

Supporting Information

Cooperative Assembly of Active Layer Utilizing the Synergistic Effect of Functional Fullerene Triad as Acceptor for Efficient and Thermally Stable P3HT-based Polymer Solar Cells

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1. Materials and synthesis

Phosphorus tribromide (99%), Tetrabutylammonium fluoride (1 mol in THF), Trimethylsilyl cyanide (97%), 4-Hydroxybenzaldehyde (99.5%), p-toluenesulfonic acid (98%) and N, N-diisopropylcarbodiimide (98%) were purchased from Energy Chemical and used without further purification. 4-dimethylaminopyridine(99%) was purchased from Chem Greatwall and used without further purification. Acetonitrile was dried over calcium hydride, and distilled before use. sodium methoxide was produced by the reaction of methanol and sodium. Anhydrous sodium sulfate, chloroform, methanol, ethyl acetate, petroleum ether, alcohol, toluene, dichloromethane and o-dichlorobenzene were purchased from Sinopharm Chemical Reagent Co.,Ltd. 3,4,5-Tris-octyloxy-phenyl-methanol and [6,6]-phenyl-C61-butyric acid (PCBA) was synthesized according to the literature method.^{1,2}

5-(bromomethyl)-1,2,3-tris(octyloxy)benzene (1). To a stirred solution of 3,4,5-Tris-octyloxy-phenyl-methanol (0.342 g, 0.695 mmol) in CH₂Cl₂ (4 mL) was added a solution of PBr₃ (0.4 g, 1.48 mmol) in CH₂Cl₂ (2 mL) at 0 °C. The mixture was allowed to react for 3 h at room temperature, and then poured into a large amount of water. The product was extracted with CHCl₃ three times. The combined organic layers were washed with brine, and dried over anhydrous Na₂SO₄. After filtration and evaporation, the residue was purified by Al₂O₃ gel chromatography with petroleum ether: ethyl ester (5/1 v/v). The yield is 61.1% as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 6.57 (s, 2H), 4.43 (s, 2H), 3.96 (m, 6H), 1.73-1.79 (m, *J* = 17.8, 7.1 Hz, 6H), 1.46 (br, 6H), 1.29 (br, 24H), 0.89 (t, 9H).

2-(3,4,5-tris(octyloxy)phenyl)acetonitrile (2). To a stirred solution of 5-(bromomethyl)-1,2,3-tris(octyloxy)benzene (1) (0.236g, 0.425 mmol) in acetonitrile (10 mL) at room temperature under nitrogen were added trimethylsilyl cyanide (TMSCN) (90 μL) and tetrabutylammonium

fluoride (TBAF) (700 μ L), and the reaction mixture was stirred for 2.5 h. The light yellow reaction mixture was concentrated under reduced pressure. The oily residue was purified by Al_2O_3 gel chromatography with petroleum ether: ethyl ester (5/1 v/v) to give compound 2 in 65% yield as a light yellow oil. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 6.48 (s, 2H), 4.06 – 3.83 (m, 6H), 3.66 (s, 2H), 1.70-1.85 (m, $J = 19.9, 12.8$ Hz, 6H), 1.46 (m, $J = 6.6$ Hz, 6H), 1.27 (br, $J = 11.1$ Hz, 24H), 0.88 (t, $J = 6.5$ Hz, 9H).

2-(3,4,5-tris(octyloxy)phenyl)-3-(4-hydroxyphenyl)acrylonitrile (3). To a mixture of the 2-(3,4,5-tris(octyloxy)phenyl)acetonitrile (0.107 g, 0.214 mmol) and p-Hydroxybenzaldehyde (0.025 g, 0.205 mmol) in EtOH (4 mL), was dropwised with the solution of EtOMe (0.034 g, 0.630 mmol) in EtOH (2 ml) with the protection of N_2 at reflux temperature, stirred at 85 $^\circ\text{C}$ for 12 h, evaporated, and the residue was purified by silica gel chromatography with petroleum ether: ethyl ester(10/1 v/v). The yield is 64.34% as a light kelly solid. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.81 (d, $J = 8.7$ Hz, 2H), 7.35 (s, 1H), 6.92 (d, $J = 8.7$ Hz, 2H), 6.81 (s, 2H), 5.43 (s, 1H), 4.01 (m, $J = 18.2, 6.5$ Hz, 6H), 1.87 – 1.71 (m, 6H), 1.48 (m, $J = 7.6$ Hz, 6H), 1.25-1.35 (m, $J = 20.4, 10.2$ Hz, 24H), 0.89 (t, $J = 6.6$ Hz, 9H).

[6,6]-phenyl-C61-butyric acid-2-(2-(3,4,5- trisoctyloxy benzyl)cyanovinyl) benzyl ester (PCBB-CN-C8). To a flask, PCBA (0.1 g, 0.112 mmol), 2-(3,4,5-tris(octyloxy)phenyl)-3-(4-hydroxyphenyl)acrylonitrile (0.0675 g, 0.112 mmol), DMAP(0.0136 g, 0.112 mmol), PTSA(0.0212 g, 0.112 mmol) was added. Then DIPC(0.0197 g, 0.157 mmol) was washed into it by dichlorobenzene(30ml), stirred at room temperature for 12 h with the protection of N_2 . Then the solution was filtered and the filtrate was purified by silica gel chromatography with petroleum ether: toluene(1/3 v/v). The crude product was suspended in methanol to give PCBB-CN-C8 in 66.5% yield as a brown solid. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.96 (d, $J = 7.3$ Hz, 2H), 7.88 (d, $J = 8.7$ Hz, 2H), 7.57 (t, $J = 7.5$ Hz, 2H), 7.50 (t, $J = 7.4$ Hz, 1H), 7.39 (s, 1H), 7.18 (d, $J = 8.6$ Hz, 2H), 6.83 (s, 2H), 4.01 (m, $J = 16.3, 6.5$ Hz, 6H), 3.02 (dd, $J = 10.0, 6.3$ Hz,

2H), 2.81 (t, $J = 7.3$ Hz, 2H), 2.42-2.24 (m, 2H), 1.92-1.68 (m, 6H), 1.48 (m, $J = 13.8, 6.4$ Hz, 6H), 1.41-1.24 (m, 24H), 0.89 (t, $J = 6.6$ Hz, 9H). ^{13}C NMR (400 MHz, CDCl_3) δ 171.13, 153.50, 151.84, 148.71, 147.68, 145.82, 145.20, 145.16, 145.05, 144.80, 144.73, 144.66, 144.51, 144.44, 144.03, 143.76, 143.14, 143.05, 143.00, 142.93, 142.23, 142.17, 142.12, 142.11, 141.03, 140.76, 140.00, 139.48, 138.05, 137.59, 136.66, 132.11, 131.46, 130.45, 129.41, 128.53, 128.36, 122.11, 117.98, 111.93, 104.81, 79.77, 73.62, 69.39, 51.67, 34.18, 33.62, 31.90, 31.83, 30.32, 29.71, 29.53, 29.37, 29.29, 26.10, 22.70, 22.68, 22.30, 14.12.

2. Measurements and characterizations.

^1H NMR spectra were measured using a Varian Mercury-400 NMR. Time-of-flight mass spectra were recorded with a Broker MALDI-TOF mass system. Thermal gravimetric analysis (TGA) was carried out on a Perkin-Elmer Pyris 6, with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ under nitrogen flow. Differential scanning calorimetry (DSC) was performed under nitrogen flushing at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ with a NETZSCH (DSC-204) instrument. 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 Ag/AgNO_3 reference electrode under N_2 atmosphere. Ferrocene was used as the internal standard. The redox potential of Fc/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 $0.1\text{ M } n\text{-Bu}_4\text{NPF}_6/\text{acetonitrile}$ solution. UV-visible absorption spectra were measured using a Shimadzu UV-3100 spectrophotometer. Atomic force Microscopy (AFM) images were recorded under ambient conditions, on a Multimode 8 microscope (Bruker). Peak force quantitative nano-mechanical scan mode with Scan Asyst-Air probe (nomial spring constants 0.4 N/m , frequency 70 kHz , purchased from Bruker) was

adopted during the measurement. The samples were prepared by spin-coating onto silicon substrate according to the optimized condition of active layer for PSCs. The transmission electron microscopy (TEM) measurements were conducted on a Tecnai G2 F20 S-Twin transmission electron microscope operated at 200 kV, and selected area electron diffraction (SAED) analysis was conducted on a FEI Tecnai F20 transmission electron microscope operated at 200 kv. Grazing incidence X-ray scattering experiment of the thin films was performed at SAXSess mc2, Anton Paar. The scattering signal was recorded on a 2-D image plate with a pixel size of 42.3 μm . The samples were 10 mm long in the direction of the beam path, and the detector was located at a distance of 251 mm from the sample center. The incidence angle of 0.35° was chosen which gave the optimized signal-to-background ratio and the X-ray wavelength was 1.542 \AA .

3. Device Fabrication and Characterization.

Photovoltaic cells were fabricated with a structure of ITO/PEDOT:PSS/P3HT:fullerene derivatives/Ca/Al. Patterned ITO glass was cleaned with detergent water, deionized water, alcohol, acetone and isopropyl alcohol. After drying with N_2 , the ITO glass was treated with UV-ozone. Then PEDOT:PSS (Clevios P VP Al 4083) was spin-coated on the ITO glass at 3500 rpm for 60 s and annealed at 120°C for 20 min to obtain a ca. 40 nm thick film. 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) in CB. The P3HT:PCBB-CN-C8 blend solution was prepared from 1:1.25 weight ratios by solution (10 mg/mL, 15 mg/ml and 20 mg/ml of P3HT) in *o*-DCB. After spin coating the blend solution at 1000-1500 rpm, or thermal annealing at 100°C for 10 min, the devices were completed by evaporating a 20 nm Ca layer protected by 80 nm of Al at a base pressure of 4×10^{-4} Pa. The effective photovoltaic area

defined by the geometrical overlap between the bottom ITO electrode and the top cathode was 5 mm². *J-V* characteristics of photovoltaic cells were taken using a Keithley 2400 source measure unit under a simulated AM1.5G spectrum. With an Oriel 9600 solar simulator, the light intensity was calibrated by KG-5 Si diode. External quantum efficiencies were measured by an Enli Technology (Taiwan) EQE measurement system.

[1] Chem. Commun. 2013, 49, 4917-4919

[2] J. Org. Chem. 1995,60, 532-538

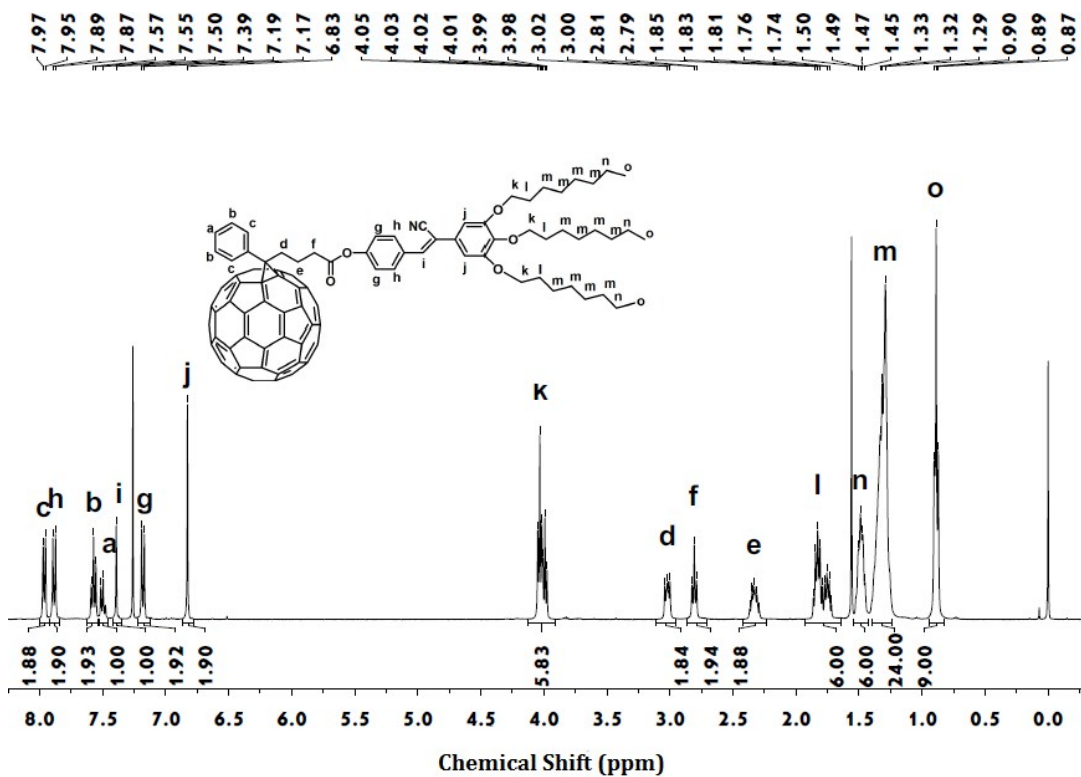


Figure S1. ¹H NMR of PCBB-CN-C8

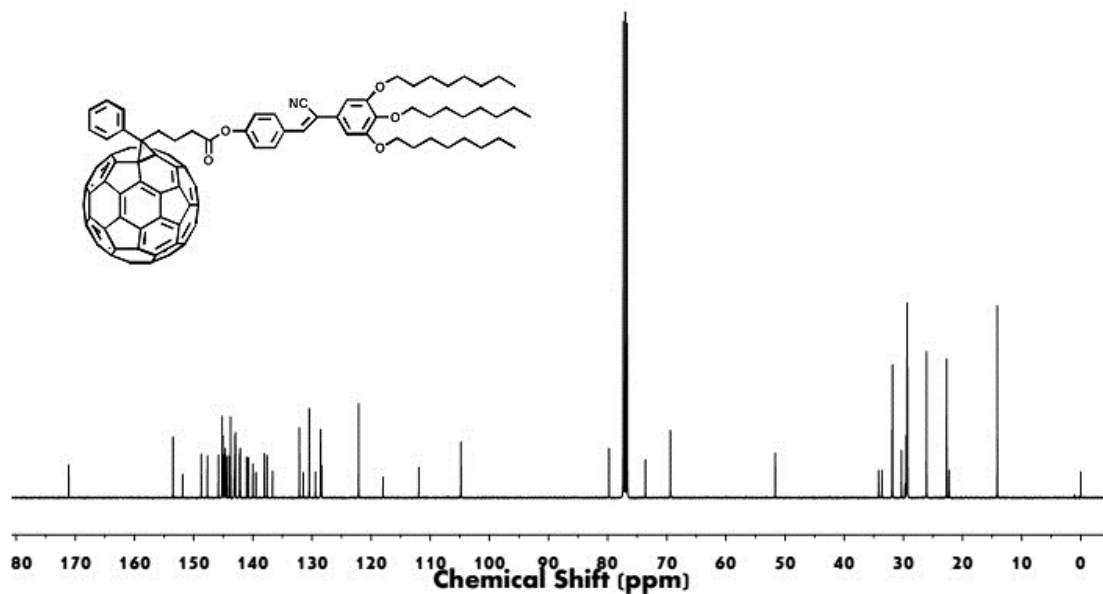


Figure S2. ^{13}C NMR of PCBB-CN-C8

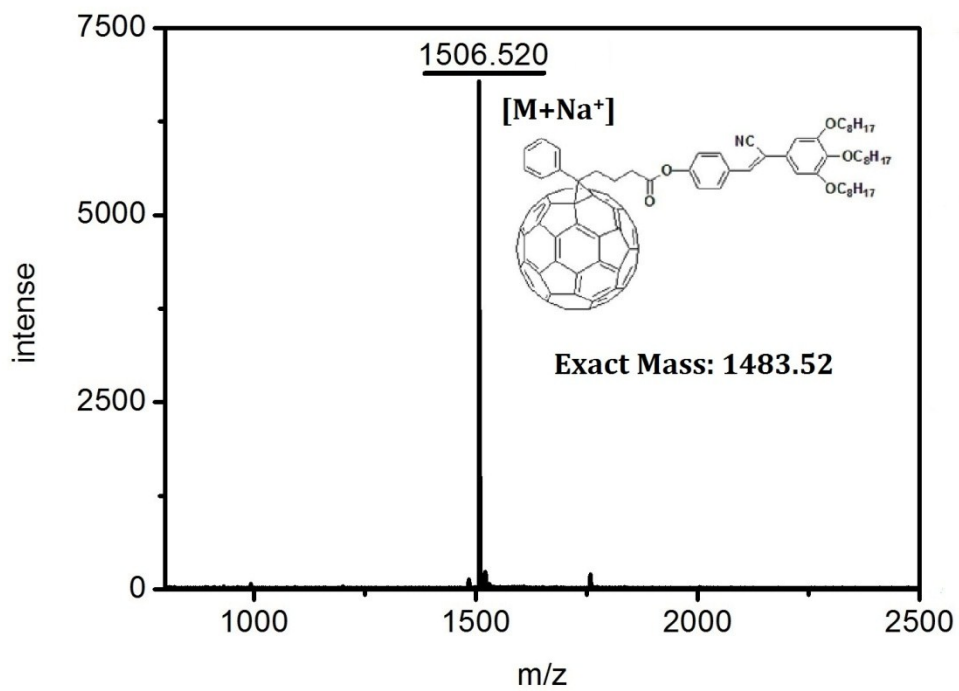


Figure S3. MALDI- TOF mass spectrum of PCBB-CN-C8

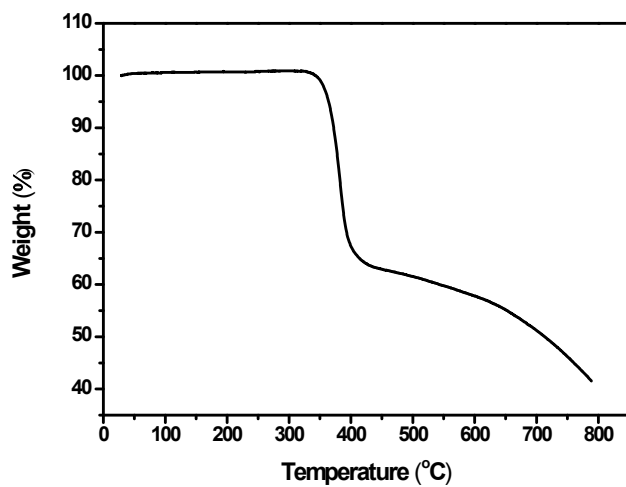


Figure S4. TGA thermogram of PCBB-CN-C8 at a heating rate of 10°C/min under N₂.

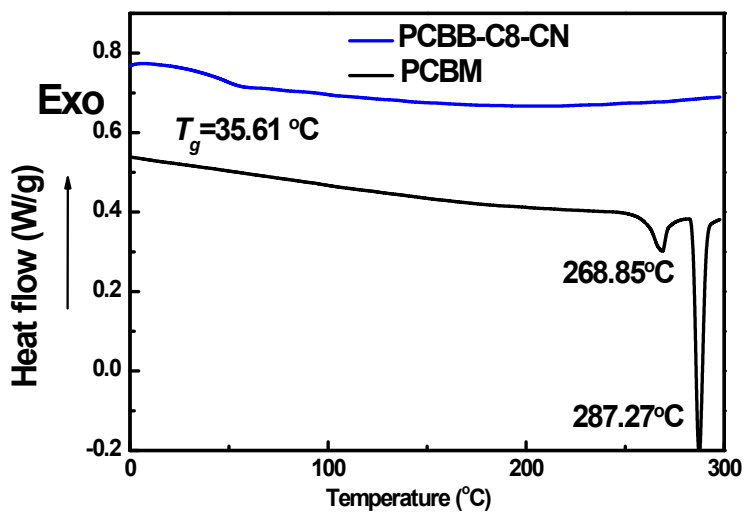


Figure S5. DSC analysis of PCBB-CN-C8 at a heating rate of 10 °C/min under N₂.

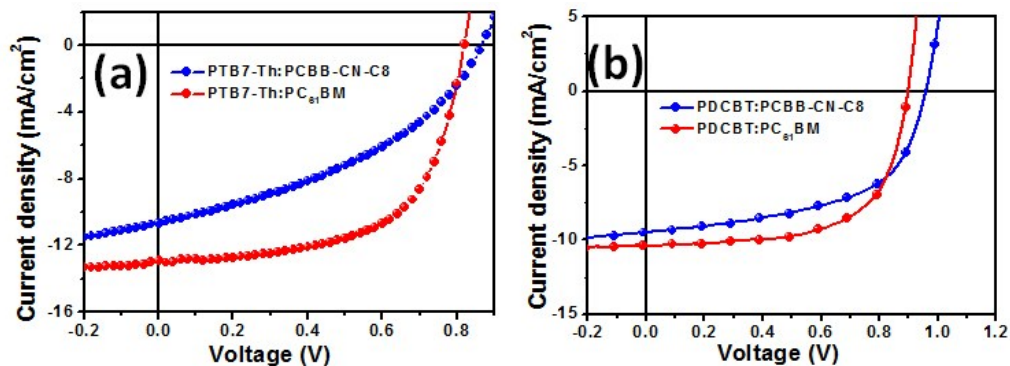


Figure S6. Current density-voltage characteristics of the PSCs based on (a) PTB7:PC₆₁BM (1:1.5 w/w) and PTB7:PCBB-CN-C8 (1:1.5 w/w) blend film spin-coated from CB solution; (b) The PDCBT:PC₆₁BM and PDCBT:PCBB-CN-C8 (1:1 w/w) blend film spin-coated from *o*-DCB solution.

Table S1. Characteristic Photovoltaic Parameters under the Illumination of AM 1.5G, 100 mW/cm².

Device	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	PCE (%)
PTB7-Th:PC ₆₁ BM with DIO (3%)	0.82	12.93	0.61	6.47
PTB7-Th:PCBB-CN-C8 without DIO	0.88	10.66	0.40	3.69
PDCBT:PCBM with without DIO	0.90	10.41	0.61	5.71
PDCBT: PCBB-CN-C8 without DIO	0.96	9.52	0.56	5.11