Supporting Information

Molecular Design towards Efficient Polymer Solar Cell with High Polymer Content

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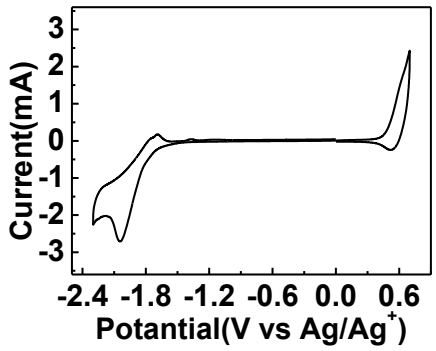


Figure s1. Cyclic voltammogram of PBT1 film on the glassy carbon electrode in 0.1 mol/L Bu_4NPF_6 in acetonitrile solution at a scan rate of 50 mV/s.

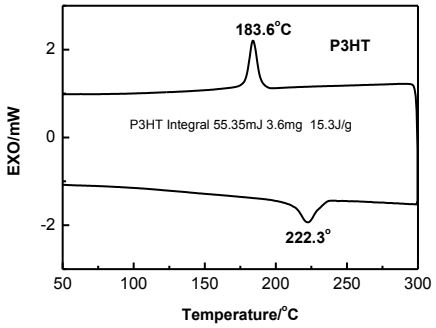


Figure s2. DSC plot of regioregular poly(3-hexylthiophene) (rr-P3HT) under inert atmosphere with a scan speed of 10°c/min.

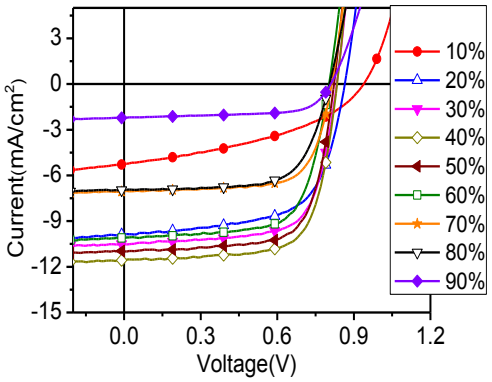


Figure s3. *J-V* curves of the PBT1-based PSCs with different $PC_{71}BM$ contents under the illumination of AM 1.5G, 100 mW/cm^2.

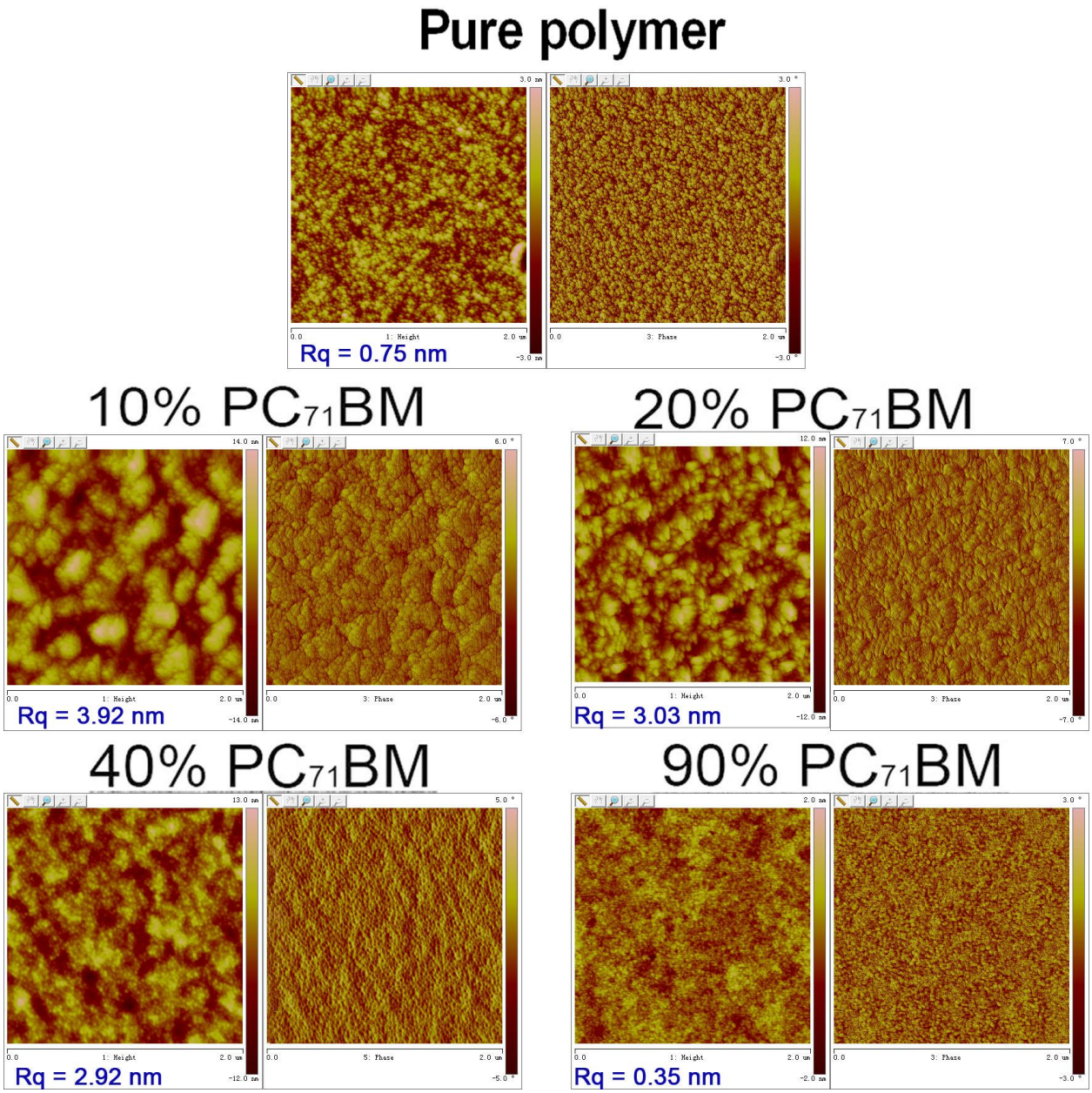


Figure s4. AFM phase images and topographies of the PBT1 pure polymer film and the PBT1:PC71BM blend films with varied PC71BM contents, 10%, 20%, 40% and 90%.

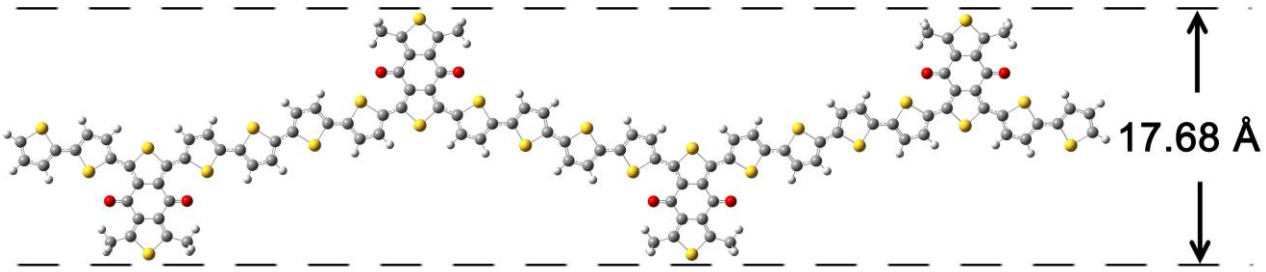


Figure s5. Backbone structure of PBT1 simulated by DFT method under b3lyp/6-31g(d,p) level.

Table s1. Photovoltaic performance based on PBT1:$PC_{71}BM$ with different ratios of DIO

DIO (%)	rpm	$PC_{71}BM$ content (%)	Voc (V)	Jsc(mA/cm^2)	FF(%)	PCE(%)
0	800	40	0.94	9.09	53.37	4.58
0.5	800	40	0.83	9.81	71.1	5.81
1	800	40	0.83	11.57	71	6.88
2	800	40	0.85	10.80	70.40	6.46

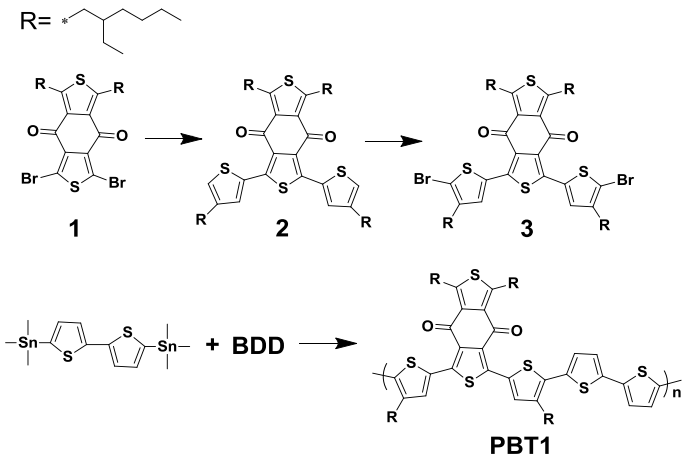
EXPERIMENTAL SECTION

Materials. 5,5'-bis(trimethylstannyl)-2,2'-bithiophene and 2,5-bis(2-ethylhexyl)thiophene were purchased from Solarmer Materials Inc.; $Pd(PPh_3)_4$ was purchased from Frontiers Scientific Inc. All of these chemicals were used as received. The other materials were common commercial level and used as received.

Instruments. ^1H and ^{13}C NMR spectra were measured on a Bruker arx-400 spectrometer in $CDCl_3$ at 293 K. UV-visible absorption spectra were taken on a Hitachi U-3100 UV-Vis spectrophotometer. The molecular weight of polymer was measured by GPC method, and polystyrene was used as a standard by using chloroform as eluent. The electrochemical cyclic voltammetry was conducted on a CHI650D Electrochemical Workstation with Pt disk, Pt plate, and Ag/Ag^+ electrode as working electrode, counter electrode and reference electrode respectively, in a 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution. X-ray data is acquired from the Advanced Light Source, which is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. AFM measurement of the surface morphology of samples was conducted on a Nanoscope III (Vecco) in tapping mode with a 2 μm scanner. TEM was performed using a JEOL 2200FS instrument at 160 kV accelerating voltage. EQE was measured by Solar Cell Spectral Response Measurement System QE-R3011 (Enli Technology Ltd., Taiwan). The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell.

Fabrication of polymer solar cells. Polymer solar cell devices were fabricated under conditions as follows: After spin-coating a ~30 nm layer of poly(3,4-ethylenedioxyth iophene):poly(styrenesulfonate) (PEDOT:PSS) onto a pre-cleaned indium-tin oxide (ITO) coated glass substrates, the polymer/PCBM blend solution which stirred for 5 hours. The concentration of the polymer:PCBM blend solution used in this study for spin-coating was 10 mg/ml (polymer/*o*-dichlorobenzene), and *o*-dichlorobenezene was used as the solvent. The additive, 1,8-diiodooctane (DIO) with 1% volume ratio was added prior to spin-coating process. The devices were completed by evaporating Ca/Al metal electrodes with an area of 4 mm^2 as defined by masks. The current-voltage curves are measured under

100 mW cm^{-2} standard AM 1.5 G spectrum using a XES-70S1 (SAN-EI ELECTRIC CO., LTD.) solar simulator (AAA grade, 70 mm × 70 mm photo-beam size). 2 cm × 2 cm Monocrystalline silicon reference cell (SRC-1000-TC-QZ) was purchased from VLSI Standards Inc.



Synthesis.

1,3-bis(2-ethylhexyl)-5,7-bis(4-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-c:4,5-c']dithiophene-4,8-dione, (2). Pd $(PPh_3)_4$ (40 mg) was added to a solution of compound 1 (3 mmol, 1.8 g) and thimethyl(thiophen-2-yl)-stannane (9 mmol, 3.4 g) in toluene. The mixture was refluxed in a nitrogen atmosphere for 12 h. After the removal of the solvent at a reduced pressure, the residue was purified by column chromatography on silica gel with petroleum ether/dichloromethane (5:1 by volume) to give a yellow solid (1.6 g, 64 %). ^{1}H NMR (400 MHz,$CDCl_3$) (ppm): 7.56 (s, 2H), 7.06 (s, 2H), 3.30(m, 4H), 2.58(d,4H),1.77 (t, 2H), 1.61(t,2H),1.42-1.29 (m, 32H), 0.93-0.82 (m, 24H). ^{13}C NMR (400 MHz, $CDCl_3$) (ppm): 177.90, 153.31, 142.78, 142.27, 133.32, 133.02, 132.48, 132.42, 125.51, 41.36, 40.51, 34.58, 33.76, 32.89, 32.63, 29.08, 28.94, 26.15, 25.74, 23.22, 23.18, 14.33, 14.29, 11.02.

1,3-bis(5-bromo-4-(2-ethylhexyl)thiophen-2-yl)-5,7-bis(2-ethylhexyl)benzo[1,2-c:4,5-c']dithiophene-4,8-dione (3). Compound 2(1.92 mmol, 1.6 g) was added into DMF(20 ml). After the solid dissolved completely, N-bromosuccinimide (NBS) (3.94 mmol, 0.7 g) was added in one portion. The reaction mixture was stirred at a room temperature for 3 h, water was added into the mixture, and the mixture was extracted with CHCl3, and the organic layer was washed with brine and dried over anhydrous sodium sulfate. The solvent was removed at a reduced pressure, the residue was purified by column chromatography on silica gel with petroleum ether/acetic ether (30:1 by volume) to give a red solid (1.35 g, 71 %). ^{1}H NMR (400 MHz, $CDCl_3$) (ppm): 7.38 (d, 2H), 3.30 (m, 4H), 2.53(d, 4H), 1.76(s, 2H), 1.64(s, 2H), 1.41-1.31(m, 32H), 0.94-0.79(m, 24H). ^{13}C NMR (400 MHz, $CDCl_3$) (ppm): 177.7, 153.9, 141.8, 141.4, 132.9, 132.7,132.1, 131.5,116.2, 41.3,40.13 33.8, 32.9, 32.6, 29.0, 26.1, 25.8, 23.2, 14.3,11.0. Elemental analysis: calculated for [$C_{50}H_{70}O_2S_4Br_2$], C, 60.59%; H, 7.12%; found: C, 60.50%; H, 7.30%.

Polymerization of PBT1. Compound 3 (0.3 mmol) and 5,5'-bis(trimethylstannyl)-2,2'- bithiophene (0.3 mmol) were dissolved in 10 ml toluene, and the solution was flushed with argon for 5 min, then 25 mg $Pd(PPh_3)_4$ was added into the solution. The mixture was again flushed with argon for 20 min. The reaction solution was heated to reflux for 12 h. The reaction mixture was cooled to room temperature and added dropwise to 100 ml methanol. The precipitate was collected and further purified by Soxhlet extraction with methanol, hexane, and chloroform in sequence. The chloroform fraction was concentrated and added dropwise into methanol. Subsequently, the precipitates were collected and dried under vacuum overnight to get polymer 230mg, yield 77%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.63 (S, 2 H), 7.17 (S, 4 H), 3.32 (S, 4 H), 2.77 (S, 4 H), 1.80-1.75(br, 4 H), 1.44-1.25 (br, 32 H), 0.98-0.83(br, 24 H). Elemental analysis: calculated for [$C_{58}H_{72}O_2S_6$], C, 69.97%; H, 7.49%; found: C, 69.03%; H, 7.48%. Mn=38 k, PDI=2.12. Td=418 °C.