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Evolution of Power Conversion Efficiency and Molecular Ordering During Thermal Annealing in P3HT:PCBM Bulk Heterojunction Solar Cells

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Supplemental J-V Charaterization

All devices were fabricated from a P3HT:PCBM BHJ at a 1:0.8 weight ratio with a total concentration of 18 mg/mL. These were spin coated at 800 rpm for 40 s and then at 2000 rpm for 5 s. The electrodes were then evaporated under vacuum (<10^{-6}torr). Lithium floride was typically evaporated at a rate of ~0.1 Å/s for a final thickness of 1 nm. Aluminum was typically evaporated at a rate of ~3 Å/s with a final thickness of >75 nm. Typically, each chip contained 5 solar cells with an area of 0.06 cm^2. Representative current-voltage curves for P3HT:PCBM BHJs annealed at 155°C for 10 min can be found in **Figure 1** with the corresponding average device characteristics in **Table 1**. Note that P3HT:PCBM BHJ solar cells made with LiF/Al electrodes showed more efficient photoconversion efficiencies due to a lower contact resistance between the active layer and electrode.

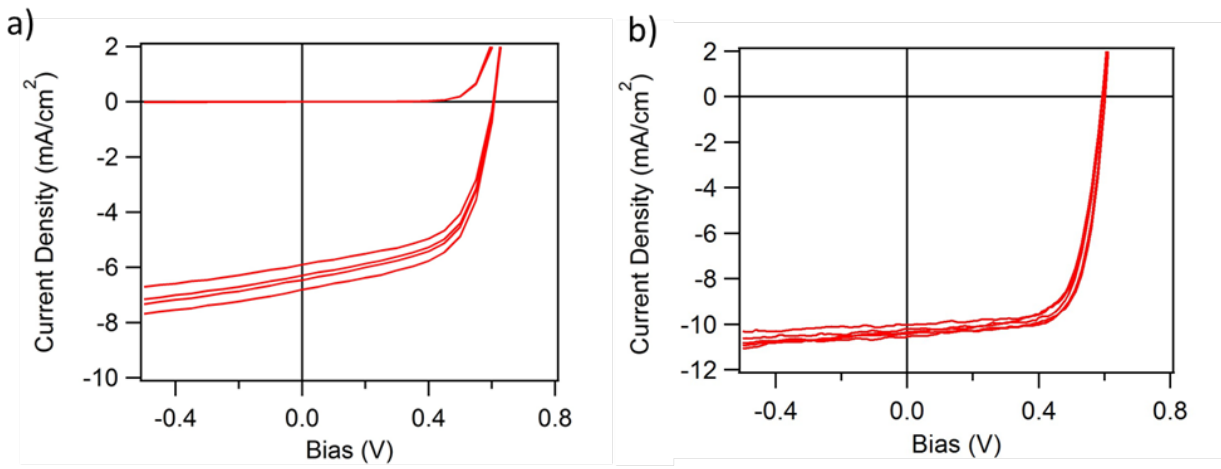

Figure S1. Current-voltage characteristics of a P3HT:PCBM (1:0.8) BHJ annealed at 155°C for 10 min measured at 100 mW/cm^2 with a a) Al (100 nm) and b) LiF (1 nm) / Al (100 nm) electrode.

Table S1. Summary of the current-voltage characteristics of a P3HT:PCBM BHJ (1:0.8) with an active layer of approximately 70 nm.

Electrode	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)
Al	6.47	0.605	0.59	2.31
LiF/Al	10.42	0.602	0.71	4.47

Stretched Exponential

A stretched exponential was used to fit the change in J_{sc} with respect to time at a certain temperature. The equation is below

$$Y=1-exp-Ktn$$

where Y is the normalized J_{sc}, t is time in minutes, and K and n are constants. The fit constants for the P3HT:PCBM BHJs used in this study are reported in **Table S2** and the fits are plotted in **Figure S2**.

Table S2. Stretched exponential constants for a P3HT:PCBM BHJ annealed at various temperatures.

Annealing Temperature	K	n
90°C	1.37	0.47
120°C	1.63	0.39
150°C	1.32	0.52

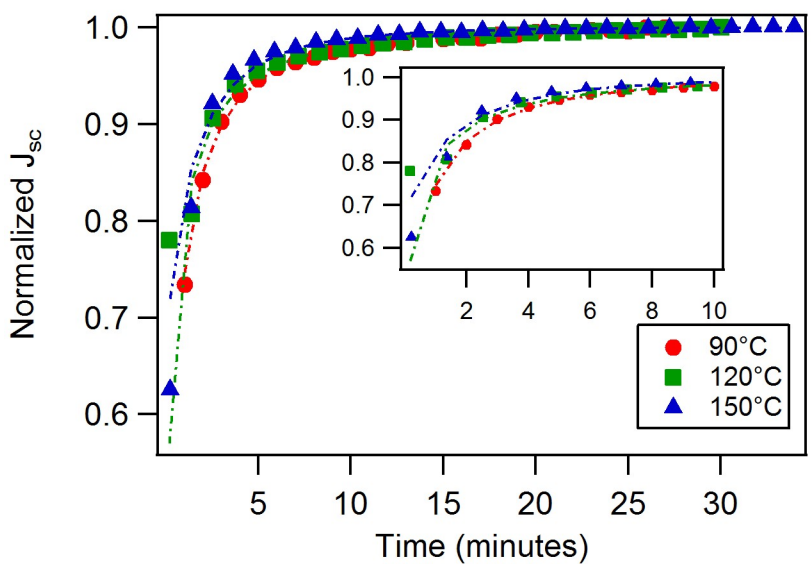

Figure S2. Normalized J_{sc} plotted against time of a P3HT:PCBM BHJ annealed at 90°C (red circles), 120°C (green squares), and 150°C (blue triangles) to determine the fit parameters according to the stretched exponential equation. The J_{sc} is normalized to the value after 25 min of isothermal annealing.

Williamson-Hall Analysis – Crystallite Thickness

Table S3. Crystallite domain size (or thickness) along the *a*-axis of P3HT crystallites in a P3HT:PCBM BHJ annealed at various times. The domain size is determined by using the Scherrer equation with the intercept from the Williamson-Hall plot in **Figure S3**. This shows a growth of crystallites with increasing annealing temperature, consist with previous studies, although the absolute values for the FWHM are much smaller in this present study (likely due to different casting solvents and film thicknesses).[1]

Sample	FHWM at Intercept ($Å^{-1}$)	Crystallite Domain Size (nm)
As Cast	0.033	21
Annealed 90°C	0.028	25
Annealed 120°C	0.025	28
Annealed 150°C	0.022	32

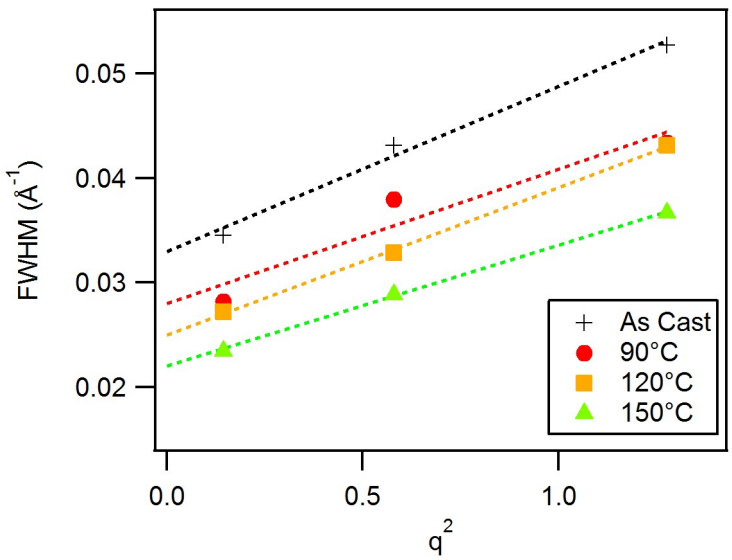

Figure S3. Full-width at half maximum of the (*h*00) peaks as a function of q^2 for a P3HT:PCBM BHJ as cast (black) and annealed at 90°C (red), 120°C (orange), and 150°C (green). The intercept of the lines were used to estimate the crystallite domain size.

2D GIWAXS Scattering Patterns

All GIWAXS patterns were normalized based on sample dimensions, exposure time, and incident beam intensity. Quasi-pole figures as a function of nominally polar angle (β) were plotted by extracting the polar arc slice with a width of 0.05 $Å^{-1}$ and a resolution of $\Delta\beta = 0.25°$. Note that the values obtained are only accurate for values of β ranging from ~10° to ~90°.

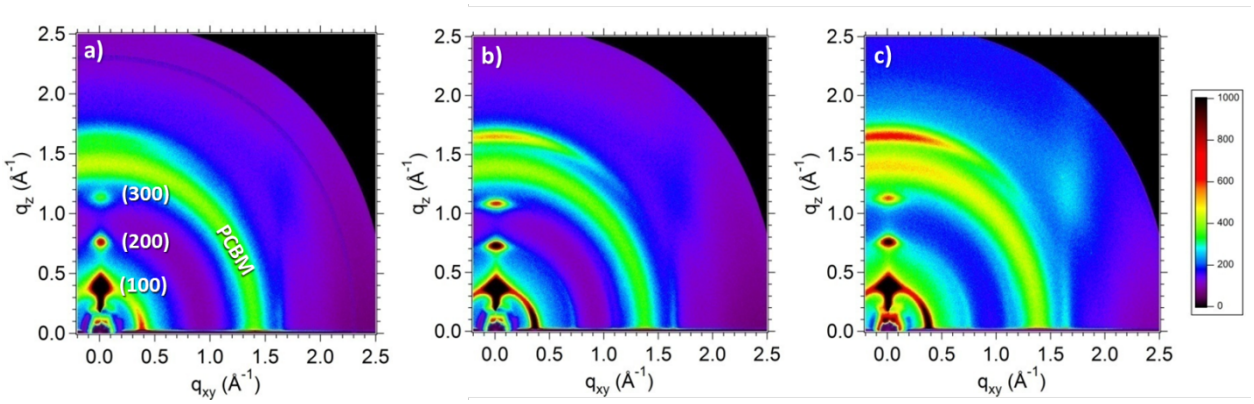

Figure S4. Two-dimensional GIWAXS of a P3HT:PCBM BHJ a) as-cast, b) measured at 90°C after heating for 5 min, and c) measured at room temperature after heating at 90°C for 20 min.

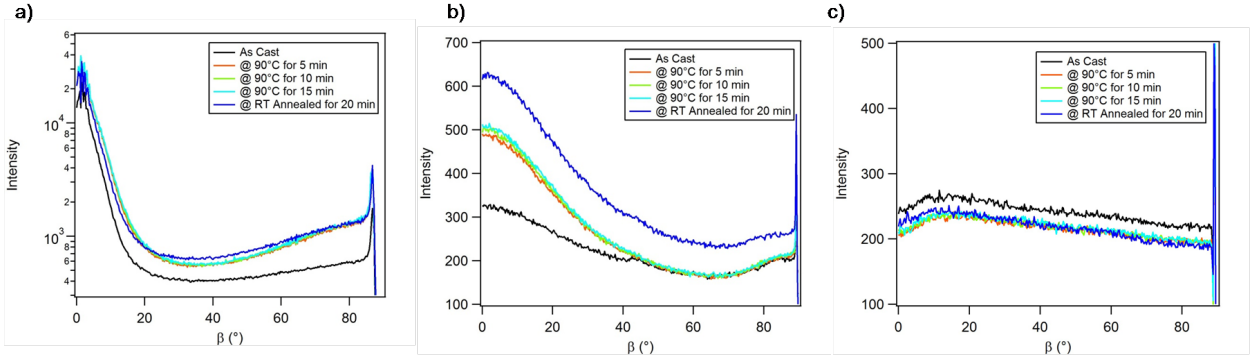

Figure S5. Quasi-pole figures as a function of nominally polar angle (β) of the a) (100) or lamellar and b) (020) or pi-stack reflections from to the P3HT crystallites and c) fullerene scattering of an as cast P3HT:PCBM BHJ (black) and measured at 90°C after annealing for 5 min (orange), 10 min (green), 15 min (aqua) and at room temperature after annealing for 20 min at 90°C (blue). Here β is the angle from the meridian in the 2D GIWAXS image. In a) and b), the sharp spike near 90° is due to refraction. The decrease at 90° in c) is due to refraction in the background used.

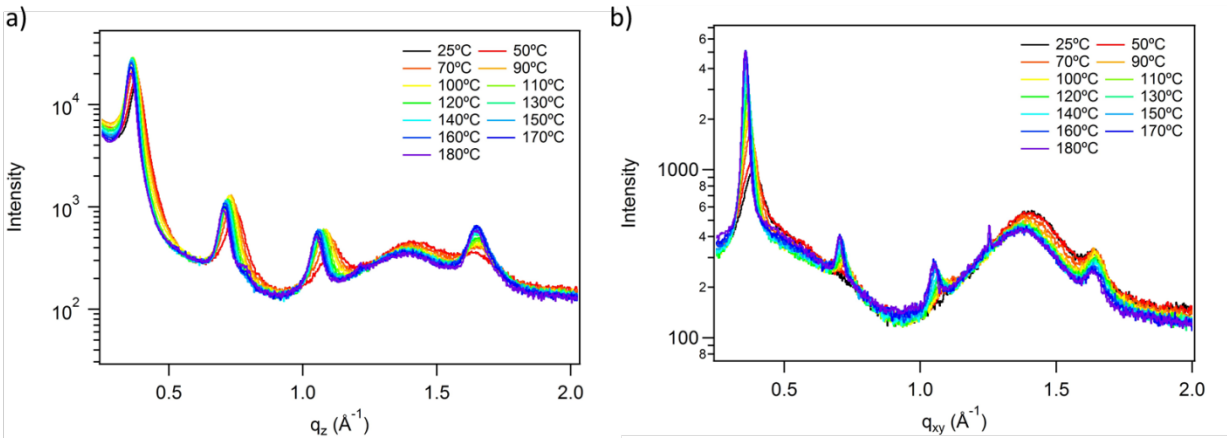

Figure S6. Integrated cake slices from a 2D GIWAXS diffraction pattern of a P3HT:PCBM BHJ a) along the meridian (near $\mathbf{q_z}$) b) along the horizon (near $\mathbf{q_{xy}}$). Patterns were collected at the temperatures noted on the graph.

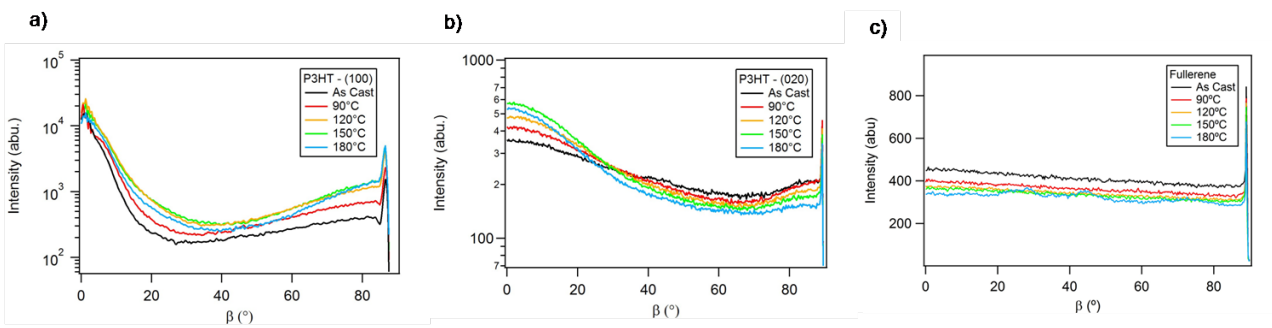

Figure S7. Quasi-pole figures as a function of β of the a) first order (100) or lamellar and b) (020) or pi-stack reflections from to the P3HT crystallites and c) fullerene scattering of a P3HT:PCBM BHJ annealed with a temperature ramp. Here β is the angle from the meridian in the 2D GIWAXS image. The sharp spike near 90° is due to refraction.

Fraction of Face-on Oriented P3HT Crystallites

Polar arcs slices at $\mathbf{q}$ = 0.39 and 1.65 Å^{-1} (with background corrections) were integrated from β_1 = 0 to 10°(meridian) and from β_2 = 80 to 90°(horizon). The ratio of β_2/β_1 at $\mathbf{q}$ = 0.39 Å^{-1} and β_1/β_2 at $\mathbf{q}$ = 1.65 Å^{-1}approximately corresponds to the relative fraction of face-on oriented P3HT crystallites. The values of the ratios were then normalized to the maximum (at 180°C) and are plotted as a function of annealing temperature in **Figure S8**. This shows an increase in face-on texture as a function of temperature, consistent with previous reports.[1]

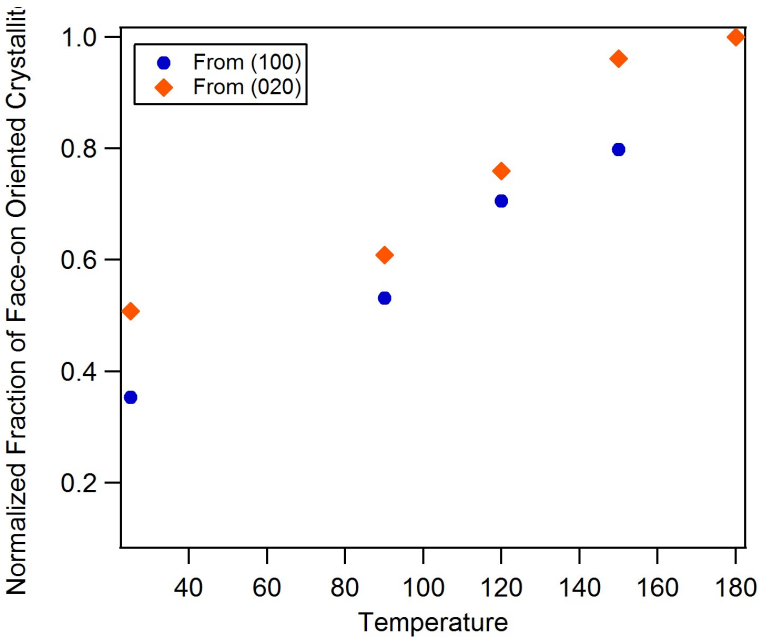

Figure S8. Normalized fraction of face on oriented crystallites calculated from the diffraction intensity of the (100) (orange diamonds) and the (020) (blue circles).

Thermochromic Shift in P3HT Absorption

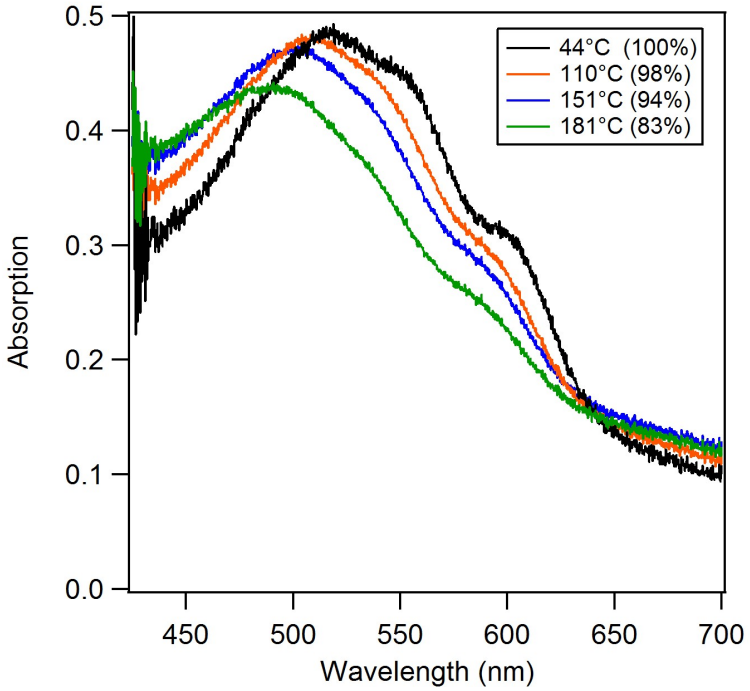

Figure S9. UV-Vis absorption spectrum of a P3HT:fullerene blend taken at 44°C (black), 110°C (orange), 151°C (blue), and 181°C (green). The values in parentheses in the annotation signify

the percent shift in the absorption spectrum of a Gaussian curve centered at 520 nm with a FWHM of 20 nm (the output of the green LED).

Optical microscopy images of P3HT:PCBM

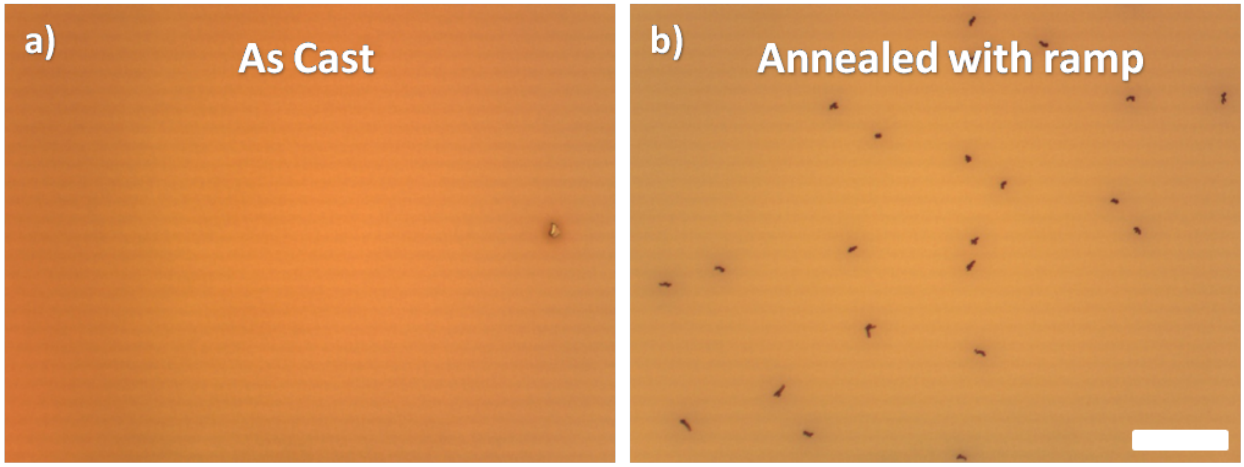

Figure S10. Transmission optical microscope images of a P3HT:PCBM BHJ solar cell a) as-cast and b) annealed with a 3°C/min temperature ramp from room temperature. Scale bar represents a length of 50 μm.

PCBM Aggregate Correlation Length Calculation

Scherrer Equation

$$q = \frac{4 \bullet \pi \bullet \sin(\theta)}{\lambda}$$

$$\lambda := 0.98 \bullet \text{Angstrom} \qquad q := 1.4105 \bullet \frac{1}{\text{Angstrom}} \qquad q_{fwhm} := 0.29972 \bullet \frac{1}{\text{Angstrom}}$$

$$\theta_B := \frac{q \bullet \lambda}{4 \bullet \pi}$$

Dropped out the sin because it doesn't change anything

$$B := 2 \bullet \frac{q_{fwhm} \bullet \lambda}{4 \bullet \pi}$$

$$\theta_B = 1.10 \times 10^{-1}$$

$$B = 4.67 \times 10^{-2}$$

λ = X-ray wavelength
B = Full-width half maximum (2θ in radians)
θ_B = Bragg Angle in radians

$$t := \frac{\lambda}{B \bullet \cos(\theta_B)}$$

$$t = 2.11 \times 10^{0}\ \text{nm}$$

1. E. Verploegen, R. Mondal, C. J. Bettinger, S. Sok, M. F. Toney and Z. A. Bao, *Advanced Functional Materials*, 2010, **20**, 3519-3529.