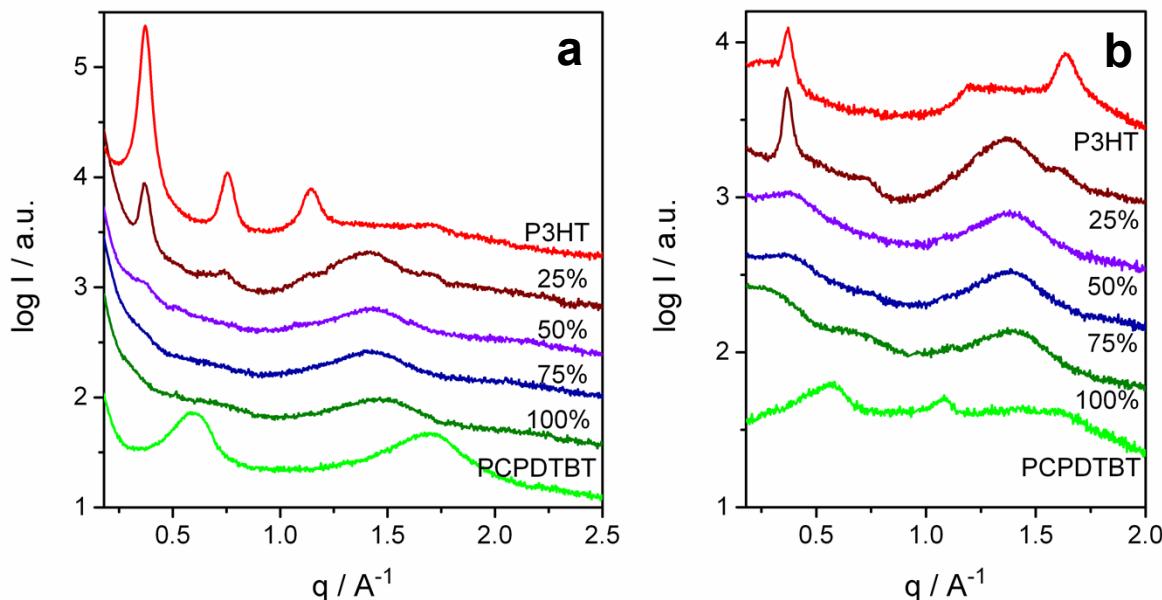


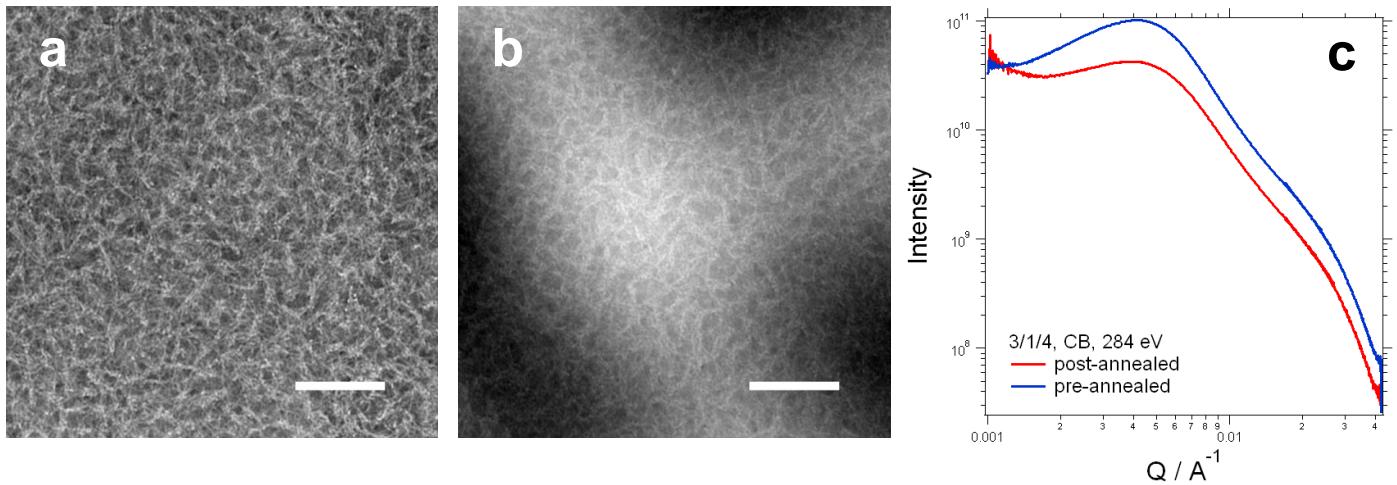
## Supporting Information

### Guided Crystallization of P3HT in Ternary Blend Solar Cell Based on P3HT:PCPDTBT:PCBM

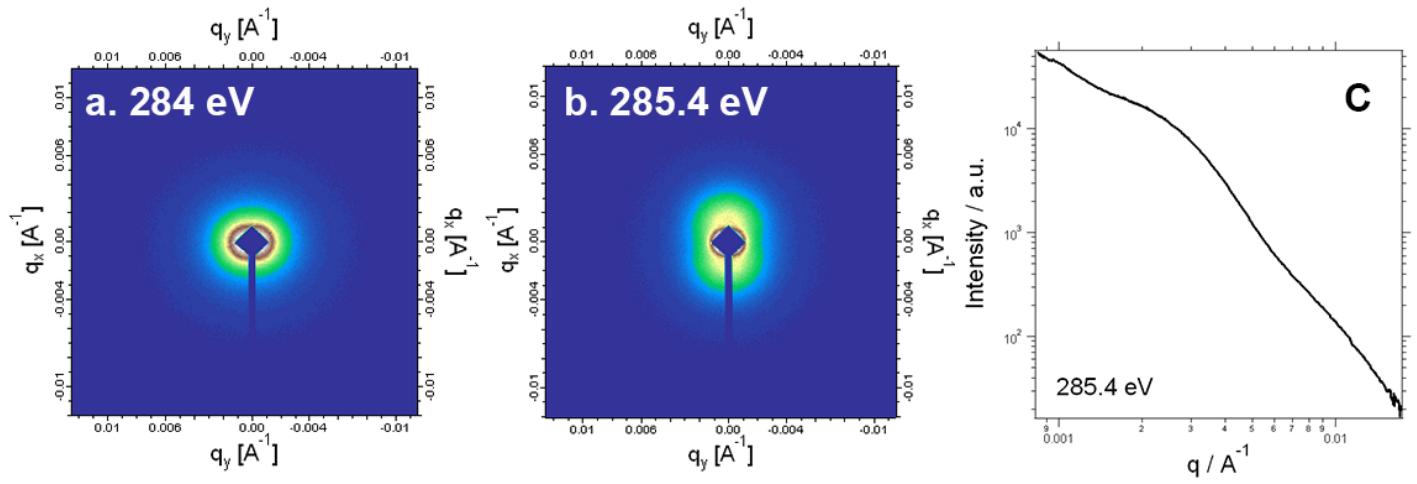
Yu Gu, Cheng Wang, Feng Liu, Jihua Chen, Ondrej E. Dyck, Gerd Duscher, Thomas P. Russell\*



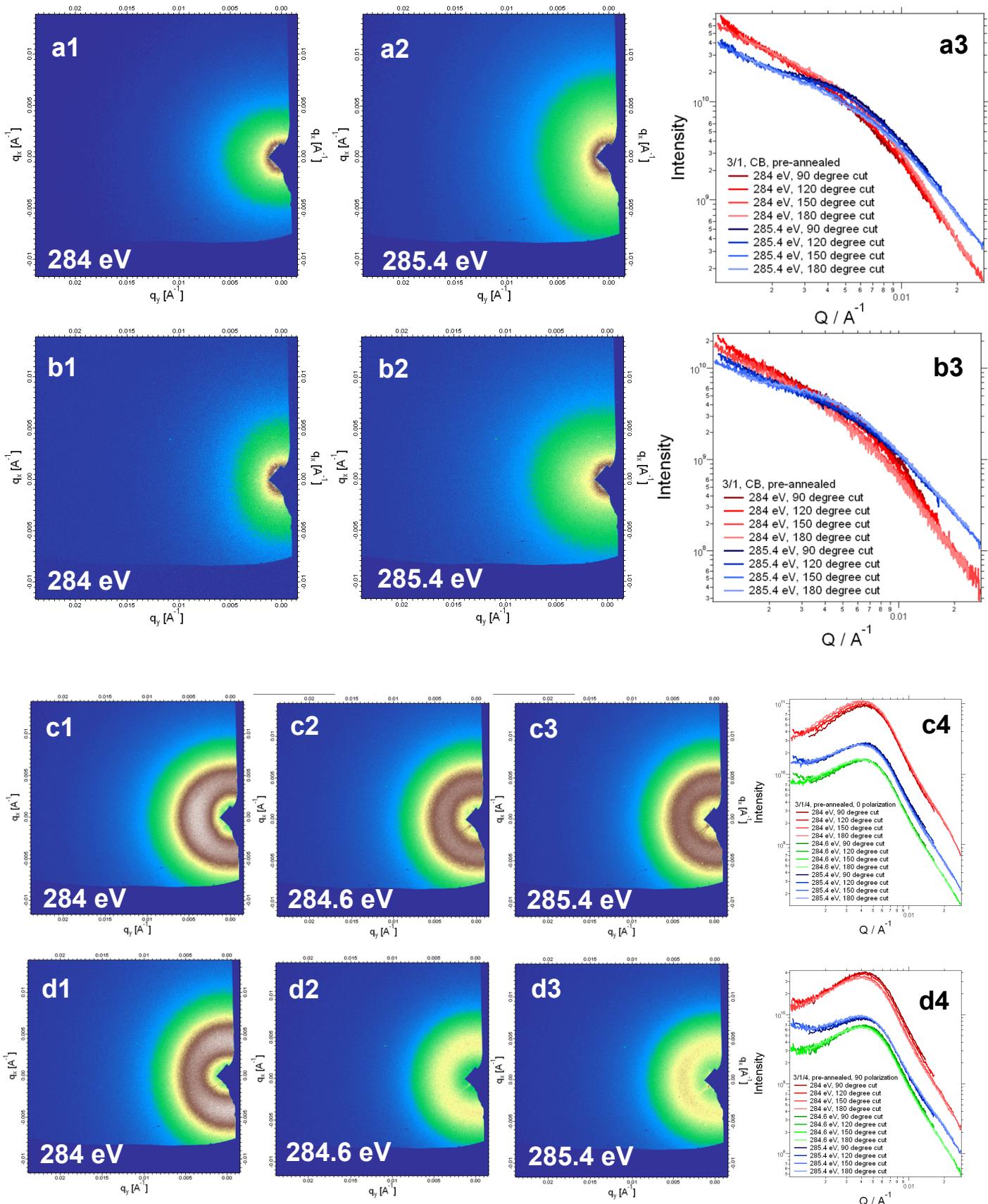
**Figure S1.** GIXD (a) OOP or (b) IP profiles for P3HT-32k:PCPDTBT:PC<sub>61</sub>BM ternary blend thin films with different PCPDTBT contents and pure P3HT or PCPDTBT films.



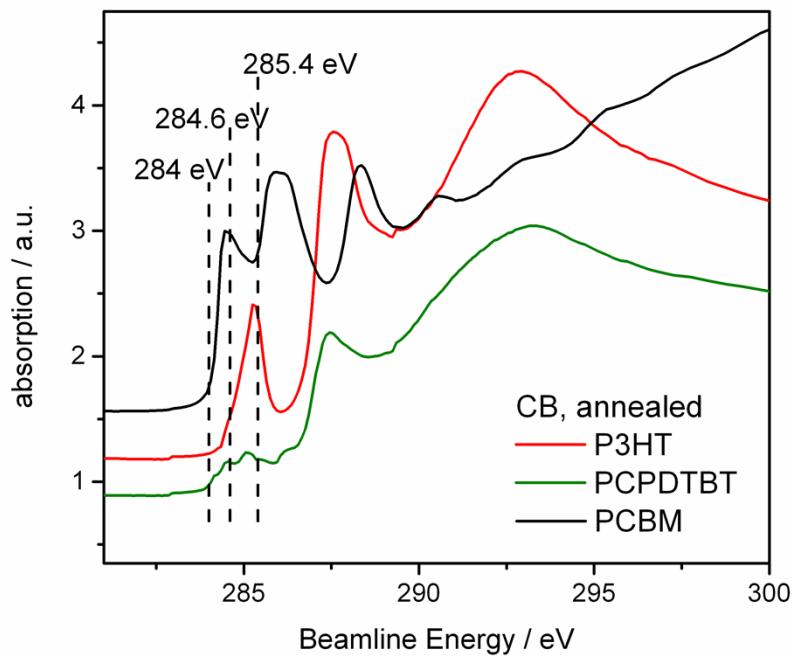
**Figure S2.** BF-TEM images for ternary blend thin films of P3HT-32k:PCPDTBT:PC<sub>61</sub>BM with weight ratio of 3/1/4 (25 wt% of PCPDTBT), spin-coated by CB, pre-annealed (a) or post-annealed (b). The scale bar is 500 nm. P-RSoXS profiles for the pre-annealed and post-annealed samples (c).



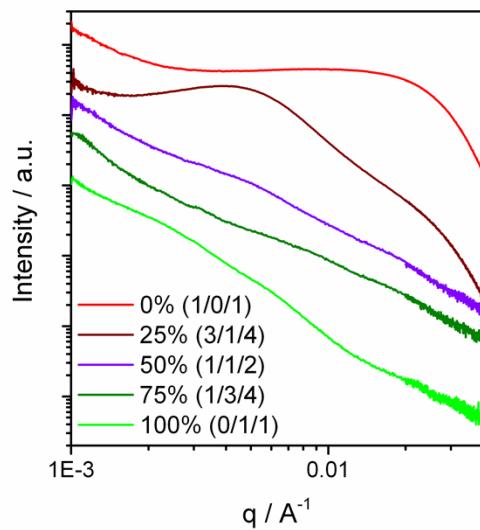
**Figure S3.** P-RSoXS patterns (a, b) and circularly averaged profile (c) for regio-random P3HT:PCPDTBT thin film (1/1 wt/wt, spin-coated by CB, pre-annealed at 150°C for 10 minutes) at horizontally polarized x-ray beam.



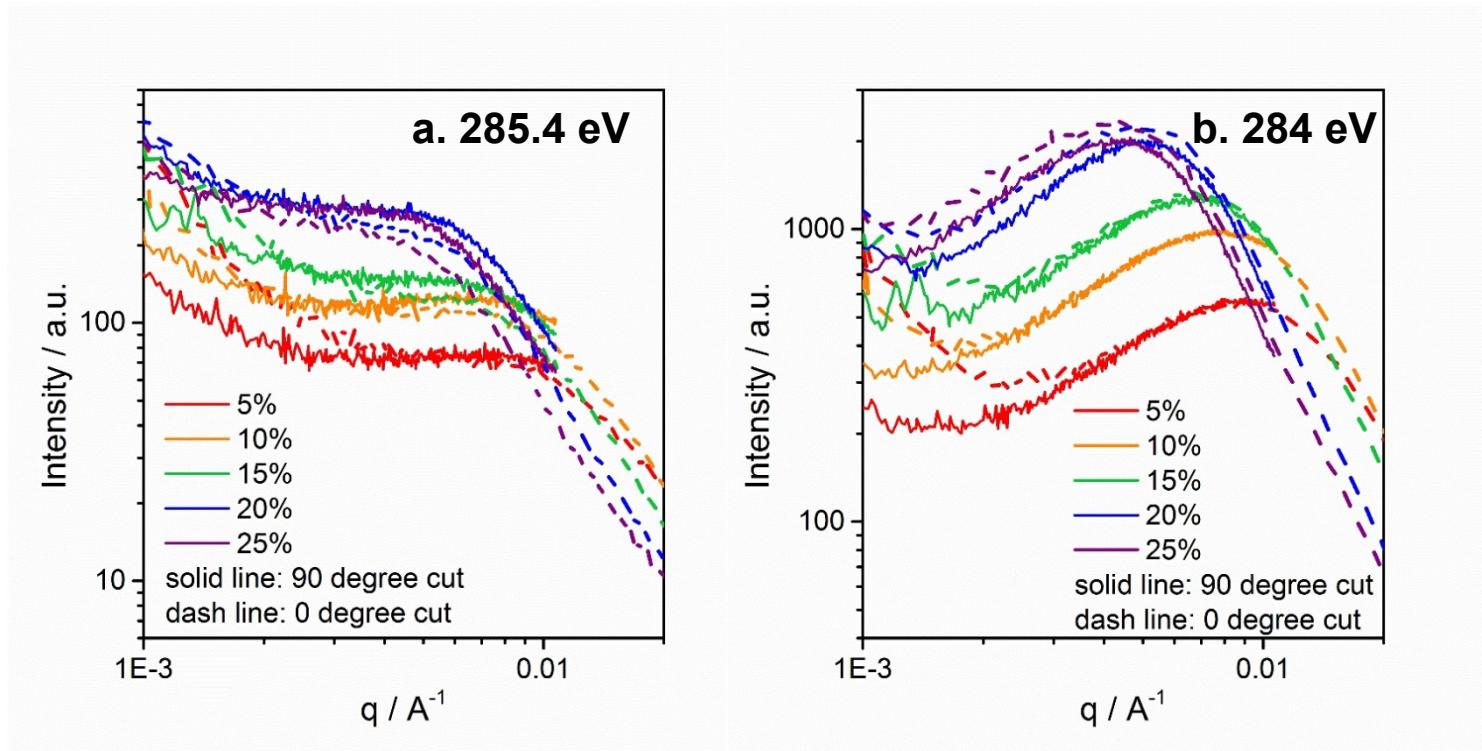
**Figure S4.** P-RSoXS scattering patterns and sector averaged profiles for P3HT-32k:PCPDTBT thin film (3/1 wt/wt, spin-coated by CB and pre-annealed) at horizontally polarized x-ray beam (a1-a3) or at vertically polarized x-ray beam (b1-b3). P-RSoXS scattering patterns and sector averaged profiles for P3HT-32k:PCPDTBT:PC<sub>61</sub>BM thin film (3/1/4, spin-coated by CB and pre-annealed) at horizontally polarized x-ray beam (c1-c4) or at vertically polarized x-ray beam (d1-d4).



**Figure S5.** NEXAFS profiles for P3HT, PCPDTBT and PCBM spin-coated by CB and annealed.

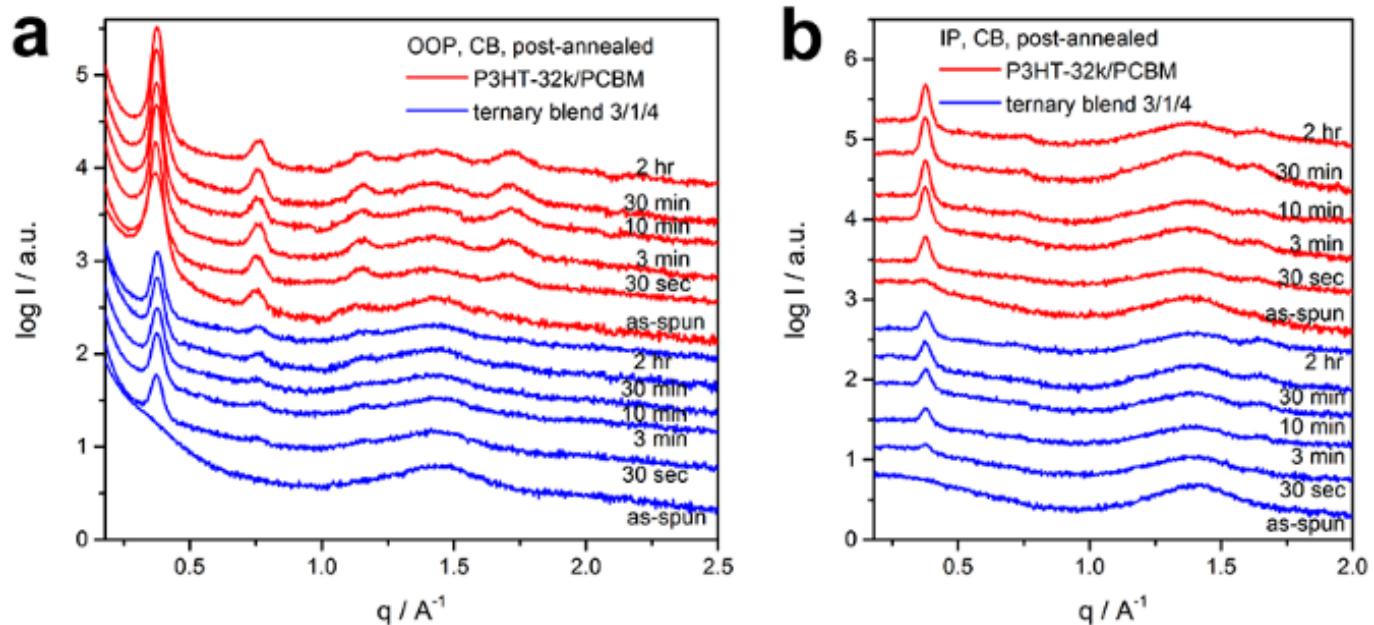


**Figure S6.** Circularly averaged P-RSoXS profiles for ternary blend thin film of P3HT-32k : PCPDTBT:PC<sub>61</sub>BM or binary references at 284 eV horizontally polarized x-ray beam. The

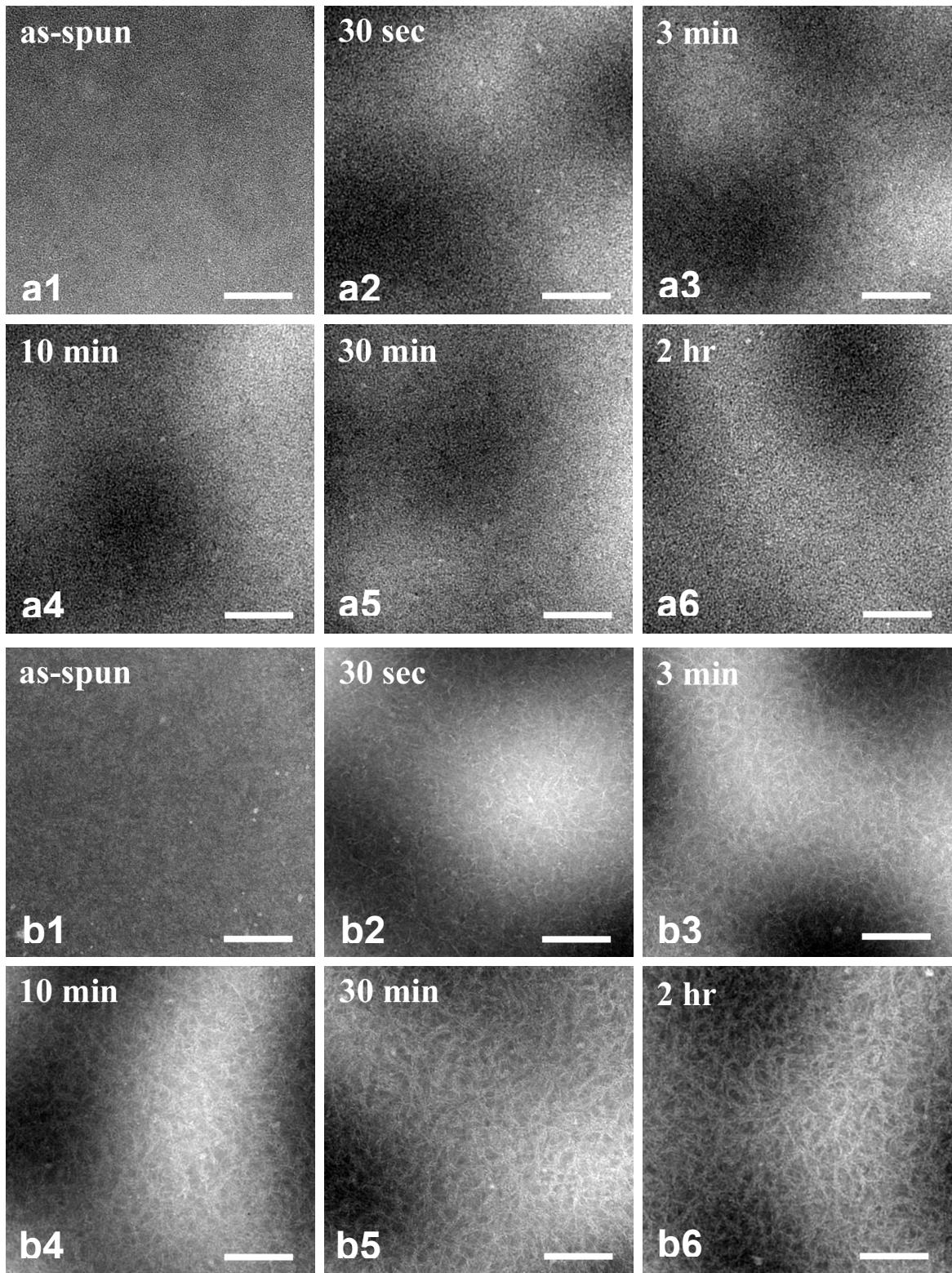


profiles are shifted to show each curve clearly.

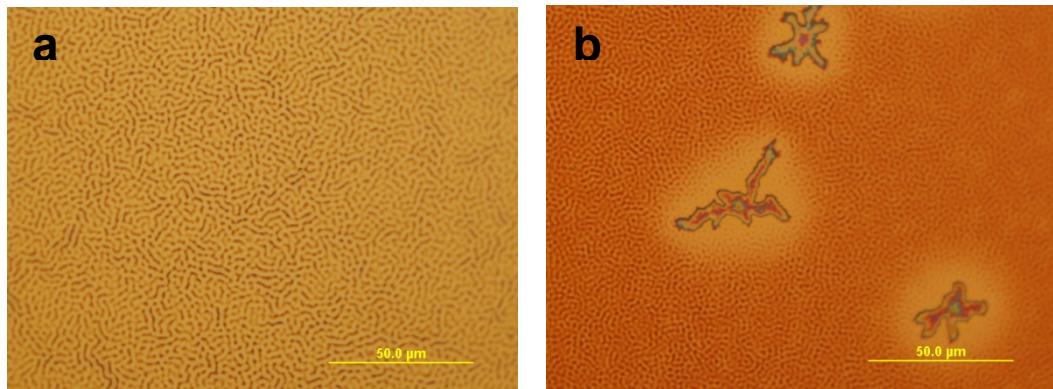
**Figure S7.** Sector averaged ( $\pm 2^\circ$ ) P-RSoXS profiles for ternary blend thin film of P3HT-32k : PCPDTBT:PC<sub>61</sub>BM with different PCPDTBT weight fractions at (a) 285.4 eV or (b) 284 eV horizontally polarized x-ray beam.



**Figure S8.** GIXD OOP (a) or IP (b) profiles for thin film of P3HT-32k:PCBM (1/1) and P3HT-32k:PCPDTBT:PC<sub>61</sub>BM (3/1/4) spin-coated by CB and post-annealed for a different time.



**Figure S9.** BF-TEM images for thin films of P3HT-32k:PC<sub>61</sub>BM (1/1) (a1-a6) or P3HT-32k:PCPDTBT:PC<sub>61</sub>BM (3/1/4) (b1-b6) post-annealed for a different time. The scale bar is 500 nm.



**Figure S10.** OM images for thin film of P3HT-32k:PCPDTBT:PC<sub>61</sub>BM (3/1/4) (a) and P3HT-32k:PC<sub>61</sub>BM (1/1) (b) spin-coated by CB and post-annealed for 2 hours. The worm-like structures on the surface are the wrinkles existing in the post-annealed samples.

**Table S1.** Device performance as a function of annealing time for thin films of P3HT-32k : PC<sub>61</sub>BM (1/1), P3HT-32k:PCPDTBT:PC<sub>61</sub>BM (3/1/4) and PCPDTBT:PC<sub>61</sub>BM (1/1) spin-coated by CB and post-annealed.

		V <sub>oc</sub> (V)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	Fill Factor (%)	Efficiency (%)
P3HT-32k: PC <sub>61</sub> BM (1:1)	as-spun	0.64±0.01	0.71±0.07	30±1	0.14±0.01
	post-30 s	0.58±0.001	6.25±0.08	55±2	1.99±0.04
	post-3 min	0.58±0.002	6.02±0.27	63±1	2.18±0.11
	post-10 min	0.58±0.005	6.47±0.11	63±2	2.35±0.05
	post-30 min	0.58±0.005	6.80±0.05	63±1	2.50±0.04
	post-2 h	0.58±0.002	6.48±0.11	62±1	2.30±0.02
P3HT-32k: PCPDTBT: PC <sub>61</sub> BM (3:1:4)	as-spun	0.54±0.01	1.54±0.10	35±1	0.29±0.02
	post-30 s	0.63±0.001	5.29±0.16	51±1	1.72±0.06
	post-3 min	0.61±0.001	7.06±0.27	48±1	2.06±0.10
	post-10 min	0.60±0.01	7.35±0.38	49±1	2.16±0.13
	post-30 min	0.60±0.004	7.48±0.31	47±1	2.13±0.06
	post-2 h	0.60±0.001	7.86±0.31	50±1	2.38±0.09
PCPDTBT: PC <sub>61</sub> BM (1:1)	as-spun	0.49±0.01	5.03±0.09	38±1	0.92±0.03
	post-30 s	0.58±0.02	5.11±0.14	35±1	1.04±0.04
	post-3 min	0.66±0.001	5.16±0.19	36±1	1.24±0.07
	post-10 min	0.66±0.005	5.37±0.18	36±1	1.28±0.05
	post-30 min	0.65±0.005	5.28±0.28	36±1	1.23±0.09
	post-2 h	0.64±0.005	5.35±0.19	36±1	1.24±0.05

**Table S2.** Device performance for the ternary blend solar cells using P3HT-28k or P3HT-19k and their binary references spin-coated by CB and post-annealed for 10 minutes.

batch of P3HT	blending ratio of P3HT:PCPDTBT:PC <sub>61</sub> BM	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	Fill Factor (%)	Efficiency (%)
P3HT-28k	1:0:1	0.55±0.004	6.84±0.16	64±2	2.39±0.02
	3:1:4	0.59±0.007	9.51±0.22	54±1	3.04±0.02
P3HT-19k	1:0:1	0.61±0.005	6.73±0.28	57±2	2.34±0.05
	3:1:4	0.65±0.008	2.95±0.42	45±2	0.86±0.16

**Table S3.** Device performance for the ternary blend solar cells using P3HT-32k with different blending ratios and binary references spin-coated by CB and post-annealed for 10 minutes.

	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	Fill Factor (%)	Efficiency (%)
PCPDTBT:PC <sub>61</sub> BM (1:1)	0.66±0.005	5.37±0.18	36±1	1.28±0.05
P3HT-32k: PCPDTBT:PC <sub>61</sub> BM (1:3:4)	0.64±0.005	4.68±0.20	37±1	1.10±0.05
P3HT-32k: PCPDTBT:PC <sub>61</sub> BM (2:2:4)	0.64±0.01	4.36±0.19	37±1	1.04±0.06
P3HT-32k: PCPDTBT:PC <sub>61</sub> BM (3:1:4)	0.60±0.01	7.35±0.38	49±1	2.16±0.13
P3HT-32k:PC <sub>61</sub> BM (1:1)	0.58±0.005	6.47±0.11	63±2	2.35±0.05