

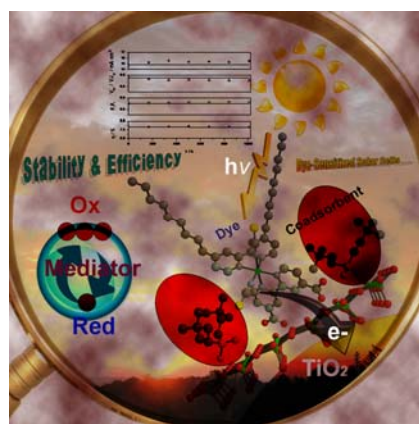
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# Probing the nanoscale phase separation in binary photovoltaic blends of poly(3-hexylthiophene) and methanofullerene by energy transfer

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The generation of charge carriers in organic photovoltaic devices requires exciton diffusion to an interface of electron donor and acceptor materials, where charge separation occurs. We report a time resolved study of fluorescence quenching in films of poly(3-hexylthiophene) containing a range of fractions of the electron acceptor [6,6]-phenyl-C61-butyric acid methyl ester (PCBM). We show that energy transfer from P3HT to PCBM helps to bring excitons to the interface, where they dissociate into charge carriers. Fluorescence quenching in blends with  $\leq 50$  wt% of PCBM is controlled by exciton diffusion in P3HT. This allows us to estimate the average size of PCBM domains to be about 9 nm in the 1:1 blend. The implications for polymer solar cells are discussed.

## Introduction

The dominant primary photoexcitations in organic semiconductors are tightly bound excitons. This means that the generation of charge carriers requires exciton diffusion to a donor-acceptor heterojunction and dissociation by charge transfer across the heterojunction. Reported exciton diffusion lengths in conjugated polymers typically fall in the range of 5–10 nm,<sup>1</sup> which is about ten times shorter than the optical path length required for substantial absorption of the incident light. Only the excitons generated within a diffusion length of the interface give photocurrent, therefore, simple bi-layer photovoltaic devices have poor photon-charge conversion efficiencies. This problem can be solved using bulk heterojunctions (BHJ) based on interpenetrating donor-acceptor networks, in which excitons are generated within their diffusion length to the donor-acceptor interface. BHJ can form by spontaneous phase separation when blended films of a conjugated polymer and a suitable electron acceptor are spin-cast from solution.<sup>2</sup> Photovoltaic devices with up to 6% power conversion efficiency of solar radiation have been reported using this approach.<sup>3</sup> BHJ of poly(3-hexylthiophene) (P3HT) and a fullerene derivative [6,6]-phenyl-C61-butyric acid methyl ester (PCBM), which is commonly known as methanofullerene, have achieved nearly 5% power conversion efficiency and good thermal stability.<sup>4</sup> Device performance strongly depends on blend morphology, which can be controlled by composition, choice of solvent, temperature, solidification time and thermal annealing. Spatial Fourier-transform analysis of images obtained by transmission electron microscopy has revealed two coexisting length scales of P3HT and PCBM domains: 1) mesoscale phase separation in a range of 20–300 nm; and 2) nanoscale phase separation on a length scale smaller than 20 nm.<sup>5</sup> Understanding the role of different length scales in charge separation and charge transport could help to develop new materials and structures. The dynamics of charge carrier photogeneration in polythiophene-PCBM blends has been

studied previously,<sup>6</sup> however its relationship with the nanoscale morphology of the blends has not yet been established.

In this paper we report a time resolved study of fluorescence quenching in P3HT-PCBM BHJ structures. We show that energy transfer from P3HT to PCBM helps to bring excitons to the interface and to speed up charge generation. Making use of a relatively slow exciton diffusion in P3HT and a fast energy transfer at the interface with PCBM, we are able to estimate the morphology length scale, which is relevant to the initial charge separation.

## Results and discussion

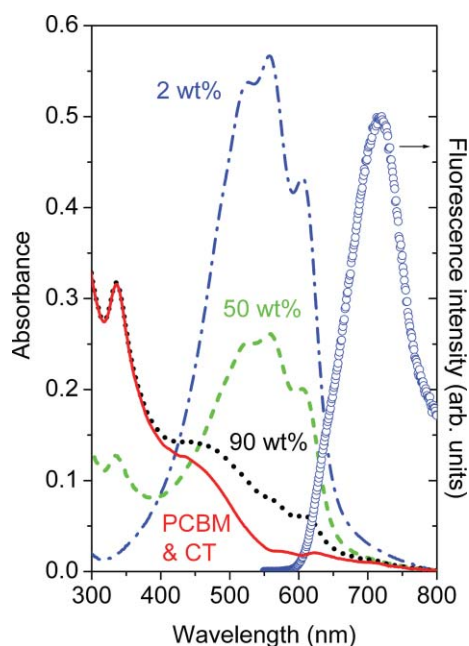
### Absorption and fluorescence spectra

Absorption spectra of blended P3HT:PCBM films show the P3HT absorption in the region of 400–650 nm and the PCBM absorption, which peaks at 340 nm (Fig. 1). In the 50 wt%-PCBM blend the absorbance of P3HT is about half of that in the 2 wt%-PCBM blend in agreement with the lower concentration of P3HT. Accordingly, the PCBM absorption doubles when PCBM amount is increased from 50 to 90 wt%. The P3HT contribution to the absorption spectrum of 90 wt%-PCBM blend can be obtained by scaling down the 2 wt%-PCBM spectrum by a factor of 9.8 as both blended films had similar thicknesses. By subtracting the P3HT contribution we obtain the absorption spectrum of PCBM (shown by the solid line in Fig. 1), which also contains a contribution from the ground state charge transfer (CT) complexes. Such complexes have been shown to form in polythiophene blends with fullerenes and to generate electron-hole pairs upon photoexcitation.<sup>7</sup> This spectrum has a finite overlap with the P3HT fluorescence spectrum, which suggests that energy can be transferred from P3HT to PCBM and to CT complexes by dipole-dipole interactions.

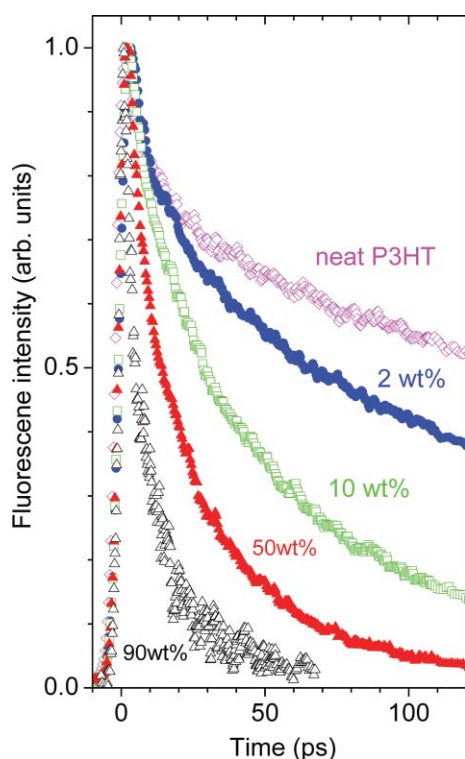
### Dynamics of fluorescence quenching

Fig. 2 shows the fluorescence kinetics in a neat P3HT film and in blends with different amounts of PCBM. Fluorescence decays

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**Fig. 1** Absorption spectra of P3HT films with different fractions of PCBM in the film. The solid red line shows the superposition of absorption by PCBM and by ground-state charge transfer complexes, which was obtained from the 90 wt%-PCBM:P3HT spectrum after subtraction of P3HT contribution. Circles show the fluorescence spectrum of the 2 wt%-PCBM:P3HT blend.



**Fig. 2** Fluorescence decays of P3HT in blended films with different fractional amount of PCBM. Initial intensities are normalised.

faster when the PCBM amount in blends is increased. In the 90 wt%-PCBM blend the  $1/e$  decay time is 10 ps, which can be taken as an upper bound of the quenching time at the interface,

because there is likely to be faster quenching within a response function of the streak camera. Time resolved fluorescence intensity  $I(t)$ , which is proportional to the exciton concentration in P3HT at time  $t$ , for  $\delta$ -function excitation can be described as

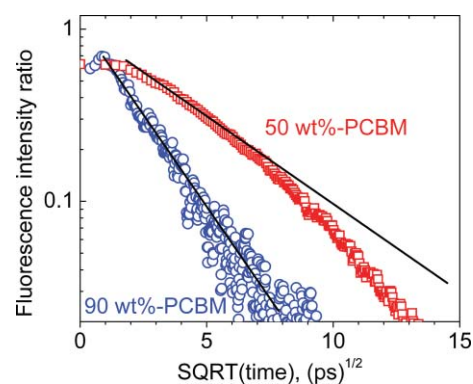
$$I(t) = I_0 \exp[-(t/\tau) - k_q(t)t] \quad (1)$$

where  $I_0$  is the fluorescence intensity at  $t = 0$ ,  $\tau$  is the fluorescence decay time in films without PCBM and  $k_q(t)$  is the quenching rate by PCBM. Taking the ratio of the time resolved fluorescence intensity measured in the blend and in the neat film allows us to eliminate the first term of the exponential in Eq. (1) and gives the quenching kinetics by PCBM. Quenching can be by electron and energy transfer to PCBM or to CT states. Previous studies have shown that both these processes compete in the dyads of a conjugated oligomer and a fullerene.<sup>8</sup>

We start the analysis of the quenching kinetics by assuming that energy transfer to PCBM by dipole-dipole interaction (Förster-type) is a dominant quenching mechanism and a random distribution of PCBM molecules in the blend. In this case the fluorescence intensity ratio  $g(t)$  can be described as<sup>9</sup>

$$g(t) = g(0) \exp[-(N_m/N_0)(\pi t/\tau)^{1/2}] \quad (2)$$

where  $N_m$  is the concentration of acceptor molecules and  $N_0$  is the 'critical concentration' defined as  $N_0 = [(4/3)\pi R_0^3]^{-1}$ , where  $R_0$  is the Förster radius. Exciton diffusion is neglected in Eq. (2). We use  $N_m = f \cdot \rho \cdot N_A / M$ , where  $f$  is the fraction of PCBM in the blend (by weight),  $\rho = 1.1 \text{ g cm}^{-3}$  is the film density,  $N_A$  is the Avogadro constant and  $M$  is the molecular mass of PCBM. Plotting the  $g(t)$  on a logarithmic scale vs the square root of time gives a linear dependence for the 90 wt%-PCBM in agreement with Eq. (2) (Fig. 3). This suggests that at least for the time  $t > 3$  ps fluorescence quenching at the interface with PCBM can be described using the Förster theory of energy transfer. It does not exclude quenching by electron transfer to PCBM, which can occur within the response function of the streak camera of 3 ps. Electron and energy transfer both lead to charge separation as energy transfer to PCBM will be followed by the hole transfer to P3HT due to an  $\sim 1$  eV offset in the ionisation potential of P3HT and PCBM.<sup>6c</sup> Energy transfer is advantageous for dissociation of excitons generated further from the interface with PCBM. Using  $\tau = 400$  ps, we get  $R_0 = 1.2$  nm from the fit to the 90 wt%-PCBM decay. This value is smaller than



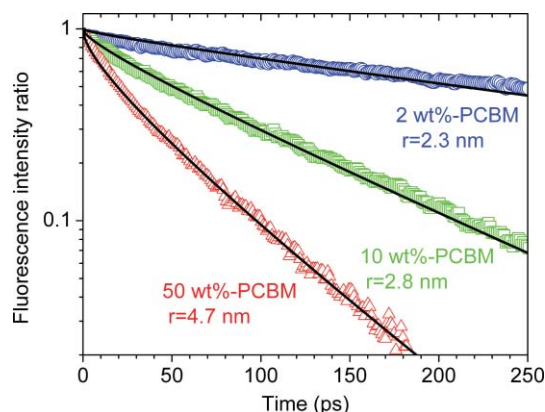
**Fig. 3** Quenching kinetics in blends with different amounts of PCBM as a function of the square root of time. The solid lines are the fits using Eq. (2) assuming quenching is by energy transfer to PCBM with  $R_0 = 1.2$  nm.

the Förster radius of 2.7 nm found in the blend of the fluorescent dye and PCBM dispersed in the polymer matrix<sup>10</sup> and consistent with a smaller spectral overlap of PCBM absorption with P3HT fluorescence (Fig. 1) than with the dye used in ref. 10 and the lower fluorescence quantum yield of P3HT. The decay in the 50 wt%-PCBM is much faster than predicted by the Förster theory for  $t > 40$  ps, which indicates that the rate of energy transfer is enhanced by exciton diffusion.

Fluorescence spectra of P3HT display no dynamical red-shift on the time scale  $t > 10$  ps at room temperature (not shown), therefore, exciton diffusion can be treated as non-dispersive. In this case the quenching rate can be described using Eq. (3)<sup>11</sup>

$$k_q = 4\pi DR_c N_d \left( 1 + \frac{R_c}{\sqrt{\pi D t}} \right) \quad (3)$$

where  $D$  is the exciton diffusion coefficient, which has been measured as  $D = 1.8 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$  by surface quenching for the same batch of P3HT,<sup>14</sup>  $R_c$  is the exciton capture radius and  $N_d$  is the concentration of the quencher, which in our case are PCBM domains. This equation has been shown to describe well the diffusion-mediated quenching in organic crystals<sup>12</sup> and is applicable to P3HT:PCBM blends because they show a spatial periodicity of P3HT and PCBM domains.<sup>5</sup> This is verified by the asymptotic quenching kinetics being exponential as the second term in Eq. (3) becomes negligible when  $t \rightarrow \infty$  and  $k_q$  is time independent (Fig. 4). In the next section we derive a relationship between  $R_c$  and  $N_d$ , which is then substituted into Eq. (3) to fit the experimental decays.



**Fig. 4** Quenching kinetics in blends with different amounts of PCBM. Solid lines are the fits using Eq. (1) in combination with Eqs. (3)-(6),  $r$  is the radius of PCBM domains obtained from the fits.

### Determining the PCBM domain size

The mass of PCBM molecules in small (nanoscale) domains in  $1 \text{ cm}^3$  is

$$m = s \cdot f \cdot \rho \quad (4)$$

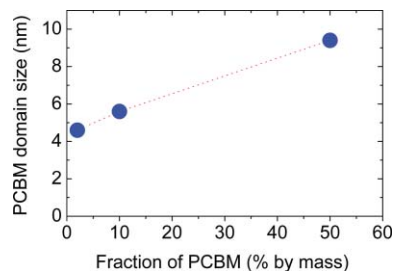
where  $f$  is the fraction of PCBM in the blend (by mass),  $\rho$  is the film density in PCBM domains and  $s$  is the PCBM fraction stored in small (<20 nm) domains. It can also be expressed as

$$m = \rho \cdot V \cdot N_d \quad (5)$$

where  $V$  is the average volume of nanoscale PCBM domains. Assuming the domains are spherical with a radius  $r$ ,

$$V = (4/3)\pi r^3. \quad (6)$$

We set  $R_c = r + d$ , where  $d$  is the distance at which energy transfer from P3HT to PCBM is much faster than the diffusion-controlled quenching. We can estimate  $d$  from the Förster formula:  $d^6 = (\tau_{ET}/\tau)R_0^6$ , where  $\tau_{ET}=10$  ps is the 1/e decay time observed in the 90 wt%-PCBM blend and  $\tau = 400$  ps is the fluorescence decay time of the neat P3HT. This gives  $d = 0.6$  nm. Substituting Eqs. (4)-(6) into Eq. (3) and assuming  $s = 1$  leaves  $r$  as the only unknown parameter, which can be determined by fitting the quenching kinetics. The fits and the  $r$  values which gave the best fits are shown in Fig. 4. The average size of PCBM domains, defined as  $2r$ , is dependent on the amount of PCBM in the blend (Fig. 5). It increases from 4.6 to 5.6 nm with the increase of the PCBM amount in the blend from 2 to 10 wt% and is found to be 9.4 nm in the 50 wt%-PCBM blend, which is a typical concentration in photovoltaic devices. The 9 nm domain size can be compared with the results obtained using the transmission electron microscopy (TEM), which showed a peak of the spatial period of two phases at around 16 nm in a blend with a similar ratio of P3HT and PCBM.<sup>5</sup> As the spatial period corresponds to the |P3HT|PCBM| domain size, the dominant PCBM domain size from TEM is about 8 nm. The length scale of <10 nm is at the resolution limit of TEM, whilst energy transfer can be used to probe even smaller length scales.



**Fig. 5** Average size of PCBM domains determined as  $2r$  as a function of the fractional amount of PCBM in the blends.

The domain size puts a restriction on the initial separation distance of the geminate electron-hole pair formed at the heterojunction. The Coulombic capture radius (distance at which the Coulomb attraction equals to the thermal energy) is about 20 nm at room temperature in materials with a dielectric constant  $\epsilon = 3$ . If charges can only be separated by 9 nm or less, then they will still be bound, and dissociation into free charge carriers has to compete with geminate recombination. This has to be taken into account when modelling polymer solar cells.

### Experimental

The P3HT with a regio-regularity of 98.5%, an average molecular weight of 76000 g/mol and polydispersity of 2.1 was supplied by Merck. The PCBM with a specified purity of >99.5% was obtained from American Dye Source Inc and used as received. Binary solutions of P3HT with 0, 2, 10, 50 and 90 wt% of PCBM by weight were prepared in chlorobenzene at a concentration of 10 mg/ml and stirred overnight at 40 °C. Films were spin-cast

at 900 rpm and their thickness was about 70 nm. Absorption and time-integrated fluorescence spectra were measured with a Varian Cary 300 UV-Vis spectrophotometer and Fluoromax 3 fluorimeter respectively. For the time-resolved PL measurements films were excited using 100 fs light pulses at a repetition rate of 80 MHz and a wavelength of 425 nm. Fluorescence was dispersed in an imaging spectrograph and detected by a Hamamatsu C6860 streak camera in synchroscan mode. To obtain the fluorescence decays of P3HT the detection window was set for the wavelength range 600–680 nm to avoid any possible PCBM fluorescence at longer wavelengths. To ensure that no fluorescence quenching by photogenerated charges occurs, the excitation intensity was attenuated to a level much lower than the onset of intensity-dependent kinetics. The fluorescence decays were measured over both short and long time ranges, which were then spliced together to give the full decay with a resolution of about 3 ps.

## Conclusions

Time resolved study of fluorescence quenching in P3HT films with different fractions of the electron acceptor [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) is reported. We found that the decay of singlet excitons generated in P3HT in the 90 wt%-PCBM blend for the time  $t > 3$  ps is described well by Förster-type energy transfer to PCBM and have determined the Förster radius  $R_0 = 1.2$  nm for energy transfer from P3HT to PCBM. Energy transfer to PCBM followed by hole transfer to P3HT is an important process contributing to the dissociation of excitons. This observation does not exclude electron transfer from P3HT to PCBM, which may occur in competition with energy transfer within our time resolution of 3 ps. We show that the rate of charge photogeneration in the bulk heterojunction structures is controlled by exciton diffusion to the interface with an electron acceptor. This allows us to estimate an average size of PCBM domains of about 9 nm in the 1:1 blend and significantly smaller in the blends with a low PCBM concentration. Domain size is smaller than the Coulombic capture radius of electron-hole pairs at room temperature, which indicates that generated charge pairs have to overcome the binding potential in order to dissociate into free charge carriers.

## Acknowledgements

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