Electronic Supplementary Material (ESI) for Energy & Environmental Science

SUPPLEMENTARY INFORMATION

On the role of intermixed phases in organic photovoltaic blends

Paul Westacott,[1,2] John R. Tumbleston,[3] Safa Shoaee,[2,4] Sarah Fearn,[1] James H. Bannock,[2,4] James B. Gilchrist,[1,2] Sandrine Heutz,[1,2] John deMello, [2,4] Martin Heeney,[2,4] Harald Ade,[3] James Durrant,[2,4] David S. McPhail,[1] & Natalie Stingelin[1,2*]

[1] *Department of Materials, Imperial College London, London, UK*
[2] *Centre for Plastic Electronics, Imperial College London, London, UK*
[3] *Department of Physics, North Carolina State University, Raleigh, N.C, USA*
[4] *Department of Chemistry, Imperial College London, London, UK*

Dynamic Secondary Ion Mass Spectrometry of Bilayers

The depth profiles of the as-prepared bilayers obtained from d-SIMS displayed subsequent layers that were sulphur rich (P3HT) and deuterium rich (PCBM) (Figure 2A top panel), agreeing with the observed contrast in TEM. It is interesting to note that the offset (the trailing edge) of the ($^{34}S^-$) P3HT layer is more gradual than the onset (the leading edge). The shape of both the leading and trailing edges at the interfaces is due to a small degree of ion beam induced mixing. However, the more extended trailing edge also indicates some intermixing of the two layers at this interface. For this reason, analysis of layer composition was performed in the central region, away from both interfaces. The annealing protocols utilised here do not appear to have led to a significant degradation of the materials, and thus the sulphur and deuterium signals can be used as a convenient probe of their parent molecules (see Materials and Methods).

We note that after annealing the depth profiles do not exhibit a diffusion profile, indicating that a diffusion equilibrium has been reached. Additionally, the H-P3HT/PCBM annealed bilayer appears to have a greater vertical compositional contrast when compared to the L-P3HT analogue. A possible explanation for this are the differences in microstructure of the neat polymers. The L-P3HT is likely to adopt an extended chain microstructure, with little interconnectivity between crystallites. This may facilitate either uptake of PCBM into the matrix or allow diffusion of these short chains into the fullerene, thereby promoting complete vertical mixing. Conversely the entangled nature of H-P3HT would act to oppose both of these processes.

Transmission Electron Microscopy

In Figure 2B, the increase in image intensity in the P3HT layer arises from the presence of the heavier sulphur atom of the thiophene unit.

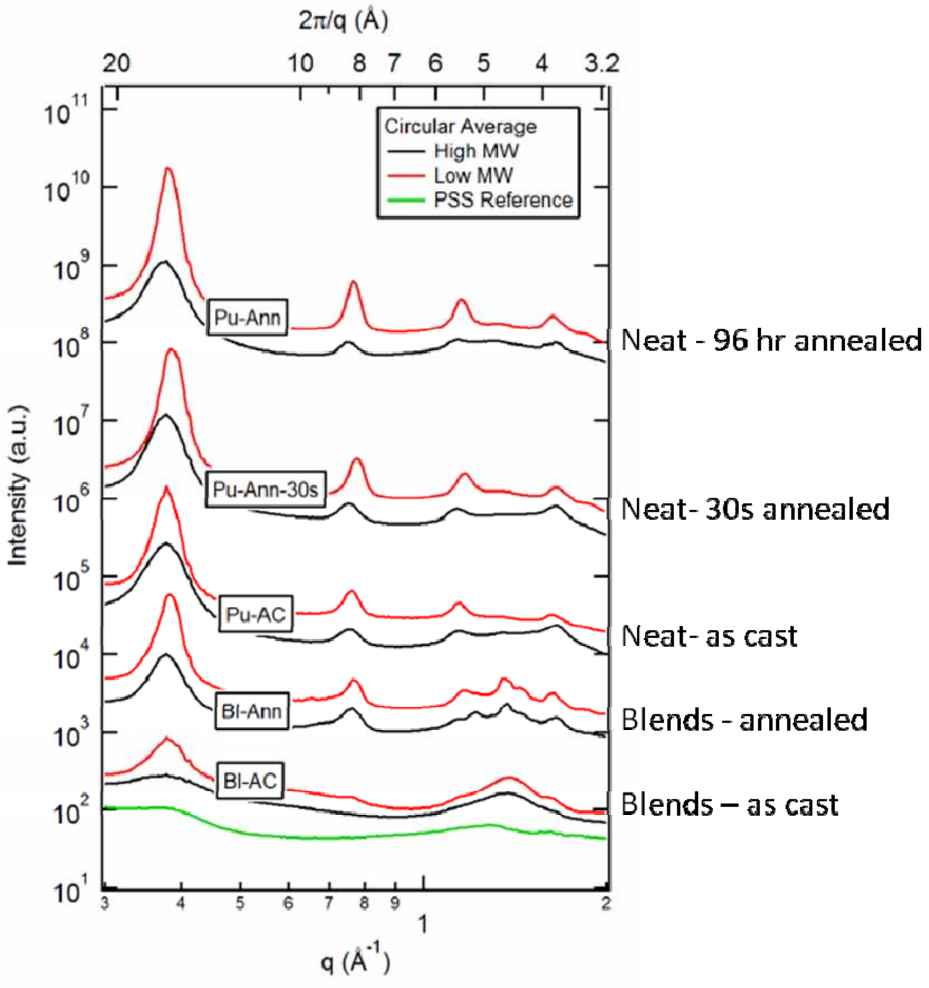
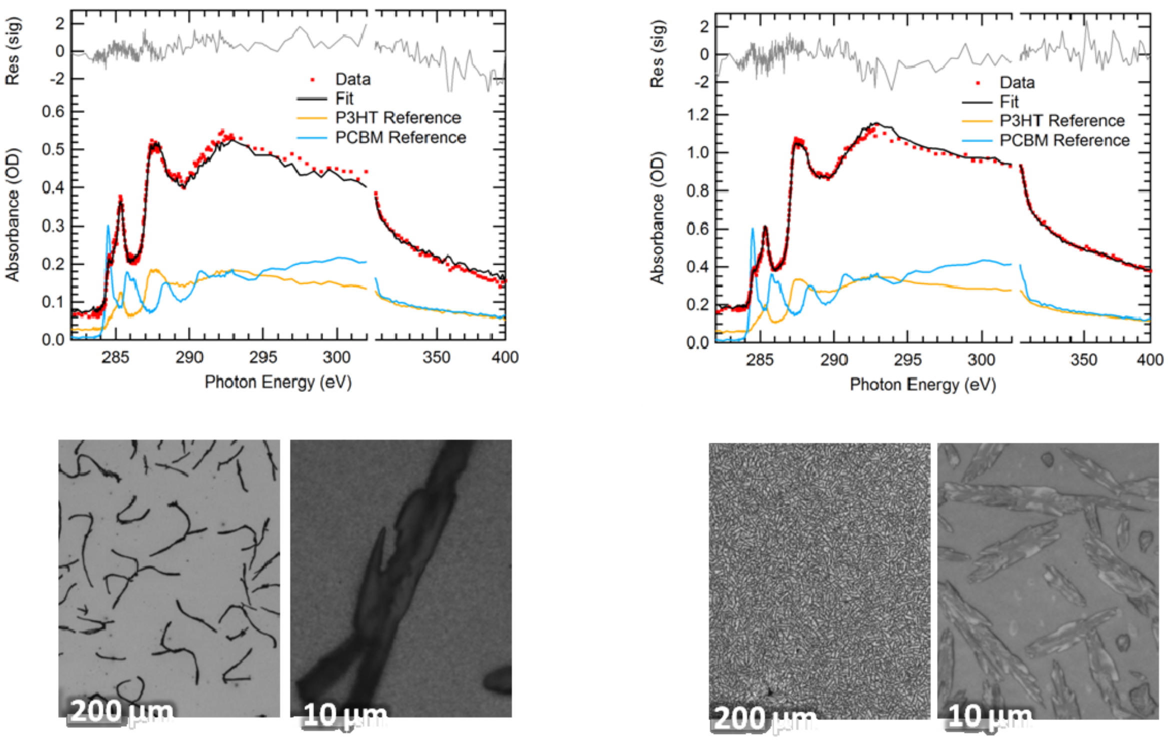


Figure S1: Circular averages of grazing incidence wide angle x-ray scattering of P3HT:PCBM blends. Showing clearly lower intensities of the reflections of H-P3HT blends compared to the corresponding samples of L-P3HT.

STXM Composition
Fit @150 C - SI



L-P3HT – 150 °C

H-P3HT – 150 °C

7.1 % PCBM

5.2 % PCBM

Figure S2: NEXAFS spectra and microscope images of 96 hour annealed blend films. STXM spectra show measured data, fit and residuals. From these fits the PCBM content of the polymer matrix (shown bottom) was calculated.

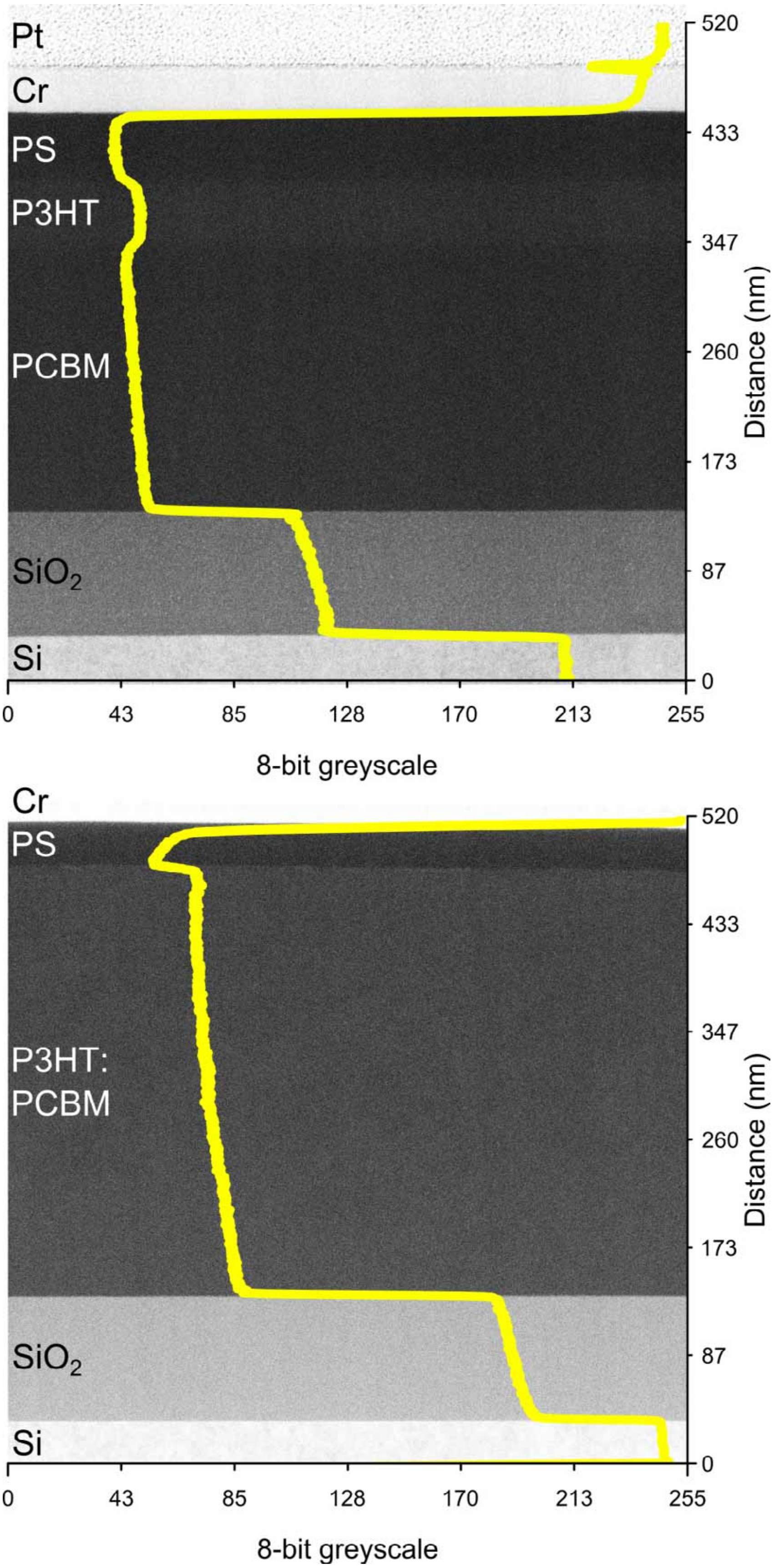


Figure S3: High resolution HAADF STEM images and overlaid integrated intensity profiles (yellow) through the vertical composition of the as-cast (top) and annealed (bottom) H-P3HT/PCBM bilayers.

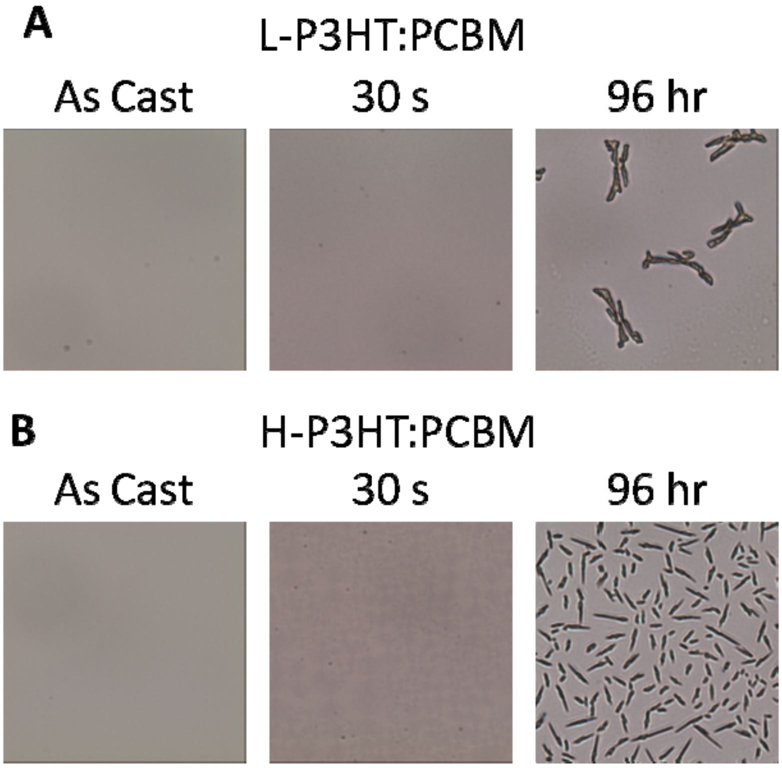
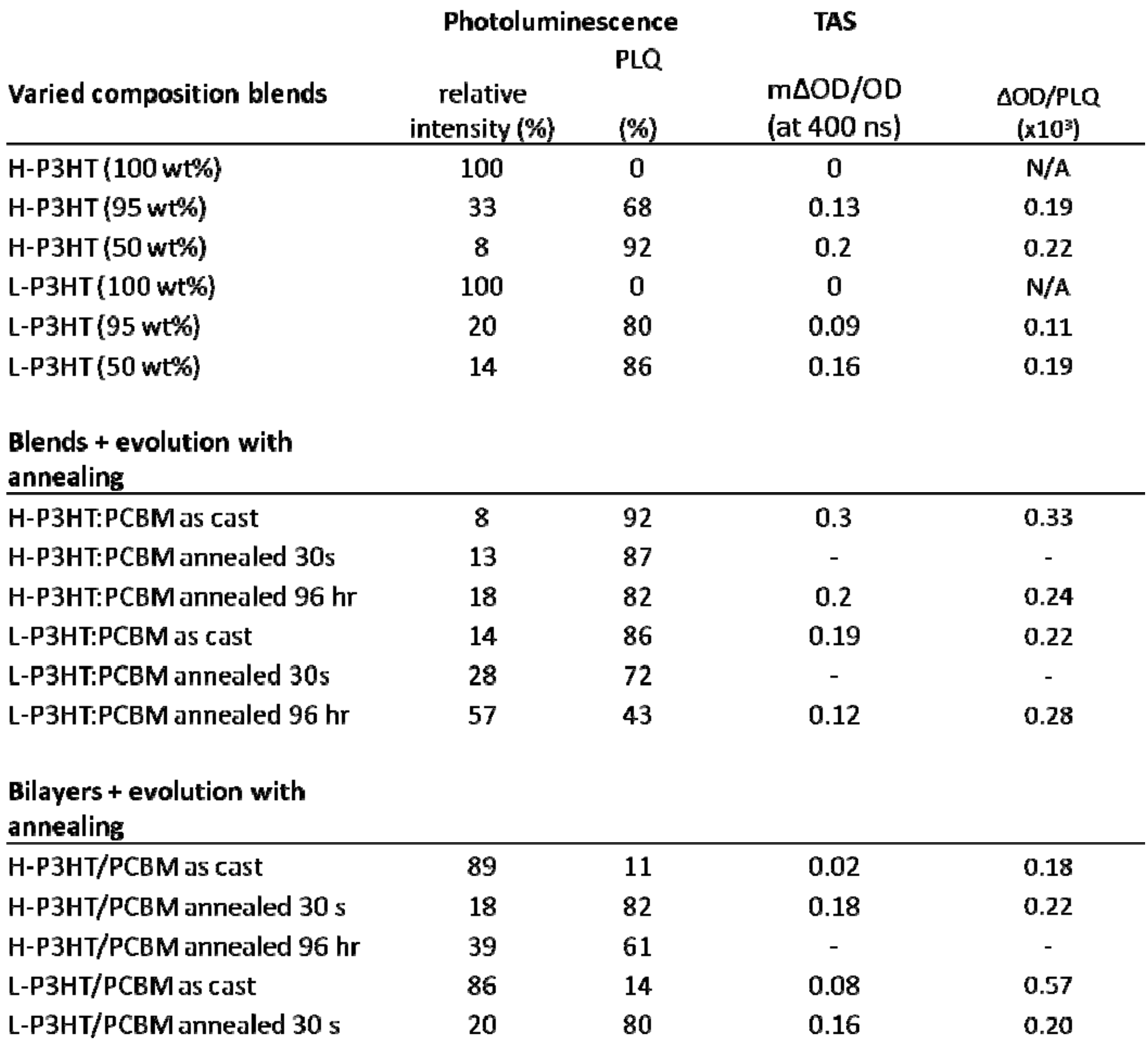


Figure S4: Optical Micrographs of blends of L-P3HT:PCBM (A) and H-P3HT:PCBM (B) after different annealing times. Between 0 s (as cast) and 30 s a clear colour change is observed, which correlates with the change in absorption spectra observed in Figure 3 All images displayed are 50 µm x 50 µm.

Table S1: Relative PL intensity, quenching and dissociated polaron yield of P3HT+PCBM systems



	Photoluminescence		TAS	
Varied composition blends	relative intensity (%)	PLQ (%)	mΔOD/OD (at 400 ns)	ΔOD/PLQ (x10³)
H-P3HT (100 wt%)	100	0	0	N/A
H-P3HT (95 wt%)	33	68	0.13	0.19
H-P3HT (50 wt%)	8	92	0.2	0.22
L-P3HT (100 wt%)	100	0	0	N/A
L-P3HT (95 wt%)	20	80	0.09	0.11
L-P3HT (50 wt%)	14	86	0.16	0.19
Blends + evolution with annealing				
H-P3HT:PCBM as cast	8	92	0.3	0.33
H-P3HT:PCBM annealed 30s	13	87	-	-
H-P3HT:PCBM annealed 96 hr	18	82	0.2	0.24
L-P3HT:PCBM as cast	14	86	0.19	0.22
L-P3HT:PCBM annealed 30s	28	72	-	-
L-P3HT:PCBM annealed 96 hr	57	43	0.12	0.28
Bilayers + evolution with annealing				
H-P3HT/PCBM as cast	89	11	0.02	0.18
H-P3HT/PCBM annealed 30 s	18	82	0.18	0.22
H-P3HT/PCBM annealed 96 hr	39	61	-	-
L-P3HT/PCBM as cast	86	14	0.08	0.57
L-P3HT/PCBM annealed 30 s	20	80	0.16	0.20