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Supplementary Information

Mixed Molecular Orientations Promote Charge Transport in Bulk Heterojunction Solar Cells

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1. Methods

Sample preparation: Indium tin oxide (ITO) coated glass substrates (Colorado Concept Coating LLC) were cleaned with DI water, acetone, and 2-propanol for 10 min each in an ultrasonic bath. The ITO was then exposed to UV-ozone treatment for 20 minutes. PEDOT:PSS (Clevios PH 1000 from Heraeus) was spin coated onto the ITO/glass at 3000 rpm for 60 s to obtain a film thickness of 30 nm. The samples were then annealed at 150 ^{o}C for 20 mins. All subsequent sample preparation steps were performed in a nitrogen filled glovebox.

Solutions of P3HT:$PC_{61}BM$ (Solaris Chem, weight ratio 3:1, P3HT MW 8.8 kDa) were prepared in chloroform from Sigma Aldrich (anhydrous, > 99% purity) with a total concentration of 2 mg/ml. Solutions were stirred at 45 °C overnight before spin coating the room temperature solution at 400 rpm for 10 s, followed by 1000 rpm for 60 s to achieve a film thickness of 24 $\pm$ 3 nm. These samples were annealed at selected temperatures of 100, 190, 195, 200, 205, and 220 ^{o}C for 45 minutes to tune the preferential orientation of P3HT crystalline domains.[1] For microelectrode deposition, TEM grids with 1.2 µm diameter holes (Quantifoil, Ted Pella, Inc.) were used as shadow masks. 50 nm of Au was thermally evaporated onto the P3HT films at a rate of 0.2 Å/s. The resulting microelectrode area was measured using C-AFM current mapping.

C-AFM measurements were performed in a nitrogen environment using an AIST Combiscope 1000 AFM with gold coated conductive probes (Budget Sensors ContE-g). The nominal cantilever spring constant was 0.2 N/m and the probe radius was under 25 nm. C-AFM scans were recorded with an applied probe-sample force of 7 nN and a 2V bias applied to the sample. For lateral current spreading measurements,[2] the bias voltage and film thickness were kept constant at 2V and 24 ± 3 nm respectively.

GIWAXS measurements were performed at the 11-BM beamline of the National Synchrotron Light Source II (NSLS-II) at Brookhaven National Laboratory using an X-ray wavelength of 0.09184 nm. The samples were illuminated at an incidence angle of about 0.1°. To quantify the orientation distribution of P3HT, we integrated the reciprocal space (100) lamellar peak along the ring at q =

0.38 $Å^{-1}$ using Fit2d GIWAXS software.[3] Background subtraction was performed by subtracting the intensity just outside of the ring for each χ. Data was not considered above $\chi = 82°$ due to Yoneda streak effects in this range, caused by interference between the incident and scattered wave.[4] Out-of-plane (100) radial peak profiles were fit with single pseudo-Voigt functions to obtain the experimental full width at half maximum (FWHM). FWHM was then adjusted for the resolution of the apparatus to determine the average grain size, using the Scherrer equation[5].

2. GIWAXS

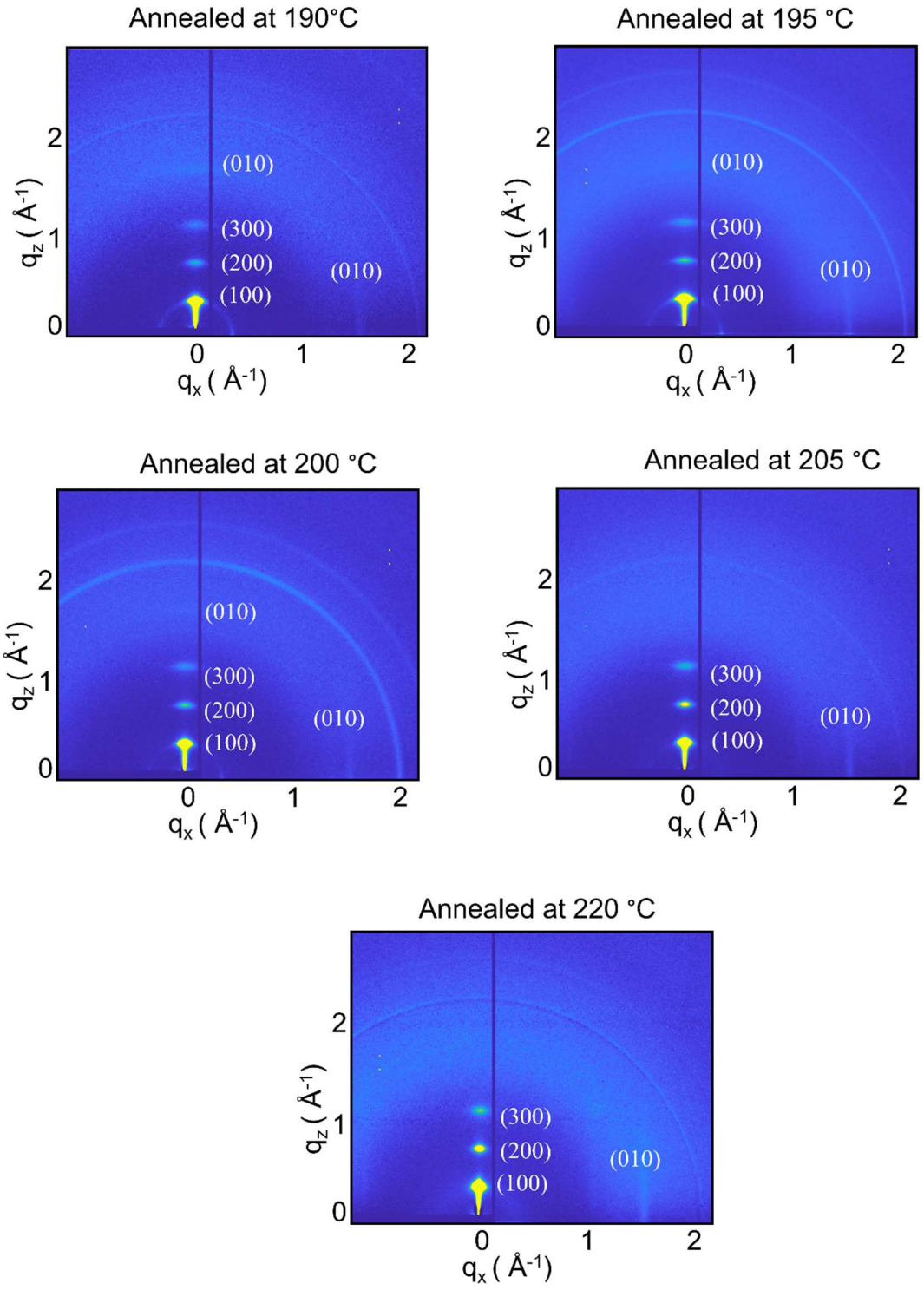

Figure S1. GIWAXS data for P3HT:$PC_{61}BM$ BHJ films.

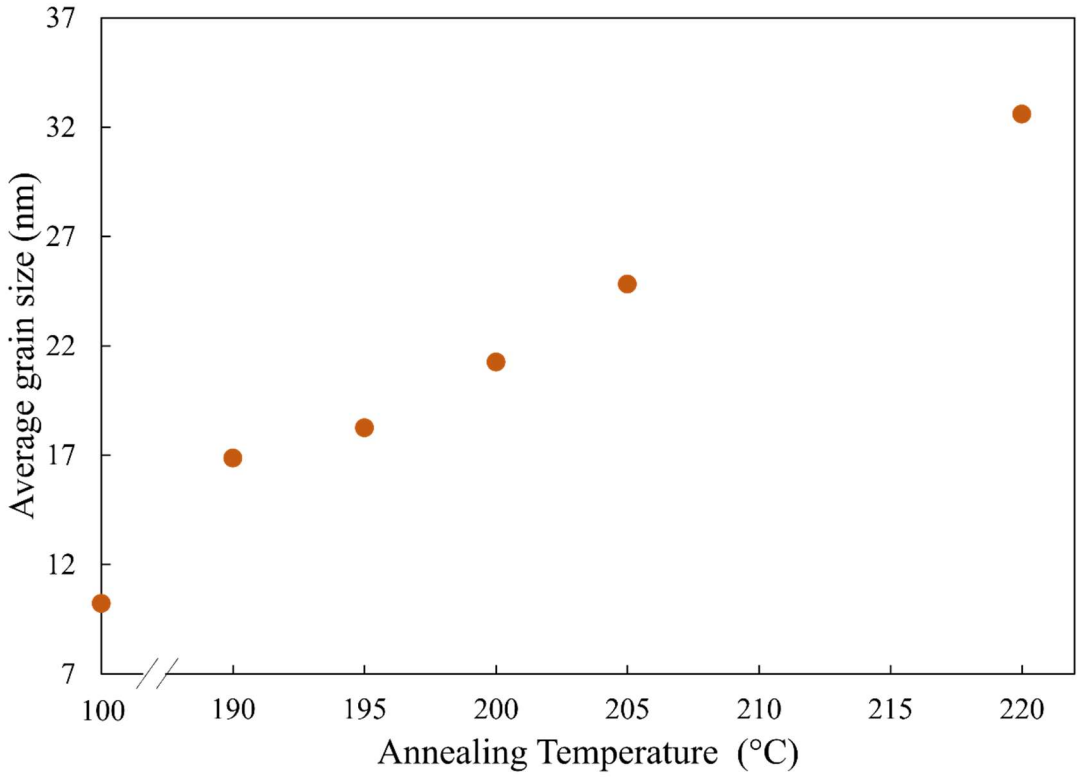

Figure S2. Dependence of P3HT average grain size on annealing temperature for P3HT:$PC_{61}BM$ BHJ films, based on the (100) out-of-plane lamellar peak.

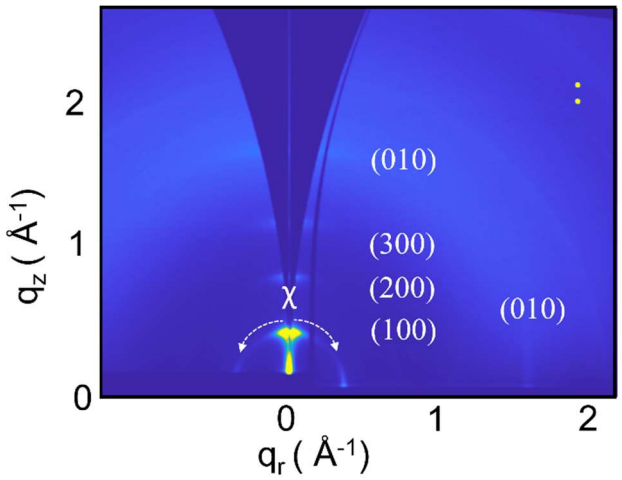

Figure S3. GIWAXS pattern corrected for the curvature of the Ewald's sphere for a P3HT:$PC_{61}BM$ BHJ film annealed at 100 °C.

3. Correlation between Current Spreading Radius and Edge-on to Face-on Ratio

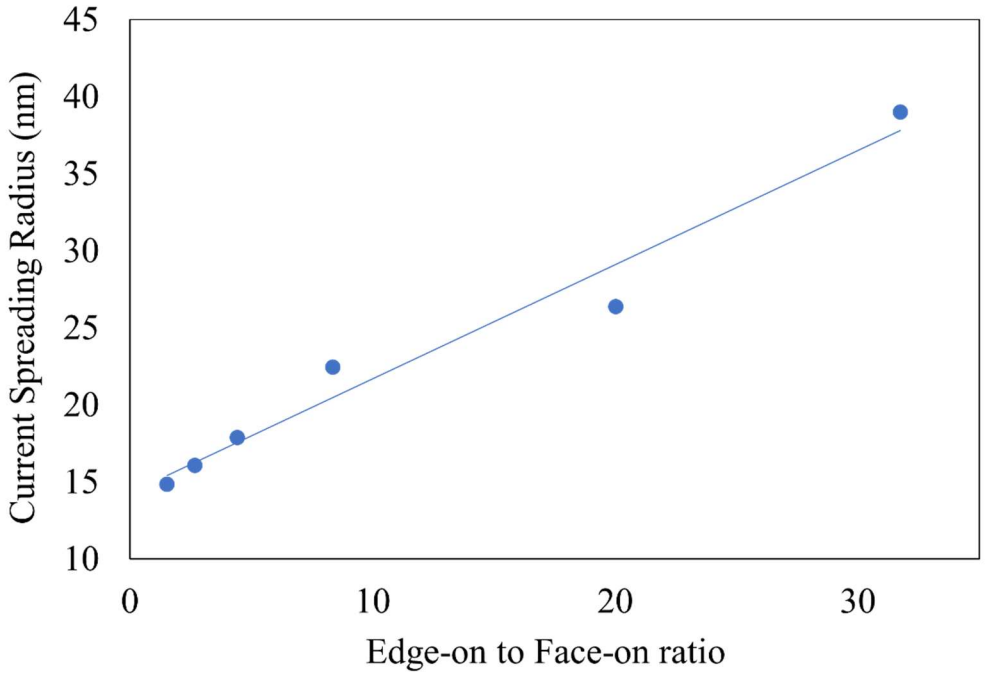

Figure S4. Current spreading radius versus edge-on to face-on ratio, showing a linear correlation, with a coefficient of determination (R^2) of 0.967.

4. C-AFM Hole Current

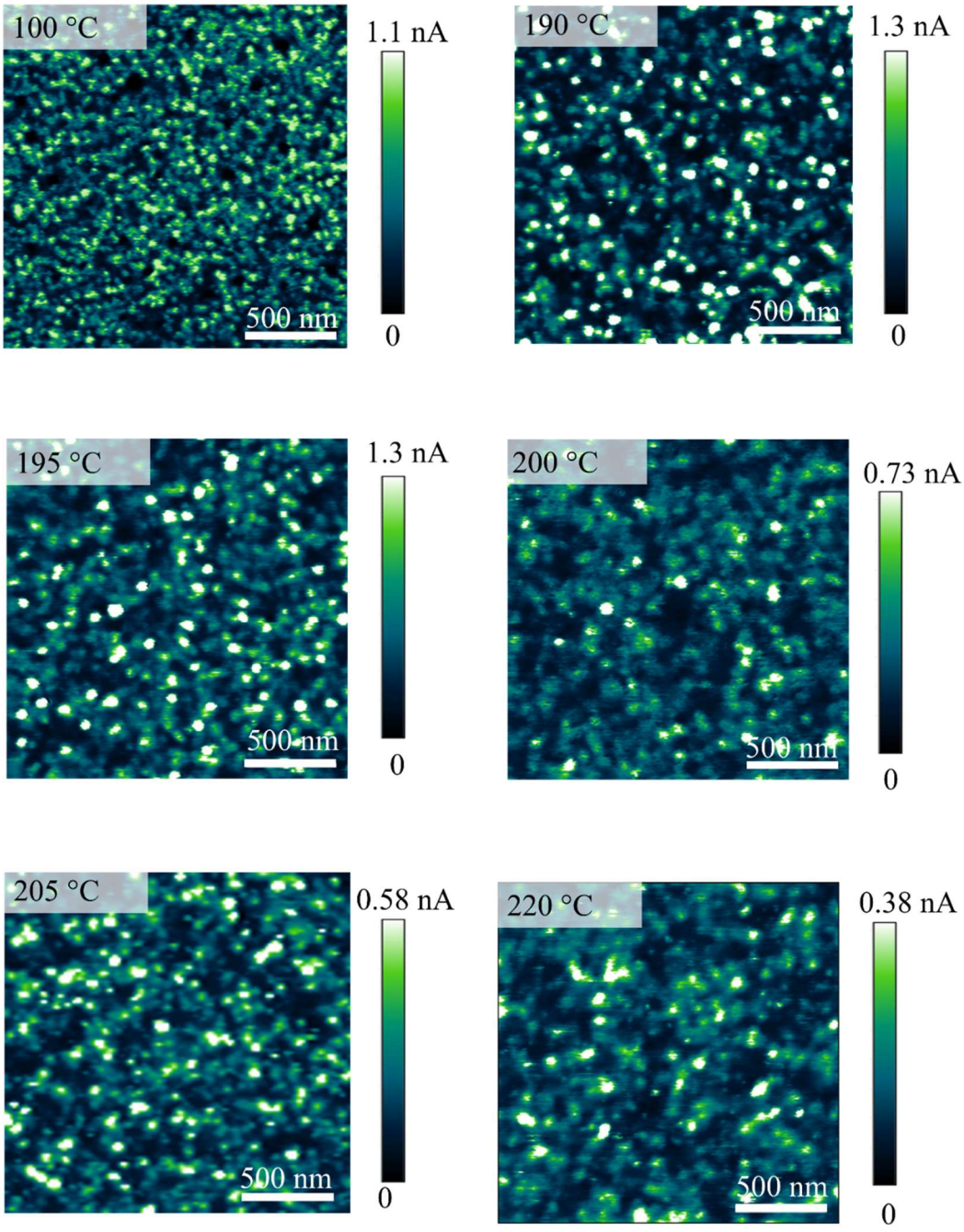

Figure S5. C-AFM hole current maps for P3HT:$PC_{61}BM$ BHJ films annealed at the noted temperatures.

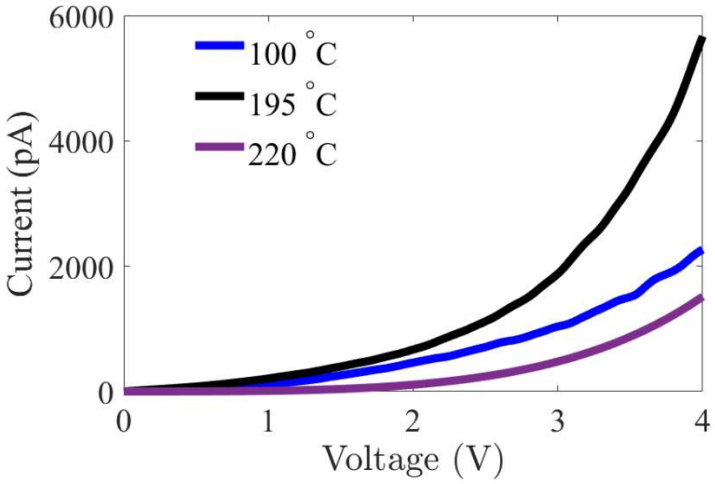

Figure S6. Current-voltage curves (averaged over 10000 sample positions) for P3HT:$PC_{61}BM$ films annealed at 100 °C, 195 °C, and 220 °C.

5. References

1 E. Verploegen, R. Mondal, C. J. Bettinger, S. Sok, M. F. Toney and Z. Bao, *Adv. Funct. Mater.*, 2010, **20**, 3519–3529.

2 P. S. Fernando, J. S. Mehta, D. M. Smilgies and J. M. Mativetsky,submitted .

3 A. P. Hammersley, S. O. Svensson, M. Hanfland, A. N. Fitch and D. Hausermann, *High Press. Res.*, 1996, **14**, 235–248.

4 F. Li, K. G. Yager, N. M. Dawson, Y.-B. Jiang, K. J. Malloy and Y. Qin, *Chem. Mater.*, 2014, **26**, 3747–3756.

5 D.-M. Smilgies, *J. Appl. Crystallogr.*, 2009, **42**, 1030–1034.