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Supporting Information for

Interface-induced Crystallization and Nanostructure Formation of [6,6]-Phenyl-C_{61}-butyric Acid Methyl Ester (PCBM) in Polymer Blend Films and Its Application in Photovoltaics

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Experimental details

PCBM and PCBNB were purchased from Frontier Carbon Corp., Japan (nanom spectra E100), and PTB7, P3HT, and PS (M_n = 18,000, M_w/M_n = 1.02, TSK standards) were from 1-Materials (Canada), Rieke Metals (USA), and TOSOH (Japan), respectively, and used without further purification. Samples for GIXRD were prepared by spin coating on pre-cleaned TiO_2 (35 nm)/ITO (100 nm)/glass substrates (washed by ultrasonication in detergent, water, acetone, and 2-propanol). TiO_2 precursor solution(NDH-510C, Nippon Soda) diluted with ethanol was spin coated on the ITO substrates at 3000 rpm for 30 s, followed by drying at 140 °C for 40 min and calcination at 500 °C for 30 min to form the TiO_2 layer. PCBM was spin coated from chlorobenzene solution (10 mg/mL) onto the TiO_2/ITO substrate, and pre-annealing was conducted on PCBM/TiO_2/ITO at 150 °C for 5 min to form the crystallized PCBM layer. To fabricate BHJ//PCBM/TiO_2/ITO samples, the contact film transfer method was used to transfer the BHJ layer onto PCBM/TiO_2/ITO samples by using poly(styrene sulfonate sodium salt) (PSS) as a sacrificial layer, following a previous method.[1,2] A PSS/glass substrate was prepared by spin coating PSS onto the pre-cleaned glass substrate. A solution of the polymer and PCBM (P3HT:PCBM = 1:1 by weight, 20 mg/mL; PTB7:PCBM = 1:1.5 by weight, 25 mg/mL; PS:PCBM = 1:0.5, 1:1, 1:1.5 by weight, 20 mg/mL) was spin coated onto the PSS/glass substrate. After the film transfer, post-annealing was conducted to induce the crystallization of PCBM in the blend layer. Unless otherwise stated, the conditions for post-annealing were fixed as 150 °C for 5 min in N_2. OSC device was fabricated by depositing MoO_3/Ag as electrode on aforementioned samples. The control devices are fabricated by spin-coating the same mixed solution onto the TiO_2/ITO substrate. *J-V* characteristics of the devices were measured using a source-meter (Model 2400, Keithley) under AM1.5 simulated solar light irradiation (PEC-L11, Peccell Technologies) at room temperature. A photomask was used to define an active area of 0.12 cm^2 for the devices. The light intensity was adjusted to 100 mW/cm^2 with a standard silicon solar cell (BS520, Bunkou Keiki, Japan).

GIXRD measurements were carried out on an X-ray diffractometer (SmartLab, Rigaku, Japan) by using monochromatized CuKα radiation ($\lambda = 0.154$ nm) generated at 45 kV and 200 mA. GIXRD patterns were measured in the in-plane geometry at an incident angle of 0.21°.2DGIXRD patterns were measured at an incident angle of 0.12 with synchrotron radiation at beamline BL19B2 of SPring-8 ($\lambda = 0.10$ nm) with the approval of the Japan Synchrotron Radiation Research Institute.

SEM was performed on 6330F (JEOL, Japan) with an acceleration voltage of 3 kV. PS:PCBM//PCBM/ITO/glass samples (treated by UV light exposure, 365 nm) after washing with acetone were used for top-views and bird's-eye views (45°). For the cross-sectional images, the samples were fabricated by mechanically breaking the samples of PTB7:PCBM//PCBM/glass. The surface was coated with Os using a Neoc-Pro osmium coater (Meiwafosis, Japan). SAED (JEM-2100F, JEOL) was performed with an acceleration voltage of 200 kV. The diameter of the selected area was 230nm. The PCBM film sample was transferred onto a Cu grid with a carbon supporting film by using CYTOP (AGC, Japan) as a support layer.

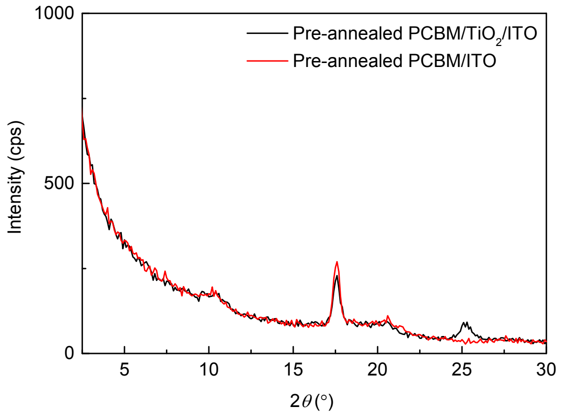

Figure S1. In-plane GIXRD patterns of PCBM films (40 nm) on ITO and TiO_2/ITO substrates after pre-annealing. The peak at 25.2° is from the TiO_2 layer. In both cases, PCBM crystallized at a similar degree, suggesting that the substrate has little effect on the crystallization of pure PCBM layers.

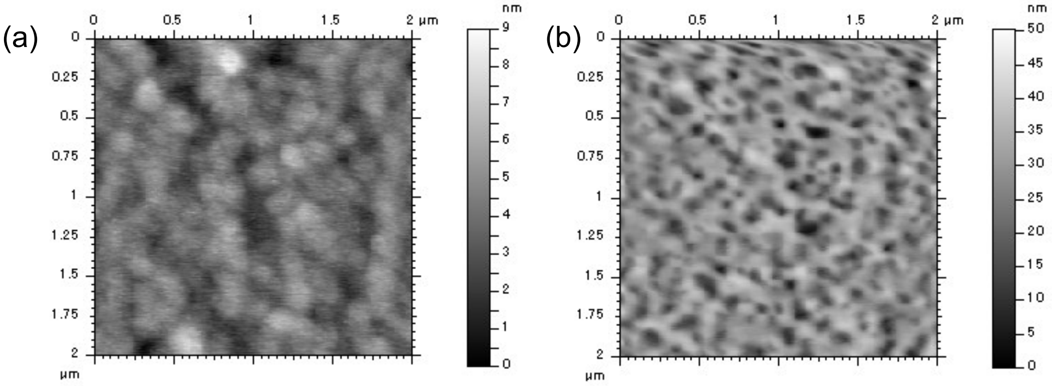

Figure S2. AFM height images of PTB7:PCBM//pre-annealed PCBM films (a) before (R_a: 0.77 nm) and (b) after post-annealing (R_a: 4.92 nm).

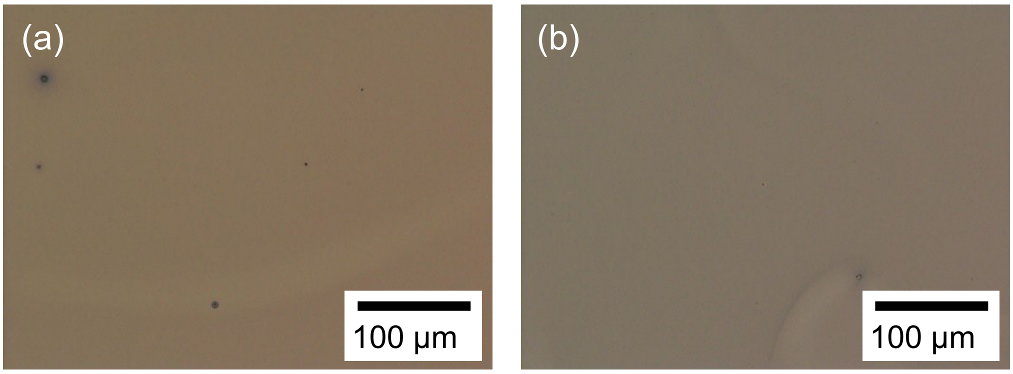

Figure S3. Optical microscopy images for PTB7:PCBM//pre-annealed PCBM films (a) before and (b) after post-annealing.

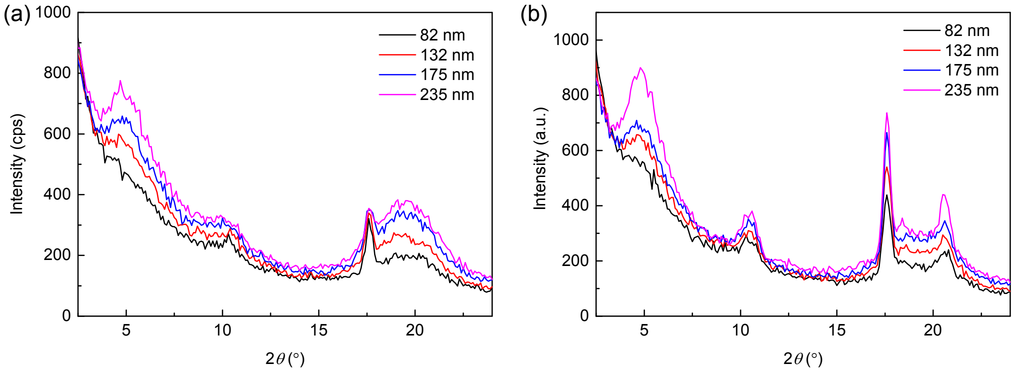

Figure S4. Thickness dependence of the in-plane GIXRD patterns for PTB7:PCBM//pre-annealed PCBM samples (a) before and (b) after post-annealing. The thickness of the PTB7:PCBM layers was changed from 82 to 235 nm.

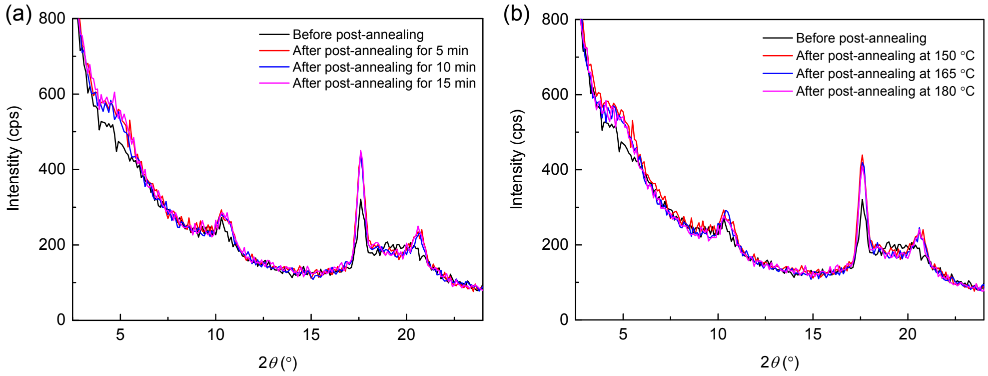

Figure S5. Dependence of in-plane GIXRD patterns on (a) annealing time (temperature fixed at 150 °C) and (b) temperature (time fixed at 5 min) for PTB7:PCBM//pre-annealed PCBM (82 nm) samples. The almost identical XRD patterns of the samples after 5 and 15 min in (a) and those at 150 and 180 °C in (b) suggested that annealing at 150 °C for 5 min was enough for the crystallization of PCBM in the PCBM:PTB7 layer to reach its limit.

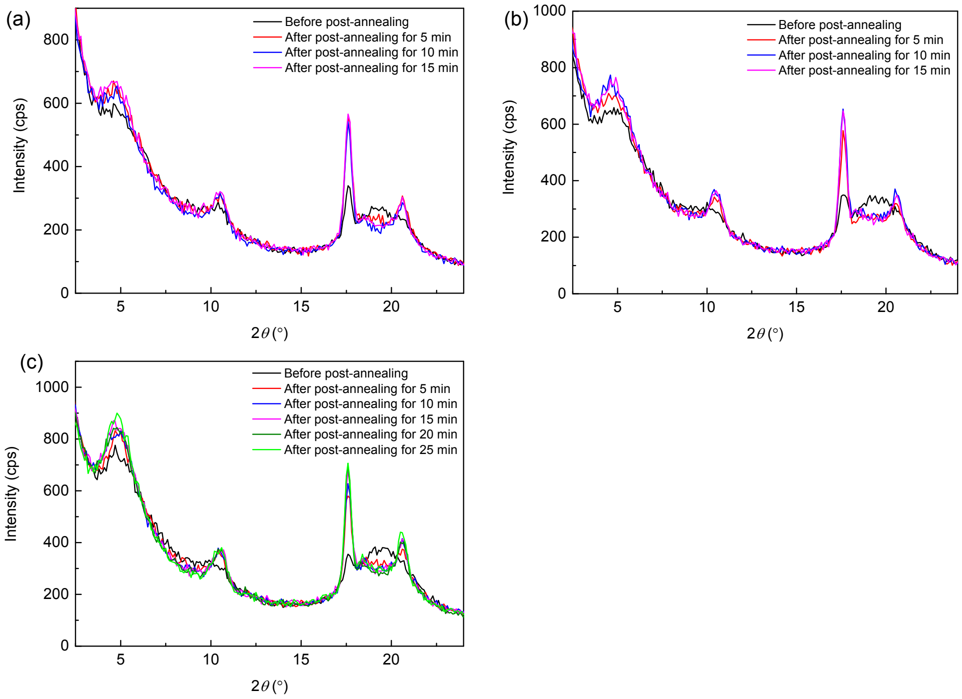

Figure S6. Dependence of in-plane GIXRD patterns on post-annealing time for PTB7:PCBM//pre-annealed PCBM samples with a PTB7:PCBM layer thickness of (a) 132, (b) 175, and (c) 235 nm. In (a), the diffraction patterns do not change after 5 min, suggesting the crystallization of PCBM reached its limit. In (b) and (c), approximately 10 and 20 min post-annealing, respectively, is necessary to reach the limit, suggesting that the diffusion of PCBM in the PTB7:PCBM layer limits the rate of the crystallization in thick films.

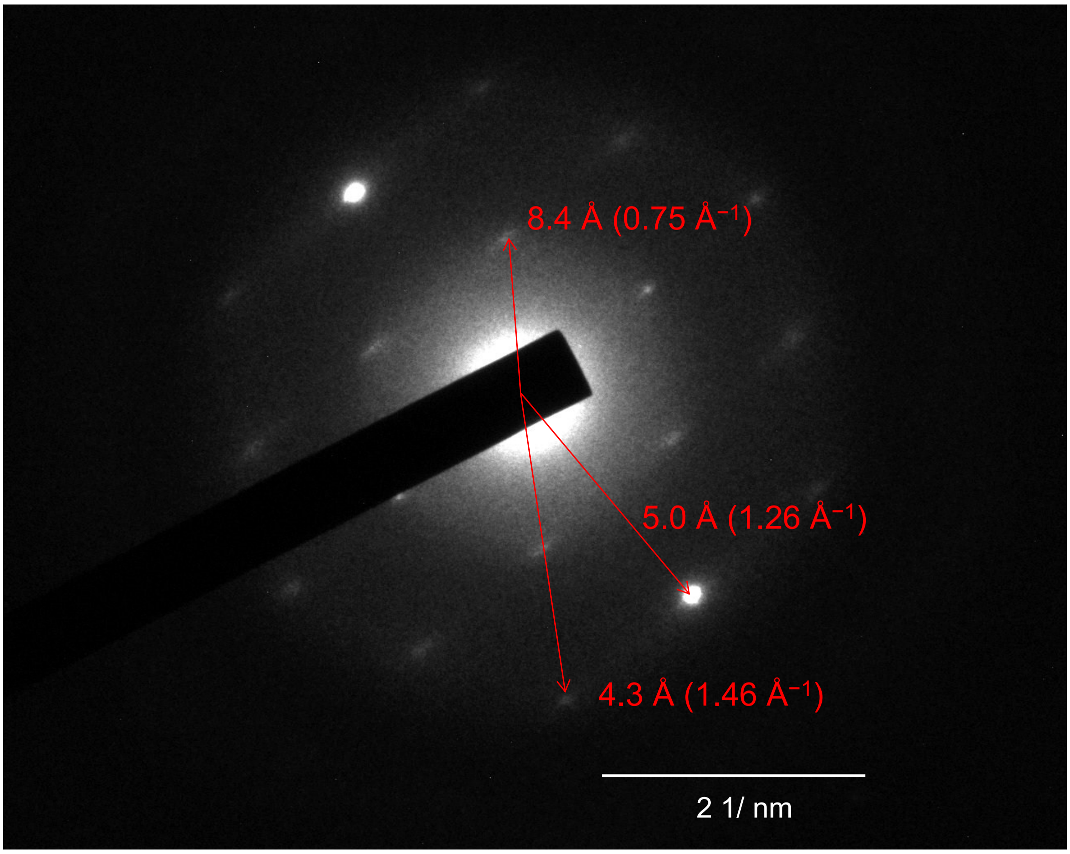

Figure S7. Selected area electron diffraction pattern of the PCBM film taken during transmission electron microscopy after pre-annealing. The diameter of the selected area is 230 nm.

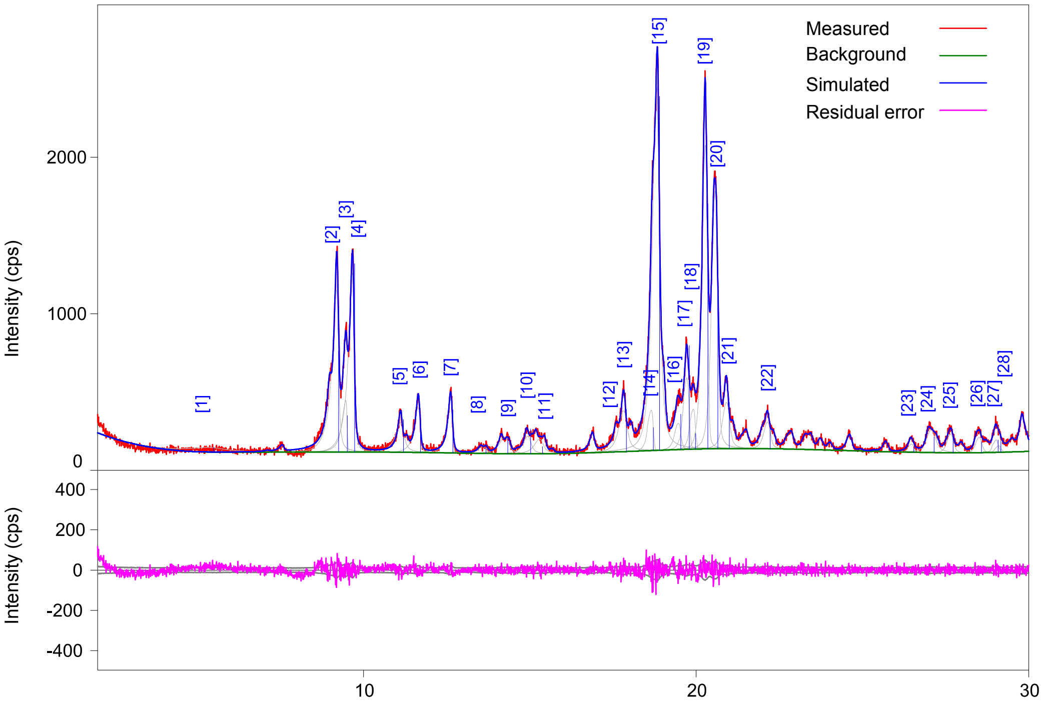

Figure S8. Powder XRD data of PCBM and fitting results with the crystal structure reported by Casalegno et al. (*Chem. Commun.*, **2013**, *49*, 4525). $C_{72}H_{14}O_2$, monoclinic, space group *P*2$_1$/*n* (#14), *a* = *13.479(3)* Å, *b* = 15.146(3) Å, *c* = 19.063(4) Å, *β* = 107.039(9)°, *V* = 3721.0(15) Å^3.

Table S1. Peak list of the fitting in Figure S13.

No.	2θ (°)	d (Å)	Height (cps)	Integrated (cps·°)	Planes	Relative intensity (a.u.)	Relative height (a.u.)
1	5.50(7)	16.06(19)	30(5)	42(4)	Unknown	7.99	1.33
2	9.2510(18)	9.5521(19)	647(25)	205(4)	PCBM (1,1,-1)	39.54	28.63
3	9.513(5)	9.290(4)	231(15)	48(3)	PCBM (1,0,1)	9.27	10.22
4	9.7314(16)	9.0815(15)	1203(35)	205(4)	PCBM (0,0,2)	39.55	53.23
5	11.201(7)	7.893(5)	209(14)	52(3)	PCBM (1,1,1)	10.06	9.25
6	11.713(3)	7.549(2)	247(16)	53(2)	PCBM (1,1,-2)	10.27	10.94
7	12.686(3)	6.9724(14)	276(17)	53.2(17)	PCBM (0,2,1)	10.23	12.20
8	13.68(2)	6.467(11)	36(6)	11(2)	PCBM (1,2,0)	2.09	1.59
9	14.339(11)	6.172(5)	100(10)	33(3)	PCBM (1,0,-3)	6.34	4.43
10	15.026(14)	5.891(5)	158(13)	28(3)	PCBM (1,2,1)	5.40	7.00
11	15.38(2)	5.756(9)	45(7)	28(5)	PCBM (2,1,0)	5.30	2.00
12	18(2)	5.1(6)	2.8(17)	0.5(15)	PCBM (2,2,-1), Unknown	0.09	0.12
13	17.906(6)	4.9497(16)	269(16)	70(3)	PCBM (1,2,2)	13.53	11.90
14	18.717(10)	4.737(2)	146(12)	36(5)	PCBM (0,2,3)	7.02	6.47
15	18.899(2)	4.6919(ssss5)	2261(48)	520(8)	PCBM (1,3,0)	100.00	100.00
16	19.542(9)	4.539(2)	226(15)	29.3(19)	PCBM (0,0,4)	5.64	9.98
17	19.793(4)	4.4820(9)	663(26)	69(2)	PCBM (2,2,1)	13.21	29.33
18	19.983(6)	4.4396(13)	99(10)	36(2)	PCBM (1,3,1)	7.00	4.36
19	20.3504(12)	4.3604(3)	1567(40)	289(6)	PCBM (2,0,-4)	55.71	69.30
20	20.6506(15)	4.2977(3)	1160(34)	280(7)	PCBM (2,2,-3)	53.90	51.32
21	20.998(6)	4.2272(12)	296(17)	63(5)	PCBM (3,1,-2)	12.17	13.09
22	22.228(7)	3.9962(12)	163(13)	33(2)	PCBM (1,3,2)	6.35	7.22
23	26.548(11)	3.3548(14)	35(6)	7.2(16)	PCBM (4,0,-2)	1.39	1.53
24	27.160(9)	3.2807(10)	102(10)	43(3)	PCBM (2,3,-4)	8.22	4.49
25	27.729(9)	3.2145(10)	104(10)	22(2)	PCBM (2,4,-2)	4.22	4.62
26	28.583(10)	3.1204(10)	71(8)	16.8(19)	PCBM (2,4,1)	3.23	3.14
27	29.08(2)	3.068(2)	79(9)	10.9(19)	PCBM (4,2,-2)	2.10	3.47
28	29.17(3)	3.059(3)	71(8)	6(9)	Unknown	1.10	3.13

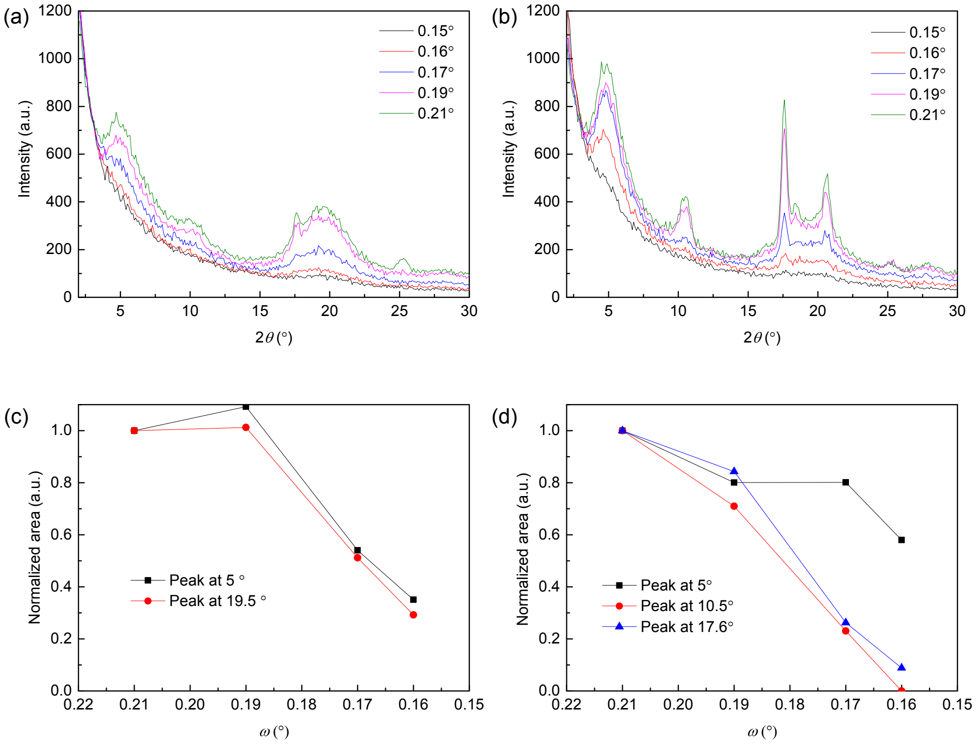

Figure S9. Incident angle dependence of the in-plane GIXRD patterns for PCBM:PTB7//pre-annealed PCBM films (a) before and (b) after post-annealing. Dependence of the peak areas on the incident angle for PCBM:PTB7//pre-annealed PCBM films (c) before and (d) after post-annealing, calculated from the patterns in (a) and (b), respectively. Each peak is fitted with a Gaussian function after baseline correction and the peak areas are normalized to those with incident angle of 0.21°.

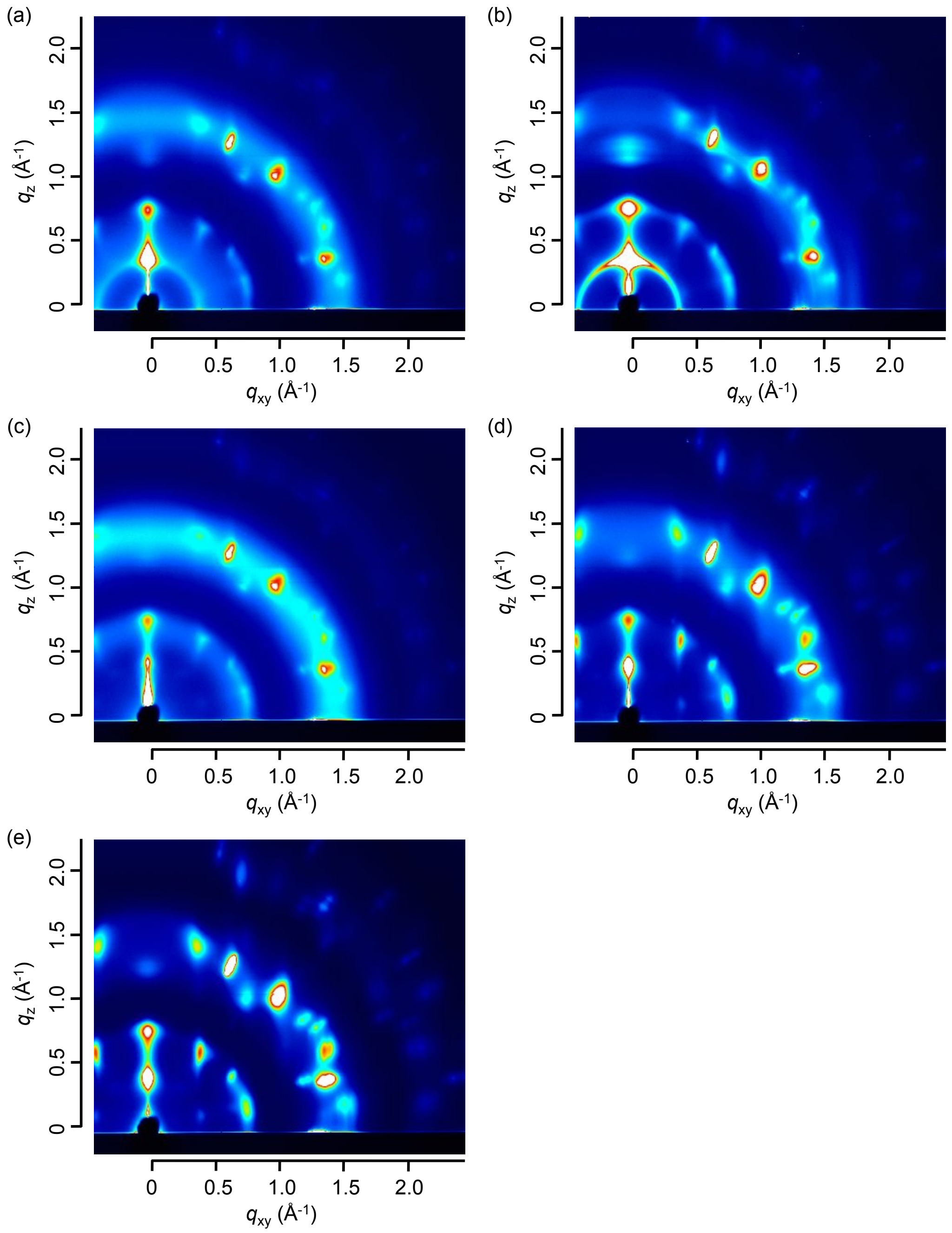

Figure S10. 2D GIXRD patterns of P3HT:PCBM//pre-annealed PCBM films (a) before and (b) after post-annealing, PS:PCBM//pre-annealed PCBM films (c) before and (d) after post-annealing, and (e) PS:PCBM//pre-annealed PCBM films after post-annealing and subsequent removal of PS by washing with acetone. A broad ring at q = 0.4 Å^{-1} in (a) and (b) originated from the lamellar structure of P3HT.

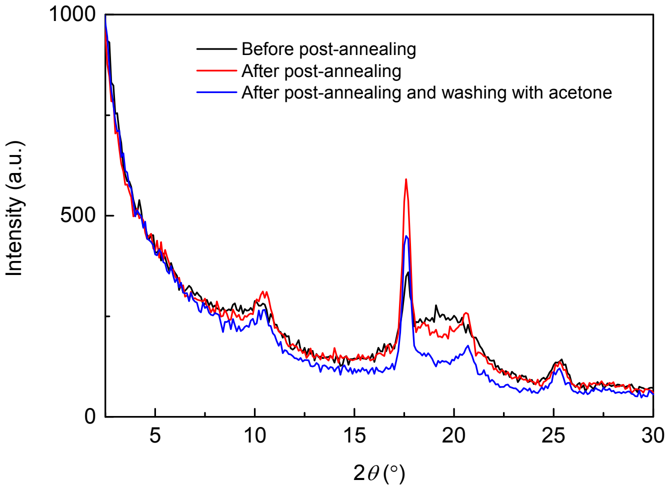

Figure S11. In-plane GIXRD patterns of PS:PCBM//pre-annealed PCBM film before and after post-annealing. The pattern was also taken after washing the post-annealed sample with acetone to remove PS selectively from the PS:PCBM BHJ layer. After washing, PCBM remained on the substrate, as indicated by the peaks at 10.5°, 17.6°, and 20.6°. Note that when the PS:PCBM//pre-annealed PCBM film was washed with acetone before post-annealing, the BHJ layer was completely removed from the seed layer.

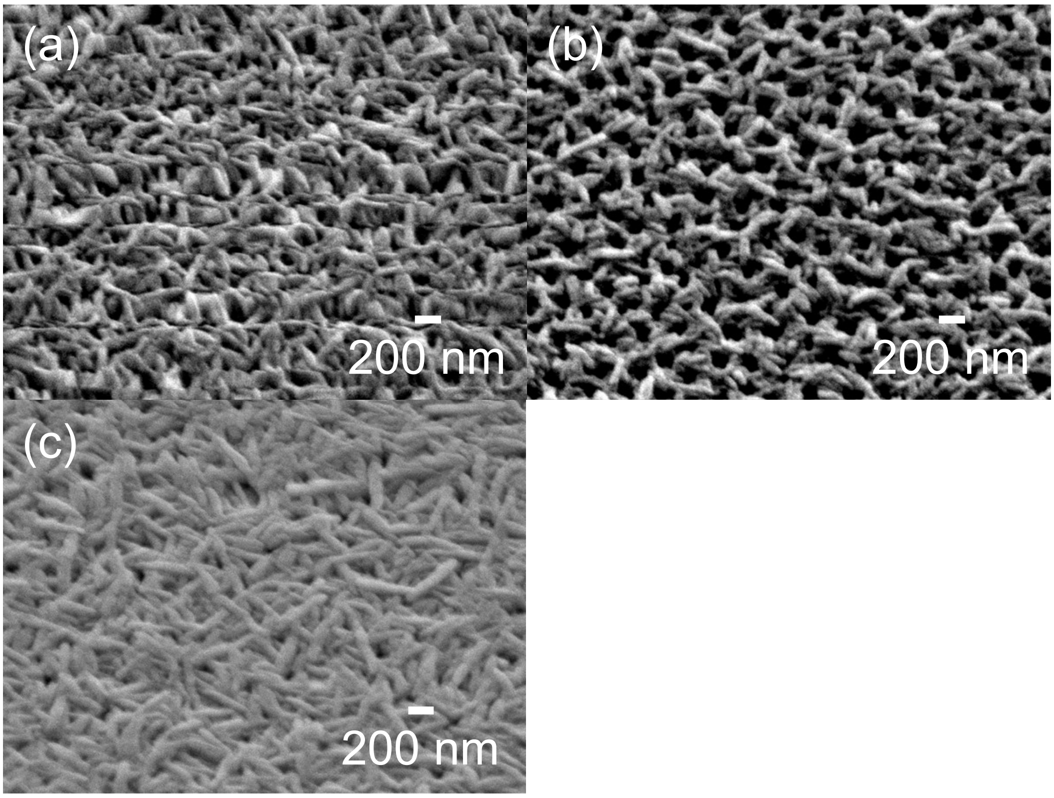

Figure S12. SEM images (tilt angle of 45°) for PS:PCBM//pre-annealed PCBM films with PCBM:PS mixing ratios of (a) 0.5:1, (b) 1:1, and (c) 1.5:1 by weight after post-annealing and washing with acetone.

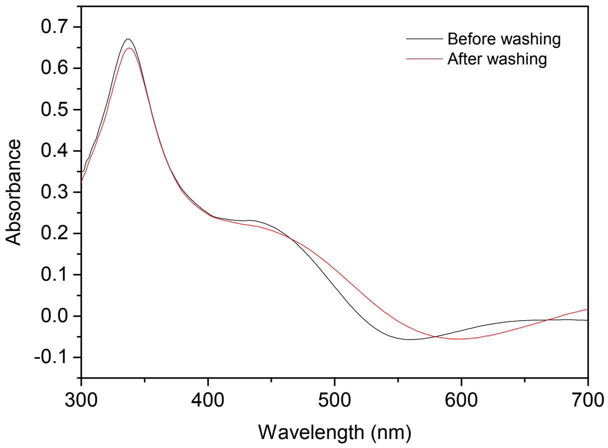

Figure S13. UV-vis absorption spectra of PS:PCBM//pre-annealed PCBM films after post-annealing at 150 °C for 5 min before and after washing with acetone.

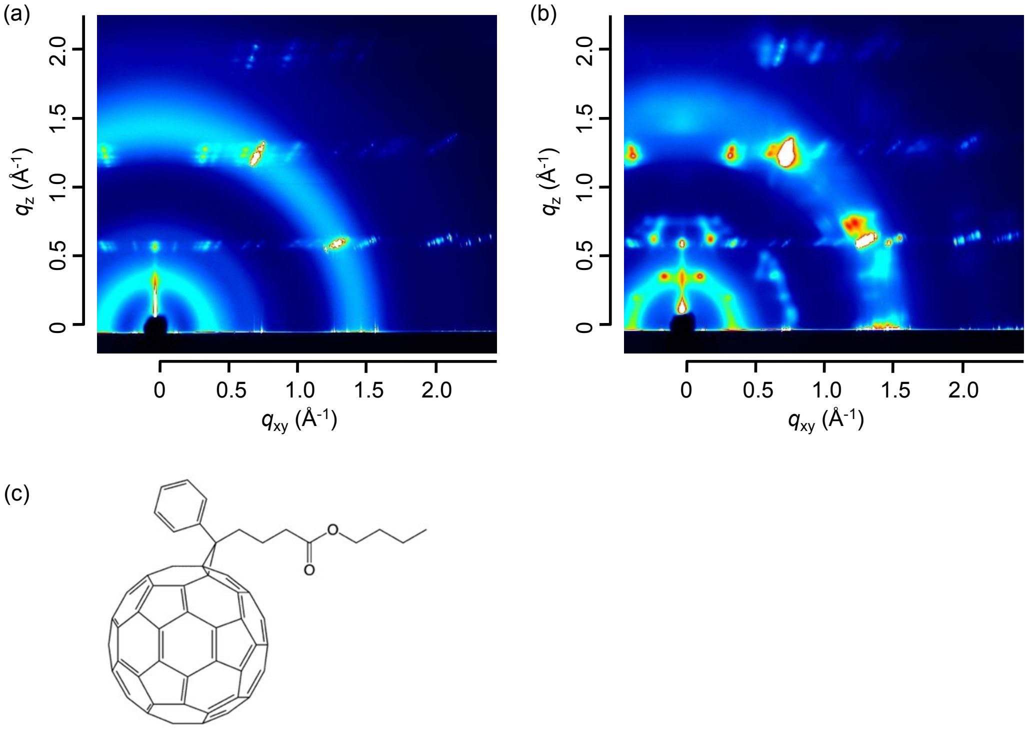

Figure S14. 2D-GIXRD pattern for PTB7:PCBM//pre-annealed PCBNB films (a) before and (b) after post-annealing. (c) Chemical structure of PCBNB.

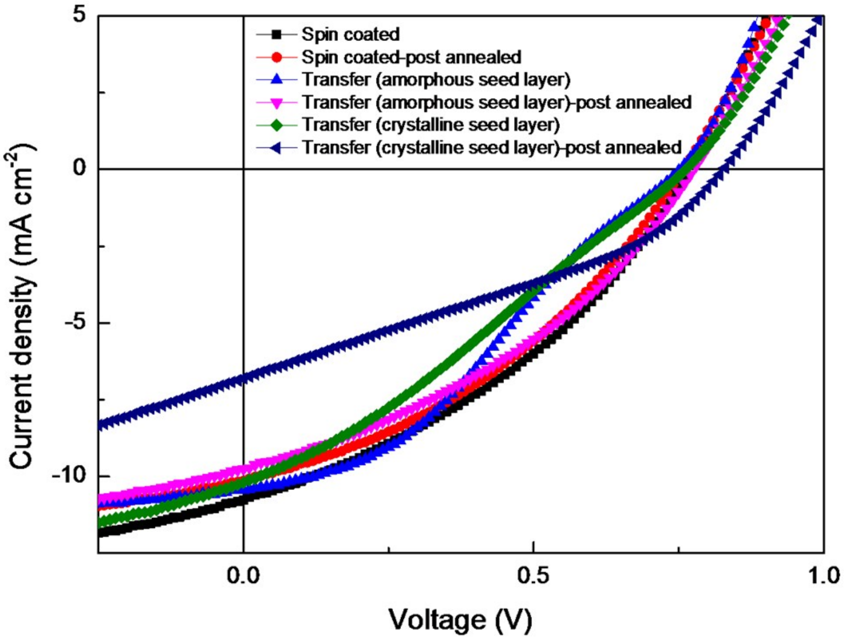

Figure S15. Typical *J-V* curves of OSCs based on PTB7:PCBM BHJ structure showed in Table 1 in the manuscript.

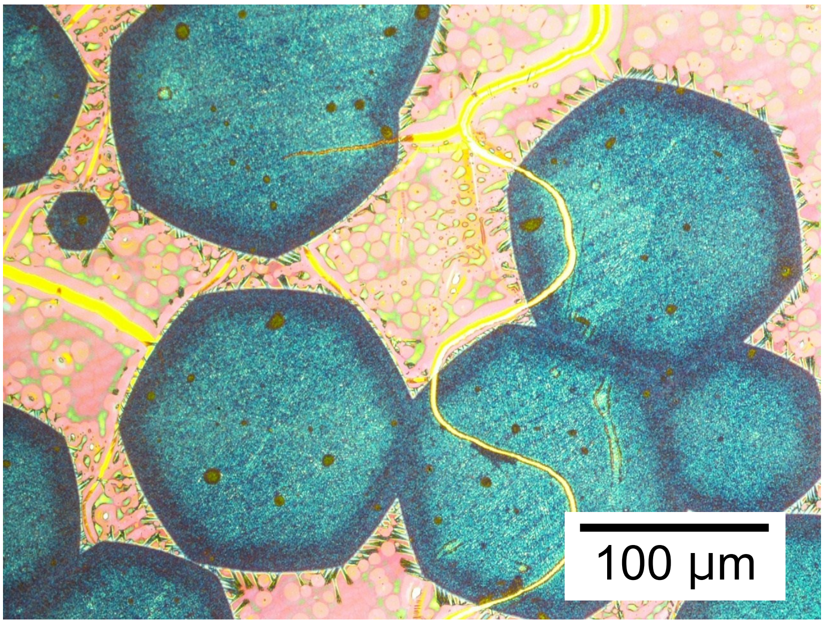

Figure S16. Optical microscopic image of PS:PCBM//pre-annealed PCBNB film after post-annealing. PS was removed by washing the sample with acetone.

References

1. Q. Wei, S. Miyanishi, K. Tajima and K. Hashimoto, *ACS applied materials & interfaces*, 2009, **1**, 2660-2666.
2. Q. Wei, K. Tajima and K. Hashimoto, *ACS applied materials & interfaces*, 2009, **1**, 1865-1868.