Electronic Supplementary Material (ESI) for Energy & Environmental Science. This journal is © The Royal Society of Chemistry 2016

Supplemental Information for

Morphology Changes Upon Scaling a High-Efficiency, Solution-Processed Solar Cell

From Spin-Coating to Roll-to-Roll Coating

Hyun Wook Ro, Jonathan Downing, Sebastian Engmann, Dean M. DeLongchamp, Lee J. Richter

Material Measurement Laboratory, National Institute of Standards and Technology

Gaithersburg, MD 20899, USA

Subhrangsu Mukherjee, Harald Ade

Department of Physics, Organic and Carbon Electronics Laboratory (ORaCEL), North Carolina State University, Raleigh, NC 27695, USA

Lethy K. Jagadamma, Maged Abdelsamie, Aram Amassian

Materials Science and Engineering Program, Division oof Physical Science and Engineering, King Abdullah University of Science and Technology, Thuwal, 23955-6900 Saudi Arabia

Yuhang Liu, He Yan

Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong



Figure S1: Detailed device parameters as a function of loading, thickness, and substrate temperature for conventional (ITO|PEDOT-PSS|BHJ|CaAl) blade-coated devices.



Figure S2: PCE of inverted and conventional blade-coated devices vs substrate temperature. Lines to guide the eye.

Polarized R-SoXS



Figure S3: R-SoXS 2d images for blade-coated a, 90 °C and b, 55 °C samples. c, Sector averaged profiles representing P-SoXS data perpendicular and parallel to the electric field polarization. All samples show greater scattering perpendicular to the electric field, reflecting face-on preferential molecular orientation with respect to donor-acceptor interfaces.

Table S1:

Blade-coated BHJ	Anisotropy
55 °C	0.07
90 °C	0.07

Composition variation of blade and spin coated films

The R-SoXS scattering profiles (Figure S4a) for the optimized blade- and spun-coat samples were corrected for absorption following the Beer-Lambert law, $I = I_0 e^{-\alpha t}$, where α is the linear absorption coefficient and t is the film thickness. The optimized spun-coat film exhibited an efficiency of 10.8% with an absolute average purity of \approx 90%, i.e. average of the pure aggregated PCBM and polymer domains and the mixed domains relative to a morphology of two pure phases, as revealed by an annealing sequence.¹ The film thicknesses were estimated from fits of a linear combination of absorption corrected material and mass density contrast functions² to the observed

scattering intensity following a procedure described in the literature.³ By integrating the scattering profiles and ensuring that scattering originates from optical contrast between polymer-rich and fullerene-rich domains, the integrated scattering intensity (ISI) reveals the relative composition variations between the blends over the length scales probed. The relative composition variation (average phase purity) of the optimized blade- and spun-coat samples thus obtained were found to be identical within the experimental uncertainty range (~5%) as shown in Figure S4b. Fits of corrected contrast function to obtain film thicknesses to the observed scattering intensities are shown in Figures S4c and d. As the morphologies have three-phases and the volume fraction of the crystalline phase affects the ISI, in order to relate the blade to the phase purity scale for the spun-coat films the relative degree of crystallinity between the spun- and blade-coat needs to be considered. The blade-coat film is found to have a lower relative degree of crystallinity. This is likely due to the blade-coating process being faster compared to spin-coating at 800 rpm (Figure 4). The results are also in agreement with earlier observations from films deposited using different spin speeds.⁴ However, the relatively small difference in the degree of crystallinity between the optimized blade and spin-coat samples imply nearly identical crystalline polymer and amorphous polymer-rich: fullrene volume fractions in the film thus validating phase-purity comparisons on an the same scale as established by the annealing limit.⁵ A average purity of 90% integrated over all domains would translate into $\sim 20\%$ PCBM in the mixed amorphous, polymer-rich domains if the degree of crystallinity is 50%.



Figure S4: (a) Lorentz-corrected and normalized R-SoXS scattering profiles (284.2 eV) from the optimized blade and spun-coat samples; (b) Average composition variation for the two samples obtained from integrations of the scattering profiles in (a); (c), (d) Film thickness (*t*) extracted from absorption corrected contrast function fits³ to the integrated scattering intensity for optimized blade and spun coat samples; (e) Volume normalized pole figures of the (100) peak from the optimized

blade- and spun-coat samples. Data in the missing wedge were extrapolated from peak fits to the intensity profiles;⁶ (f) relative degrees of crystallinity (DoC) extracted from the first index peak for the lamellar directions. The uncertainties in (b) are from differences in average composition values calculated at different material contrast energies as well as uncertainties in the film thickness. The uncertainties in (f) are from uncertainties in the film thickness and sample length measurements.



S5 GIXD and GISAXS for PBTff4T-2OD processed at a) high (90 °C) and b) low T (70 °C). Like PffBT4T-2OD, PBTff4T-2OD exhibits clear edge on morphology when coated at high temperature, from the disaggregated state and a face on morphology when coated from the cooler solution. Interestingly, crystallization of the PCBM-71 is observed for the low temperature PBTff4T-2OD BHJ.



S6 Top Row, in-situ UV-Vis normal incidence transmission during spin-coating of an initially 110 °C substrate and 110 °C solution.

Bottom Row, in-situ UV-Vis p-polarized transmission (51°) during blade-coating of a 90 °C solution on a 90 °C substrate.

	Q (n00) [Å ⁻¹]	FWHM [Å ⁻¹]	Q (010)[Å-1]	Lc
	(d ₁₀₀)	(Lc)	d ₀₁₀	
Y5 90C w/	0.277 (22.6 nm)	0.048 (13. nm)	1.731 (3.63 Å)	0.148 (4.2 nm)
Y5 55C w/	0.285 (22.0 nm)	0.028 (22. nm)	1.757 (3.68 Å)	0.146 (4.3 nm)
BHJ 90C w/	0.280 (22.4 nm)	18. (nm)	1.738 (3.61 Å)	0.132 (4.7 nm)
BHJ 55C w/	0.284 (22.1 nm)	26. (nm)	1.778 (3.53 Å)	0.135 (4.6 nm)

Table S2 GIXD feature values

D₁₀₀ position taken from least squares fit to first 3 orders to eliminate calibration artifacts

PoleFigure & Hermann Orientation Parameter

Assuming cylindrical symmetry around the sample normal, the corrected intensity equals $I(\omega)^*sin(\omega)$, with ω being the pole angle. The integral is then a relative measure for the crystal volume. Due to geometric restrictions of the gracing incidence experiment not the whole momentum space (q_{xy}, q_z) is accessible which leads to a small missing "wedge" in the X-ray data. The within the manuscript reported relative crystallinity values assume a top hat distribution across this wedge, perfectly aligned diffraction planes with normal parallel to q_z are neglected leading to an underestimation of the overall crystallinity.



Figure S7: (a) Raw detector image obtained from a BHJ cast at 90C. (b) Detector image after conversion to reziprocal space. Note the "missing wedge" near $q_{xy} = 0$. (c) (100)-pole figure and $\sin(\omega)$ weighted intensity as obtained from the corrected detector image.

Additionally, to the integral of the corrected pole figure the Hermann's orientation factor, defined as

$$\langle P_2 \rangle = \frac{\int_0^{90} I(\omega) \sin(\omega) \cdot P_2 \, d\omega}{\int_0^{90} I(\omega) \sin(\omega) \, d\omega} \quad \text{with} \quad P_2 = \frac{3}{2} \cos^2(\omega) - \frac{1}{2}$$

can be calculated. The orientation factor of an isotropic sample will equal zero, while taking unity for preferential orientation parallel to the sample normal and minus 1/2 for perpendicular orientation for the feature of interest. Bimodal or multimodal distributions are not well described by this parameter, as orientations parallel and perpendicular are weighted differently. It is readily seen that a bimodal distribution assuming perfectly oriented equal populations for parallel and perpendicular orientation to the director yields 1/4. The calculated Herman's orientation parameter for the (100) is 0.82 and -0.09 for the film blade-coated at 90 °C and 55 °C respectively, indicating a strong edge-on orientation for the high temperature condition. In case of the lower temperature coating the Herman's orientation factor indicates a slight face-on orientation (lamellar separation and (100) perpendicular to surface normal).



Linear –Linear Plots of Fig. 4, Fig. 5 & Fig.6

Figure S8: Film thickness (black) and absorbance (red) from in-situ UV-Vis absorption studies during spincoating and blade-coating at optimized conditions.



Figure S9: Results from in-situ GIXD during blade-coating as a function of temperature. Top row: falsecolor plot of (100) pole figure vs time. Bottom row: film thickness and integrated pole figure vs time for blade-coated 90 °C (left panel) and 55 °C (right panel) samples.



Figure 10: In-situ GISAXS as a function of time and temperature for 90 °C (left panel) and 55 °C (right panel) blade-coated samples. Top row: Kratky plots of Iq^2 , middle row: false-color image of Iq^2 vs time, bottom row: film thickness and pseudo-TSI vs time.

Comparison of GISAXS, R-SoXS and TEM

Because of both the truncation of the q-range, and the approximation of a 3D scattering distibution, the psuedo TSI derived from GISAXS may introduce systematic errors. Show below are comparisons of the the GISAXS from films blade coated at 55C and 90 C to the R-SoXS and to the FFT of plain-view LAADAF STEM. One sees excellent agreement between the GISAXS and R-SoXS and STEM over the q-range probed.



S11 Shown below are comparisons of the 'Relative' TSI from R-SoXS and relative psuedo TSI from GISAXS. The psuedo TSI from the GISAXS captures the same trends of the R-SoXS; however, the q-truncation clearly biases the pseudo GISAXS.





S11 Schematic of prototype R2R coater installed at NIST. Slot die head and support wheel are temperature controlled via heat transfer fluid. 2m drier is temperature controlled by forced air from the rectangular heater. Two regions in the heater are open to allow transmission spectroscopies. The entire length can be probed by reflection spectroscopies. For the present studies, an additional heater was located between the coating head and the drier to maintain the web at constant temperature over the entire length from head to end of drier. Arrow indicates location of slot-die coater, that is equipped with a low-pressure backing system (not visible) for high-speed coating.

References

- 1. Y. Liu, J. Zhao, Z. Li, C. Mu, W. Ma, H. Hu, K. Jiang, H. Lin, H. Ade and H. Yan, *Nat Commun*, 2014, **5**, 5293.
- 2. J. R. Tumbleston, A. C. Stuart, E. Gann, W. You and H. Ade, *Advanced Functional Materials*, 2013, 23, 3463-3470.
- 3. S. Mukherjee, C. M. Proctor, G. C. Bazan, T.-Q. Nguyen and H. Ade, *Advanced Energy Materials*, 2015, **5**, 1500877.
- 4. W. Ma, G. Yang, K. Jiang, J. H. Carpenter, Y. Wu, X. Meng, T. McAfee, J. Zhao, C. Zhu, C. Wang, H. Ade and H. Yan, *Advanced Energy Materials*, 2015, **5**, 1501400.
- 5. W. Ma, J. R. Tumbleston, M. Wang, E. Gann, F. Huang and H. Ade, *Advanced Energy Materials*, 2013, **3**, 864-872.
- 6. R. Steyrleuthner, R. Di Pietro, B. A. Collins, F. Polzer, S. Himmelberger, M. Schubert, Z. Chen, S. Zhang, A. Salleo, H. Ade, A. Facchetti and D. Neher, *J Am Chem Soc*, 2014, **136**, 4245-4256.