<Supporting information>

The Effect of Irregularity from Asymmetric Random $\pi$-Conjugated Polymers on the Photovoltaic Performance of Fullerene-Free Organic Solar Cells

Um Kanta Aryal,$^a$ Junwoo Lee,$^b$ Kakaraparthi Kranthiraja,$^a$ Saripally Sudhaker Reddy,$^a$
Vijaya Gopalan Sree,$^a$ Taiho Park,$^b$ Myungkwan Song$^c$ and Sung-Ho Jin$^a$

$^a$Department of Chemistry Education, Graduate Department of Chemical Materials, Institute for Plastic Information and Energy Materials, Pusan National University, Busan, 46241, Republic of Korea. E-mail: shjin@pusan.ac.kr

$^b$Department of Chemical Engineering, Pohang University of Science and Technology, Gyeongbuk 37673, Republic of Korea. E-mail: taihopark@postech.ac.kr

$^c$Surface Technology Division, Korea Institute of Materials Science, Gyeongsangnam-do 51508, Republic of Korea. E-mail: smk1017@kims.re.kr

$^2$U. K. Aryal, Junwoo Lee, and K. Kranthiraja made equal contribution for this article
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Experimental Section

Materials and Instruments

All the chemicals and solvents were purchased from Sigma-Aldrich, Alfa aesar and used directly without further purification. ITIC were obtained from Solarmer (China) and Solemme BV (Netherlands), respectively. Zinc acetate dihydrate (99.9%), 2-methoxy ethanol (99.8%), ethanolamine (99.5%), chlorobenzene, toluene were obtained from Sigma Aldrich (Korea). The UV-vis absorption spectra and emission spectra were recorded on a JASCO V-570 spectrophotometer (USA) and Hitachi F-4500 fluorescence spectrophotometer (Japan), respectively at room temperature. The number-average and weight-average molecular weights (Mn and Mw) of PBDTP and asy-PBDTPBT was determined relative to a polystyrene standard with tetrahydrofuran as the eluent at 25 °C using gel permeation chromatography (Agilent GPC 1200 series, Germany). Cyclic voltammetry (CV) analyses were carried out with a CHI 600C potentiostat (CH Instruments) at a scan rate of 100mV s⁻¹ in 0.1 M solution of tetrabutylammonium perchlorate in acetonitrile. A platinum wire was used as the counter electrode and an Ag/AgCl electrode was used as the reference electrode. Atomic force microscopy images were acquired with a XE-100 (Park system corp., Korea) in tapping mode.
Blend solutions

Photoactive blend solutions were prepared using chlorobenzene and these solutions were vigorously stirred at room temperature for 12 h before spin-coating. ZnO precursor solutions were prepared by dissolving zinc acetate dehydrate and ethanolamine in 2-methoxyethanol, were stirred at 60 °C for 1 h and then at room temperature for 12 h prior to spin-coating.

Device fabrication

Indium-tin-oxide (ITO) substrates were sequentially cleaned with deionized (DI) water, acetone and isopropanol by sonication process. Cleaned ITO substrates were dried and kept in UV-ozone for 20 minutes, and then ZnO solution is spin-coated on top of ITO at 3000 rpm for 40 s, for 40 nm thickness. The samples were baked at 160 °C for 15 minutes. After annealing, the samples were transferred into N₂ glove box and the photoactive layer. For non-fullerene acceptor case, Polymer:ITIC-Th (1:1 weight ratio in CB) was spin-coated on the top of ZnO layer. The thickness of photoactive layer of both fullerene and non-fullerene acceptor cases, were optimized about 100 nm. Finally, 7 nm of MoO₃ and 100 nm Ag anode were thermally evaporated under high vacuum with adjusting 0.11 cm² device area, as defined by the aperture area on mask.

Device measurement and characterization

The performances of solar cells were measured using a calibrated air mass (AM) 1.5 G solar simulator (Oriel Sol3A Class AAA solar simulator, models 94043A, Newport Stratford, Inc., USA) with a light intensity of 100 mW/cm² adjusted using a standard PV reference cell (2 cm × 2 cm monocrystalline silicon solar cell, calibrated at NREL, Golden, CO) and a computer controlled Keithley 2400 (Keithley Instruments, Inc. USA) source measure unit. The external quantum efficiency spectrum was determined by using Oriel IQE-200 with a 250W quartz tungsten halogen lamp Oriel IQE-200 (Newport Stratford, Inc., USA) equipped
with a 250W quartz tungsten halogen lamp as the light source and a monochromator, an optical chopper, a lock-in amplifier, and a calibrated silicon photodetector. While measuring the $J$-$V$ curves, a black mask was used and only the effective area of the cell was exposed to light irradiation. VersaSTAT-3 (Princeton Applied Research, USA) work station with an ac signal of 25 mV in the frequency range of 500 Hz-1 MHz in the dark was applied for EIS measurement. The experimental data were fitted using commercial Z-view software. Hole mobility measurements of the devices were performed with a hole only device structure ITO/MoO$_3$/active layer/MoO$_3$/Al. The mobility calculated by fitting the dark $J$–$V$ curve into the space charge limited current model (based on the equation derived by the Mott-Gurney law). For the measurement of thickness of the different layers of the device, Alpha-step IQ surface profilometer USA with an accuracy of $\pm 1$ nm was applied. Atomic force microscopy images were determined with a XE-100 (Park system corp., Korea) in tapping mode.
Synthesis of monomers and polymers

The monomers BDT (0.27 mmol), and P (0.27 mmol), were dissolved in anhydrous chlorobenzene (4 mL) and purged with nitrogen for 15 min before the addition of Pd$_2$ (dba)$_3$ (5.4 mg, 2 mol%), and (o-tol)$_3$P (16 mg, 16 mol%) and continued the purging for 15 min, heated to 150 °C for 1 h. After completion of the reaction, cooled the reaction mixture and precipitated into the methanol. Then soxhlet extraction was carried out with methanol, hexane, acetone and chloroform, the chloroform fraction was evaporated and precipitated from methanol to get new polymer. For new set of random conjugated polymers an additional BT acceptor (25%) was also incorporated.

**PBDTP (70%)**: $M_n = 55000 \text{ g/mol}; \text{PDI}=2.3$; Anal. Calcd for C$_{84}$H$_{101}$F$_2$NO$_4$S$_7$: C, 69.52; H, 7.02; F, 2.6; N, 0.97 Found C, 69.42; H, 6.96; N, 0.99. $^1$H NMR (300 MHz, CDCl$_3$, $\delta$): 7.27-7.58 (br, 8H), 6.88 (br, 6H), 3.84 (br, 4H), 3.52 (br, 2H), 2.02-2.93 (br, 4H), 1.70-1.74 (m, 3H), 1.29-1.55 (m, 48H), 0.89 (m, 24H).

**asy-PBDTPBT (67%)**: $M_n = 60000 \text{ g/mol}; \text{PDI}=2.3$; Anal. Calcd for C$_{109}$H$_{129}$F$_2$N$_3$O$_6$S$_{10}$: C, 67.63; H, 6.72; F, 1.96; N, 2.17 Found C, 67.33; H, 6.27; N, 2.08. $^1$H NMR (300 MHz, CDCl$_3$, $\delta$): 6.88-7.58 (br, 18H), 3.84 (br, 8H), 3.52 (br, 2H), 2.02-2.93 (br, 4H), 1.29-1.55 (m, 71H), 0.89 (m, 30H).
Fig. S1 $^1$H NMR of PBDTP.

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Table S1 Dihedral angles of the PBDTP and asy-PBDTPBT.

<table>
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<th>Polymer</th>
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<th>02</th>
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<th>05</th>
<th>06</th>
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<td>PBDTP</td>
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<td>asy-PBDTPBT</td>
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<td>32.67</td>
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