Electronic Supplementary Material (ESI) for Nanoscale.
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Supporting information

Insight into nanoscale lateral and vertical phase separation in organic bulk heterojunctions via scanning probe microscopy

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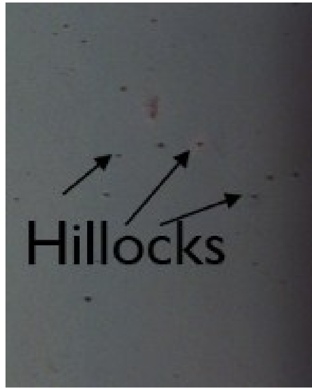
S1: Application note on WF calibration of AFM tip:

Precise work function(WF) calibration is a challenge in non-UHV conditions. The reason is partly because of the variation in the WF measured due to the water layer absorbed on the surface of both tip and sample. Furthermore, the WF value is a fickle function varying with local measurement conditions. Since the measurements are done in controlled environment which reflect high vacuum (HV) conditions, calibration of WF of AFM tip in these conditions is necessary.

Highly oriented pyrolitic graphite (HOPG) is one material whose WF remains constant in air, HV or UHV. We have examined several HOPG samples, exposed to air, N_2, Ar, freshly cleaved in and measured using several tips for statistical significance on the WF value to come to a conclusion on the WF of the AFM cantilever (error bar/noise level of 100 mV).

S2: Thermally degraded sample:



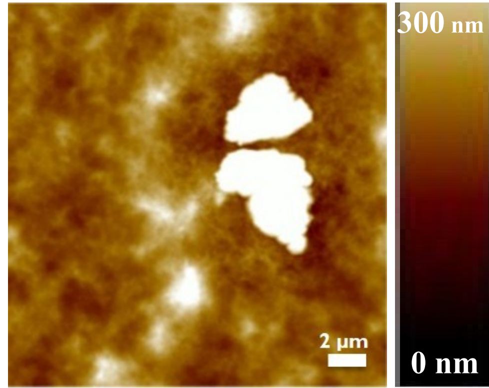


Figure S2. (a) Optical image of thermally degraded sample showing hillocks on the surface. (b) AFM topography image of scan size (20 µm X 20 µm). The height of the hillock is ~500 nm.

S3: Topography in the craters:

The RMS roughness of the surface is ~10 nm. The effect of Gas clustered ion beam (GCIB) ablation on the surface topography can be verified by the roughness of the craters. Figure S3 shows surface

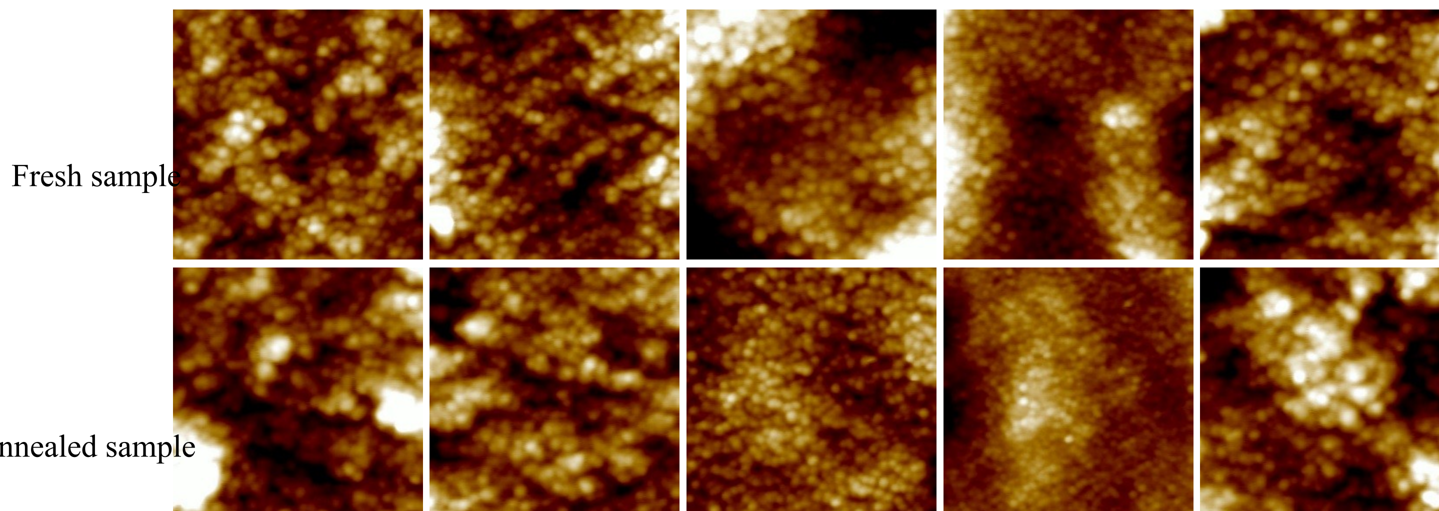


Figure S3. Topography of various craters after exposing to GCIB for material removal. Scan size (1µm × 1µm), Z-scale 40 nm. Top row shows the surface topography of fresh samples. Bottom row shows the topography of annealed samples.

topography of the craters. The RMS roughness of the AFM scans is around 10 nm, showing that there is no considerable inconsistencies in the removal rate of polymer and fullerene.

S4:Photoluminescence:

Photoluminescence (PL) spectroscopy measurements of Thermally annealed vs fresh samples of the P3HT:PCBM blend films is shown in Figure S4. PL spectroscopy of thermally annealed samples showed that the detected PL intensity of P3HT:PCBM blend samples increases (almost double) after thermal annealing. This means that the photoluminescence quenching decreases with annealing the blend. The conducted PL measurements used 405 nm laser source to excite the blend. The excitation wavelength falls in the region where both P3HT and PCBM have good absorption coefficient. The increase in the PL

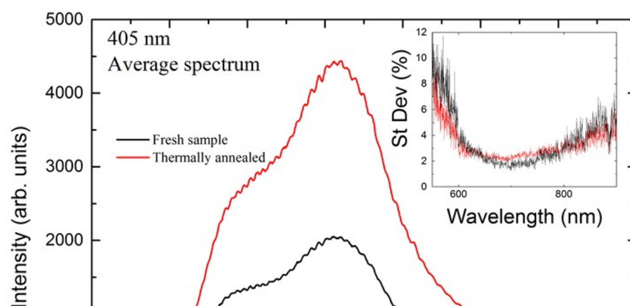


Figure S4. Photoluminescence (PL) spectra of fresh and thermally annealed samples. Measurements were acquired at 30 different locations and the average information is presented here. The PL intensity doubles for thermally annealed sample when compared to fresh sample.

intensity is a direct measure of increase in the phase separation of the acceptor and the donor materials, leading to larger areas of P3HT and PCBM which leads to less efficient exciton dissociation to electron and hole pair

S5: TOF-SIMS depth profile:

Figure S5, shows the TOF-SIMS based composition depth profile of the fresh and annealed samples. The TOF-SIMS analysis area is (300 µm × 300 µm), changes after 1 h annealing are not reflected in TOF-SIMS information as this is averaged over larger area.

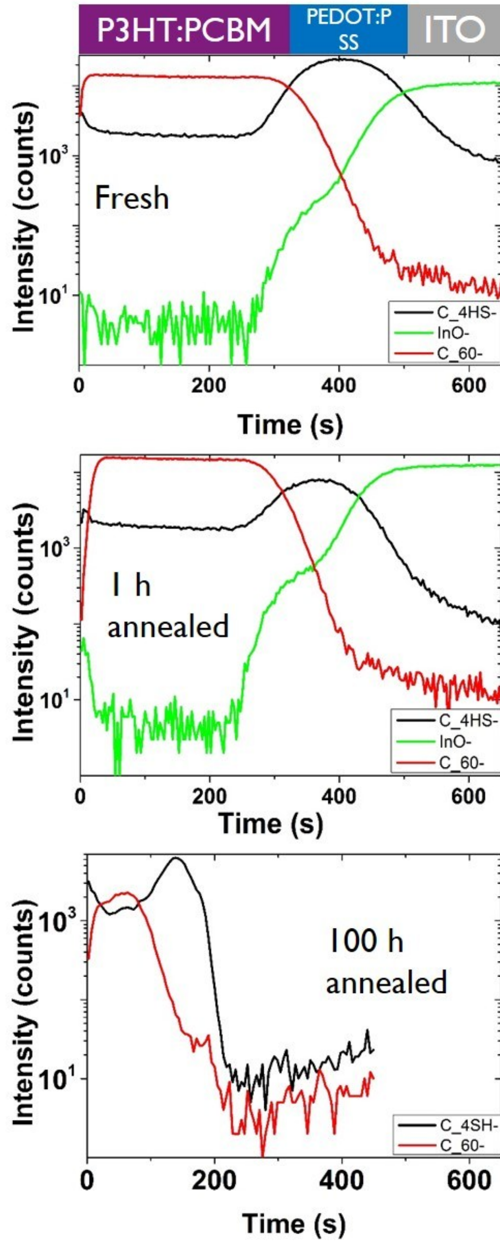


Figure S5. TOF-SIMS depth profile of fresh, 1 h annealed, 100 h annealed samples.