Electronic Supplementary Information

Spectroscopic Investigations of Three-Phase Morphology Evolution in Polymer: Fullerene Solar Cell Blends

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Figure S1: Comparison of normalised Raman spectra for RR-P3HT and RRa-P3HT under non-resonant (top left) and resonant (top right) conditions, showing the difference between the C=C peaks of ordered and disordered polymer. Bottom: Predicted variation in C=C peak position and FWHM with changing regiorandom contribution to overall Raman intensity.
The degree of molecular order was calculated from each Raman spectrum by fitting with RR-P3HT and RRa-P3HT reference spectra (to represent ordered and disordered phases respectively) according to Equation 1.

\[
F_{RR} = \frac{I_{RR}}{I_{RR} + I_{RRa} \sigma_{RRa}/\sigma_{RR}}
\]  

(1)

where \(F_{RR}\) is the relative degree of molecular order, \(I_{RR}\) and \(I_{RRa}\) are the intensities of the ordered and disordered components obtained by fitting, and \(\sigma_{RRa}/\sigma_{RR}\) is the Raman scattering cross-section of RRa-P3HT relative to that of RR-P3HT, reported by Tsoi et al. as 1.69x.\(^{21}\)

Figure S2: Film thicknesses for annealed P3HT:PCBM blends of different compositions, measured by profilometry.

Figure S3: Absorption spectra (left) and maximum absorption (at \(\lambda_{\text{max}}\)) of P3HT (right) for as-cast P3HT:PCBM films with different compositions, before and after annealing.
Figure S4: Absolute (left) and normalised (right) absorption spectra for annealed P3HT:PCBM films of different compositions. Normalisation was done to $A_{\text{max}}$ of P3HT.

Figure S5: Normalised Raman (left) and PL (right) spectra for annealed P3HT:PCBM films of different compositions.
Figure S6: Normalised Raman spectra during *in situ* heating of P3HT:PCBM blends with different compositions.
Figure S7: Evolution of C=C peak position (red) and calculated degree of molecular order (black) during in situ heating of P3HT:PCBM blends with different compositions. Glass transition temperatures were estimated by linear fitting of trends in molecular order below and above the onset of reorganisation.
Figure S8: Normalised PL spectra during in situ heating of P3HT:PCBM blends with different compositions, plotted against Raman shift across a range equivalent to 522-865 nm.
Figure S9: Evolution of integrated PL intensity during *in situ* heating of P3HT:PCBM blends with different compositions. PL was integrated over photon energy rather than wavelength or Raman shift, across a range equivalent to 522-865 nm, and values are relative to the intensity from an as-cast film of neat P3HT. Glass transition temperatures were estimated by linear fitting of C=C peak position trends below and above the onset of reorganisation.