Electronic Supplementary Information

Ternary Conjugated D-A Copolymer Yields over 9.0% Efficiency in Organic Solar Cells

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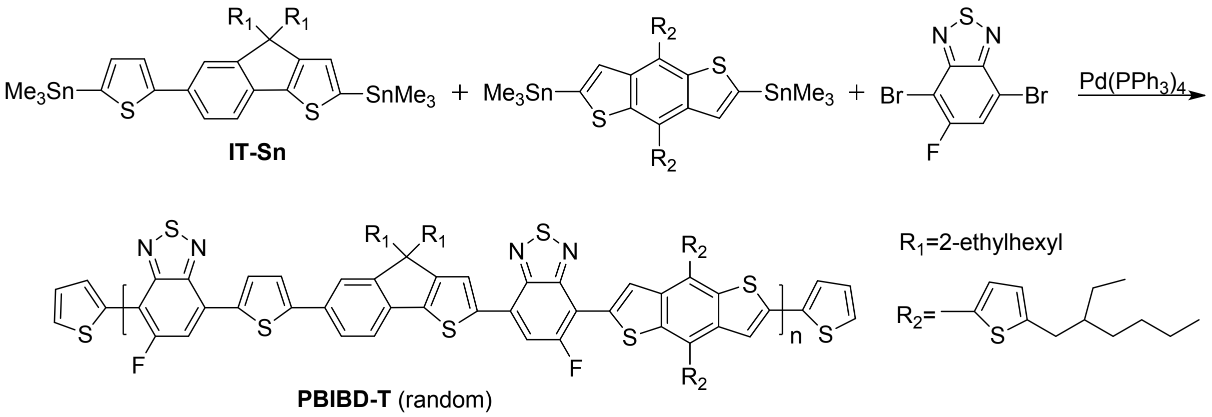
Instruments

Column chromatography was conducted with silica gel (300–400 mesh). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE-400 spectrometer operating at 400 and 100 MHz, respectively. Mass spectroscopy (MS) measurements were performed on an Ion Spec 4.7 T spectrometer. Linear absorption spectra were collected on a UV-Vis spectrophotometer (Lambda 365 UV/vis). The molecular weight and polydispersity index (PDI) of the copolymer were estimated by the gel permeation chromatography (GPC) method in 1,2,4-trichlorobenzene at 150 ^{o}C (polystyrene as the internal standard). Thermogravimetric analysis (TGA) was taken on a NETZSCH STA 449C Simultaneous Thermal Analyzer. Differential scanning calorimetry (DSC) was performed at a NETZSCH DSC 200 F3 instrument. Cyclic voltammogram was obtained by a CHI 700E electrochemical workstation. The atomic force microscopy (AFM) images of the active layers were obtained by a Bruker Dimension ICON at a tapping mode.

Materials: 5-Fluoro-4,7-diiodobenzo[c][1,2,5]thiadiazole,[1] (4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane),[2,3] (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane),[4] IT-Sn,[5] and 2,9-bis(3-(dimethylamino)propyl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone[6] were synthesized according to the literature procedures. Reagents, unless otherwise stated, were purchased from Aladdin-Reagent Inc., Aldrich Inc. or Adamas beta Ltd. and used as received.



Scheme S1. Synthesis of random **PBIBD-T**.

Synthesis of compound **1.** Compound **IT-Sn** (1.10 g, 1.37 mmol), 5-fluoro-4,7-diiodobenzo[c][1,2,5]thiadiazole (1.28 g, 4.10 mmol), and $Pd(PPh_3)_4$ (70 mg) were dissolved in 100 mL degassed toluene. After heated at 90 °C over night, the solvent was removed in vacuum. The crude product was further purified by silica column chromatography with petroleum ether:dichloromethane (10/1, v/v) as the eluent to give a dark red powder (1.09 g, 85%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 8.20-8.16 (m, 2H), 7.77-7.73 (m, 2H), 7.69-7.67 (m, 2H), 7.53 (d, J = 8.4 Hz, 1H), 7.47 (d, J = 4.0 Hz, 1H), 2.16-2.04 (m, 4H), 1.08-0.88 (m, 16H), 0.75-0.60 (m, 14H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 162.05, 159.55, 156.75, 154.67, 154.34, 148.92, 147.92, 144.12, 139.58, 138.19, 136.15, 131.12, 130.27, 128.35, 127.45, 125.33, 124.66, 124.10, 123.91, 121.19, 119.85, 119.66, 115.26, 114.78, 96.05, 95.74, 54.60, 43.72, 43.66, 35.22, 35.14, 34.24, 34.03, 28.56, 27.51, 22.80, 22.66, 14.09, 13.96, 10.81, 10.67, 10.61, 10.46. MS m/z: calculated for $C_{43}H_{42}Br_2F_2N_4S_4$, (M+H$^+$): 939.06; found: 939.07.

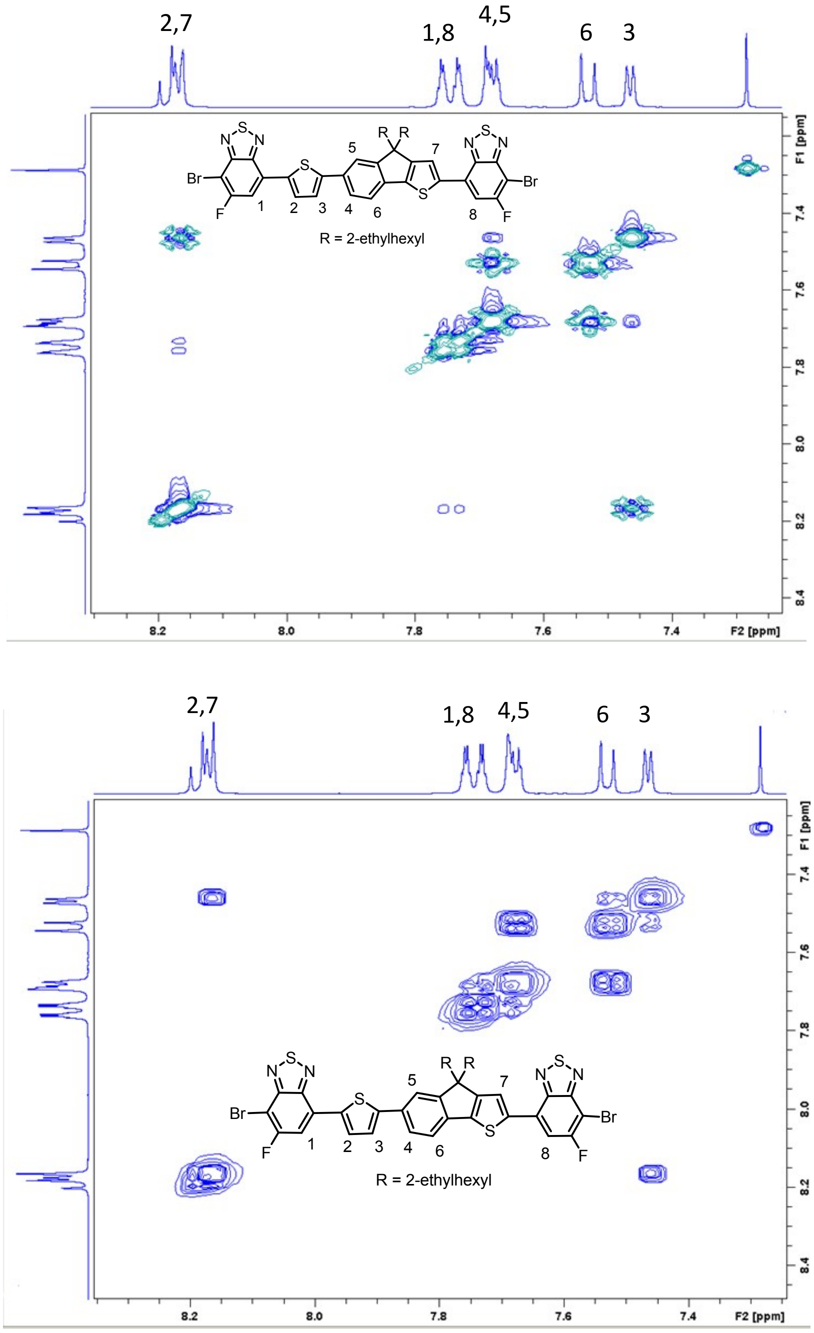


Figure S1. Aromatic regions of 2D ^1H-^1H NOESY (top) and ^1H-^1H COSY (bottom) NMR spectra of compound **1** in $CDCl_3$

Synthesis of **PBIBD-O**. Compound **1** (0.30 g, 0.32 mmol), (4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (0.25 g, 0.32 mmol), 25 ml of anhydrous toluene were added into a 50 ml flask. The mixture was degassed by bubbling with nitrogen for 1 h, then 6 mg of $Pd(PPh_3)_4$ were added. After refluxed gently for 18 h, 0.20 ml of 2-tributylstannylthiophene was added to the mixture solution and reacted for 12 h. Then, 0.4 ml of 2-bromothiophene was added to the mixture and heat for another 12 h to complete the end-capping reaction. After cooled to room temperature, the mixture was precipitated into methanol. The polymer was collected by filtration and further purified in a Soxhlet setup with methanol, acetone, hexane and dichloromethane for 24 h each. Then the residue solid was redissolved in chloroform and precipitated into methanol. Finally, the product polymer was collected by filtration and dried in vacuum at 55 °C overnight to give a black solid with a metallic luster (0.25 g, 63%). ^{1}H NMR ($C_2Cl_4D_2$, 400 MHz, ppm): 8.91-8.81 (br, 2H), 8.35-8.24 (br, 2H), 7.97-7.55 (m, 5H), 7.37-7.34 (br, 1H), 4.57-4.30 (m, 4H), 2.30-1.62 (m, 22H), 1.44-0.75 (m, 42H). GPC (in 1,2,4-trichlorobenzene): M_n = 14.0 KDa, PDI = 1.74.

Synthesis of **PBIBD-T.** Polymer **PBIBD-T** was prepared according to the same procedure as that for **PBIBD-O**. Yield: 0.67 g (77%). ^{1}H NMR ($C_2Cl_4D_2$, 400 MHz, ppm): 9.04-8.86 (br, 2H), 8.31-8.18 (br, 2H), 7.86-7.34 (m, 7H), 7.20-7.06 (m, 3H), 3.12-3.04 (m, 4H), 2.26-1.90 (m, 6H), 1.79-1.46 (m, 16H), 1.39-1.00 (m, 28H), 0.96-0.67 (m, 14H). GPC (in 1,2,4-trichlorobenzene): M_n = 21.9 KDa, PDI = 1.78.

Electrochemical Cyclic Voltammetry (CV): The CV measurements were performed by using a three electrode cell system in a 0.1 mol/L nitrogen-saturated tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution at a scan rate of 0.1 V/s. This system consisted of a Pt disk working electrode coated with a polymer film, a Ag/Ag$^+$ (0.1 M $AgNO_3$ in MeCN) reference electrode, and a Pt wire counter electrode. The onset oxidation potential ($E_{1/2\ ox}$) of ferrocene in this system was measured to be -0.02 V *versus* Ag/Ag$^+$. It was assumed that the redox potential energy level of Fc/Fc$^+$ has an absolute value of -4.80 eV to vacuum. Thus, the HOMO and LUMO energy levels, and electrochemical bandgap of the polymer can be calculated according to the following equations.

$$E_{\mathrm{HOMO}} = -(\varphi_{\mathrm{ox}} + 4.82)\ (\mathrm{eV}) \tag{1}$$

$$E_{\mathrm{LUMO}} = -(\varphi_{\mathrm{red}} + 4.82)\ (\mathrm{eV}) \tag{2}$$

$$E_g^{\mathrm{ec}} = (\varphi_{\mathrm{ox}} - \varphi_{\mathrm{red}})\ (\mathrm{eV}) \tag{3}$$

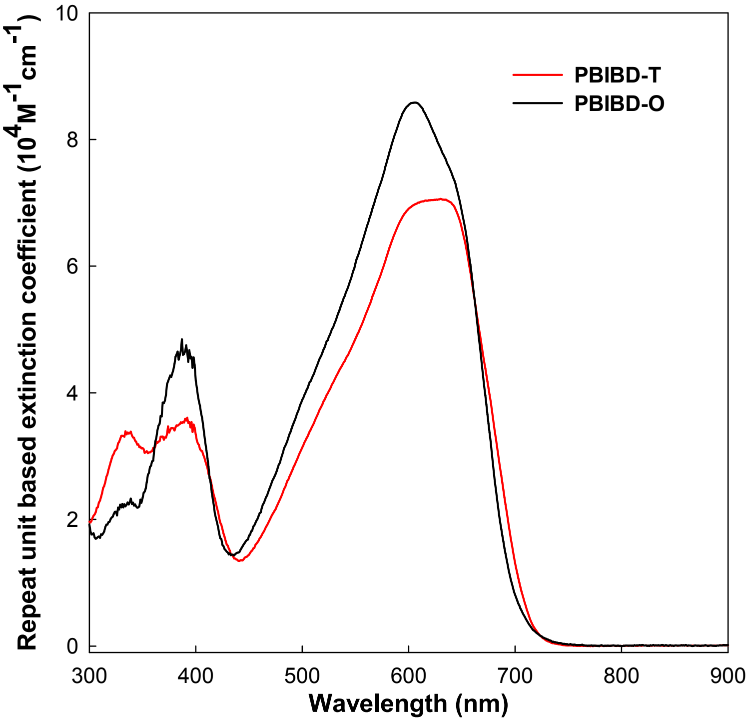


Figure S2 Repeat unit based extinction coefficients for the copolymers in solution.

Fabrication and Characterization of PSCs: The PSCs were fabricated in the traditional sandwiched structure: indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS)/polymer:PC$_{71}$BM/PDIN/Al. ITO glass was cleaned by ultrasonication sequentially in detergent, water, acetone, and isopropyl alcohol for 30 min each and then dried in an oven at 80 °C overnight. After the ITO glass substrates were subjected to ultraviolet/ozone treatment for 15 min, PEDOT:PSS (Baytron PVPAI 4083) was spin-coated on the ITO substrates at 3000 rpm for 60 s. Then the film-loaded substrates were dried at 140 °C in the air for 15 min. Polymer was blended with PC$_{71}$BM (1:2.2, w/w) and then dissolved in chlorobenzene (with or without 2 vol % diphenyl ether) at a concentration of

18 mg/mL and stirred overnight at 80 °C. Then the active layer was prepared by spin-coating the polymer: $PC_{71}BM$ solution at 1200 rpm for 60 s. To facilitate efficient electron injection, a methanol solution of PDIN (1.5 mg/mL containing 0.2% acetic acid) was spin-coated at 3000 rpm for 30 s to form an electron injection interlayer. Eventually, the negative electrode was prepared by thermally depositing about 100 nm Al. The device areas of the PSCs were fixed at 6 mm^2. All devices were encapsulated in glove box and tested in air. J–V characteristics of PSCs were measured by a Keithley 2440 source measurement unit under AM 1.5 G irradiation (100 mW/cm^2) from an Oriel sol3A simulator (Newport) which had been accurately calibrated with a National Renewable Energy Laboratory (NREL)-certified silicon reference cell. The EQE spectra were performed on a Newport EQE measuring system.

Grazing Incidence Wide-Angle X-ray Scattering (GIWAXS) Characterization: GIWAXS measurements were performed at beamline 7.3.3[7] at the Advanced Light Source (ALS). Samples were prepared on Si substrates using identical blend solutions as those used in PSC devices. The 10 keV X-ray beam was incident at a grazing angle of 0.11–0.15°, selected to maximize the scattering intensity from the samples. The scattered X-rays were detected using a Dectris Pilatus 2M photon counting detector.

Resonant Soft X-Ray Scattering (R-SoXS): R-SoXS transmission measurements were performed at beamline 11.0.1.2[8] at the Advanced Light Source (ALS). Samples for R-SoXS measurements were prepared on a PEDOT:PSS modified ITO substrate under the same conditions as those used for device fabrication, and then transferred by floating in water to a 1.5 mm × 1.5 mm, 100 nm thick Si_3N_4 membrane supported by a 5 mm × 5 mm, 200 μm thick Si frame (Norcada Inc.). 2D scattering patterns were collected on an in-vacuum CCD camera (Princeton Instrument PI-MTE). The sample detector distance was calibrated from diffraction peaks of a triblock copolymer poly(isoprene-b-styrene-b-2-vinyl pyridine), which has a known spacing of 391 Å. The beam size at the sample is approximately 100 μm × 200 μm.

Fabrication and characterization of hole-only devices: The structure for the hole-only device is ITO/PEDOT:PSS/copolymer:$PC_{71}BM/MoO_3/Au$. The hole-only devices were prepared by following the same procedures as those for the conventional PSC fabrication except that the electron injection interlayer and cathode were changed to MoO_3 (10 nm) and gold (60 nm), respectively. These devices were recorded by an Agilent 4155C semiconductor parameter analyzer in dark. The thicknesses of the blended films were estimated by the Bruker Dektak XT surface profilometer. With the space charge limited current (SCLC) model, the hole mobilities were estimated by the following equation:[1]

$$J = \frac{9}{8}\varepsilon_r \varepsilon_0 \mu \frac{V^2}{L^3}$$

where J is the current, ε_r is the dielectric constant of the polymer (assumed to be 3), ε_0 is the permittivity of free space (8.85×10^{-12} F m^{-1}), μ is the carrier mobility, V is the voltage drop across the device ($V = V_{appl} - V_a - V_{bi}$, where V_{appl} is the applied voltage to the device, V_a is the voltage drop due to contact resistance and series resistance across the electrodes, and V_{bi} is the built-in voltage due to the difference in work function of the two electrodes), and L is the film thickness of the active layer.

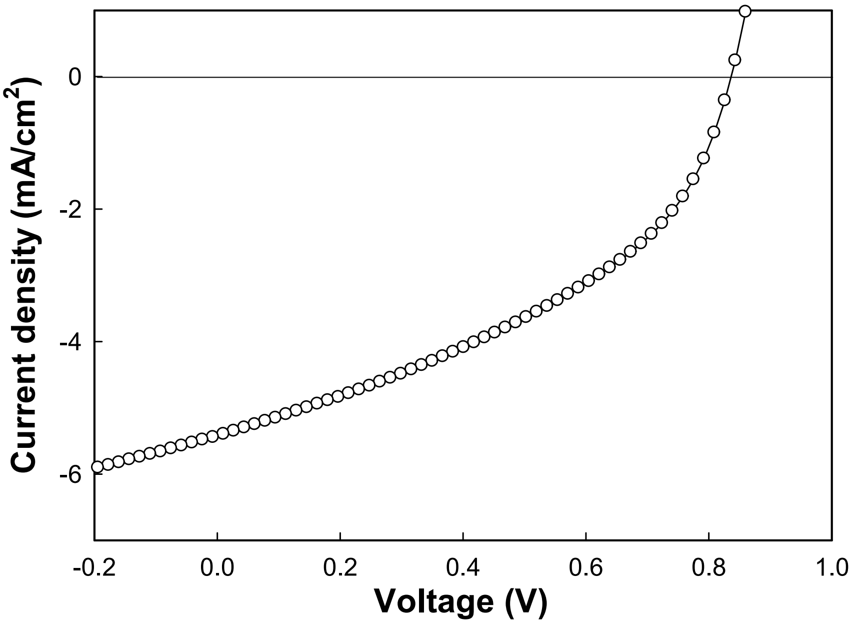


Figure S3. Current-voltage characteristic of fullerene polymer solar cells based on a random isomer of PBIBD-T.

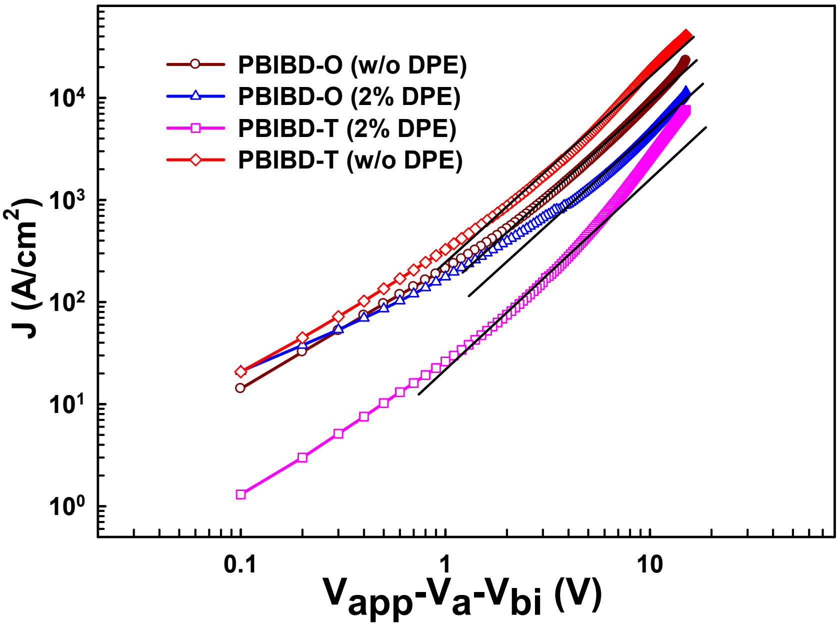


Figure S4. *J~V* characteristics of hole-only devices based on copolymer:PC$_{71}$BM blends with or without DPE.

References

1. S. Albrecht, S. Janietz, W. Schindler, J. Frisch, J. Kurpiers, J. Kniepert, S. Inal, P. Pingel, K. Fostiropoulos, N. Koch, and D. Neher, *J. Am. Chem. Soc.*, **2012**, *134*, 14932.
2. J. H. Hou, M.-H. Park, S. Q. Zhang, Y. Yao, L.-M. Chen, J.-H. Li, and Y. Yang, *Macromolecules*, **2008**, *41*, 6012.

3. Y. Y. Liang, Y. Wu, D. Q. Feng, S.-T. Tsai, H.-J. Son, G. Li, and L. P. Yu, *J. Am. Chem. Soc.*, **2009**, *131*, 56.
4. M. J. Zhang, X. Guo, S. Q. Zhang and J. H. Hou, *Adv. Mater.*, **2014**, *26*, 1118.
5. M. Wang, D. D. Cai, Z. G. Yin, S.-C. Chen, C.-F. Du, Q. D. Zheng, *Adv. Mater.* **2016**, *28*, 3359.
6. Z.-G. Zhang, B. Y. Qi, Z. W. Jin, D. Chi, Z. Qi, Y. F. Li, J. Z. Wang, *Energy Environ. Sci.* **2014**, *7*, 1966.
7. A. Hexemer, W. Bras, J. Glossinger, E. Schaible, E. Gann, R. Kirian, A. MacDowell, M. Church, B. Rude, H. Padmore, *J. Phys. Conf. Ser.* **2010**, *247*, 012007.
8. E. Gann, A. T. Young, B. A. Collins, H. Yan, J. Nasiatka, H. A. Padmore, H. Ade, A. Hexemer, C. Wang, *Rev. Sci. Instrum.* **2012**, *83*, 045110.