

Supporting Information

Fullerene-dependent miscibility in the silole-containing copolymer PSBTBT-08

Brian A. Collins¹, Zhe Li², Christopher R. McNeill³, and Harald Ade¹

¹Department of Physics, North Carolina State University, Raleigh, North Carolina 27695, United States

²Cavendish Laboratory, University of Cambridge, J J Thomson Avenue, Cambridge, CB3 0HE, U.K.

³Department of Materials Engineering, Monash University, Clayton, Victoria, 3800, Australia

Material Information

PSBTBT-08 or Poly[(4,4-octyldithieno(3,2-b:2',3'-d)silole)-2,6-diyl-alt-(2,1,3-benzothiadiazole)-4,7-diyl] was purchased from 1-Material under lot number YY1-170, which was measured to have a peak molecular weight (M_p) of 24 kg/mol and a polydispersity of 2.1 as measured via GPC as quoted from the manufacturer. PC₆₁BM was purchased from Nano-C and PC₇₁BM from American Dye Source. A UV-vis spectrum of pure PSBTBT-08 films is shown in S1, which agrees well with a previous report of the material in solution.^[16] This indicates that there is no crystallization occurring in this material.

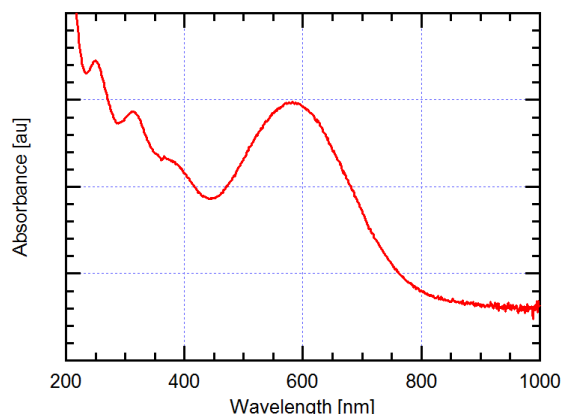


Figure S1. UV-vis Spectrum of a pure PSBTBT film.

PSBTBT-08 GIWAXS

Pure PSBTBT films (same material batch) were cast from chlorobenzene onto NaPSS/Si substrates to assess their level of crystallinity. The GIWAXS data was also taken at the ALS beamline 7.3.3 in a Helium environment but this time using a Pilatus 1M detector. Data at incident angles below and above the critical angle were taken with no qualitative change in the scattering pattern. In both the as cast and annealed films, there is no detectable diffraction signal above the NaPSS/Si background as shown in S2. In these profiles, only the polymer amorphous scattering at $q=14 \text{ nm}^{-1}$ can be seen above that of the NaPSS, further confirming the lack of crystallinity in this polymer.

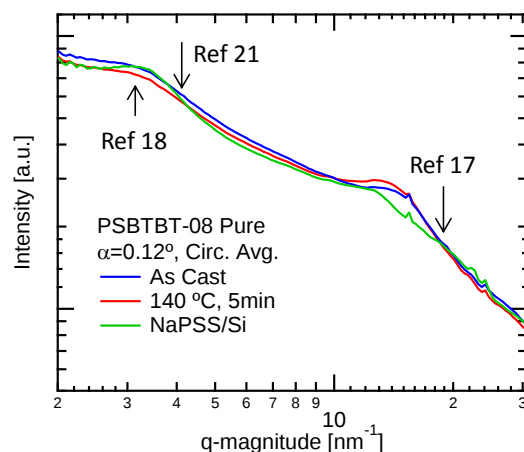


Figure S2: Circularly averaged profiles of pure PSTBTB-08 films. Arrows indicate locations of crystallographic reflections reported in the literature.

PSTBTB:PC₆₁BM GIWAXS Correlated to PC₆₁BM

Figure S3 demonstrates how the texture of the low-q diffraction peaks in the PSTBTB:PC₆₁BM are correlated to one another. Several of these peaks correlated with GIWAXS of pure PC₆₁BM (Figure S4) and through the symmetry of the texture pattern, each peak here must also be associated with these crystals. Additionally, the speckle-like texture of the diffraction rings is prevalent in all rings here whereas this does not occur in any of the other data for this study. This shows that this is not an artifact of the instrument and reinforces the origin of the diffraction pattern as being from fullerene crystals.

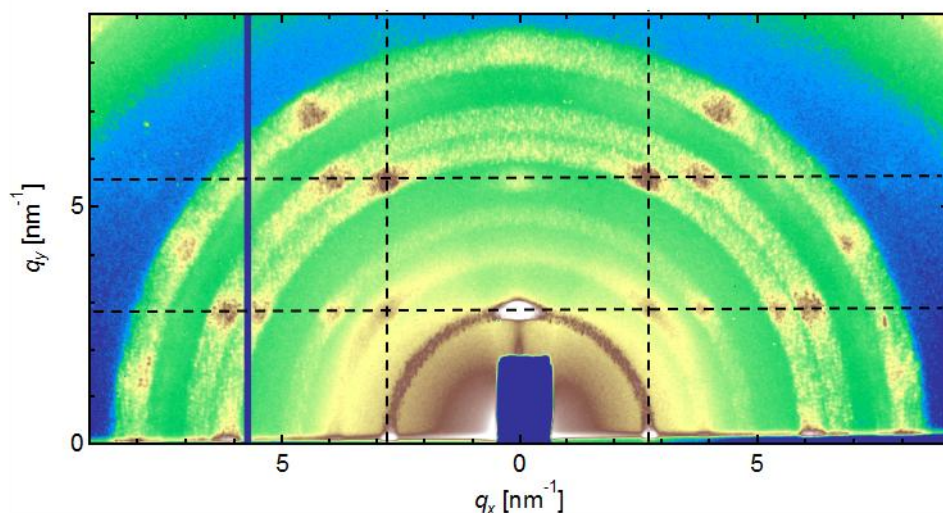


Figure S3: Zoom of the GIWAXS data on the PSTBTB:PC₆₁BM blend film showing the correlation of the texture pattern that includes that of the low-q diffraction peak at 2.74 nm⁻¹. Additionally, all peaks contain the same speckle-like pattern from individual nanocrystals.

Pure PC₆₁BM films drop cast from chlorobenzene onto Si substrates were investigated via GIWAXS to compare with that of the PSBTBT:PC₆₁BM blend films. Common peaks between the films ($q < 10 \text{ nm}^{-1}$) are identified as those at 4.0 nm^{-1} , 6.7 nm^{-1} , 7.6 nm^{-1} and 8.1 nm^{-1} , while those in the blend film not matched appear at 2.8 nm^{-1} , 4.8 nm^{-1} and 6.1 nm^{-1} . Analyzing the texture pattern in Figure S3, shows these unpaired peaks to be from the same crystal species as the others. Thus it is highly likely that all the diffraction peaks here are from the fullerene crystals easily identified and avoided in the miscibility measurement.

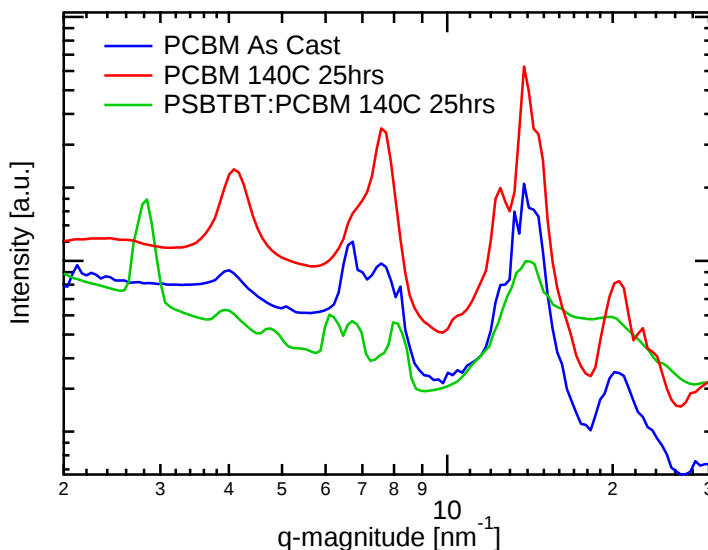


Figure S4: Comparison of circularly averaged GIWAXS profiles from pure PC₆₁BM and the PSBTBT:PC₆₁BM blend.

PSBTBT-08 Processing and Device Testing

Devices were fabricated on PEDOT:PSS-coated indium tin oxide (ITO) glass substrates. After deposition of PEDOT:PSS from an aqueous solution (spin-coated to form $\sim 40 \text{ nm}$ thick films with subsequent annealing at $150 \text{ }^{\circ}\text{C}$ for 30 mins under flowing nitrogen) substrates were transferred to a nitrogen glove box for deposition of the active layer. PSBTBT-08:PC₇₁BM blends ($\sim 100 \text{ nm}$ thick) were deposited by spin-coating chlorobenzene solutions with a weight ratio of 1:1 and total concentration of about 30 mg/ml . For some devices chloronaphthalene was used as a solvent additive as described in Ref 17, while others an additional pre-annealing step of $140 \text{ }^{\circ}\text{C}$ for was employed (Ref 19). Devices were completed by the deposition of a top aluminum electrode through an 8-pixel shadow mask, and were encapsulated prior to removal from the glove box and testing.

Devices were testing by measuring both the external quantum efficiency (EQE) spectra and the device current-voltage characteristics under a solar simulator. EQE spectra were measured using a 100 W tungsten halogen lamp dispersed through a monochromator with a Keithley 237 source meter unit

(SMU) used to measure the short circuit current at various wavelengths. Incident light intensity was continuously monitored during measurement by a reference photodiode calibrated by a Hamamatsu S8746-01 calibrated photodiode. Current-voltage characteristics were measured under $\sim 100 \text{ mW/cm}^2$ AM 1.5G conditions using the Keithley 237 SMU with illumination provide by an ABET class AAA solar simulator calibrated to a silicon reference cell, correcting for spectral mismatch.

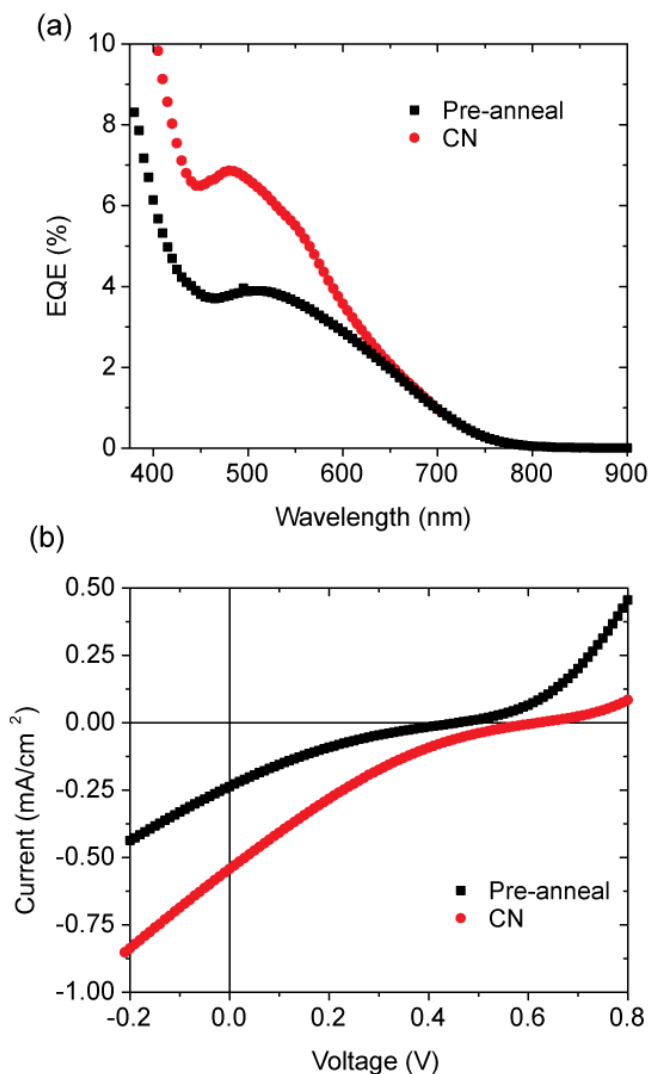


Figure S5. Device study using PSBTBT-08:PC₇₁BM films. a) External quantum efficiency and b) J-V curves of devices made using two previously reported fabrication methods.