

Electronic Supplementary Information (ESI)

Directly Probing the Molecular Order of Conjugated Polymer in OPV Blends Induced by Different Film Thicknesses, Substrates and Additives

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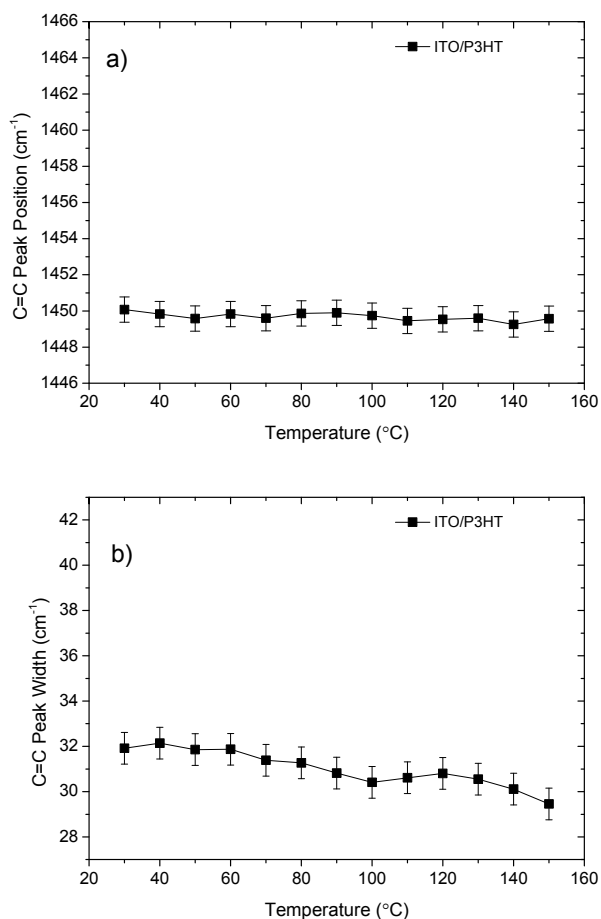


Figure S1: Evolution of C=C peak position (a) and FWHM (b) for a neat P3HT film on ITO during stepped heating at 10°C/min. Neat P3HT showed no change in peak position and only a small reduction in FWHM during heating, we believe the latter is due to some reorganisation occurring within the neat film but in general there is no phase transition like that seen in the blend.

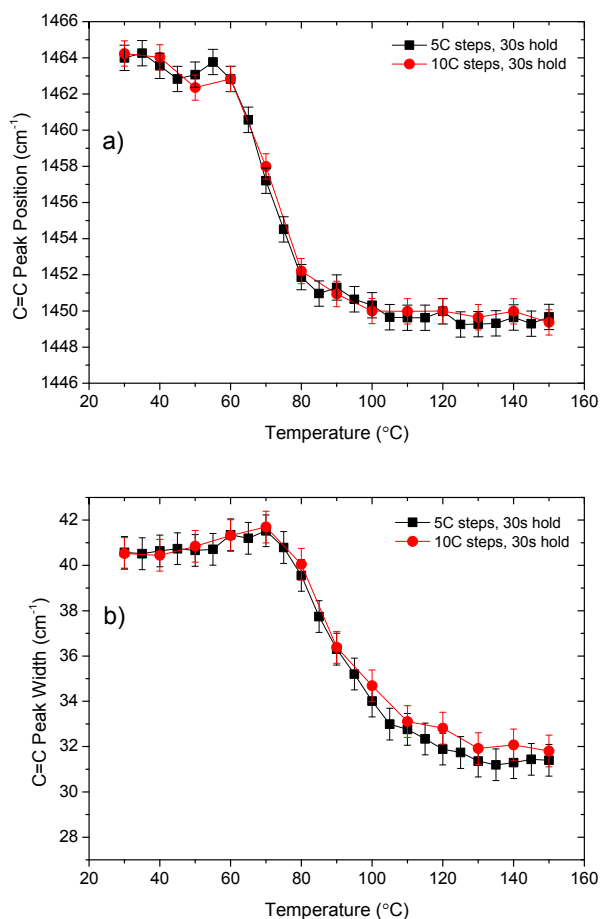


Figure S2: Evolution of C=C peak position (a) and FWHM (b) for P3HT:PCBM films on ITO when heated at different rates: 10°C steps at 10°C/min, or 5°C steps at 5°C/min. Measured peak properties were the same regardless of the heating rate used, which establishes that our measurements are not dependent on the heating rate and that the sample's internal temperature closely matches that recorded by the thermal stage even when heated at 10 °C/min.

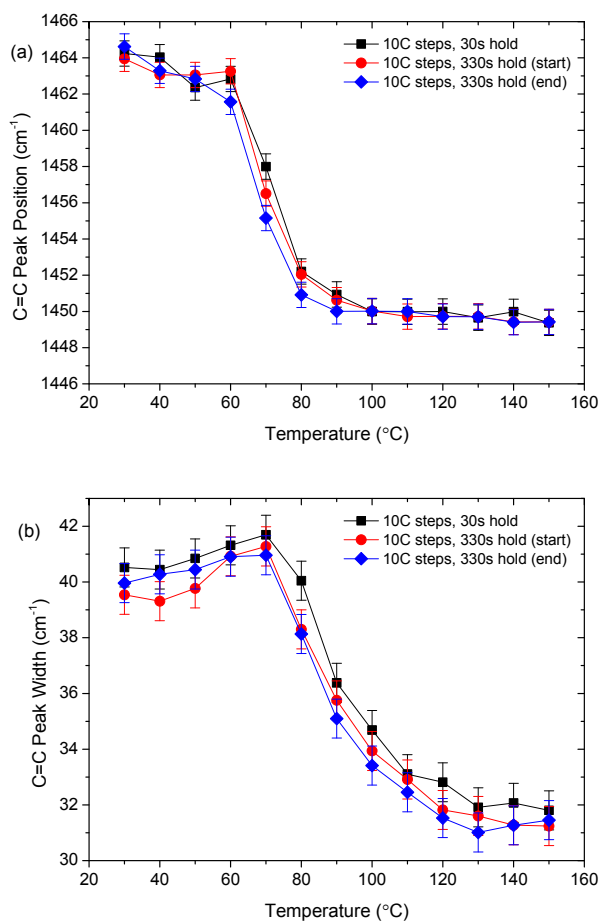


Figure S3: Evolution of C=C peak position (a) and FWHM (b) for P3HT:PCBM films on ITO heated in 10 °C steps at 10 °C/min with holding times of either 30 or 330 seconds (the latter has Raman spectra taken at the start and end of the holding time). Measured peak properties showed some dependence on the duration of holding time after each heating step, but most variation was within the error bars. Variation was largest during the phase transition, as a sample held at 70 °C was more ordered after 5 minutes than after 30 seconds.

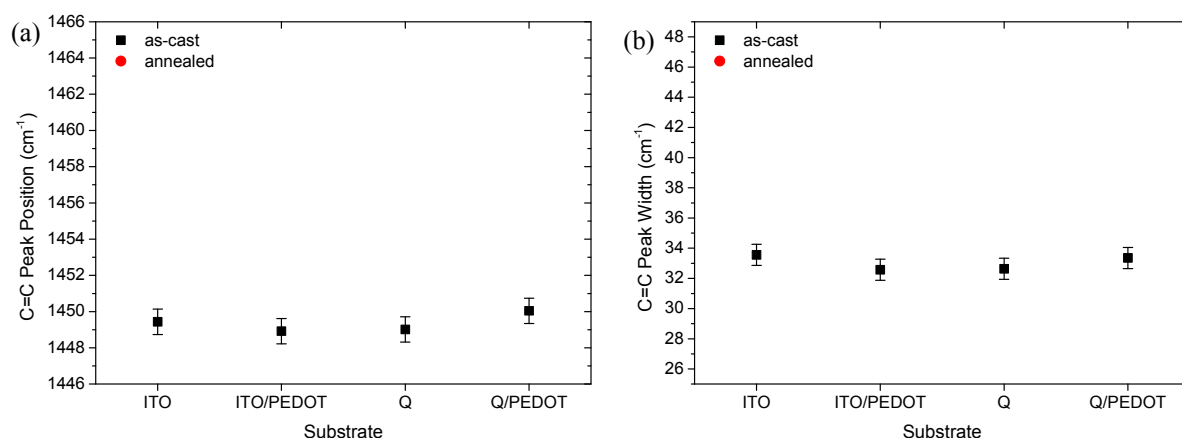


Figure S4: C=C peak position (a) and FWHM (b) for neat P3HT films on different substrates, before and after annealing. Variation in both peak position and FWHM was negligible for neat P3HT films spin-coated onto different substrates, due to the lack of blend structure and therefore no vertical phase separation to vary between substrates.

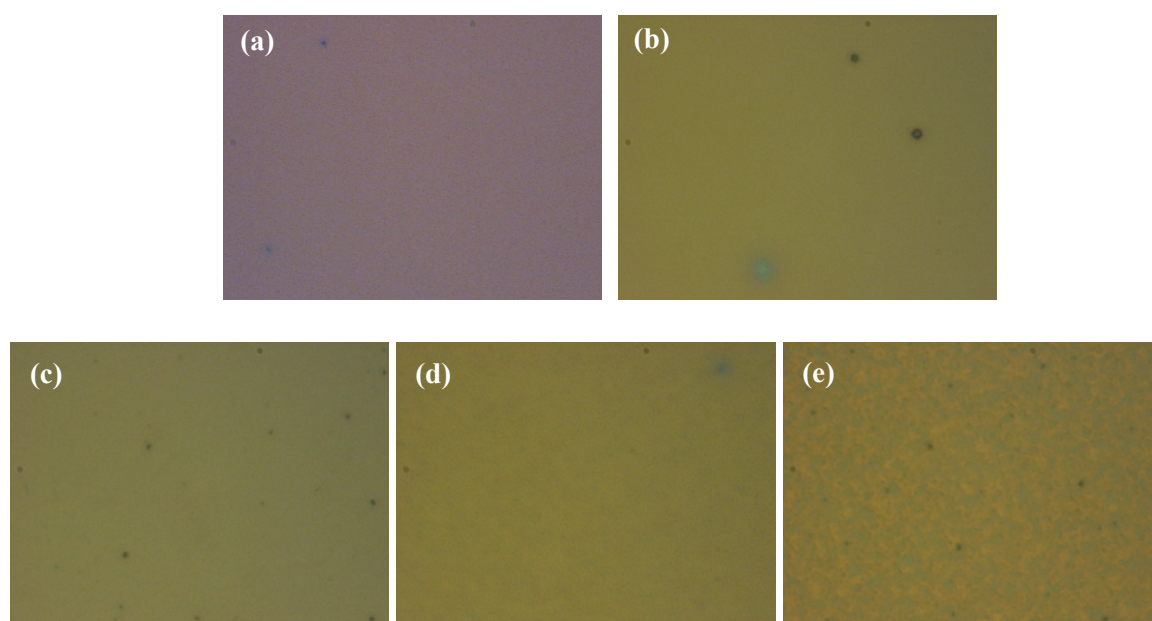


Figure S5: Optical microscopy images (at 50x magnification) of as-cast (a) and annealed (b) P3HT:PCBM, and as-cast P3HT:PCBM treated with 1% (c), 2% (d), 3% (e) and 9% (f) ODT. Large phase separation was only observed using optical microscopy for films treated with 3% and 9% ODT. Some micron-sized features can be seen but do not resemble the many PCBM aggregates observed in thermally-treated films, which only appear when the blend is heated above $\sim 120^\circ\text{C}$.

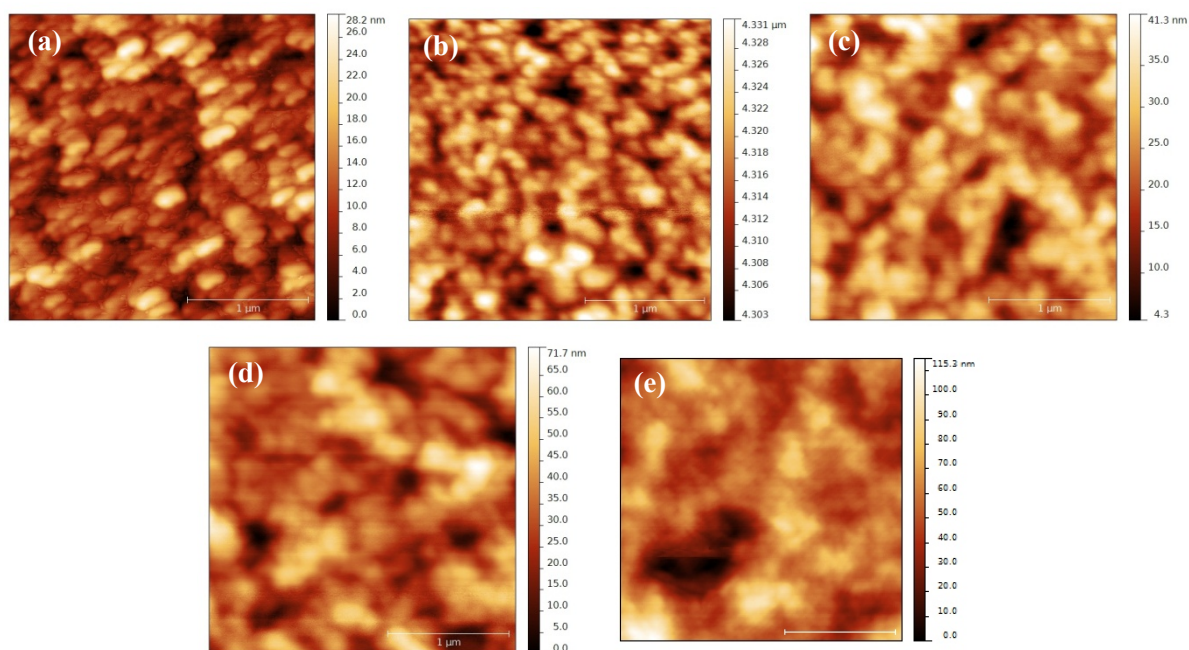


Figure S6: AFM images of P3HT:PCBM surfaces, from solutions treated with 0.5% (a), 1% (b), 2% (c), 3% (d) and 9% (e) ODT. All lateral scale bars are 1 μm , vertical scales are 28.2 nm, 28 nm, 36.9 nm, 71.7 nm and 115.3 nm respectively. Increasing roughness with ODT concentration for treated films is accompanied by increasing domain sizes, as shown by AFM images, indicating larger degree of phase separation.

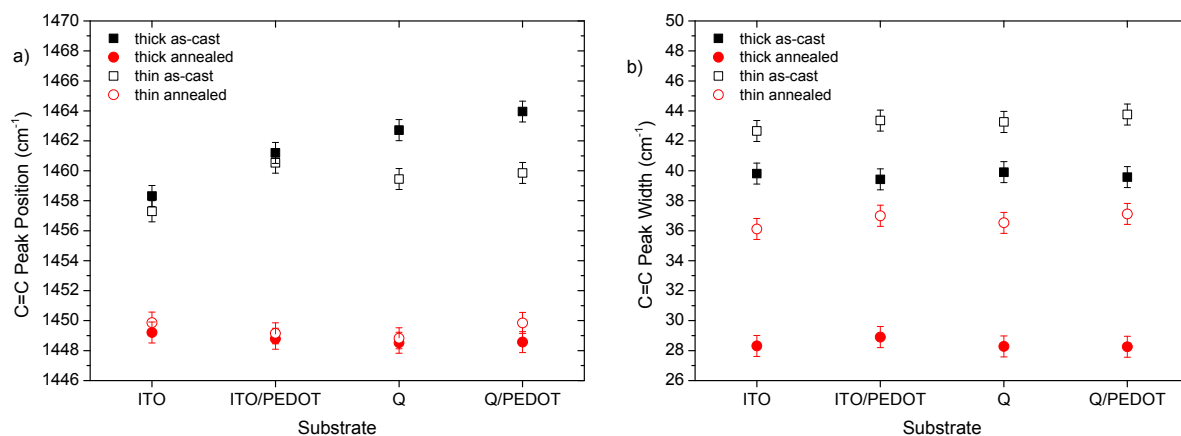


Figure S7: Comparison of C=C peak position (a) and FWHM (b) for thick and thin P3HT:PCBM films on different substrates, before and after annealing.

Thick and ultra-thin films show a similar trend in peak properties when PEDOT:PSS is included as an interlayer.