Supporting Information

Manipulating the Morphology of P3HT-PCBM Bulk Heterojunction Blends with Solvent Vapor Annealing

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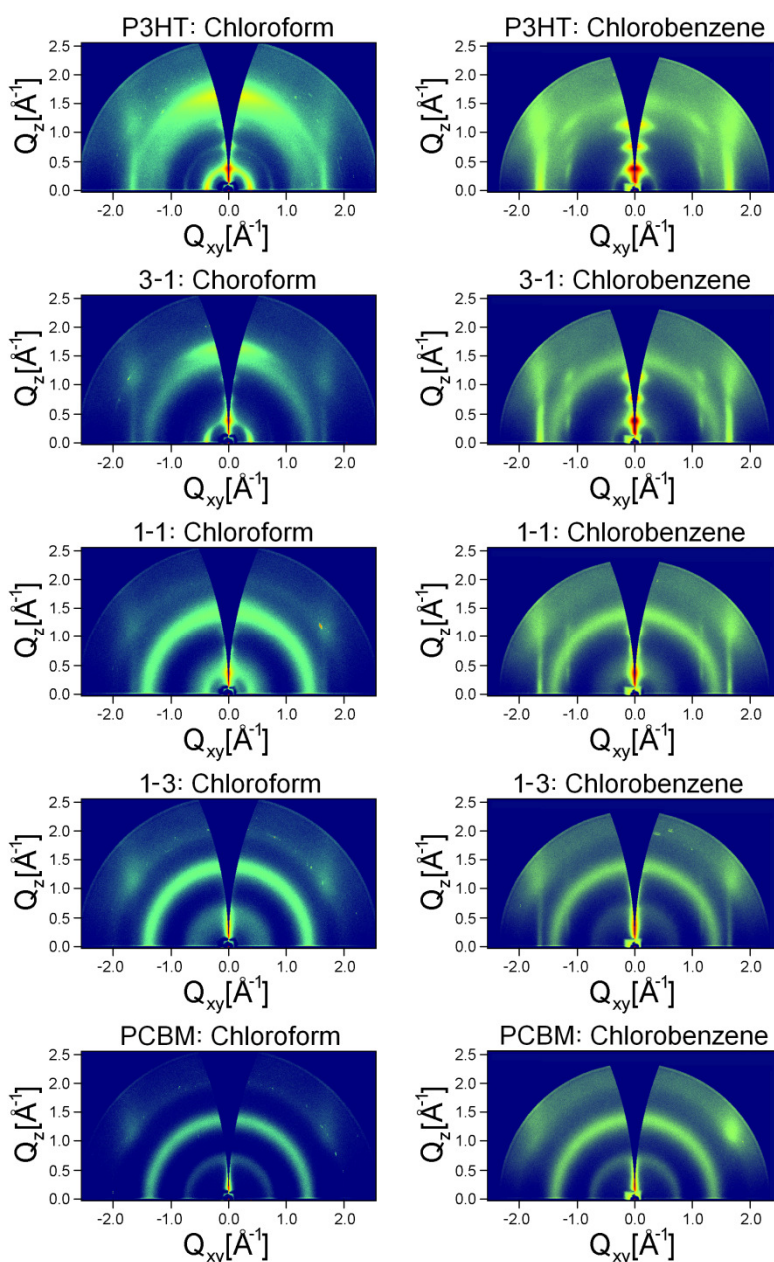[2]Stanford Synchrotron Radiation Lightsource, Menlo Park, CA 94025

Figure S1. 2-D GIWAXS images as-cast thin films, top to bottom: of P3HT, 3:1 P3HT-PCBM blend, 1:1 P3HT-PCBM blend, 1:3 P3HT-PCBM blend, and PCBM. The images on the left are spin cast from 2 mg/mL in chloroform, and the images in the right are spin cast from 2 mg/mL in chlorobenzene.
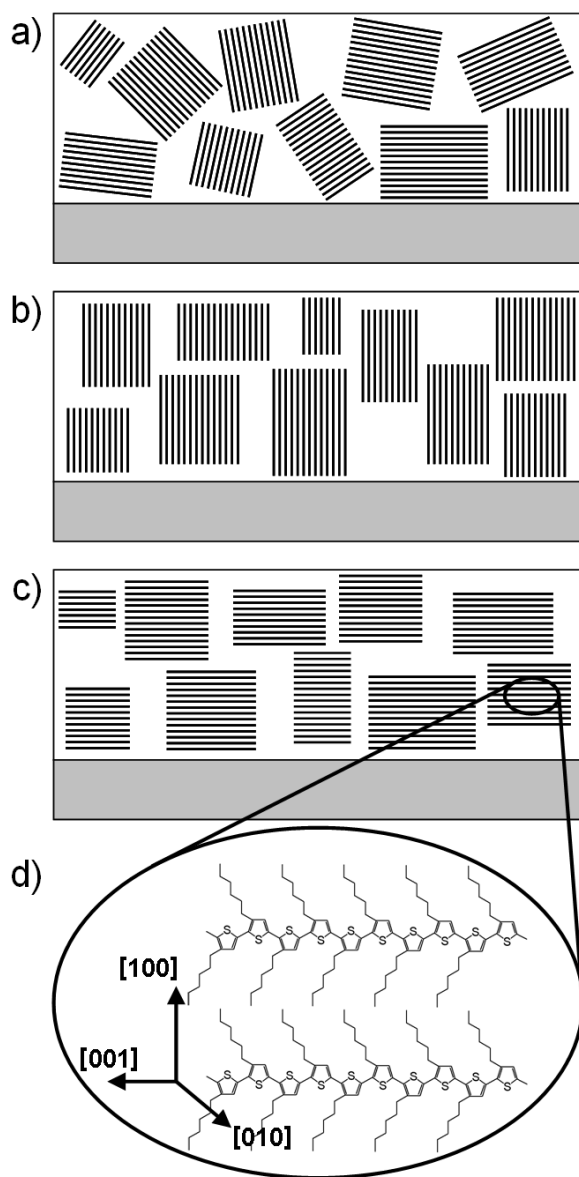
Figure S2. Cartoons of P3HT thin films with a) random, b) perpendicular, and c) parallel P3HT lamellae orientations relative to the substrate. The crystallographic directions are shown relative to the molecular structure in d). The P3HT layers lie in the (100) plane, the [100] direction is normal to the P3HT layers, the π-face lies in the (020) plane, the π-π stacking direction is along the [010] direction, and the chain backbone is along the [001] direction. (Figure taken from Verploegen et.al. *Advanced Functional Materials* **2010,** 20, (20), 3519-3529)

Table S1. Layer spacing and FWHM of P3HT in thin films spin cast from 2 mg/mL in chloroform and 2 mg/mL in chlorobenzene (see Figure S1). The layer spacing was determined by integration of the nominally out-of-plane (200) peak (The region selected for subsequent quantitative analysis is shown in Figure S3 of the supplementary information).

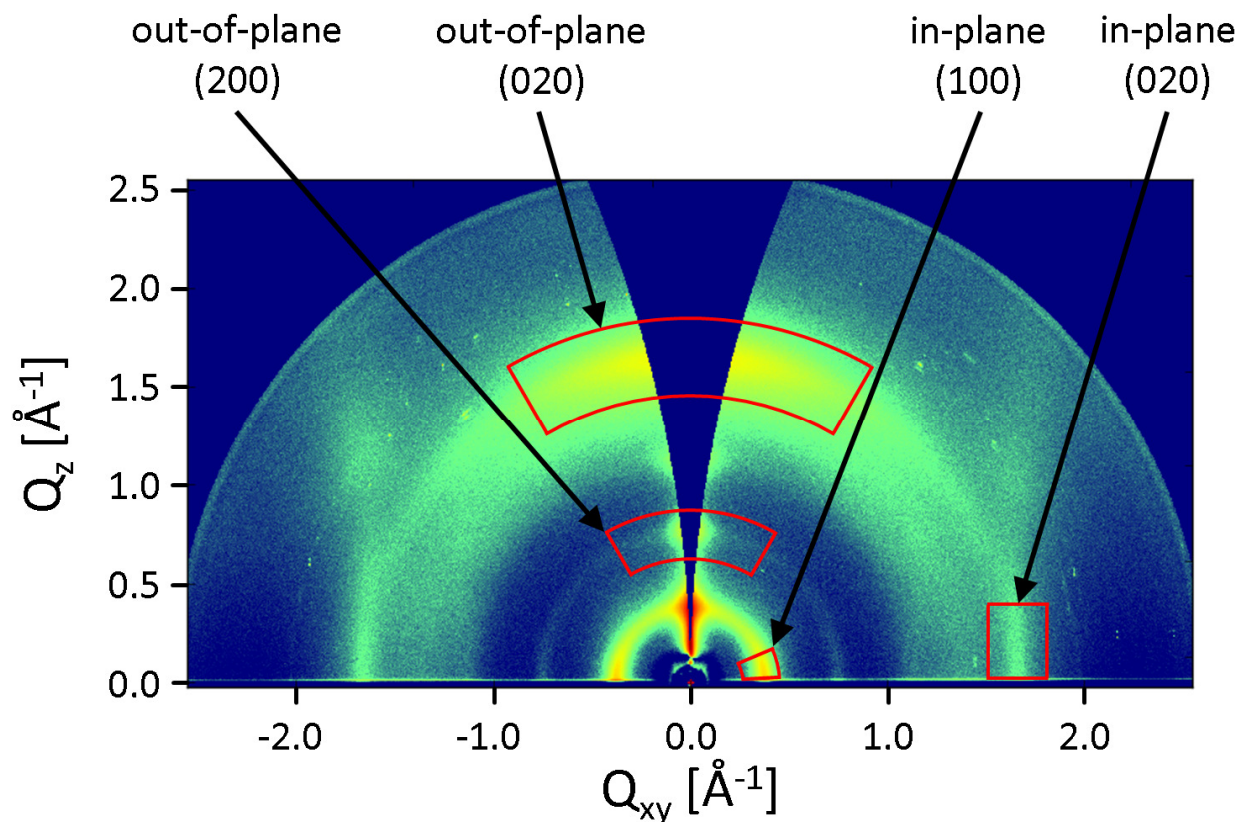| Blend	Spin casting solvent	Layer spacing (Å)	FWHM ($Å^{-1}$)	Boiling Point (°C)
P3HT	Chloroform	16.68	0.103	61
P3HT	Chlorobenzene	16.41	0.081	131
3-1	Chloroform	16.72	0.107	61
3-1	Chlorobenzene	16.41	0.084	131
1-1	Chloroform	16.86	0.121	61
1-1	Chlorobenzene	16.78	0.109	131

Figure S3. 2-D GIWAXS image of as-cast P3HT thin film. The red boxes indicate the region where the peak integration takes place. A cake slice was taken from q = 0.26 $Å^{-1}$ to 0.45 $Å^{-1}$ and chi = 3° to 20 was used for analysis of the in-plane (100) peak. A cake slice was taken from q = 0.62 $Å^{-1}$ to 0.86 $Å^{-1}$ and chi = 60° to 120° was used for analysis of the nominally out-of-plane (200) peak. A cake slice was taken from q = 1.45 $Å^{-1}$ to 1.85 $Å^{-1}$ and chi = 60° to 120° was used for analysis of the nominally out-of-plane (020) peak, and a box from q_{xy} = 1.5 $Å^{-1}$ to 1.8 $Å^{-1}$ and q_z = 0.03 $Å^{-1}$ to 0.40 $Å^{-1}$ was used for analysis of the in-plane (020) peak.

Table S2. P3HT layer spacing, layer FWHM, π-π stacking distance, π-π FWHM for each solvent, before, during, and after SVA; for neat P3HT, 3-1, and 1-1 blends spin cast from 2 mg/mL in chloroform. Percent change can be found in Table S3 below. Layer spacing values were determined by integration of the in-plane (100) peak, and the π-π stacking distance was determined by integration of the nominally out-of-plane (020) peak (The regions selected for subsequent quantitative analysis is shown in Figure S3).

Film composition	Solvent vapor	Layer spacing			Layer FWHM			π-π stacking distance			π-π FWHM		
		before	during	after	before	during	after	before	during	after	before	during	after
	Chloroform	16.73	17.24	17.00	0.054	0.046	0.045	3.83	3.80	3.76	0.152	0.129	0.132
P3HT	Hexane	16.72	17.35	16.96	0.056	0.058	0.054	3.81	3.81	3.80	0.146	0.146	0.144
	THF	16.67	17.10	16.73	0.058	0.049	0.047	3.81	3.79	3.75	0.142	0.128	0.133
	Chloroform	16.62	17.17	17.09	0.059	0.049	0.049	3.83	3.79	3.72	0.147	0.124	0.136
3:1	Hexane	16.70	17.27	16.97	0.059	0.058	0.056	3.83	3.83	3.82	0.143	0.145	0.143
	THF	16.62	16.98	16.78	0.060	0.050	0.049	3.83	3.81	3.75	0.146	0.129	0.130
	Chloroform	16.55	17.07	17.15	0.083	0.049	0.049	-	-	-	-	-	-
1:1	Hexane	16.55	17.25	17.01	0.089	0.063	0.057	-	-	-	-	-	-
	THF	16.44	16.89	16.82	0.096	0.045	0.045	-	-	-	-	-	-

Table S3: P3HT percent change for layer spacing, layer FWHM, π-π stacking distance, π-π FWHM for each solvent, before, during, and after SVA (for neat P3HT, 3-1, and 1-1 blends spin cast from 2 mg/mL in chloroform). Layer spacing values were determined by integration of the in-plane (100) peak, and the π-π stacking distance was determined by integration of the nominally out-of-plane (020) peak (The regions selected for subsequent quantitative analysis is shown in Figure S3 of the supplementary information).

| Film composition	Solvent vapor	Layer spacing		Layer FWHM		π-π stacking distance		π-π FWHM	
		% during	% after	% during	% after	% during	% after	% during	% after
	Chloroform	3.04	1.60	-13.75	-16.54	-0.94	-2.01	-15.11	-12.86
P3HT	Hexane	3.79	1.45	4.11	-3.04	0.03	-0.24	0.07	-1.44
	THF	2.56	0.37	-15.13	-18.26	-0.53	-1.55	-10.20	-6.61
	Chloroform	3.32	2.81	-16.84	-16.33	-1.15	-2.87	-15.47	-7.57
3:1	Hexane	3.40	1.62	-2.53	-6.41	0.11	-0.14	1.65	-0.23
	THF	2.20	0.96	-16.72	-18.39	-0.57	-1.91	-11.90	-10.81
	Chloroform	3.11	3.60	-41.66	-41.54	-	-	-	-
1:1	Hexane	4.28	2.81	-28.86	-35.96	-	-	-	-
	THF	2.73	2.30	-53.07	-53.28	-	-	-	-
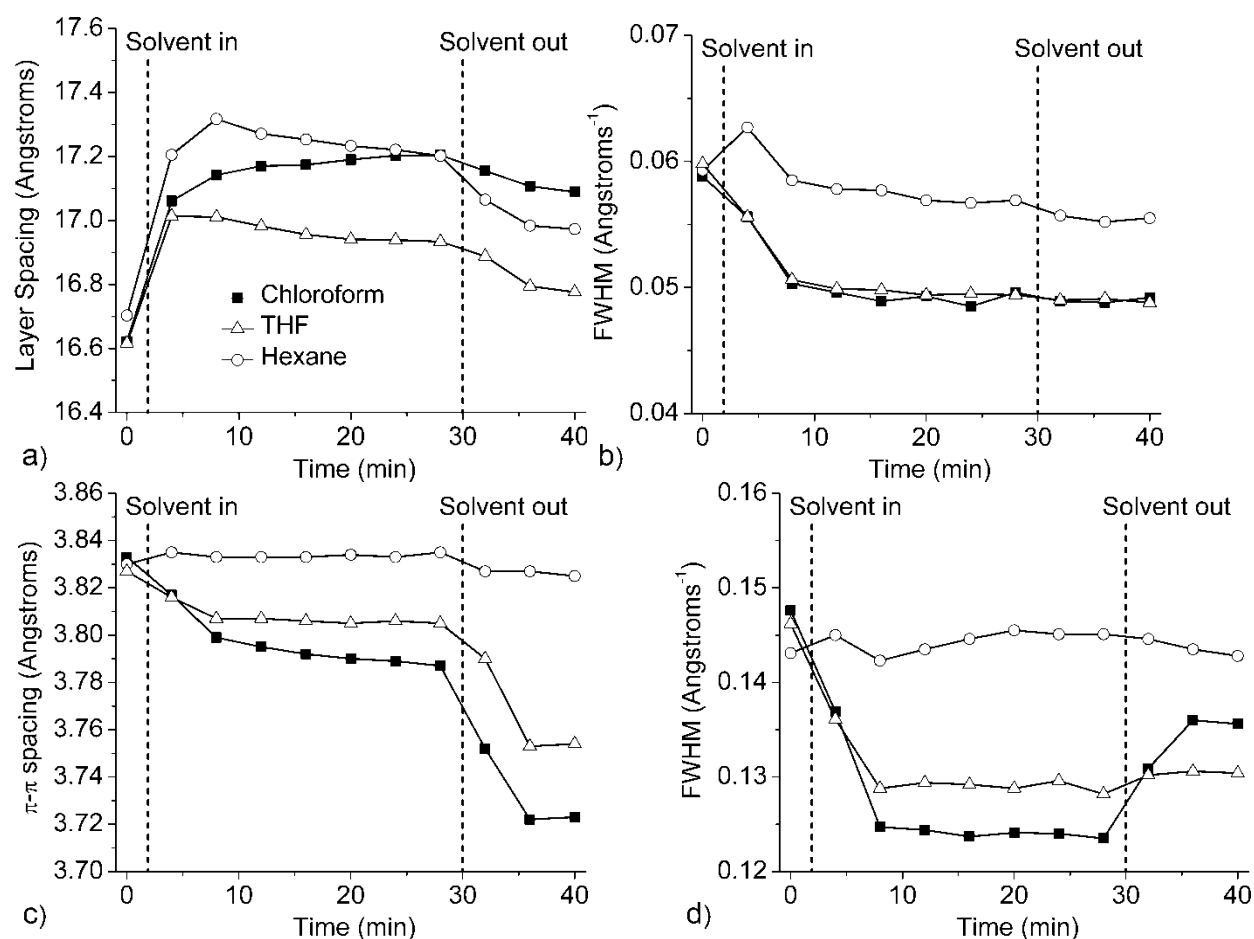
Figure S4. a) Layer spacing, b) Layer FWHM, c) π-π stacking distance, d) π-π FWHM for 3:1 blend thin films spin cast from 2 mg/mL in chloroform. The thin films exposed to chloroform vapor (solid squares), hexane vapor (open circles), and THF vapor (open triangles) are shown. Layer spacing values were determined by integration of the in-plane (100) peak, and the π-π stacking distance was determined by integration of the nominally out-of-plane (020) peak.

Table S4. P3HT layer spacing, layer FWHM, π-π stacking distance, π-π FWHM for each solvent, before, during, and after SVA (for neat P3HT, 3-1, and 1-1 blends spin cast from 10 mg/mL in chloroform). Percent change can be found in Table S5 in the supporting information. Layer spacing values were determined by integration of the in-plane (100) peak, and the π-π stacking distance was determined by integration of the nominally out-of-plane (020) peak.

Film composition	Solvent vapor	Layer spacing			Layer FWHM			π-π stacking distance			π-π FWHM		
		before	during	after	before	during	after	before	during	after	before	during	after
P3HT	Chloroform	16.61	17.08	16.72	0.062	0.056	0.055	3.82	3.79	3.77	0.172	0.133	0.148
	THF	16.63	17.04	16.70	0.063	0.056	0.055	3.82	3.81	3.78	0.175	0.147	0.153
3:1	Chloroform	16.64	17.08	16.68	0.063	0.051	0.051	3.84	3.81	3.81	0.145	0.116	0.124
	THF	16.64	17.00	16.63	0.063	0.051	0.050	3.84	3.82	3.82	0.148	0.120	0.127
1:1	Chloroform	16.59	16.82	16.71	0.088	0.048	0.049	-	-	-	-	-	-
	THF	16.38	16.70	16.55	0.084	0.047	0.047	-	-	-	-	-	-

Table S5: P3HT percent change for layer spacing, layer FWHM, π-π stacking distance, π-π FWHM for each solvent, before, during, and after SVA (for neat P3HT, 3-1, and 1-1 blends spin cast from 10 mg/mL in chloroform). Layer spacing values were determined by integration of the in-plane (100) peak, and the π-π stacking distance was determined by integration of the nominally out-of-plane (020) peak.

| Film composition	Solvent vapor	Layer spacing		Layer FWHM		π-π stacking distance		π-π FWHM	
		% during	% after	% during	% after	% during	% after	% during	% after
P3HT	Chloroform	2.82	0.69	-9.85	-11.15	-0.58	-1.13	-22.80	-14.44
	THF	2.48	0.42	-10.19	-11.78	-0.37	-1.07	-16.27	-12.67
3:1	Chloroform	2.65	0.28	-18.57	-18.89	-0.63	-1.41	-20.51	-14.87
	THF	2.16	-0.07	-19.05	-20.79	-0.52	-1.28	-19.10	-14.24
1:1	Chloroform	1.37	0.70	-44.86	-44.41	-	-	-	-
	THF	1.92	1.01	-44.19	-44.19	-	-	-	-
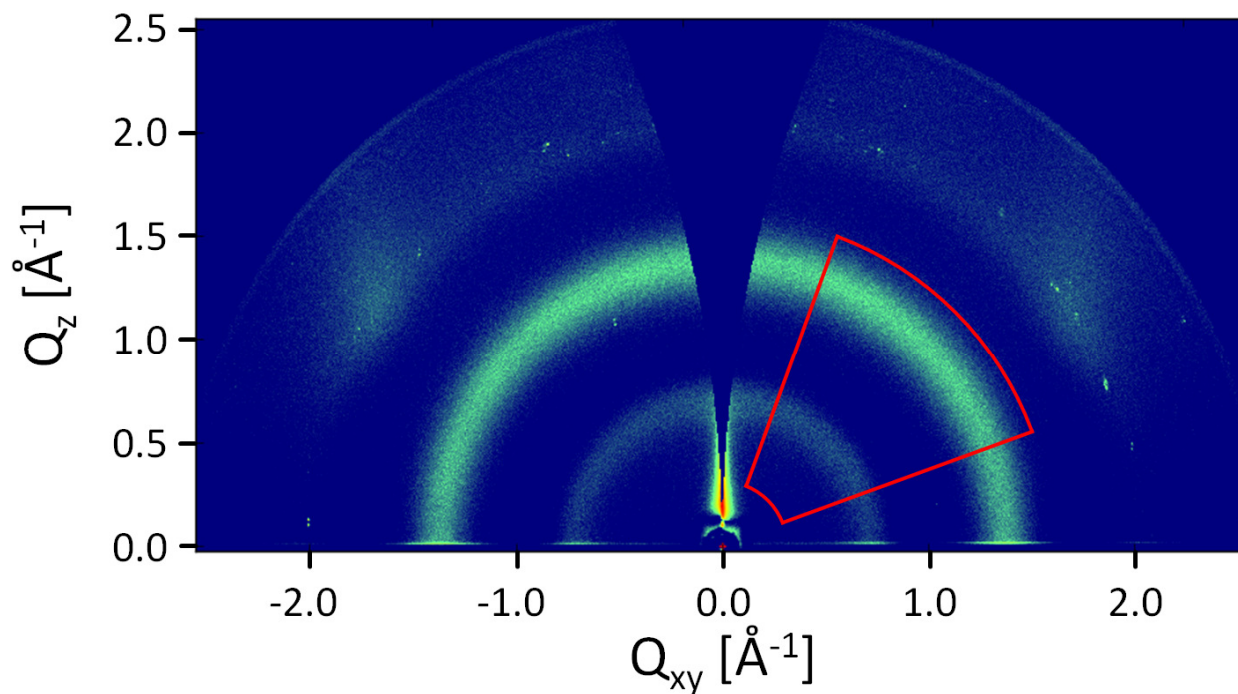
Figure S5. 2-D GIWAXS image of as-cast PCBM thin film. The red box indicates the region where the peak integration was taken (q = 0.3 to 1.6 Å^{-1} and β = 20 to 70°)

PCBM as-cast

PCBM THF vapor annealed
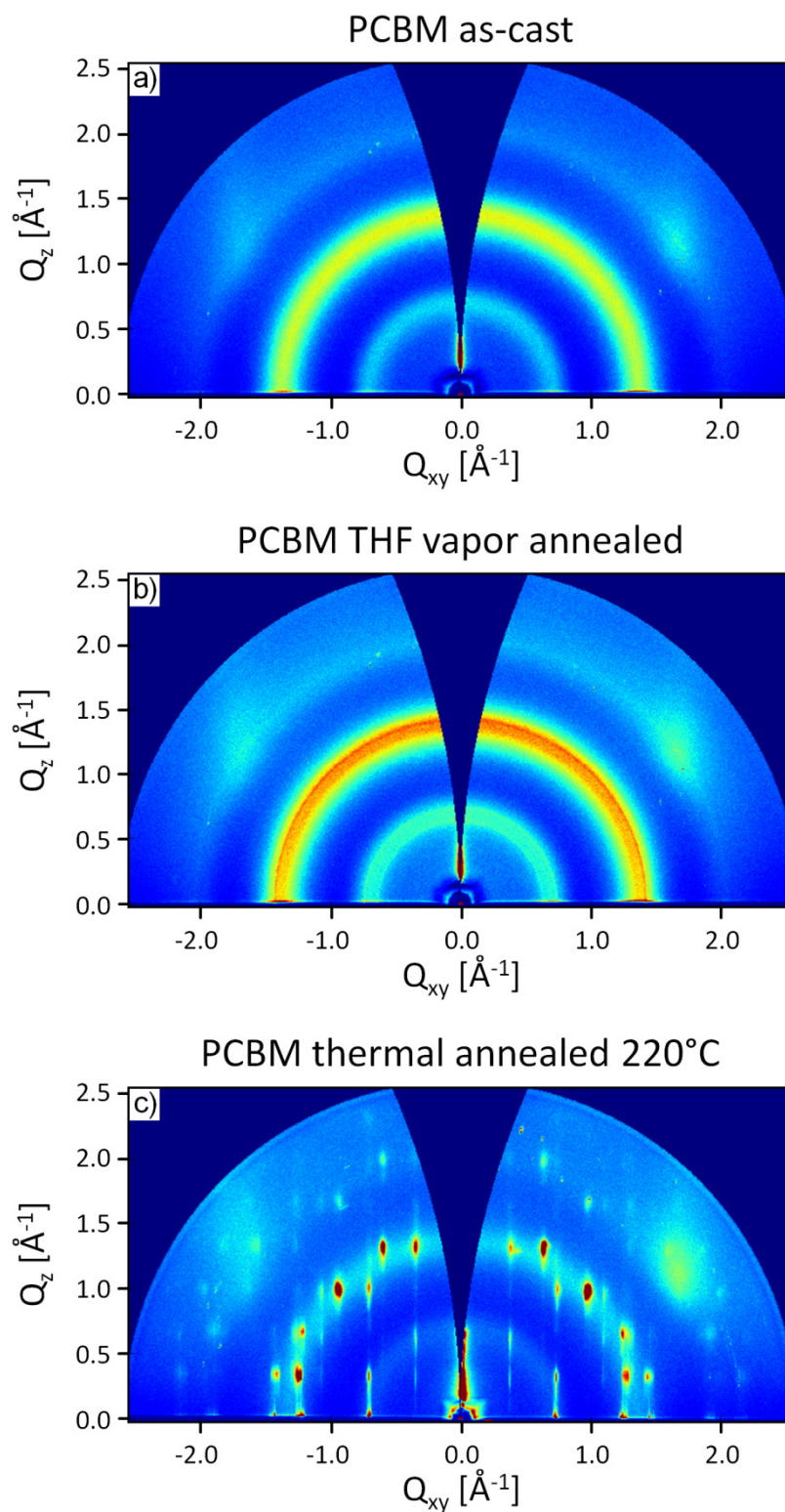

PCBM thermal annealed 220°C

Figure S6. 2-D GIWAXS images of neat PCBM thin films spin cast from 10 mg/mL in chloroform a) as-cast, b) after exposure to THF vapor for 30 minutes, and c) after thermal annealing at 220 °C.
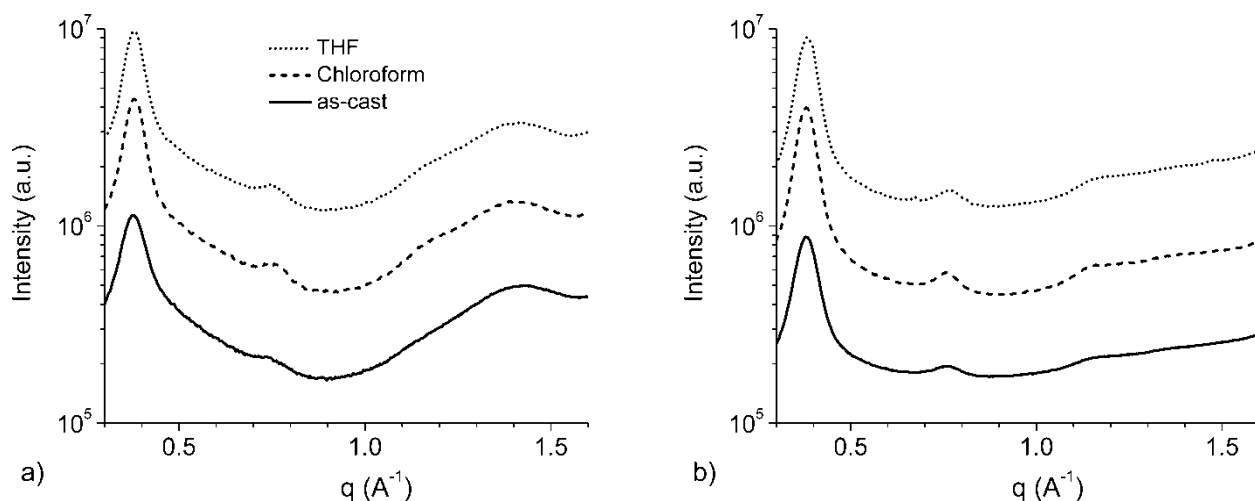
Figure S7. GIWAXS of a) 3:1 P3HT-PCBM blend and b) neat P3HT thin films spin cast from 10 mg/mL in chloroform. The as-cast thin films (solid line), thin films exposed to chloroform vapor (dashed line), and thin films exposed to THF vapor (dotted line) are shown. The data are presented with *arbitrary units* and have been *shifted for clarity*. The region selected for subsequent quantitative analysis is shown in Figure S5 of the supplementary information. The peaks observed at q ~ 0.37 Å^{-1} and ~ 0.75 Å^{-1} are the (100) and (200) peaks of the P3HT component, respectively.
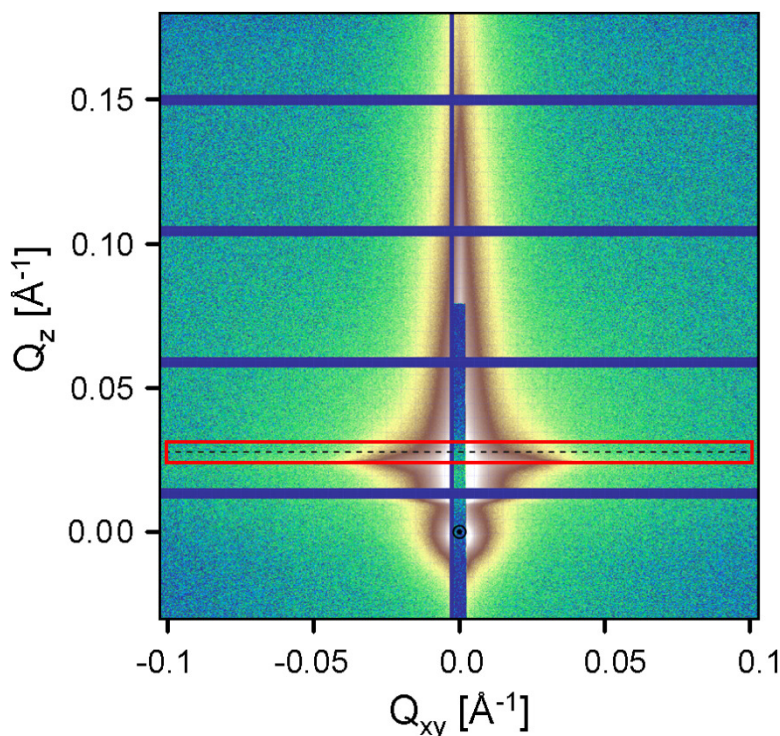

Figure S8. 2-D GISAXS image of a 1:1 P3HT-PCBM blend thin film. The red boxes indicate the region where the peak integration takes place (q_{xy} = -0.1 to 0.1 Å^{-1} and q_z = 0.0239 to 0.0303 Å^{-1}). The lines with no scattering intensity are the gaps between the individual detectors.

Table S6. Domain sizes and Porod exponent determined by fitting the unified equation to the in-plane GISAXS data.

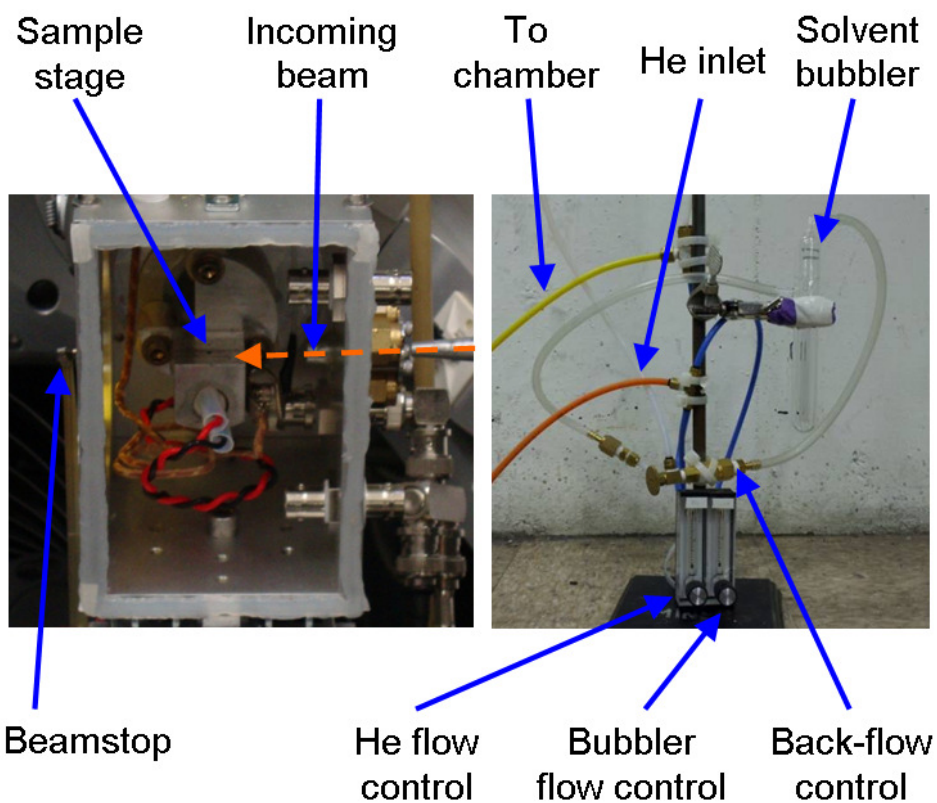| Annealing Conditions	Domain sizes [Å]	Porod exponent
as-cast	-	2.4
SVA with hexane	-	2.0
SVA with THF	61.6	3.1
SVA with chloroform	52.1	3.5
Thermal annealing at 140°C	86.3	3.2
Thermal annealing at 175°C	120.8	2.8

Figure S9. Images of in-situ solvent vapor annealing chamber.