

Electronic Supplementary Information for

# **Fullerene Dyad with Trioctyloxybenzene Moiety Induced Efficient Nanoscale Active Layer for the Poly(3-hexylthiophene)-Based Bulk Heterojunction Solar Cells Application**

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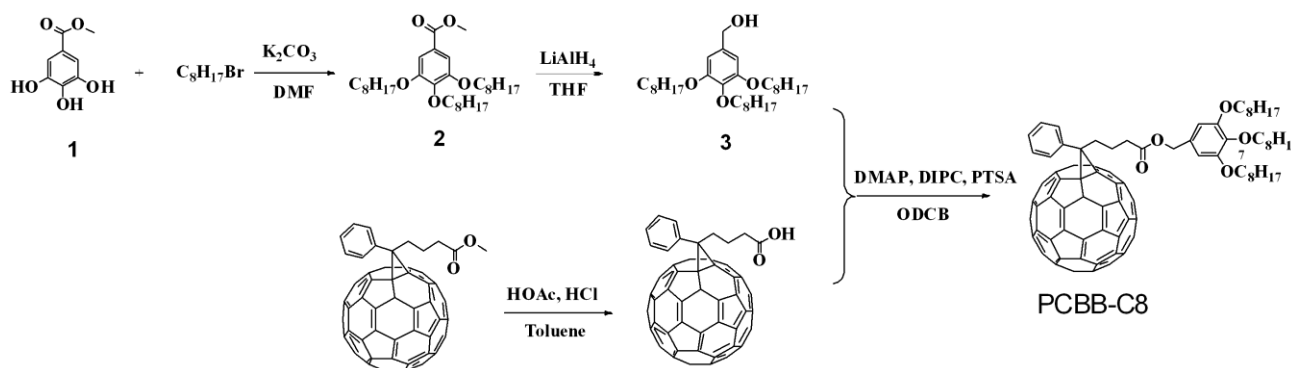
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## Synthesis



Scheme S1. Synthesis of PCBB-C8.

**3,4,5-Tris(octyloxy)benzoic acid methyl ester (2).** 3,4,5-Trihydroxy-benzoic acid methyl ester (11 mmol) was dissolved in DMF (50 mL). When stirred,  $C_8H_{17}Br$  (38 mmol) was added resulting in a brown solution. The mixture was stirred at 80 °C for 24 h and then extracted into toluene 150 mL, washed with water three times, and dried with  $Na_2SO_4$ . The crude product was chromatographed on silica with petroleum ether: ethyl acetate (v/v, 30/1) as the eluent. The yield is 85% as a yellow oil.  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  (ppm) 7.25 (s, 2H), 4.01 (td,  $J = 6.5, 2.5$  Hz, 6H), 3.91 – 3.86 (m, 3H), 1.78 (ddd,  $J = 28.2, 14.3, 7.2$  Hz, 6H), 1.50 – 1.21 (m, 30H), 0.88 (t,  $J = 6.3$  Hz, 9H).

**3,4,5-Tris(octyloxy)phenylmethanol (3).** To a solution of 3,4,5-Tris(octyloxy)benzoic acid methyl ester (3.8 mmol) in THF (25 mL) was added  $LiAlH_4$  (5.7 mmol) in parts at 0 °C and then slowly allowed to warm to room temperature. The solution was stirred overnight under Nitrogen atmosphere and then quenched with diluted HCl solution. The mixture was extracted into ethyl ester, washed with water and then dried with  $Na_2SO_4$ . The crude product was chromatographed on silica with petroleum ether: ethyl acetate (v/v, 5/1) as the eluent. The yield is 88.5% as a yellow solid.  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  (ppm) 6.56 (s, 2H), 4.59 (s, 2H), 3.99 – 3.90 (m, 6H), 1.86 – 1.70 (m, 6H), 1.55 – 1.12 (m, 32H), 0.88 (t,  $J = 6.4$  Hz, 9H).

**[6,6]-phenyl-C61-butanoic acid-3,4,5-tris(octyloxy)benzyl ester (PCBB-C8).** To a solution of [6,6]-phenyl-C61-butanoic acid (PCBA) (0.11 mmol) and 3,4,5-Tris(octyloxy)phenylmethanol (0.11 mmol) in 1,2-dichlorobenzene (40 mL) were added DMAP (0.11 mmol), PTSA (0.11 mmol) and DIPC

(0.165 mmol). The solution was stirred at room temperature under Nitrogen atmosphere for 12 h. The solution was concentrated in vacuo and then chromatographed on silica with toluene as the eluent. After concentration the residue was suspended in methanol. The precipitate was collected by filtration, washed three times with methanol. The yield is 65% as a brown solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 7.91 (d,  $J = 7.4$  Hz, 2H), 7.61 – 7.41 (m, 3H), 6.52 (s, 2H), 5.00 (s, 2H), 3.94 (q,  $J = 6.8$  Hz, 6H), 2.97 – 2.86 (m, 2H), 2.58 (t,  $J = 7.4$  Hz, 2H), 2.20 (s, 2H), 1.85 – 1.67 (m, 6H), 1.37 (d,  $J = 71.5$  Hz, 30H), 0.88 (t,  $J = 6.2$  Hz, 9H).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm): 172.8 153.1 148.7 147.7 145.7 145.1 144.6 143.9 143.6 142.9 142.0 140.9 140.6 137.9 137.5 136.6 132.0 130.6 128.3 106.9 79.7 73.3 69.0 66.7 51.7 34.0 33.5 31.8 30.2 29.3 26.1 22.6 22.3 14.1. MALDI-TOF-MS  $m/z$ : 1480.5 ( $(\text{M}+\text{Ag})^+$ ).

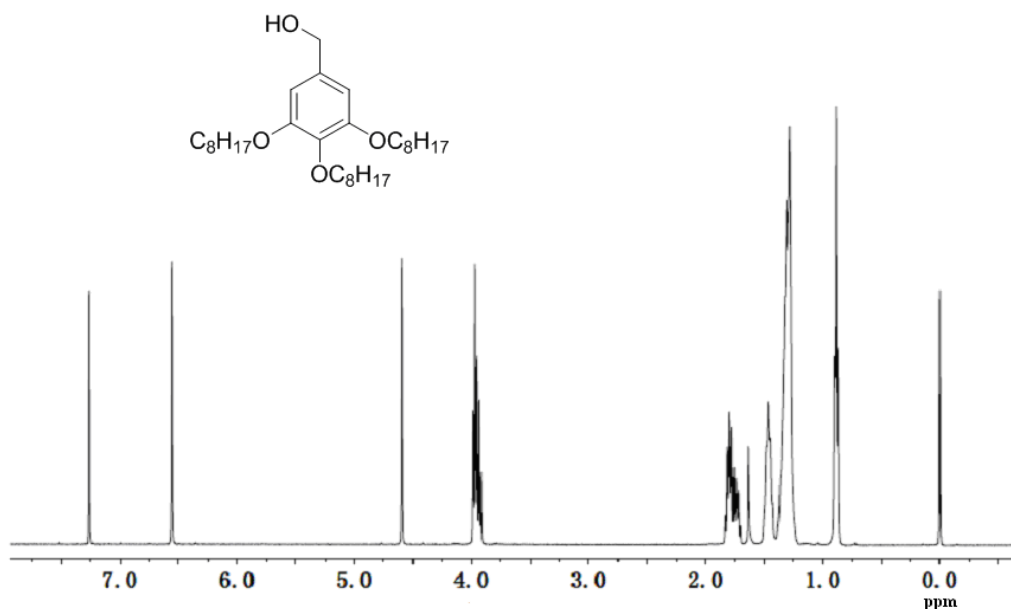


Fig. S1.  $^1\text{H}$  NMR of 3,4,5-Tris(octyloxy-phenyl)-methanol

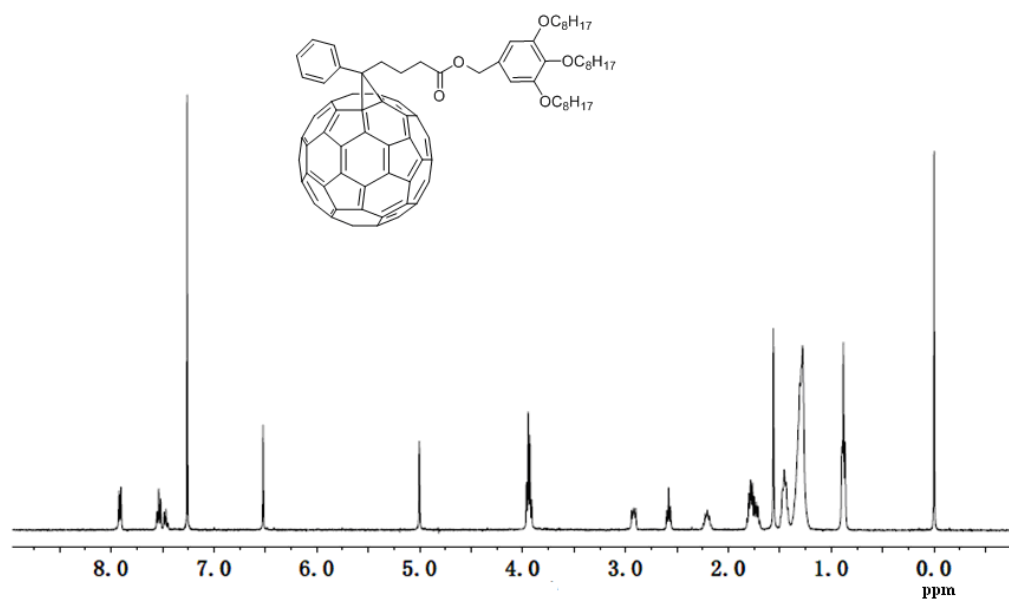


Fig. S2. <sup>1</sup>H NMR of PCBB-C8

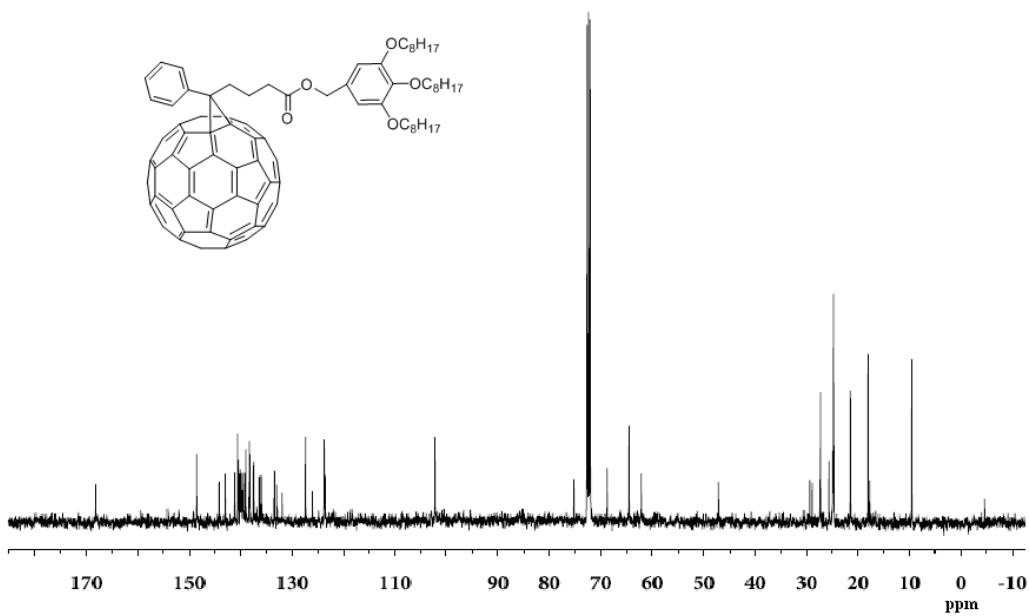


Fig. S3. <sup>13</sup>C NMR of PCBB-C8

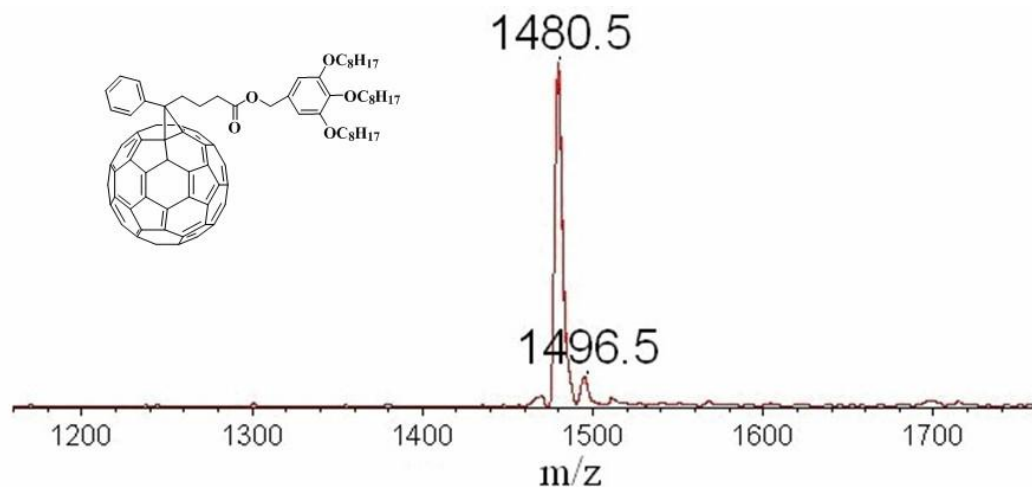


Fig. S4. MALDI- TOF mass spectrum of PCBB-C8

### Thermal property

PCBB-C8 exhibits good thermal stability with 5% weight loss temperatures ( $T_d$ ) higher than 312 °C under  $N_2$ , as revealed by thermogravimetric analysis (TGA) (Fig. S5).

### Measurements and characterizations.

Differential scanning calorimetry (DSC) was performed under nitrogen flushing at a heating rate of 10 °C/min with a NETZSCH (DSC-204) instrument. Thermal gravimetric analysis (TGA) was carried out on a Perkin-Elmer Pyris 6, with a heating rate of 10°C/min under nitrogen flow. Electrochemical measurements of these derivatives were performed with a Bioanalytical Systems BAS100 B/W electrochemical workstation. The cyclic voltammetry (CV) diagrams of the fullerene derivatives were obtained by using  $n\text{-Bu}_4\text{NPF}_6$  as supporting electrolyte in acetonitrile solution with a glass carbon working electrode, a platinum wire counter electrode and a  $\text{Ag}/\text{AgNO}_3$  reference electrode under  $N_2$  atmosphere. Ferrocene was used as the internal standard. The redox potential of  $\text{Fc}/\text{Fc}^+$  which has an absolute energy level of -4.8 eV relative to the vacuum level for calibration is located at 0.09 V in 0.1 M  $n\text{-Bu}_4\text{NPF}_6/\text{acetonitrile}$  solution.  $^1\text{H}$  NMR spectra were measured using a Varian Mercury-400 NMR. Time-of-flight mass spectra were recorded with a Kratos MALDI-TOF mass system. POM observations

were carried out on a polarizing microscope (Olympus Corporation, BX51-P) at a magnification ( $\times 200$ ) which was coupled with a computer-controlled video camera. UV-visible absorption spectra were measured using a Shimadzu UV-3100 spectrophotometer. Atomic force Microscopy (AFM) images were recorded under ambient conditions, using a Veeco Digital Instrument Multimode Nanoscope IIIa operating in the tapping mode regime. The samples were prepared by spin-coating onto silica at 800 rpm from sample solutions in chloroform. X-ray diffraction (XRD) analysis was performed on an X'Pert-Pro MPD diffractometer with a Cu K radiation source at room temperature. The transmission electron microscopy (TEM) measurements were conducted on a Tecnai G2 F20 S-Twin transmission electron microscope operated at 200 kV.

### **Device Fabrication and Characterization.**

The active layer contained a blend of P3HT as electron donor and PCBM or PCBB-C8 as electron acceptor, which was prepared from 1:1 weight ratios by solution (10 mg/mL of P3HT) in chlorobenzene. After spin coating the blend from solution at 1100 rpm, the devices were completed by evaporating a 0.8 nm LiF layer protected by 100 nm of Al at a base pressure of  $4 \times 10^{-4}$  Pa. The effective photovoltaic area defined by the geometrical overlap between the bottom ITO electrode and the top cathode was 12 mm<sup>2</sup>. Current-voltage characteristics of the solar cells in the dark and under illumination of 100 mW/cm<sup>2</sup> white light from a Hg-Xe lamp filtered by a Newport 81094 Air Mass Filter, using a GWinstek SFG-1023 source meter. Monochromatic light from a Hg-Xe lamp (Newport 67005) in combination with monochromator (Oriel, Cornerstone 260) was modulated with a mechanical chopper. The response was recorded as the voltage over a 50  $\Omega$  resistance, using a lock-in amplifier (Newport 70104 Merlin). A calibrated Si cell was used as reference. All the measurements were performed under ambient atmosphere at room temperature.

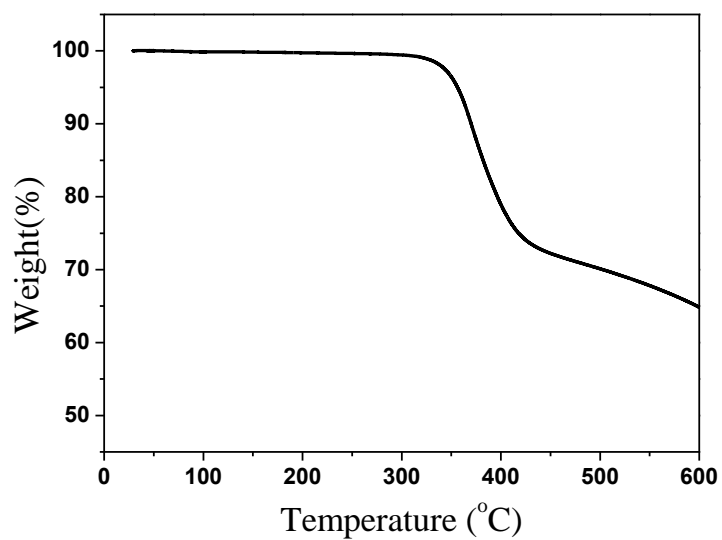


Fig. S5. TGA thermogram of PCBB-C8 at a heating rate of 10°C/min under N<sub>2</sub>.

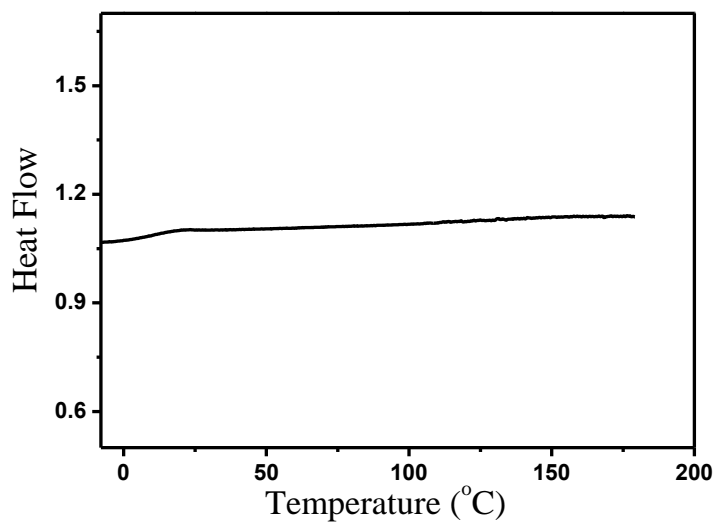


Fig. S6. DSC analysis of PCBB-C<sub>8</sub> at a heating rate of 10°C/min under N<sub>2</sub>.

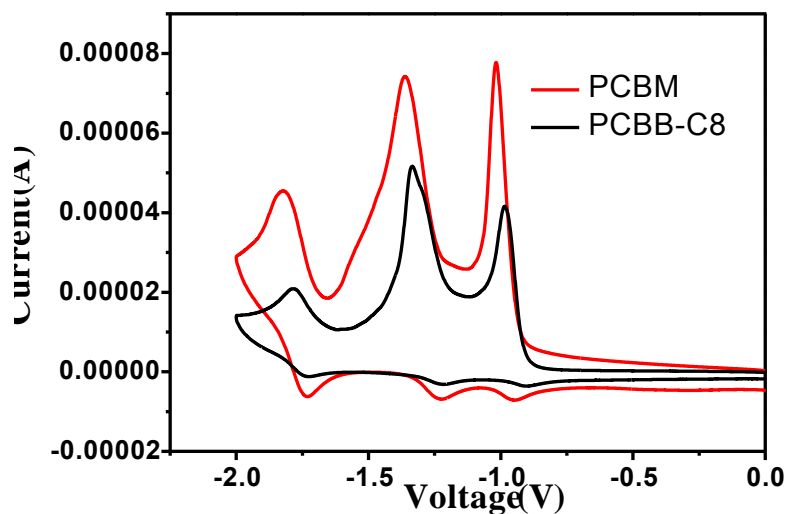


Fig. S7. Cyclic voltammograms scans of PCBB-C8 and PCBM.

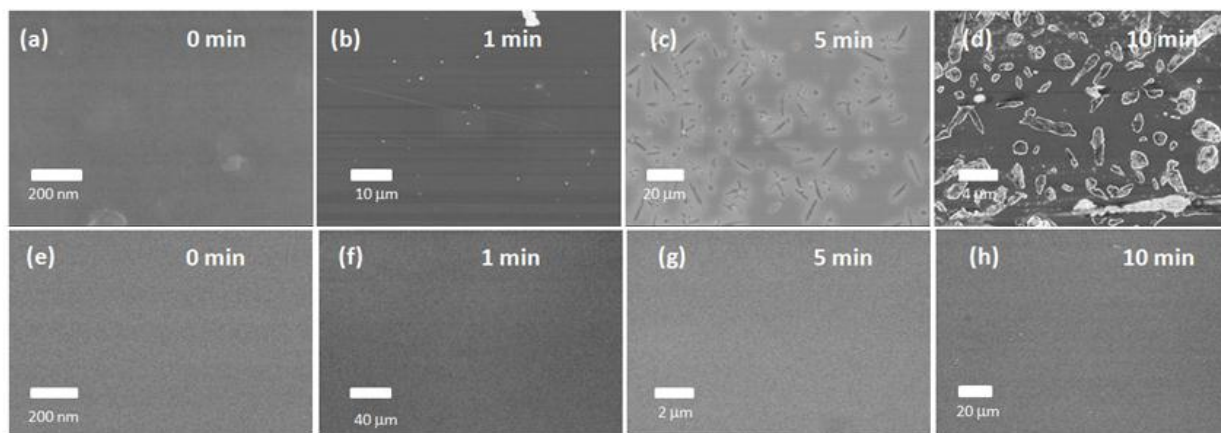


Fig. 8. SEM images of P3HT:PCBM blend film with different thermal annealing time (a) 0 min; (b) 1 min; (c) 5 min; (d) 10 min and P3HT:PCBB-C8 blend film with different thermal annealing time (e) 0 min; (f) 1 min; (g) 5 min; (h) 10 min.



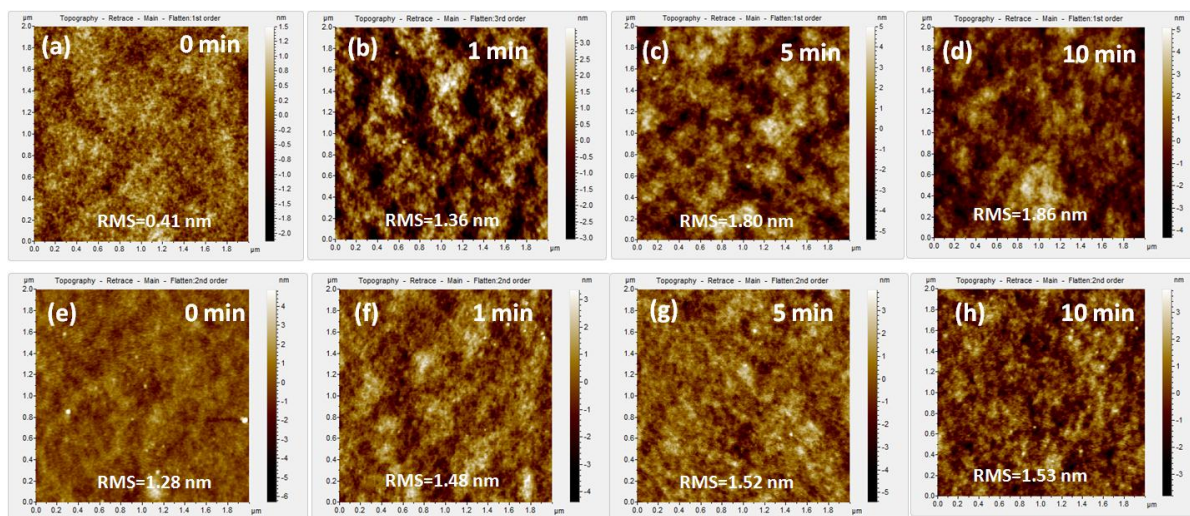


Fig. S9 AFM images of P3HT:PCBM blend film with different thermal annealing time (a) 0 min; (b) 1 min; (c) 5 min; (d) 10 min and P3HT:PCBB-C8 blend film with different thermal annealing time (e) 0 min; (f) 1 min; (g) 5 min; (h) 10 min. RMS (root mean square)

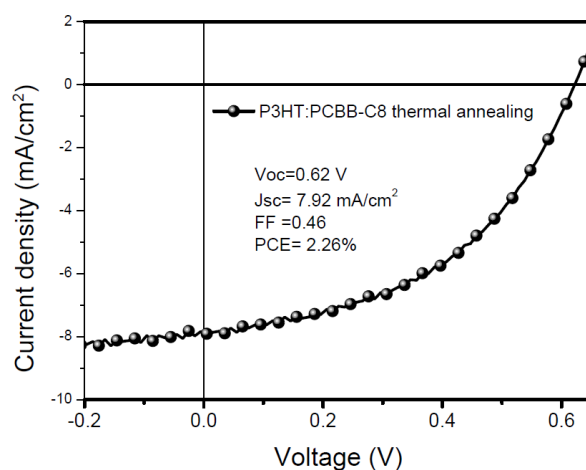


Fig. S10 Current–voltage characteristics of photovoltaic cells based on P3HT:PCBB-C8 with thermal annealing for 10 min.

**Table S1.** Characteristic Current-voltage Parameters from Device Testing at AM 1.5G White Light Conditions.

Active layer	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (V)	FF	PCE(%)	$R_s$ (Ω cm <sup>2</sup> )	$R_{sh}$ (Ω cm <sup>2</sup> )
P3HT/PCBM <sup>a</sup>	1.99	0.70	0.34	0.47	228	606
P3HT/PCBM <sup>b</sup>	8.87	0.55	0.62	3.02	10.8	653.6
P3HT/PCBB-C8 <sup>a</sup>	8.70	0.56	0.49	2.40	15.7	346
P3HT/PCBB-C8 <sup>b</sup>	7.92	0.62	0.46	2.26	--	--

<sup>a</sup> The active layer without thermal annealing process; <sup>b</sup> The active layer with thermal annealing at 150 °C for 10 min.