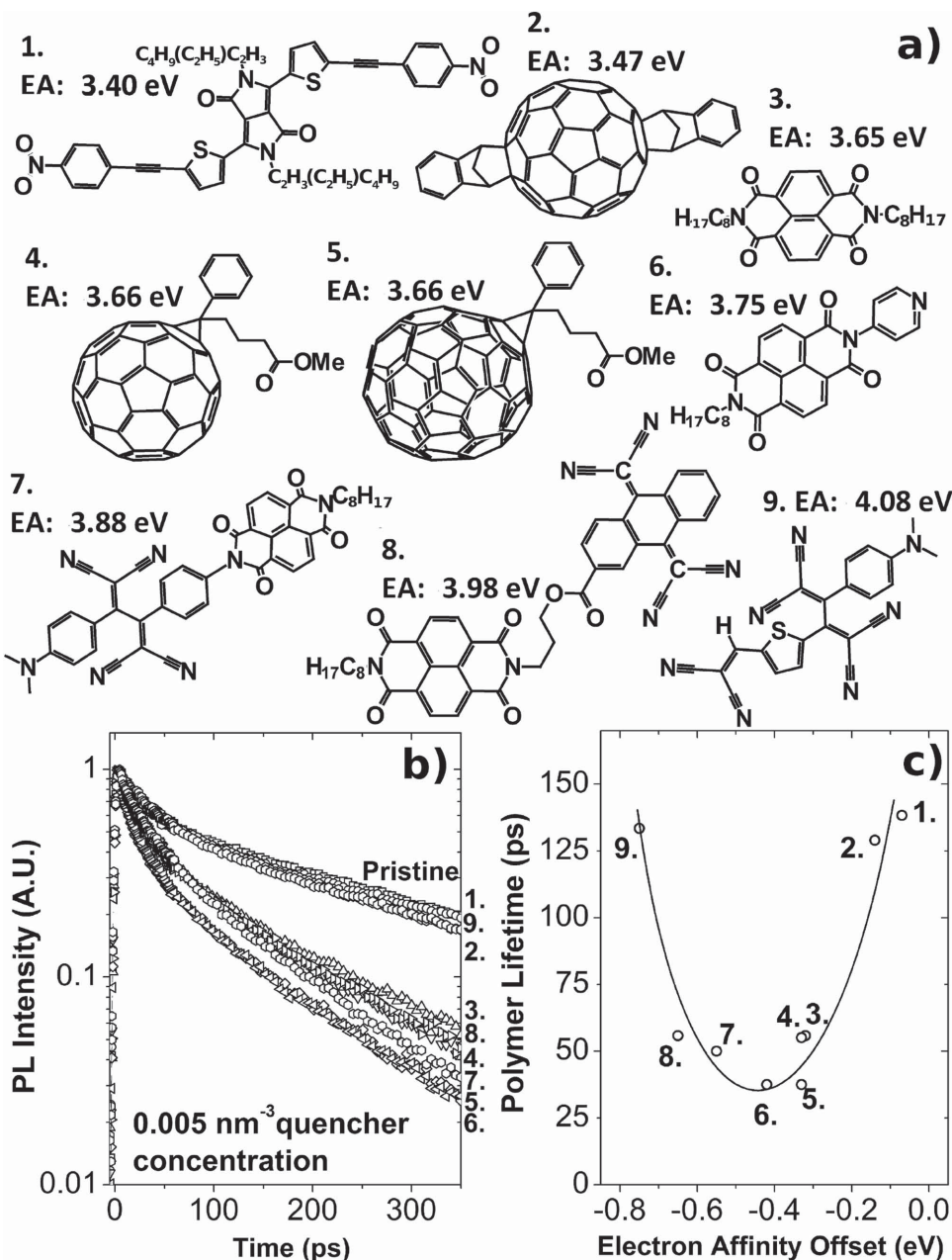


Figure 1. a) Chemical structures and EA of the electron acceptors used in this work; b) time-resolved PL of PTB7 films doped with the numbered acceptors at a concentration of 0.005 nm^{-3} detected in the spectral window of 685–770 nm; and c) the PL decay time to $1/e$ plotted against the difference of EA of donor and acceptor ($EA_D - EA_A$). The line is a guide for the eye.

relative values of their EA, not the absolute values are relevant. Figure 1b shows the photoluminescence (PL) kinetics of a pristine PTB7 film and of the PTB7 blends with a fixed 0.005 nm^{-3} concentration of the electron acceptor. Strong dependence on the EA of the acceptor is observed. The time taken for the PL intensity to decrease to $1/e$ of the initial value is shown in Figure 1c indicating that the blend lifetime decreases significantly more for acceptors with optimum EA offset between the donor and acceptor when compared with blends with precisely the same number concentration of acceptor sites but sub-optimum EA offset.

The PL intensity is proportional to the exciton concentration $[E]$. The decay rate of excitons in a blend $d[E]/dt$ is a sum of the spontaneous decay rate with a rate constant k_f and an acceptor-induced decay rate with the rate constant k_q

$$\frac{d[E]}{dt} = -k_f [E] - k_q [Q][E] \quad (1)$$

where $[Q]$ is the acceptor concentration which is time independent. It has been shown previously that for such a monomolecular quenching process^[6]

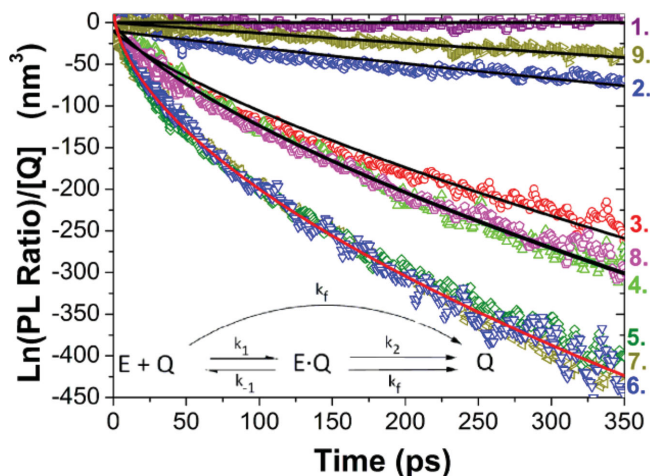


Figure 2. Natural logarithm of the PL intensity ratio $I_{\text{Doped}}/I_{\text{Pristine}}$ measured in doped films I_{Doped} and in the pristine PTB7 film I_{Pristine} divided by the acceptor concentration (0.005 nm^{-3}). Solid lines are fits to the scheme shown in the inset and described by Equation (3).

$$k_q = - \frac{d}{[Q] dt} \ln \left[\frac{I_{\text{Doped}}}{I_{\text{Pristine}}} \right] \quad (2)$$

where I_{Doped} is the normalized PL intensity of the film with acceptors and I_{Pristine} is the normalized PL intensity of the pristine PTB7 film. Using this approach, the rate constant of quenching (k_q) is isolated from the rate constant of unquenched, spontaneous decay of excitons (k_f). The time dependence of $\ln(I_{\text{Doped}}/I_{\text{Pristine}})/[Q]$ shown in **Figure 2** is linear for acceptors 2 and 9 indicating that k_q is time independent. In contrast, for strongly quenching acceptors 3–8 k_q clearly slows down with time. The slowing down of k_q can be due to dispersive exciton diffusion which brings exciton to the acceptor^[10] or due to long-range FRET to the acceptor.^[6,11a] In order to evaluate possible FRET to the acceptor we have measured molar extinction coefficients of all the acceptors used in this work and calculated Förster radii as described in the Supporting Information. Absorption by acceptors 3, 6, and 8 occurs at much shorter wavelengths than the fluorescence of PTB7 as shown in Figure S3, Supporting Information, so FRET should be negligible, yet they show much faster quenching than acceptors 1, 2, and 9 which have nonzero spectral overlap with PTB7 fluorescence as shown in Figure S4, Supporting Information. Negligible FRET from PTB7 to any of acceptors used in this work can be explained by more rapid back FRET from these acceptors to PTB7. For example, the Förster radius for energy transfer from PTB7 to the acceptor 5 is calculated to be 1.4 nm (Table S1, Supporting Information), whereas Förster radius for the back FRET from the acceptor 5 to PTB7 has been found to be 2.17 nm^[3] therefore, the rate of the back energy transfer to PTB7 should be ≈ 14 times higher than that of the forward energy transfer from PTB7. On the basis of these observations we exclude FRET to the acceptor and analyze the PL quenching as diffusion-assisted ET using the scheme shown in the inset of Figure 2. Here k_1 is a second order rate constant which describes the formation of an encounter complex $E \cdot Q$, k_{-1} is a first order rate constant which describes the escape of exciton

from $E \cdot Q$ and k_2 is a rate constant of ET to an acceptor in an encounter complex.

When the populations of the encounter complexes are in a quasi-steady state, then the exciton quenching rate constant by an acceptor can be expressed as^[12]

$$k_q = \frac{k_1 k_2}{k_{-1} + k_2} \quad (3)$$

From inspection of Equation (3), it is clear that when $k_2 \gg k_{-1}$ then $k_q \approx k_1$ and quenching is diffusion limited. We make the observation that quenching kinetics in Figure 2 are very similar for acceptors 5, 6, and 7, which give the fastest quenching indicating that quenching is diffusion limited in these blends. We can fit quenching kinetics for these acceptors with the time dependent $k_q = k_0 t^{-h}$ as shown by the solid line in Figure 2 with $k_0 = 9.1 \text{ nm}^3 \text{ ps}^{-0.66}$ and $h = 0.34$.

In order to determine k_2 we have measured PL quenching in blends of PTB7 with very high concentration of acceptors where ET is much faster than exciton diffusion. These results are shown in **Figure 3a**. The blend with acceptor 5 shows very fast PL decay which is limited by the streak camera resolution ($< 2 \text{ ps}$). In contrast, the PL decay in the blend with acceptor 2 is significantly slower and can be described by an exponential decay with a time constant of 9 ps. By taking into account the initial PL decay in the pristine PTB7 film with a time constant of 100 ps we can determine the rate of quenching is equal to 0.1 ps^{-1} in this blend. Bulky side groups of PTB7 allow only two acceptor molecules to be very close to the polymer backbone, so in order to determine k_2 as defined in the scheme inset in Figure 2, we divide the measured rate by two to account for the two possible acceptor molecules available to each PTB7 chromophore, this gives $k_2 = 0.05 \text{ ps}^{-1}$. Then using $k_q = 0.19 \text{ nm}^3 \text{ ps}^{-1}$ for acceptor 2 determined from its gradient in Figure 2, and assuming the same time dependence for k_{-1} as for k_1 , because both rates are controlled by exciton diffusion, we determine the ratio $k_1/k_{-1} \approx 4 \text{ nm}^3$ using Equation (3). Assuming that populations of excitons and of the encounter complexes are at equilibrium and that the exciton distribution in the film is uniform, we obtain

$$\frac{k_1}{k_{-1}} = \frac{[E \cdot Q]_{\text{eq}}}{[E]_{\text{eq}} [Q]} = \frac{N_q V_q}{V} \frac{1}{[Q]} = V_q \quad (4)$$

where V_q is the volume around the acceptor in which an encounter complex is formed, N_q is the total number of acceptor molecules in the film, and V is the total film volume. Then the value $k_1/k_{-1} \approx 4 \text{ nm}^3$ implies that the radius of the action sphere around an acceptor to form an encounter complex is about 1 nm. This is acceptable because ET requires wavefunction overlap between donor and acceptor. Using $k_1/k_{-1} = 4 \text{ nm}$ as well as k_0 and h determined above we fit the kinetics in Figure 2 and obtain k_2 for each acceptor, as shown in Figure 3b. To estimate the driving force ΔG^0 for ET we use the enthalpy difference between the initial and final states and consider that the entropy change by ET is insignificant, thus $\Delta G^0 = EA_A - EA_D - \Delta E_b$, where EA_D and EA_A are EA of the donor and acceptor and ΔE_b is the difference of the binding energies of a polymer exciton and of a charge pair generated by ET. We set $\Delta E_b = 0.15 \pm 0.1 \text{ eV}$ to the $EA_A - EA_D$ value

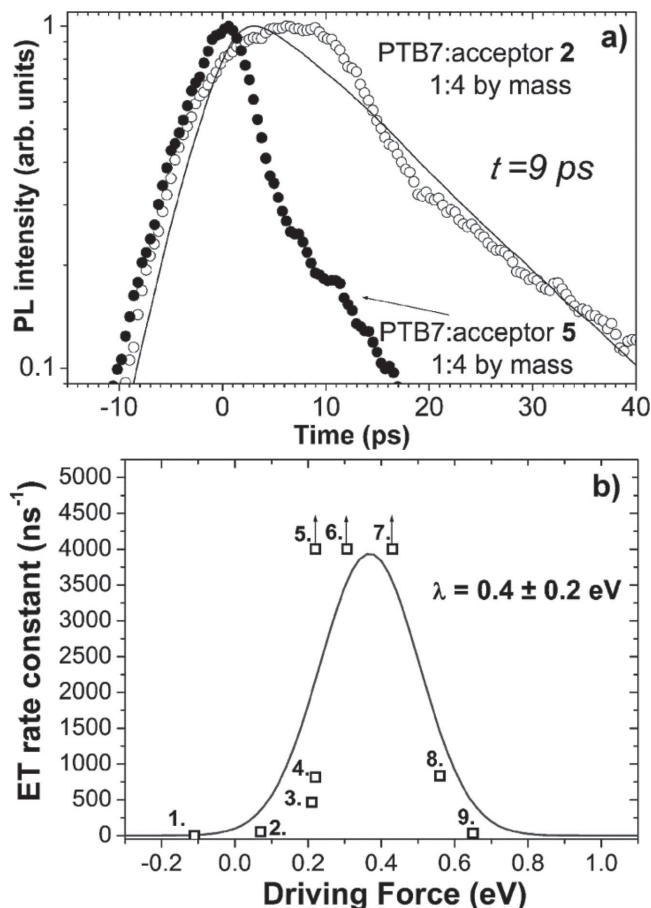


Figure 3. a) PL kinetics in 1:4 blends of PTB7 with the numbered acceptors by the mass ratio detected in a window of 750–850 nm after excitation at 650 nm. The solid line is a fit to exponential decay with a 9 ps time constant. b) ET rate constant k_2 to each acceptor. The solid line is a fit to Equation (4) with reorganization energy $\lambda = 0.4$ eV, the arrows above points 5, 6, and 7 indicate that these points are lower limits.

of PTB7 and acceptor 2 which gives small but clearly detectable PL quenching. This ΔE_b value is consistent with the difference in binding between charge pairs in PTB7 blends with the acceptor 4 of 0.07 ± 0.04 eV^[13] and typical exciton binding energies of 0.4 eV.^[14] Uncertainty in ΔE_b gives a systematic error in the driving force and does not affect general conclusions of our work. We note that the electron affinity in the film will be higher than that measured in solution due to the polarization of the electron density in surrounding π -conjugated molecules in the solid film.^[15] However, this polarization effect will cancel when calculating the driving force from the difference between two EA measured in solution using the same technique.

The determined rates of k_2 initially increase with respect to the driving force, reaching a maximum at ≈ 0.4 eV and then falling with increasing driving force. Such a dependence is typical for nonadiabatic ET and can be described using the Marcus formula^[16]

$$k_{\text{ET}} \propto \exp \left[-\frac{(\Delta G^0 + \lambda)^2}{4\lambda k_B T} \right] \quad (5)$$

where ΔG^0 is the driving force, λ is the reorganization energy, k_B is the Boltzmann constant, and T is the temperature. Though usually applied to describe the ET rate,^[17] recently the theory has been shown to fit the relative yield of free charge carriers in donor–acceptor blends by Coffey *et al.*^[5] An interesting implication of Equation (5) is that when the energetic driving force is greater than the reorganization energy then the rate of ET decreases with increasing driving force which is known as the “Marcus inverted region.” The fit to the values of k_2 using Equation (4) is shown by the solid line in Figure 3b and gives $\lambda = 0.4 \pm 0.1$ eV. As the position and breadth of the Gaussian fit is dictated by a single free parameter, λ , the fact that the data can be fitted to this simple model is extremely encouraging. The small value of the reorganization energy is good not just for charge generation but also for charge transport^[18] and so is an important factor contributing to the high photovoltaic performance of PTB7 blends with fullerene derivatives. Similar values of 0.22–0.27 eV were calculated for other efficient photovoltaic blends of poly[2,6-(4,4-bis-(2-ethylhexyl)dithieno[3,2-b:2',3'-d]silole)-alt-4,7-(2,1,3-benzothiadiazole)](Si-PCPDTBT) with fullerene derivatives.^[19] For comparison, Coffey *et al.* found slightly larger λ values between 0.4 and 0.8 eV in blends of fluorene–thiophene copolymers with fullerene derivatives.^[5] Knowing the reorganization energy of high performance photovoltaic materials is critically important to the rational design of solar cell materials. A small reorganization energy means that efficient ET is possible with a relatively small energy offset between the EA of the donor and acceptor. This means less energy is lost to thermalization during charge generation and a higher open-circuit voltage is possible. For acceptors 5, 6, and 7 which give the fastest quenching we can only determine the lower limit of the ET rate which estimates that ET should be faster than 250 fs. This is similar to previously observed ultrafast charge generation in PTB7 blends with acceptor 5.^[31,20] Our study shows that for the optimal driving force ET from a thermally relaxed exciton can be as fast as those reported for hot excitons.^[31]

In conclusion, the presence of an optimum driving force for ET is shown by strong dependence of the fluorescence lifetime of the donor doped with a small concentration of the acceptor. Fitting the measured rates to a Marcus model allowed us to determine that the reorganization energy $\lambda = 0.4 \pm 0.2$ eV for ET from PTB7 to a range of acceptors, suggesting that it is mainly the polymer which reorganizes upon ET. Our study shows that ET from thermally relaxed excitons can be very efficient for processes with the optimal driving force. Understanding that the reorganization energy of the polymer is important for charge separation is very important to the community, as being able to produce a polymer with a small reorganization energy will be extremely beneficial in the development of highly efficient solar cells. This is because it lowers the energetic driving force required to rapidly separate excitons and hence allows a greater proportion of the photon energy to be harvested. This could be one contributing factor to why the highest efficiency P3HT solar cells (power conversion efficiency 6.43%) experience voltage losses ($E_g - V_{\text{OC}}$) of 1.4 eV^[21] whereas the highest efficiency PTB7 devices experience voltage losses of just 0.9 eV.^[8]

Experimental Section

Sample Preparation: PTB7 with a molecular weight of 92 000 Da and a polydispersity of 2.6 was purchased from 1-Material. Acceptors **2**, **4**, and **5** were purchased from Solenne. Synthesis and purification of acceptors **1**, **3**, **6**, **7**, **8**, and **9** is described in the Supporting Information. Blend films with low concentration of acceptors were produced by spin-coating from a 13.6 mg mL⁻¹ chlorobenzene solution of PTB7 containing ≈0.07 mg mL⁻¹ of acceptor. The exact quantity of acceptor was chosen so that a film spun from this solution would give a number density of acceptors of 0.005 nm⁻³ assuming a PTB7 mass density of 1.12 g cm⁻³.^[22] The films were spin-coated from solutions onto fused silica substrates at 2000 rpm under a nitrogen atmosphere.

Time-Resolved PL: It was measured in a nitrogen atmosphere with a synchroscan streak camera C6860 from Hamamatsu. The excitation for blends with low concentration of acceptors was with 100 fs pulses at 400 nm and 80 MHz repetition rate. Blends with high concentration of acceptors shown in Figure 3a were excited at 650 nm and 100 kHz.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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