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Molecular versus crystallite PCBM diffusion in P3HT:PCBM blends

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The diffusion of PCBM in P3HT:PCBM blend films has been investigated using multi-wavelength scanning absorption microscopy (MWSAM). By studying the depletion of PCBM in the vicinity of the phase segregated PCBM-rich regions that form upon thermal annealing, we are able to measure the diffusion constant and activation energy for PCBM diffusion in P3HT:PCBM blend films. The measured kinetic parameters are consistent with the diffusion of nanoscale PCBM crystallites rather than molecular PCBM. We show that the presence of two distinct diffusion processes in these blend materials provides an explanation for the large differences that have been reported for PCBM diffusion in P3HT:PCBM blends. This insight allows us to develop a unified model for PCBM mass transport in these materials.

The diffusion and crystallisation of polymer:fullerene blends is a key optimization process in organic electronic device fabrication. Thermal or solvent annealing is typically used to alter the morphology of the device active layer on the nanoscale. However, the blend film structure is a complex interplay of crystalline and amorphous mixed and demixed regions. Understanding the formation of the optimal film morphology therefore requires knowledge of the key factors that govern mass transport in these materials.

For the highly studied P3HT:PCBM system, the diffusion of PCBM in the P3HT matrix is recognised as a key parameter, since it governs the formation of an intricate film structure that incorporates both crystalline and amorphous P3HT regions. In particular, the phase segregation of PCBM is known to influence ordering of the polymer regions and hence device function. The diffusion constant of PCBM in P3HT has been investigated as a function of dPCBM volume fraction and temperature; reporting a diffusion constant of 2.5 x 10^{-10} cm^2 s^{-1} for PCBM diffusion in a P3HT matrix at 140 °C. Subsequently, Labram et al. used electron field-effect mobility models to estimate a diffusion constant of 5 x 10^{-14} cm^2 s^{-1} for PC_61BM diffusion and 1.1 x 10^{-14} cm^2 s^{-1} for PC_71BM diffusion in P3HT matrices at 130 °C and 160 °C respectively. In an alternative approach, Treat et al. used dynamic secondary ion mass spectrometry (DSIMS) to probe the diffusion of deuterated PCBM (dPCBM) into P3HT:dPCBM blends. Their initial studies reported an interdiffusion coefficient of 3.0 x 10^{-10} cm^2 s^{-1}. More recently, however, they have extended their approach to obtain diffusion constants for dPCBM diffusion in P3HT:dPCBM blends as a function of dPCBM volume fraction and temperature; reporting a diffusion constant of 2.2 x 10^{-11} and 5.7 x 10^{-11} cm^2 s^{-1} for diffusion at 50 °C and 70 °C respectively.

In this letter, we use multi-wavelength scanning absorption microscopy (MWSAM) to probe the diffusion of PCBM in P3HT:PCBM blend materials and obtain diffusion constants and activation energies for the governing mass transport processes in this system. We show that the formation

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of PCBM-rich phase segregated features in these systems occurs via the diffusion of PCBM crystallites rather than molecular PCBM. The recognition that there are two distinct diffusion processes allows us to resolve the controversy over the measured diffusion constant for PCBM in P3HT and hence present a unified picture for mass transport in these important organic electronic materials.

Figure 1(a) shows the multi-wavelength scanning absorption microscopy (MWSAM) image for a PCBM-rich structure formed by annealing a 1:1 P3HT:PCBM film on a glass substrate for 40 minutes at 140°C. All P3HT:PCBM blend films used throughout this investigation were spin

![Figure 1](image_url)

**FIG. 1.** (a) Scanning absorption microscopy (SAM) composition map of a film containing a PCBM-rich, phase segregated feature. Profiles were taken along the black lines and used to calculate diffusion rates both perpendicular and parallel to the major axis. The colour side scale bar indicates the fraction of PCBM in the film, whilst the lateral scale bar is 10 μm. (b) The perpendicular PCBM composition profile showing the highlighted data points used to determine the feature boundary. The feature edge points are marked as red filled circles and fitted with a straight line, while the depletion edge points are plotted as blue filled squares and fitted with a quadratic function. The intersection between the straight line and quadratic was taken to be the boundary (large open red circle). (c) Experimental perpendicular PCBM composition profile (red dots) along with the fitted solution to the diffusion equation (solid blue line). The error bars are estimated from the standard deviation of the PCBM concentration profile far from the phase segregated region.
coated from a 25 mg/ml chloroform solution with a blend ratio of 1:1 (w/w). The P3HT used was synthesised in-house at the Centre for Organic Electronics, University of Newcastle, and had a molecular weight of 43 kg mol\(^{-1}\) and a regioregularity of 95% while the PCBM was used as received from Solenne. The MWSAM technique generates quantitative composition maps of thin organic films\(^{17}\); in this case the contrast map gives the PCBM weight fraction in the film. The image clearly shows the presence of an asymmetric PCBM-rich feature surrounded by an annular depletion region of lower PCBM concentration. Moreover, the depletion region is larger along the long (major) axis, and smaller along the short (perpendicular) axis, of the feature.

We have previously shown that the growing PCBM-rich structure creates a localized sink for PCBM diffusion within the P3HT matrix resulting in the observed depletion region.\(^9\) Thus, by annealing the 1:1 P3HT:PCBM films at different temperatures, and assuming an initial even distribution of PCBM, the resulting composition maps can be used to determine the diffusion rate of PCBM in the P3HT matrix from Fick’s second law of diffusion\(^9\):

\[
\frac{\partial \phi}{\partial t} = -D \frac{\partial^2 \phi}{\partial x^2}
\]

Where \(\phi\) represents the PCBM concentration, \(D\) is the diffusion constant and \(x\) and \(t\) represent dimensions of space and time respectively. The effect of vertical stratification of P3HT:PCBM blends\(^{18–21}\) can be ignored as the film is only \(\sim 100\) nm thick; 2 orders of magnitude smaller than the lateral diffusion which extends over \(\sim 10\)–20 \(\mu\)m.

Figure 1(b) shows the 1-D perpendicular PCBM composition profile from the centre of the phase segregated region. The boundary of the depletion region was found from the intersection of a straight line fitted to the falling edge of the PCBM-rich feature and a quadratic fitted to the rising edge of the depletion region (red and blue highlighted points in Figure 1(b) respectively). The PCBM diffusion constant was obtained by fitting the PCBM composition profile to the 1-D solution to Fick’s second law\(^9\):

\[
\phi = \phi_b + (\phi_0 - \phi_b) \frac{4}{\pi} \sum_{m=1}^{\infty} \frac{1}{m} \sin \left( \frac{m\pi x}{L} \right) e^{-D\pi^2(m^2)}
\]

Where \(\phi_0\) and \(\phi_b\) represent the initial PCBM concentration within the film and the equilibrium concentration found at the base of the aggregate and \(L\) is the distance between neighbouring aggregates.

Figure 1(c) shows the fit to the solution to Fick’s Law along with the experimental PCBM composition profile across the depletion region (the PCBM-rich feature is treated as a sink and is omitted from the profile). There is excellent agreement between experiment and fit, which yields a diffusion constant of \(1.1 \times 10^{-11}\) cm\(^2\) s\(^{-1}\) in the direction perpendicular to the major axis. A similar analysis was carried out for the parallel profile as well as for phase segregated structures formed at higher temperatures. At higher temperatures, the anneal time was reduced in order to keep the phase segregated regions roughly the same size and the results are summarised in Table I. We speculate that the greater diffusion constant perpendicular to the aggregate axis can be attributed to a greater concentration gradient found in the depletion region along the long edge of the aggregate compared to the depletion regions at the ends. Further modelling and experimentation is underway to determine the underlying cause of the asymmetry in the aggregate.

**TABLE I.** Diffusion constants for PCBM diffusion perpendicular and parallel to the major aggregate axis in a P3HT matrix at various temperatures.

<table>
<thead>
<tr>
<th>Anneal Temperature (°C)</th>
<th>Anneal Time (min)</th>
<th>(D_{\text{perpendicular}}) (cm(^2) s(^{-1}))</th>
<th>(D_{\text{parallel}}) (cm(^2) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>140</td>
<td>40</td>
<td>(1.1 \times 10^{-11})</td>
<td>(0.88 \times 10^{-11})</td>
</tr>
<tr>
<td>150</td>
<td>15</td>
<td>(3.4 \times 10^{-11})</td>
<td>(2.2 \times 10^{-11})</td>
</tr>
<tr>
<td>160</td>
<td>10</td>
<td>(16.5 \times 10^{-11})</td>
<td>(3.4 \times 10^{-11})</td>
</tr>
<tr>
<td>170</td>
<td>4</td>
<td>(16.7 \times 10^{-11})</td>
<td>(6.3 \times 10^{-11})</td>
</tr>
</tbody>
</table>
The diffusion of PCBM in a P3HT matrix can be modelled as an Arrhenius process such that:

\[ D = A e^{-\frac{E_a}{RT}} \]

Where \( D \) is the diffusion constant, \( E_a \) is the activation energy for the diffusion, \( R \) is the universal gas constant, \( T \) is the temperature and \( A \) is the pre-exponential factor. Figure 2 shows the plot of the natural logarithm of the diffusion rate against the inverse of temperature at which that diffusion occurred. The calculated slopes of the straight line fits to the data reveal that the activation energy for diffusion perpendicular to the aggregate major axis is \( 148 \pm 36 \text{ kJ mol}^{-1} \) (~1.53 eV/molecule) and parallel to the axis is \( 97 \pm 9 \text{ kJ mol}^{-1} \) (1 eV/molecule), where the uncertainties in the measurements were taken from the standard deviation of the slope.

The measured activation energies lie well outside the range \( (50 \text{ kJ mol}^{-1} – 80 \text{ kJ mol}^{-1}) \) (0.52 eV/molecule – 0.83 eV/molecule) for molecular diffusion in polymers.\(^{22,23}\) As such, the diffusion behaviour reported here is consistent with a model whereby the phase segregated structures formed during the annealing of P3HT:PCBM blends are not single crystals but rather consist of aggregates of smaller PCBM crystallites of dimension \( \sim 50 \text{ nm} \). By contrast, the activation energy of 65.5 kJ mol\(^{-1}\) (0.68 eV/molecule) for dPCBM diffusion in P3HT:dPCBM films with very low PCBM content \( (\phi_{\text{PCBM}} = 1\% ) \) reported by Treat et al. does lie within the range expected for molecular diffusion of PCBM in a P3HT matrix.\(^{16}\)

In order to understand the effect of diffusing moiety size upon the diffusion constant, let us consider the mobility of both molecular PCBM and PCBM crystallites within a P3HT matrix. In general, the diffusion constant, \( D \), for a particle of a given radius, \( R \), is given by the Stokes-Einstein equation\(^{24}\):

\[ D = \frac{k_B T}{6\pi \eta R} \]

Where, \( k_B \) is the Boltzmann constant; \( T \) is the temperature and \( \eta \) is the viscosity of the P3HT matrix, which varies with temperature for linear polymers such as P3HT.\(^{25}\) The corollary is that for a fixed annealing temperature the viscosity of the P3HT matrix is invariant. Thus, for the same polymer matrix at a fixed temperature, a particle’s mobility decreases as \( R^{-1} \) and, consequently, the diffusion constant for molecular PCBM (\( R = 0.5 \text{ nm} \)) will be 50 times greater than that of the PCBM crystallites (\( R = 25 \text{ nm} \)). Therefore, in order to compare the diffusion constants of PCBM crystallites with molecular PCBM, we have corrected our data by this Stokes-Einstein factor.

We have observed that there are two distinct mass transport processes involved in phase segregation of PCBM in a P3HT:PCBM blend matrix. Firstly, there is the rapid formation of PCBM crystallites of diameter \( \sim 50 \text{ nm} \), which (based on Treat’s work\(^{15}\)) occurs spontaneously upon film formation on the timescale of seconds at the typical annealing temperatures used for P3HT:PCBM
blends. Secondly, diffusion of PCBM crystallites occurs to form macroscale aggregates, which occurs on the timescale of minutes to hours. Therefore, the value of the diffusion constant that is measured depends on the overriding process, which is, in turn, a function of the precise details and timescale of the experimental set-up.

The observation that two distinct mass transport processes are involved in the phase separation of P3HT:PCBM blends has important implications for the formation of stable device morphologies. The initial rapid diffusion and crystallisation of the PCBM results in the formation of metastable morphology consisting of nanoscale crystallites throughout the blend film. Importantly, it is the formation of corresponding regions of PCBM depletion which act to stabilise the film morphology by restricting nanocrystallite growth. After this initial crystallisation, the film will be left in a metastable state since the second mass transport process of the nanocrystals has a higher activation energy. This higher activation energy for the diffusion of the nanocrystals explains why larger aggregates are not observed in P3HT:PCBM active layer blends until they have been annealed at elevated temperature or after extended periods of time.

Since Watt’s et al. observed PCBM phase segregation on the timescale of minutes to hours, the prevailing mass transport process must involve the diffusion of nanoscale PCBM crystallites rather than molecular PCBM. To test this hypothesis, we have applied the same Stokes-Einstein correction factor for a PCBM crystallite ($R = 25$ nm) to the reported diffusion constant ($2.5 \times 10^{-10} \text{cm}^2\text{s}^{-1}$).

Figure 3(a) shows an Arrhenius plot of diffusion constants from this study and the value reported by Watts et al. as well as the values (and straight line fits) for dPCBM diffusion in P3HT:dPCBM blends.

![Diagram](image-url)

**FIG. 3.** (a) Diffusion constants for diffusion perpendicular to (open red squares) and parallel to (open red diamonds) the major axis, as well as the constant (open red triangle) measured by Watts et al. Also plotted are the diffusion rates for dPCBM diffusing through a P3HT matrix with different dPCBM volume fractions: 0 (filled grey circles), 0.001 (open grey circles) and 0.05 – 0.1 (open circles). Also shown are the composition independent diffusion rates (filled black circles). The dashed lines show the extrapolated straight line fits to the diffusion constants in Ref. 16. (b) Same as for (a) where the diffusion constants for diffusion perpendicular to (filled red squares) and parallel to (filled red diamonds) the major axis, as well as the constant (filled red triangle) measured by Watts et al. have been adjusted using the Stokes-Einstein size ($R=25$nm) correction factor.
films as a function of dPCBM volume fraction reported by Teat et al. Figure 3(a) highlights the apparent discrepancy between the two sets of data, indicating that the measured diffusion constants differ by around 2 orders of magnitude. Figure 3(b) shows the effect of applying the Stokes-Einstein size correction to the diffusion constants. We now observe an excellent correlation between the two datasets, with all of the data lying within, or very close to, the extrapolated straight line fits. Moreover, the diffusion constants presented in this work lie closest to the values for dPCBM diffusing in a P3HT:dPCBM blend with a higher dPCBM content; consistent with our experimental conditions for crystallite diffusion. The remaining small differences between the three datasets can now readily be explained by differences in the P3HT matrices used (e.g. polymer molecular weight).

In summary, PCBM mass transport in P3HT:PCBM blends is highly complex and occurs via two distinct mechanisms: (a) diffusion of molecular PCBM and/or (b) diffusion of PCBM crystallites of dimension ~50 nm. By identifying these two diffusion mechanisms, we have been able to reconcile the significant differences in the diffusion constant reported previously. We show that for PCBM volume fractions relevant to P3HT:PCBM device blends, the formation and diffusion of PCBM crystallites is a significant process and occurs with a diffusion constant in the range of $10^{-11} - 10^{-10}$ cm$^2$ s$^{-1}$ and an activation energy of 97 - 148 kJ mol$^{-1}$ for temperatures relevant to P3HT:PCBM device processing. Further work is underway to determine the key thermodynamic and kinetic drivers for the formation of these crystallites and subsequent aggregates.

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22 P. Neogi, Diffusion in Polymers (Marcel Dekker, New York, 1996).