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Supporting information for "New Insights into Dynamics and Morphology of P3HT:PCBM Active Layers in Bulk Heterojunctions"

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Simulation protocol

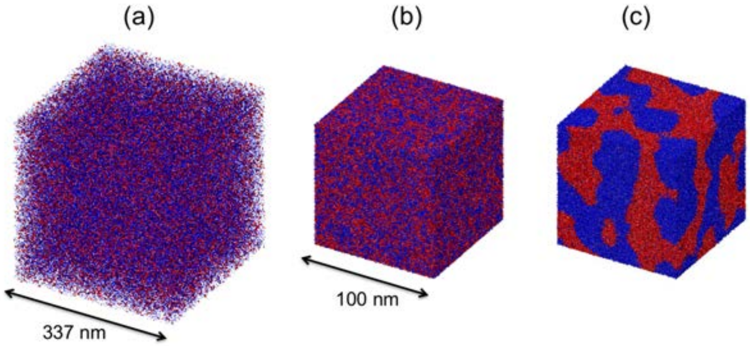


Fig. S 1: Simulation steps showing the thermal annealing of an active layer for a P3HT:PCBM bulk heterojunction structure at 423 K where the P3HT monomers and PCBM beads are colored in red and blue respectively. (a) Initial configuration of the P3HT:PCBM system with N=100, m=32,400 and $\phi_m = 0.5$. (b) Configuration after compression at constant T using Langevin thermostat and initial configuration of the isobaric-isothermal runs. (c) Final configuration (t = 400 ns) of the isobaric-isothermal run.

Persistence length, l_p of the coarse-grained P3HT model

The coarse-grained polymer chain is a chain model with hindered rotations and the persistence length l_p is half the Kuhn length b_k. The equation of the Kuhn length is[1]

$$b_k = \frac{b}{\cos(\theta_0/2)}\left(\frac{1+\cos(\theta_0)}{1-\cos(\theta_0)}\right)\left(\frac{1+\langle\cos(\phi)\rangle}{1-\langle\cos(\phi)\rangle}\right) \tag{S-1}$$

The force field that defines the polymer chain already specifies the values of b, which is the equilibrium bond length of the harmonic bond; and θ_0, which is the equilibrium bond angle of the harmonic angle. The average value of the cosine of the dihedral angle, $\langle\cos(\phi)\rangle$ of the P3HT chain can be estimated from the probabilities determined by the Botlzmann factor $e^{(-U_{dihedral}(\phi_i)/k_BT)}$

$$\langle\cos(\phi)\rangle = \frac{\int_0^{2\pi}\cos(\phi)e^{(-U_{dihedral}(\phi_i)/k_BT)}d\phi}{\int_0^{2\pi}e^{(-U_{dihedral}(\phi_i)/k_BT)}d\phi} \tag{S-2}$$

Single P3HT chain simulations and P3HT melt simulations of m = 1,200 chains with degree of polymerization N = 100 were carried out to calculate the persistence length of the P3HT chain in vacuum and in the melt. The single chain simulation was carried out in a periodic simulation box with the size of its dimensions equal to $4Nb$, which is large enough to minimize the interaction of the polymer chain with its periodic image. The temperature in the NVT ensemble was set to 423 K and controlled using a Langevin thermostat with a coupling constant of 0.1 ps. The P3HT melt simulation was performed at an NPT ensemble using a Nose-Hoover thermostat and barostat with set points equal to $T = 423$ K and $P = 1$ atm and with coupling constants 0.1 ps for the temperature and 1.0 ps for the pressure. The calculated persistence length l_p and the average values of the bond length b, cosine of the angle between two neighboring bonds $\langle \cos(\theta) \rangle$ and the cosine of the torsion angle $\langle \cos(\phi) \rangle$ from the force field parameters, single chain simulation and melt simulation are tabulated in table 1. The expected value of the persistence length is 37.8 Å, which is in the vicinity of the chain in vacuum (35.0 Å), melt simulations (35.6 Å), and experiments (24 Å, 33 Å).

Table. S 1: Persistence length calculated from the force field, single P3HT chain and P3HT chain in the melt

Parameter	Force Field Set Point	Single Chain	P3HT Melt
Bond length, $\langle b \rangle$	3.82 Å	3.82 ± 0.06 Å	3.82 ± 0.06 Å
Bond angle[a], $\langle \cos(\theta) \rangle$	0.882	0.873 ± 0.04	0.873 ± 0.04
Torsion angle[b], $\langle \cos(\phi) \rangle$	0.0948	0.092 ± 0.6	0.099 ± 0.6
Persistence length, l_p	37.8 Å	35.0 Å	35.6 Å

[a] $\theta = 0$ pertains to collinear bonds.
[b] $\phi = 0$ pertains to the trans torsion angle.

PCBM diffusion coefficient, D

We estimated the diffusion coefficient of PCBM isolated by P3HT monomers by calculating the mean square displacement $\langle \Delta r(t)^2 \rangle$, of isolated PCBM beads. By employing the radical Voronio tessellation [2] these beads were identified and their trajectories were used in the calculation of $\langle \Delta r(t)^2 \rangle$. The three dimensional diffusion coefficient is proportional to the mean squared displacement

$$D = \lim_{t \to \infty} \frac{1}{6t} \left\langle [\vec{r}(t + \Delta t) - \vec{r}(t)]^2 \right\rangle \tag{S-3}$$

The results of the mean squared displacement calculations using the trajectories from 250 to 400 ns were plotted in figure S2 where the data from 2-5 ns were fitted with the equation

$$\left\langle [\vec{r}(t + \Delta t) - \vec{r}(t)]^2 \right\rangle = \left\langle \Delta r(t)^2 \right\rangle = 6Dt + \alpha \tag{S-4}$$

where α is a constant and D is the diffusion coefficient. The calculated diffusion coefficient, $D = 33.94$ Å^2/ns is 679 times the reported value by Treat *et al.*[3] which makes the simulation 679 times faster than experiments. The equivalent "real" time that the simulations were ran is approximately 0.27 ms.

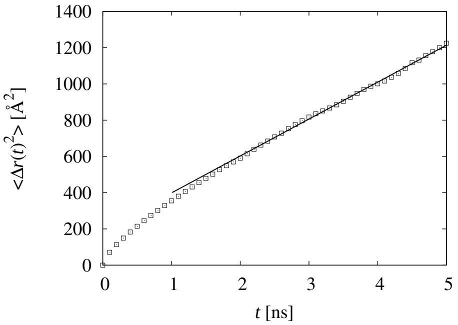


Fig. S 2: Mean squared displacement $\langle \Delta r(t)^2 \rangle$, of isolated PCBM beads in the P3HT matrix for the P3HT:PCBM system with $N = 100$, $\phi_m = 0.5$ and $m = 1200$. The line corresponds to eq S-4 where $D = 33.94$ Å^2/ns and $\alpha = 195.2$ Å^2.

Flory-Huggins χ paramter

In the calculation of the free energy of the Flory-Huggins[4] equation for polymer solutions, the free energy consists of two parts, which are the entropy of binary mixing and the energy of binary mixing. In the latter term, the energy change on mixing per lattice site is

$$\Delta U_{mix} = \chi \phi_v (1 - \phi_v) k_B T \tag{S-5}$$

where χ is the Flory interaction parameter and ϕ_v is the polymer volume fraction. The energy change on mixing per lattice site ΔU_{mix} can be estimated by running three separate NPT ensemble simulations; (1) simulation of pure PCBM beads, (2) simulation of pure P3HT polymers and (3) simulation of the mixture. In each of the three simulations, the pair energy per bead is [5]

$$U/n_{\mathrm{TOTAL}} = 2\pi\rho \int_0^\infty r^2 u(r) g(r) dr \tag{S-6}$$

where ρ is the number density, $u(r)$ is the Lennard-Jones pair potential and $g(r)$ is the radial distribution function. Fortunately, in molecular dynamics the pair energy is evaluated in order to evaluate the forces acting on each of the particle. In this regard, the pair energy per bead is readily available and equation S-6 need not be evaluated.

In the third simulation, the probability of the P3HT monomer finding another P3HT monomer is equal to the P3HT volume fraction ϕ_v such that the number of sites occupied by the P3HT polymer chains is equal to $n\phi_v$ where n is equal to the number of sites in the mixture. The number of lattice sites n is equal to the combined volume of the P3HT polymers and the PCBM beads (volume of the simulation box of the 3$^{\mathrm{rd}}$ simulation) divided by the smallest unit volume v_0, which is the volume of the solvent or the volume of the PCBM bead.

The volume fraction of P3HT ϕ_v can be estimated by taking the ratio of the voronio volumes belonging to the P3HT monomer divided by the volume of the simulation box. The radical voronio tessellation code in the voro++[2] library was used to determine the voronoi cell volumes where the size of the P3HT monomers and PCBM beads were used for the tessellation weights. In a similar fashion, the smallest unit volume v_0, was estimated by averaging the volume of the PCBM voronoi cells that does not touch a P3HT monomer. For the system with N = 75, m =1,200 and ϕ_m = 0.5, the value of the P3HT volume fraction is ϕ_v = 0.476 and the lattice volume, v_0 = 891 Å^3. The energy change of mixing per lattice site is therefore

$$\begin{aligned} \Delta U_{mix} =& \frac{(n_{\mathrm{P3HT}} + n_{\mathrm{PCBM}})_3 (U/n_{\mathrm{TOTAL}})_3}{(V/v_0)_3} \\ &- \frac{(n_{\mathrm{P3HT}})_3 (U/n_{\mathrm{TOTAL}})_2}{(V/v_0)_3} \\ &- \frac{(n_{\mathrm{PCBM}})_3 (U/n_{\mathrm{TOTAL}})_1}{(V/v_0)_3} \end{aligned} \tag{S-7}$$

where the subscript in the parenthesis denotes the type of simulation where the value is derived (*i.e.* $(\ldots)_1$,$(\ldots)_2$ and $(\ldots)_3$ denotes the values were derived from the pure PCBM, pure P3HT polymer and the mixture of P3HT and PCBM simulations respectively). For the system with N = 75, m = 1,200 and ϕ_m = 0.5, ΔU_{mix} is equal 0.193 kcal/mol and using equation S-7 will result to a Flory interaction parameter χ that is equal to 0.92 ± 0.10.

Interface-to-volume ratio γ

Radical Voronoi tessellation was performed using the coordinates of the Lennard-Jones beads in the simulation box using the voro++[2] library. The size of the Lennard-Jones beads are calculated using the method by Barker and Henderson[6] shown in eq 4 of the text in the main article and were used as the weights for the radical Voronoi tessellation. Figure S3 shows the Voronoi faces of the P3HT/PCBM interface of the P3HT:PCBM system with N=100, m=1200 and ϕ_m = 0.5.

Pore size distribution $P(D_{\mathrm{PSD}})$

To quantify the domain size of the P3HT polymer matrix, we used the method described by Bhattacharya and Gubbins [7] where we calculated the pore size distribution by removing all the P3HT chains in the simulation box and calculating the pore size of the remaining PCBM network. The PCBM network is analogous to the pore cavity wall and the PCBM beads that were dissolved in the polymer matrix were removed in determining the pore size distribution. Figure S4(a) illustrates how the pore size diameter was determined. The simulation box was divided into grid points e.g. P and spheres were grown that encompasses the grid point P. The maximum radius encompassing the point P is the pore diameter at this point. A cumulative histogram was constructed $H(D_{\mathrm{PSD}})$ where $H(D_{\mathrm{PSD}})$

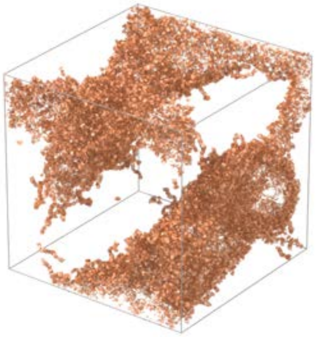
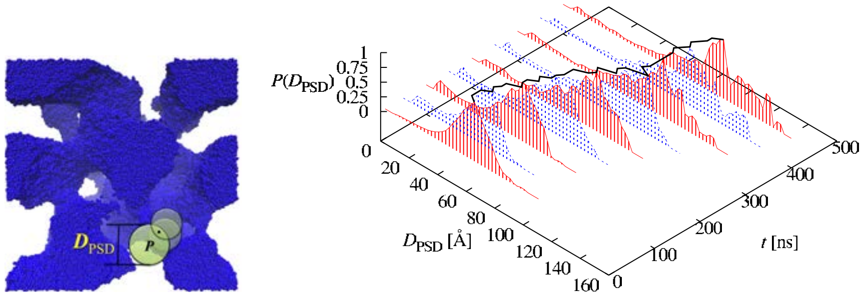


Fig. S 3: Voronoi faces of the P3HT/PCBM interface calculated, using radical Voronoi tessellation using voro++[2] library, of the P3HT:PCBM system with N=100, m=1200 and $\phi_m = 0.5$.



(a) (b)

Fig. S 4: $D_{\rm PSD}$ is the diameter of the largest sphere that encompasses point P without intersecting the cavity wall defined by the coordinates of the PCBM beads (a). Evolution of the pore size distribution $P(D_{\rm PSD})$ of the P3HT:PCBM system with $N = 100$, $\phi_m = 0.5$ and $m = 32{,}400$ where the black curve is the location of the $P(D_{\rm PSD})$ peak (b).

represents the probability of finding a point in the simulation box with a pore size greater than or equal to $D_{\rm PSD}$ and the pore size distribution $P(D_{\rm PSD})$ is equal to the negative of the derivative of $H(D_{\rm PSD})$ with respect to $D_{\rm PSD}$

$$P(D_{\rm PSD}) = -\frac{{\rm d}H(D_{\rm PSD})}{{\rm d}D_{\rm PSD}} \tag{S-8}$$

The evolution of the pore size distribution $P(D_{\rm PSD})$ for most of the $N \times m = 3,240,000$ P3HT:PCBM blends were calculated with a resolution of 2.5 Å and an average error of 0.05%. Figure S4(b) shows the evolution of $P(D_{\rm PSD})$ for P3HT:PCBM blend with $N = 100$, $\phi_m = 0.5$ and $m = 32{,}400$. The calculation of $P(D_{\rm PSD})$ is not accurate in initial configurations before the onset of domain formation. The plot in Fig. 4(b) do not show values for $P(D_{\rm PSD})$ when greater than 80% of the PCBM molecules have no contact with other PCBM molecules.

Scattering function, $S(q,t)$

We used the scattering function $S(\vec{q})$ of the P3HT chains where $S(\vec{q})$ is defined as

$$S(\vec{q}) = \frac{1}{N \times m} \sum_{k,j}^{N\times m} \exp(\imath(\vec{q} \cdot (\vec{r}_k - \vec{r}_j))) \tag{S-9}$$

The summation is taken all over the total number of P3HT coarse-grained monomer beads in the system $N \times m$ and $\vec{r}_k$ is the radius vector of the k_{th} monomer. The scattering function can be obtained by taking the Fourier transform of the spatial density distribution of the P3HT monomers,

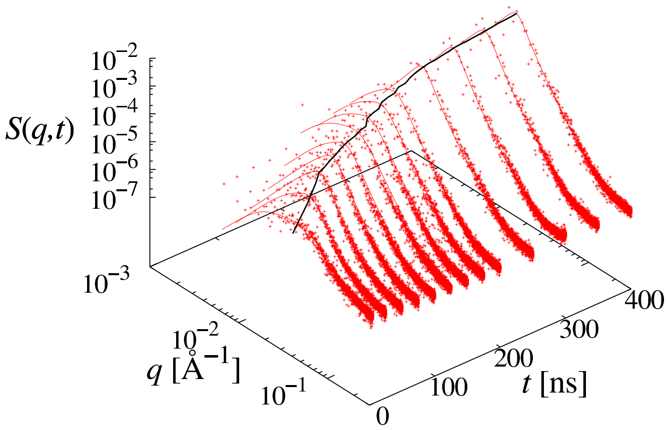


Fig. S 5: Evolution of the scattering function $S(q,t)$ of P3HT monomers for the P3HT:PCBM system with $N = 100$, $\phi_m = 0.5$ and $m =$ 32,400 (c). The red curves are fits using eq 7 and the black curve is the plot peak of the $S(q,t)$ vs. t plot.

$$\rho(\vec{q}) = \sum_{k,j}^{N\times m} \exp(\imath(\vec{q}\cdot\vec{r}_k)) \tag{S-10}$$

Such that the scattering function $S(\vec{q})$ can be written in terms of $\rho(\vec{q})$ as

$$S(\vec{q}) = \frac{1}{N\times m}\langle\rho(\vec{q})\rho(-\vec{q})\rangle \tag{S-11}$$

In one snapshot or frame of the molecular dynamics simulation, the calculation of the Fourier transform of the density distribution can be done by using the Fast Fourier Transform (FFT) method where the monomer density distribution are represented in a 3 dimensional grid of size $\Delta\times\Delta\times\Delta$ such that the total number of grids N_g is equal to $(L/\Delta)^3$ where L is the length of one side of the simulation box. $N_g^{1/3}$ is equal to the rounded off value to the nearest integer of ($L/10$ Å) such that Δ is approximately equal to 1 nm. The Fourier space density distribution $\rho(\vec{q})$ is now represented as

$$\rho(\vec{q}) = \rho(u,v,w) = \sum_{k,j}^{N\times m} \exp\left(\imath\frac{2\pi}{N_g}(lx+ly+lz)\right) n(x,y,z) \tag{S-12}$$

where $n(x,y,z)$ is the number of monomers in the grid with coordinates x, y and z. The 3 dimensional wave vector has its three components as $q_x = 2\pi u/L$, $q_y = 2\pi v/L$, $q_z = 2\pi w/L$ and magnitude equal to $q = (q_x^2+q_y^2+q_z^2)^{1/2}$. The result of the FFT calculation is the complex function $\rho(u,v,w)$ and the scattering function $S(u,v,w)$ is equal to the product of the complex conjugates of $\rho(u,v,w)$ and normalized by the number of P3HT monomers

$$S(u,v,w) = \frac{1}{N\times m}\left[(\Re(\rho(u,v,w)))^2 + (\Im(\rho(u,v,w)))^2\right] \tag{S-13}$$

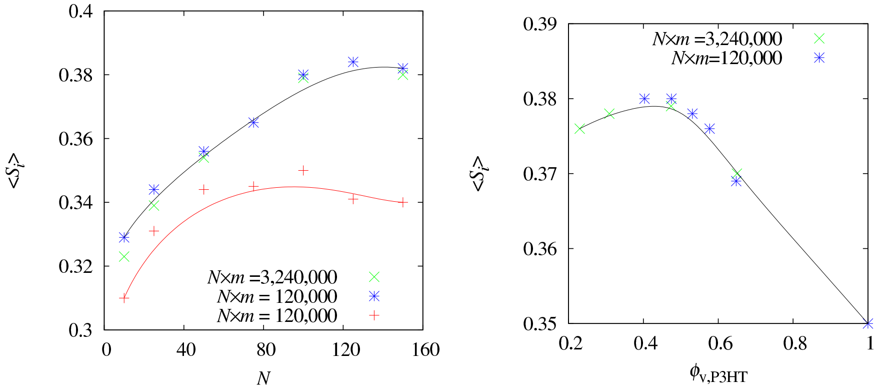
where $\Re(\rho(u,v,w))$ and $\Im(\rho(u,v,w))$ are the real and imaginary parts of the function $\rho(u,v,w)$.

Orientational order parameter, S_i

The local orientational order parameter of bond i, S_i, is defined as the average of the second Legendre polynomial of $\cos(\theta_i)$ where θ_i is the angle made by the P3HT bond to the director unit vector $\vec{n}_i$:

$$S_i = \langle P_2(\cos\theta_i)\rangle = \left\langle\frac{3\cos^2\theta_i - 1}{2}\right\rangle \tag{S-14}$$

The director unit vector $\vec{n}_i$ was determined by taking the minimum of $\sum_j(1-(\vec{n}_i\cdot\vec{n}_j)^2)$ for a set unit vectors defined by bonds that are the nearest neighbor bonds of bond i. Bond i is included in the set of bonds. The list of nearest neighbors of bond i was determined by using the radical Voronoi tessellation where a bond was considered as a single particle with a radius equal to two P3HT monomers and the location is defined by the center of mass of



(a) (b)

Fig. S 6: Average local orientational order parameter $\langle S_i \rangle$ for the P3HT melt (red) and P3HT blend at $\phi_m = 0.5$ (green and blue) at different P3HT degrees of polymerization N(a). Average orientational order parameter $\langle S_i \rangle$ for the P3HT blend with $N = 100$ and different P3HT volume fractions ϕ_v (b).

the two P3HT monomers. The PCBM beads were included in the Voronoi tessellation to serve as domain boundaries when the director unit vector is calculated.

Figure S6 plots the relationship of the average local orientational order parameter $\langle S_i \rangle$ for $\phi_m = 0.5$ and $\phi_m = 1.0$ and different degrees of polymerization N (fig S6(a)) and at constant value of N and different values of ϕ_m. (fig S6(b)). We can observe from figure S6(a) that the neat polymer has a lower orientational order parameter for all chain degrees of polymerization. This indicates that the presence of PCBM induces local alignment.

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