Electronic Supplementary Information

**Strong Polymer Molecular Weight–Dependent Material Interactions: Impact on Formation of Polymer/Fullerene Bulk Heterojunction Morphology**

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Fig. S1. (a) Material contrast followed by integrated scattering intensity (ISI), extracted from R-SoXS profiles of PDPP3T:PC$_{71}$BM blends. PDPP3T has three different MWs of 43, 73, and 102 kDa. (b) Scattering anisotropy of the blend films, obtained from three MWs of PDPP3T and three solvent combinations. Anisotropy does not seem to be distinctly changing for all applied blend films. The molecular orientation relative to the heterointerface does not change much in these set of samples.  

Fig. S2. Contact angle measurements from droplets of DIO and DCB on the PDPP3T films with different molecular weights (MWs).

**Understanding the aggregation and solvation behavior of polymer chains**

UV-Vis absorption spectra was exploited to exhibit the effect of different solvent/additives on the aggregation of polymer chains for different MW polymers in their
blend (Fig. S3) and pristine solution (Fig. S5). The measurements were performed at different temperatures to simulate the formation of aggregations in the blend solution and compared with the spectra of the blend film. As inferred from UV-Vis data, the solution UV-vis spectra of the high MW polymer approaches the spectra of the blend film. The peak intensities of $A_{0-1}$ at ~730 nm denote the homocoupling and peaks of $A_{0-0}$ at ~790 nm represent the interchain interactions which are less developed at high temperatures. The red-shift and increasing $A_{0-0}/A_{0-1}$ peak ratio in normalized UV-Vis spectra were observed for the low temperature solutions for all applied MWs and solvent combinations. The increasing peak ratio manifests the increasing planar conformation of polymer chains.\textsuperscript{2,3} For higher MWs, DIO additives induced more interchain interactions among polymer chains in their blend solution. The DIO additive seems to hardly affect the aggregation behavior for the low MW PDPP3T but it enhanced the emerging aggregation for the higher MW PDPP3T. The higher MW and DIO additives induced the aggregation in the solution which created the multiple polymer seeds in the solution. On the contrary, PC\textsubscript{71}BM peaks at 375 and 460 nm were not changed much for the different temperatures, MWs, and additives. Therefore, it can be inferred that during the film formation, PC\textsubscript{71}BM particles are intercalated into the spaces among the polymer chains once the polymer chains form aggregated guidance during the morphology formation, corroborated well with the low $\chi$ between PC\textsubscript{71}BM and DCB.
Fig. S3. Normalized UV-Vis spectra of PDPP3T and PC$_7$BM blend solutions from various MWs and solvents, measured as varying temperatures ranging from 25 to 100 °C. The solution UV-Vis spectra were compared with the spectra from corresponding blend films (dotted lines) to show the film formation processes.
Fig. S4. Swelled volume of pristine PDPP3T films from different MWs. The films were exposed to (a) CF, (b) DCB, and (c) DIO during measurements.
Fig. S5. UV-Vis spectra of pristine PDPP3T solutions from various MWs in DCB solvent, measured with varying temperatures ranging from 25 to 100 °C. Peak ratio of $A_{0,0}/A_{0,1}$ increases for the higher MW solution which is the same trend of the solution UV from the blend solutions.

Fig. S6. (a) 2D GIWAXS patterns and (b) 1D profiles of the PDPP3T and PC$_{71}$BM blends from the polymer MWs of 43, 73, and 102 kDa and solvent combinations of DCB and DCB/CF/DIO.
Fig. S7. (a) light absorption, and (b) IQE results of devices from PDPP3T with different MWs and PC\textsubscript{71}BM blends, cast from DCB and DCB/CF/DIO solvents. Light absorption was calculated from refractive index, evaluated by an ellipsometry.\textsuperscript{4}

Table S1. Photovoltaic properties of devices from 43, 73, and 102 kDa PDPP3T and solvent combinations of DCB and DCB/CF/DIO.

<table>
<thead>
<tr>
<th>Blend from polymer in solvent</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
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<tbody>
<tr>
<td>Blend from 43 kDa polymer in DCB</td>
<td>0.572 ± 0.005</td>
<td>4.14 ± 0.11</td>
<td>58.9 ± 0.4</td>
<td>1.40 ± 0.02</td>
</tr>
<tr>
<td>Blend from 73 kDa polymer in DCB</td>
<td>0.654 ± 0.002</td>
<td>8.47 ± 0.30</td>
<td>60.5 ± 0.5</td>
<td>2.90 ± 0.25</td>
</tr>
<tr>
<td>Blend from 102 kDa polymer in DCB</td>
<td>0.634 ± 0.003</td>
<td>11.1 ± 0.53</td>
<td>62.4 ± 1.5</td>
<td>4.30 ± 0.14</td>
</tr>
<tr>
<td>Blend from 43 kDa polymer in DCB/CF/DIO</td>
<td>0.622 ± 0.024</td>
<td>11.5 ± 0.46</td>
<td>65.1 ± 0.6</td>
<td>4.65 ± 0.27</td>
</tr>
<tr>
<td>Blend from 73 kDa polymer in DCB/CF/DIO</td>
<td>0.663 ± 0.006</td>
<td>16.3 ± 0.34</td>
<td>65.2 ± 1.3</td>
<td>7.02 ± 0.03</td>
</tr>
<tr>
<td>Blend from 102 kDa polymer in DCB/CF/DIO</td>
<td>0.627 ± 0.004</td>
<td>16.0 ± 0.43</td>
<td>60.5 ± 1.2</td>
<td>6.07 ± 0.10</td>
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Evaluation of the interactions between polymer and fullerene by STXM
The effect of $\chi_{\text{PDPP3T-PC}}$ were evaluated from the miscibility of the amorphous mixed regions of equilibrium morphologies. Polymer:fullerene BHJ films were thermally annealed at 180 °C for three consecutive days and then imaged by a scanning transmission X-ray microscope (STXM) near carbon edge 284.4 eV (Fig. S9), from which the degree of miscibility was evaluated. The miscibilities of PDPP3T:PC$_{71}$BM blend films were evaluated by analyzing the PC$_{71}$BM compositions at equilibrium condition. Accordingly, the miscibilities of the low MW, medium MW and high MW polymers were found to be 4.9, 4.4, and 3.2 %, respectively (Fig. S9d). The decreasing trend of fullerene miscibility with MW is consistent with the observed increase of polymer–fullerene repulsive interaction as denoted by large $\chi_{\text{PDPP3T-PC}}$. 

(a) 

(b) 

(c) 

(d)
Fig. S8. Fitted STXM spectra of PDPP3T from (a) 43, (b) 73, and 102 kDa and PC_{71}BM blend films, acquired at 284.4 eV. (d) Fullerene miscibility in amorphous mixed region at equilibrium morphology correlated with $\chi_{PDPP3T-PC_{71}BM}$.

References