

Supporting Information

Novel Photovoltaic Donor 1-Acceptor-Donor 2-Acceptor Terpolymers with Tunable Energy Levels Based on Difluorinated Benzothiadiazole Acceptor

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Material: Tris(dibenzylideneacetone)dipalladium, PC₇₁BM (99.9%), Al (99.998%), LiF (99.99%), and other materials were purchased from Alfa, Shanghai Reagent Co., Ltd., or Aldrich and without further purification. Indium-tin oxide (ITO) glass was purchased from Delta Technologies Limited, whereas PEDOT: PSS (Baytron PA14083) was obtained from Bayer Inc. 5,6-Difluoro-4,7-diodobenzo[c][1,2,5]thiadiazole was prepared following the reported literature procedure.^[1]

Synthetic procedure

Synthesis of 4,7-bis(4-hexylthienyl)-5,6-difluoro-2,1,3-benzothiadiazole (1). In a reaction flask equipped with a magnetic stirrer, 5,6-difluoro-4,7-diodobenzo[c][1,2,5]thiadiazole (424 mg, 1 mmol, 1 equiv), tributyl(4-octylthiophen-2-yl)stannane (1213 mg, 2.5 mmol, 2.5 equiv) and tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) (30 mg) were mixed. The flask was purged with nitrogen (N₂) before adding 15 mL of toluene as a solvent. After stirring the mixture at 110 °C for 36 h under N₂ atmosphere, the reaction was quenched by adding dichloromethane. The crude product was extracted with dichloromethane, and purified by column chromatography with hexane and

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dichloromethane. Compound (1) was obtained as yellow solid (500 mg, 90% yield). ¹H-NMR (CDCl₃, 400 MHz): δ (ppm) 8.053(s, 2H), 7.140 (s, 2H), 2.647 (t, 4H), 1.635 (t, 4H), 1.300-1.187 (m, 22H), 0.832-0.798 (m, 8H). ¹³C-NMR (CDCl₃, 400 MHz): δ (ppm) 151.10, 150.90, 148.47, 148.32, 143.66, 132.17, 131.19, 123.70, 110.05, 31.88, 30.53, 30.46, 29.44, 29.35, 29.28, 22.67, 13.68.

Synthesis of 4-(5-bromo-4-octylthiophen-2-yl)-5,6-difluoro-7-(4-octylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (2). In a round-bottom flask, NBS (40 mg, 0.22 mmol, 1.2 equiv) was added into a solution of (1) (100 mg, 0.18 mmol) in mixture of chloroform (10 mL) and three drops of Acetic Acid. After stirring the mixture overnight at 0 °C in the dark, the reaction was quenched by adding water. The crude product was extracted with dichloromethane and the organic layer was washed with water and was dried over anhydrous Na₂SO₄. After removal of the solvent, the products were purified by recrystallization from chloroform and hexane (yellowish red solid, 80 mg, 70% yield). ¹H-NMR (CDCl₃, 400 MHz): δ (ppm) 8.105 (s, 1H), 7.936 (s, 1H), 7.198 (s, 1H), 2.720-2.627 (dt, 4H), 1.740-1.615 (m, 4H), 1.363-1.280 (m, 20H), 0.993-0.862 (d, 6H). ¹³C-NMR (CDCl₃, 400 MHz): δ (ppm) 148.20, 143.68, 142.51, 132.41, 132.32, 131.63, 131.54, 124.17, 124.10, 31.87, 30.52, 30.44, 29.74, 29.54, 29.43, 29.37, 29.33, 29.24, 22.66, 14.09.

Synthesis of 4,7-bis(5-bromo-4-octylthiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazole (3). In a round-bottom flask, NBS (80 mg, 0.45 mmol, 2.5 equiv) was added into a solution of (1) (100 mg, 0.18 mmol) in mixture of chloroform (15 mL) and three drops of Acetic Acid. After stirring the mixture overnight at room temperature in the dark, the reaction was quenched by adding water. The crude product was extracted with dichloromethane and the organic layer was washed with water and was dried over anhydrous Na₂SO₄. After removal of the solvent, the products were purified by recrystallization from chloroform and hexane (red solid, 100 mg, 80% yield). ¹H-NMR (CDCl₃, 400 MHz): δ (ppm) 7.957 (s, 2H), 2.655 (t, 4H), 1.664 (t, 4H), 1.360-1.254 (m, 22H), 0.885-0.867 (br, 6H). ¹³C-NMR (CDCl₃, 400 MHz): δ (ppm) 150.97, 150.75, 148.38, 148.17, 142.46, 131.74, 130.99, 114.13, 31.88, 29.74, 29.53, 29.38, 29.26, 22.67, 14.11.

Synthesis of 4-(5-(7-(5-(5,6-difluoro-7-(4-octylthiophen-2-yl)benzo[c][1,2,5]thiadiazol-4-yl)-3-octylthiophen-2-yl)-9,9-dioctyl-9H-fluoren-2-yl)-4-octylthiophen-2-yl)-5,6-difluoro-7-(4-octylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (4). In a reaction flask equipped with a magnetic stirrer, (2) (300 mg, 0.47 mmol, 2.2 equiv), 2-(9,9-dioctyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-fluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (F-2BO) (137 mg, 0.21 mmol, 1 equiv), K₂CO₃ (500 mg) and three drops of Aliquat 336 were added under the protection of nitrogen. After adding 15 mL toluene and 5 mL water, the mixture was degassed for 10 min. Pd(PPh₃)₄ (60 mg, 0.051 mmol) was added, then the mixture was heated to 100 °C and stirred for 36 h. The reactant was extracted with dichloromethane and the organic layer was washed with water and was dried over anhydrous Na₂SO₄. After removal of the solvent, the products were purified by column chromatography with hexane and dichloromethane. Compound (4) was obtained as red solid (302 mg, 85% yield). ¹H-NMR (CDCl₃, 400 MHz): δ (ppm) 8.186 (s, 2H), 8.141(s, 2H), 7.793(d, 2H), 7.555-7.514 (m, 4H), 7.213 (s, 2H), 2.810 (t, 4H), 2.725 (t, 4H), 2.054 (br, 4H), 1.732-1.592 (m, 10H), 1.405-1.100 (m, 80H), 0.936-0.799 (m, 24H). ¹³C-NMR (CDCl₃, 400 MHz): δ (ppm) 151.31, 143.65, 140.26, 139.20, 133.01, 132.45, 130.75, 128.67, 38.59, 31.78, 31.13, 30.55, 30.29, 30.06, 29.68, 29.47, 29.34, 28.90, 23.69, 22.90, 22.73, 14.02, 10.97.

Synthesis of 4-(5-bromo-4-octylthiophen-2-yl)-7-(5-(7-(5-(7-(5-bromo-4-octylthiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazol-4-yl)-3-octylthiophen-2-yl)-9,9-dioctyl-9H-fluoren-2-yl)-4-octylthiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazole (5). Compound (5) was similarly prepared from (1) to (3), giving red solid in 90% yield. ¹H-NMR (CDCl₃, 400 MHz): δ (ppm) 8.185 (s, 2H), 7.968 (s, 2H), 7.790 (d, 2H), 7.649-7.511 (m, 4H), 2.863 (t, 4H), 2.666 (t, 4H), 2.052 (br, 4H)1.729-1.677 (m, 8H), 1.377-1.091 (m, 60H), 0.830-0.779 (m, 24H). ¹³C-NMR (CDCl₃, 400 MHz): δ (ppm) 151.24, 142.73, 142.55, 140.25, 139.32, 133.99, 132.90, 131.52, 128.18, 123.62, 119.92, 55.20, 40.36, 31.87, 31.78, 31.13, 30.12, 29.76, 29.64, 29.56, 29.48, 29.38, 29.34, 29.30, 29.25, 29.04, 22.67, 22.52, 14.00, 13.68.

PBDT-DTffBT Compound (3) (120 mg, 0.17 mmol, 1equiv), BDT-2Sn (131 mg, 0.17 mmol, 1 equiv) and tri(o-tolyl)phosphine (P(o-tolyl)₃) (18 mg) were placed in a 100 ml reaction flask equipped with a magnetic stirrer. After purged with N₂ for 5 min, dry chlorobenzene (CB, 6 mL) and Pd₂(dba)₃ (7 mg) were added under N₂. Then the mixture was heated at 110 °C for 48 h. After cooling to room temperature, the reaction solution was poured into 150 mL of methanol and 10 mL of concentrated hydrochloric acid and stirred overnight to remove the stannylated end-groups. The polymers were subjected to Soxhlet extraction with acetone, hexanes and chloroform for 24 h each. Then poured into 150 ml of methanol, obtain dark solid after suction filtration (120 mg, 70%). ¹H-NMR (CDCl₃, 400 MHz): δ (ppm) 8.187-7.983 (m, 1H), 7.810-7.649 (m, 1H), 7.525-7.339 (m, 2H), 7.016-6.881 (m, 1H), 4.375-3.986 (m, 3H), 3.056-2.855 (m, 4H), 1.668-1.241 (m, 42H), 1.129-0.847 (m, 12H).

PF-DTffBT Compound (3) (120 mg, 0.17 mmol, 1equiv), F-2BO (109 mg, 0.17 mmol, 1 equiv), tri(o-tolyl)phosphine (P(o-tolyl)₃) (18 mg), K₂CO₃ (500 mg) and three drops of Aliquat 336 were placed in a 100 ml reaction flask equipped with a magnetic stirrer. After purged with N₂ for 10 min, dry toluene (6 mL), demineralised water and Pd₂(dba)₃ (7 mg) were added under N₂. Then the mixture was heated at 110 °C for 72 h after which the crude polymer was precipitated in methanol (100 mL). The polymers were subjected to Soxhlet extraction with acetone, hexanes and chloroform for 24 h each. Then poured into 150 ml of methanol, obtain crimson solid after suction filtration (100 mg, 63%). ¹H-NMR (CDCl₃, 400 MHz): δ (ppm) 8.240-8.175 (m, 1H), 7.836-7.750 (m, 1H), 7.578-7.529 (m, 2H), 2.896-2.764 (m, 4H), 2.099-1.710 (m, 6H), 1.574-1.085 (m, 28H), 0.874-0.744 (m, 12H).

PBDT-DTffBT-F-DTffBT This polymer was prepared from compound (5) and BDT-2Sn in a procedure similar to that for PBDT-DTffBT as a black solid (75%). ¹H-NMR (CDCl₃, 400 MHz): δ (ppm) 8.202-8.140 (m, 1H), 7.797-7.685 (m, 2H), 7.481-7.341 (m, 4H), 6.949-6.896 (m, 1H), 4.415-4.032 (m, 4H), 2.951-2.911 (m, 6H), 1.963-1.789 (m, 4H), 1.518-1.252 (m, 32H), 1.125-0.770 (m, 24H).

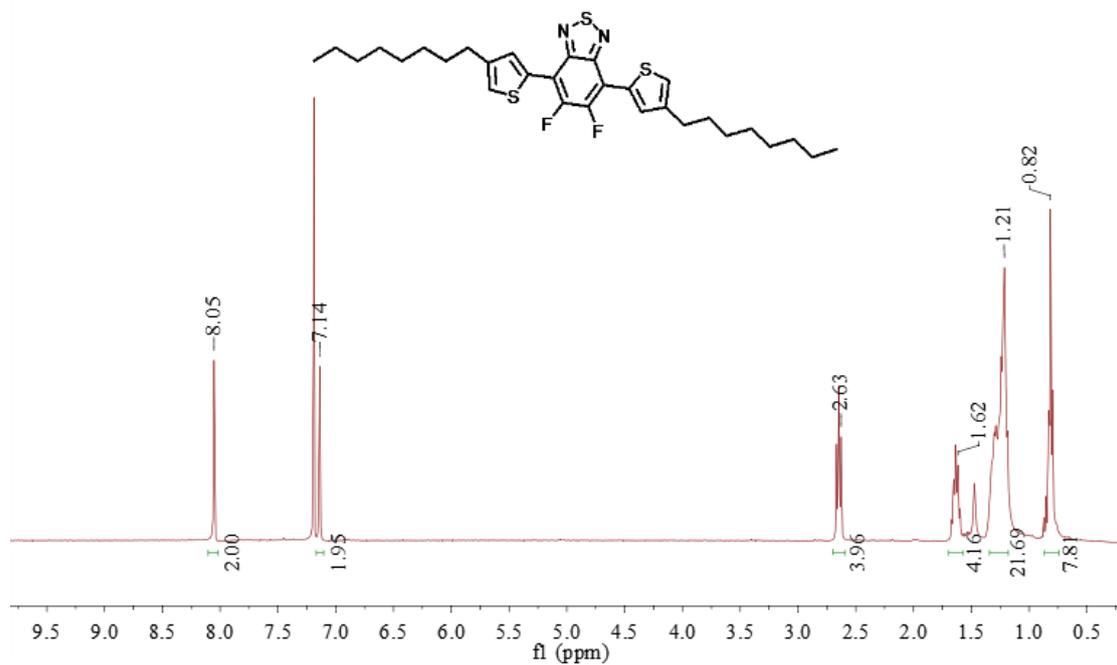


Figure SI 1. ^1H NMR spectra of (1).

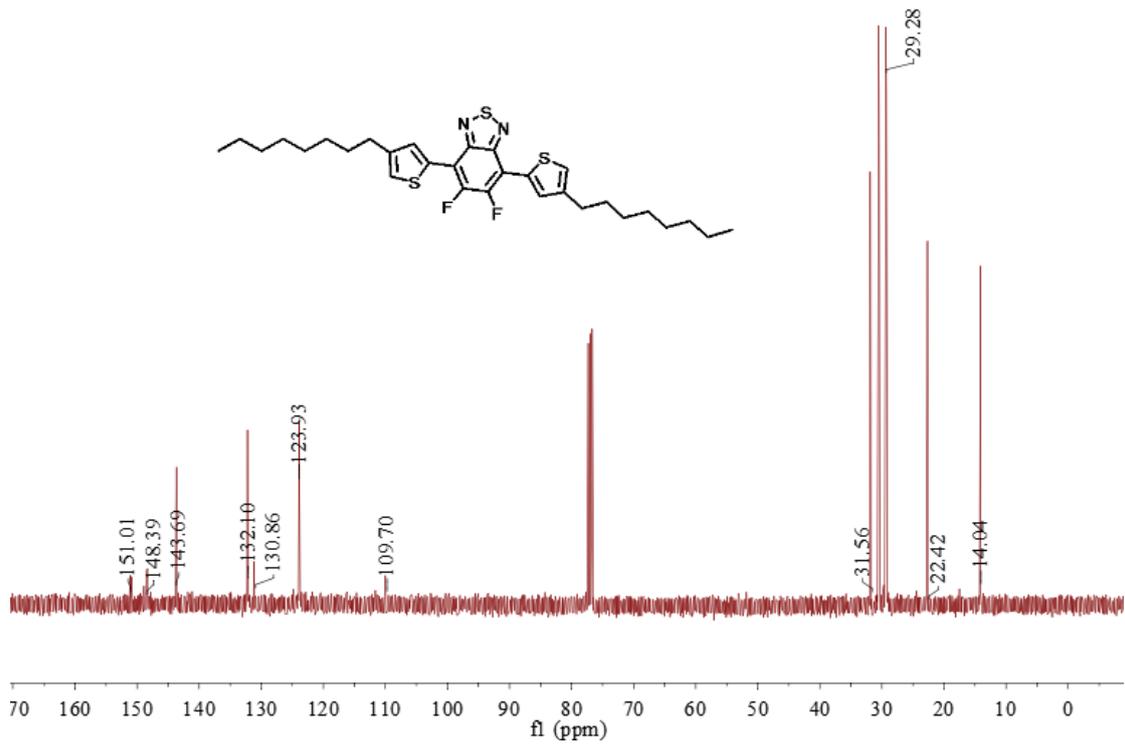


Figure SI 2. ^{13}C NMR spectra of (1).

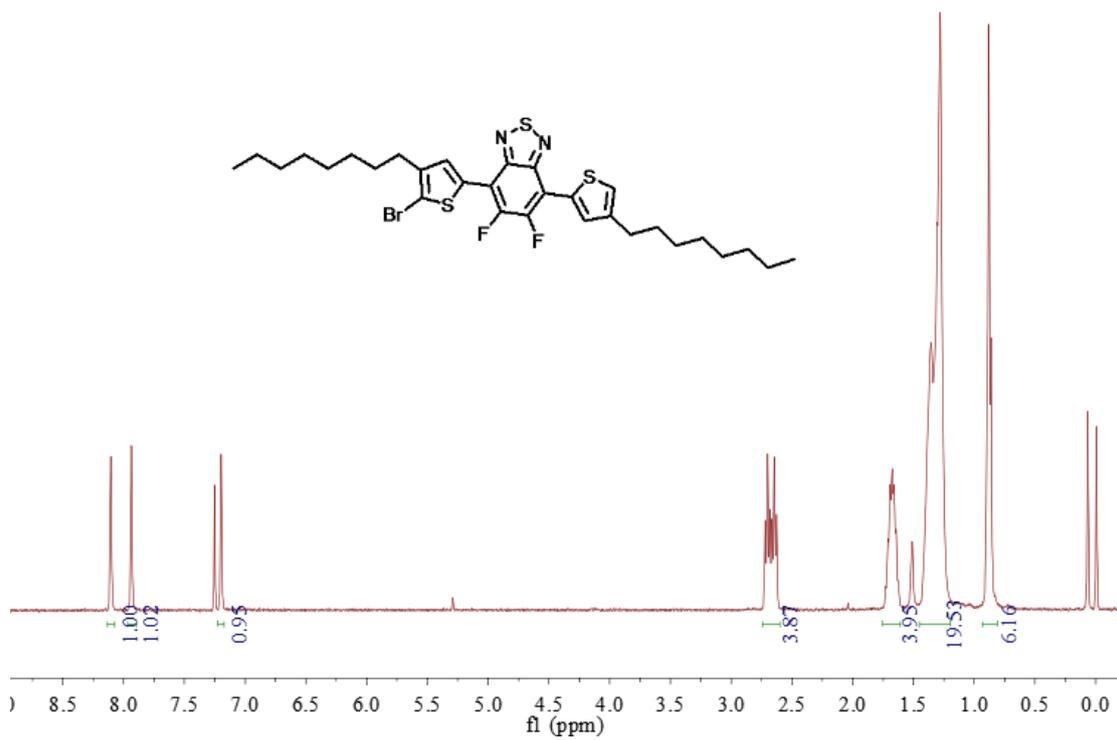


Figure SI 3. ¹H NMR spectra of (2).

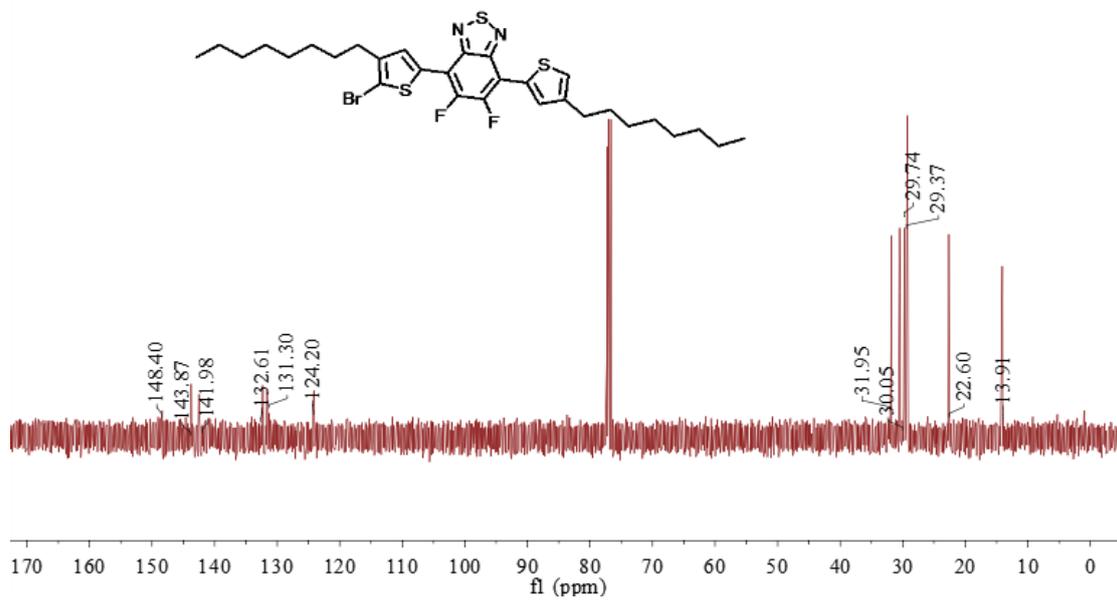


Figure SI 4. ^{13}C NMR spectra of (2).

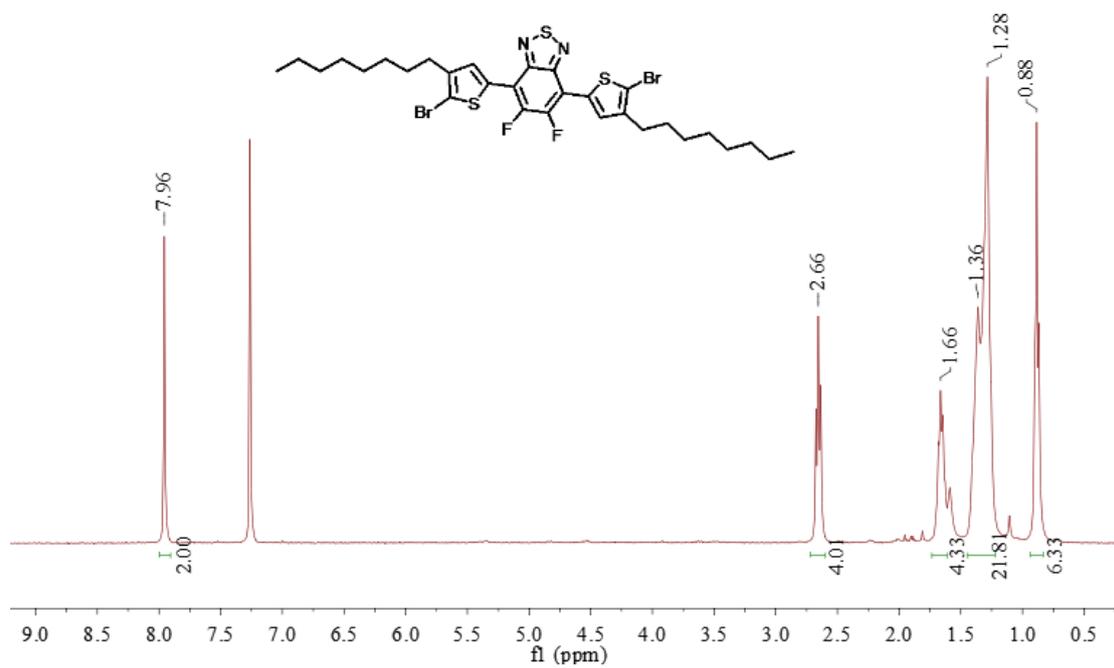


Figure SI 5. ^1H NMR spectra of (3).

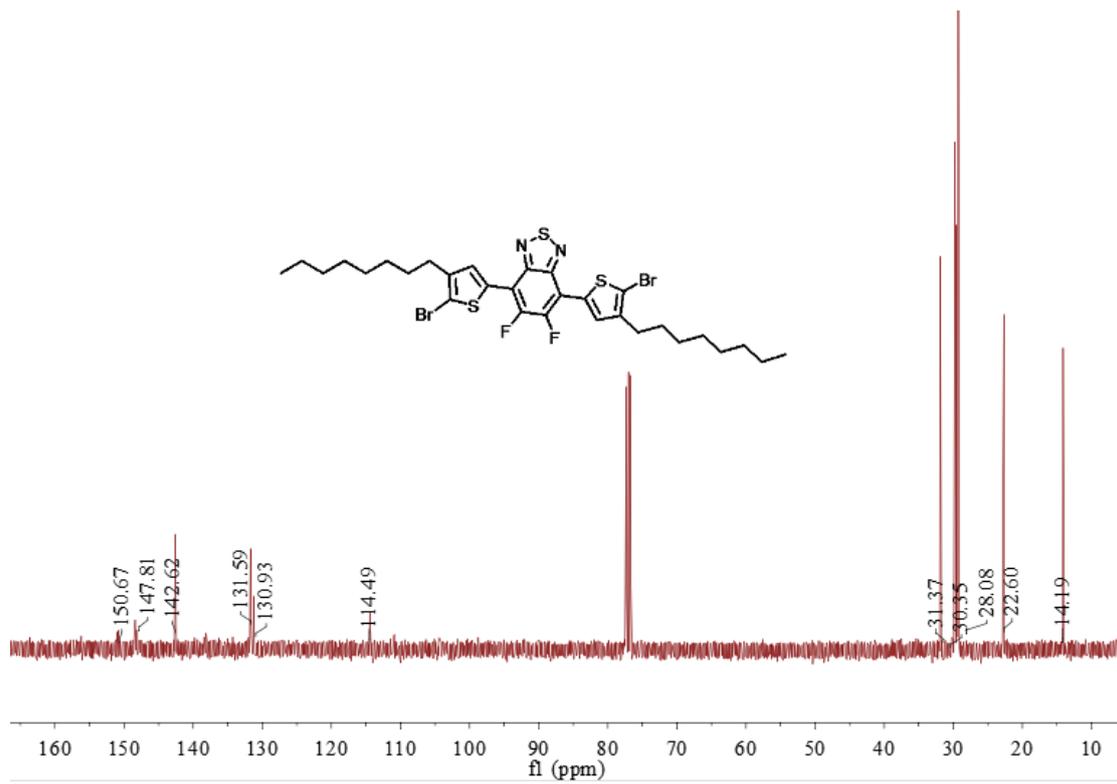


Figure SI 6 ¹³C NMR spectra of (3).

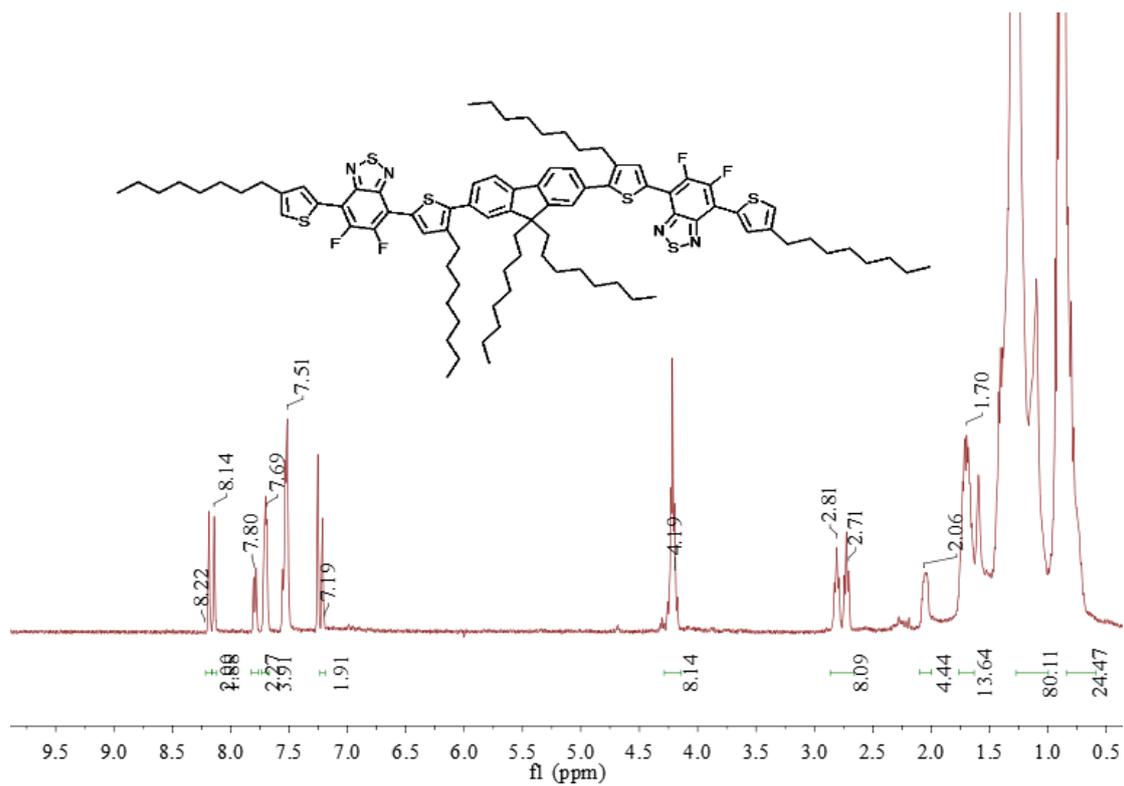


Figure S1 7. ^1H NMR spectra of (4).

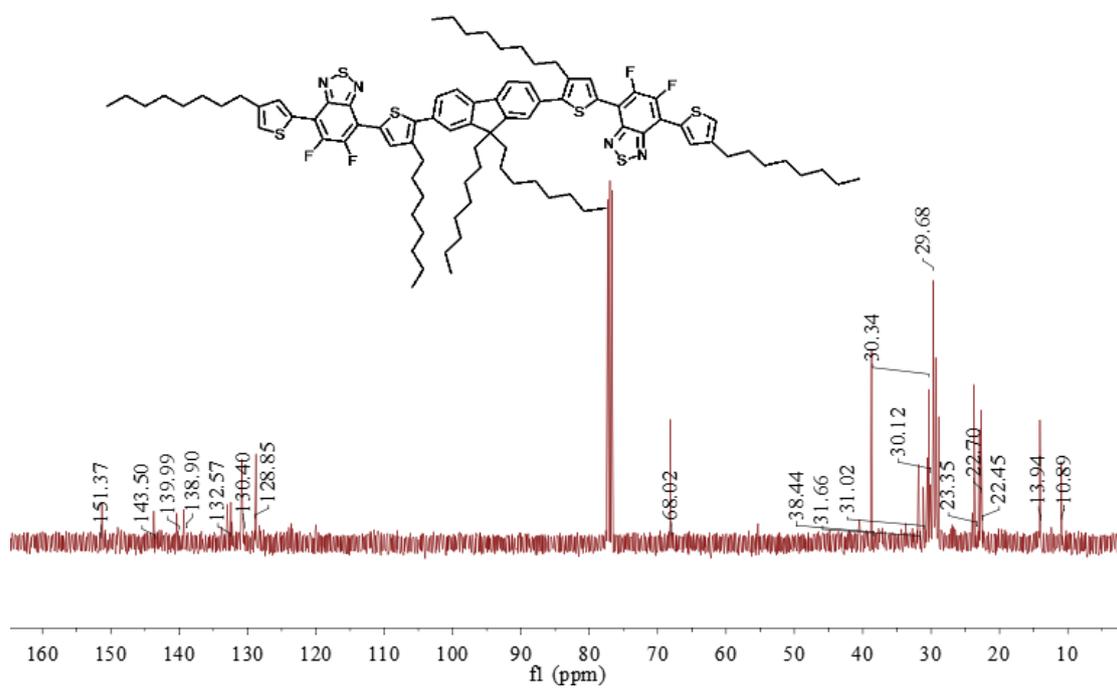


Figure SI 8 ^{13}C NMR spectra of (4).

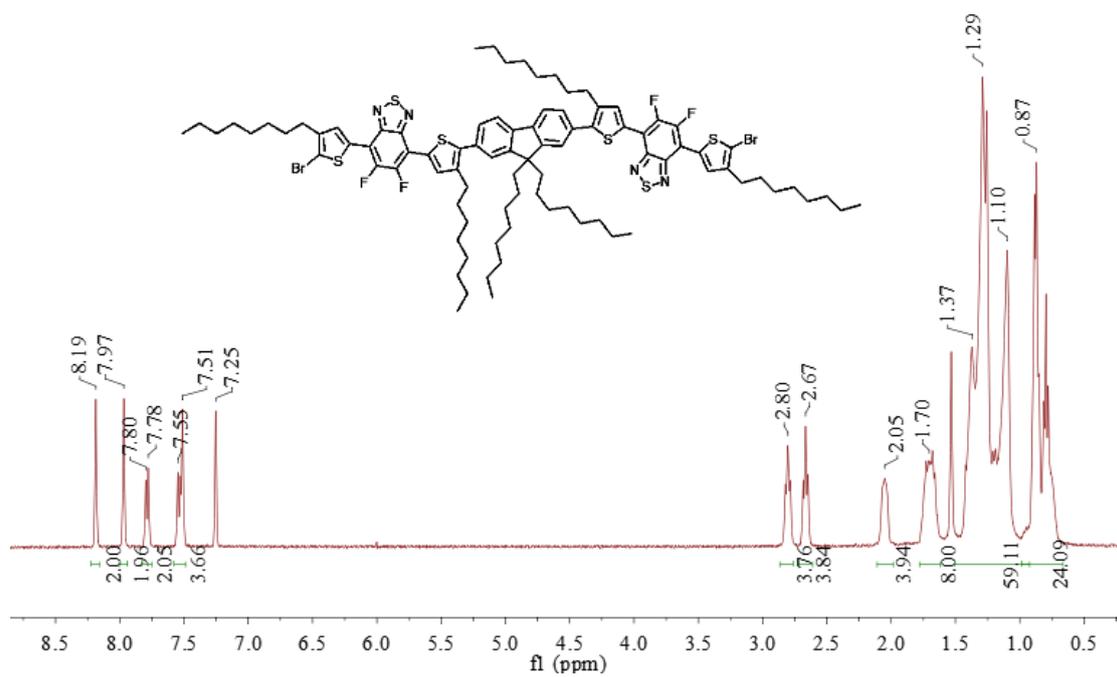


Figure SI 9. ¹H NMR spectra of (5).

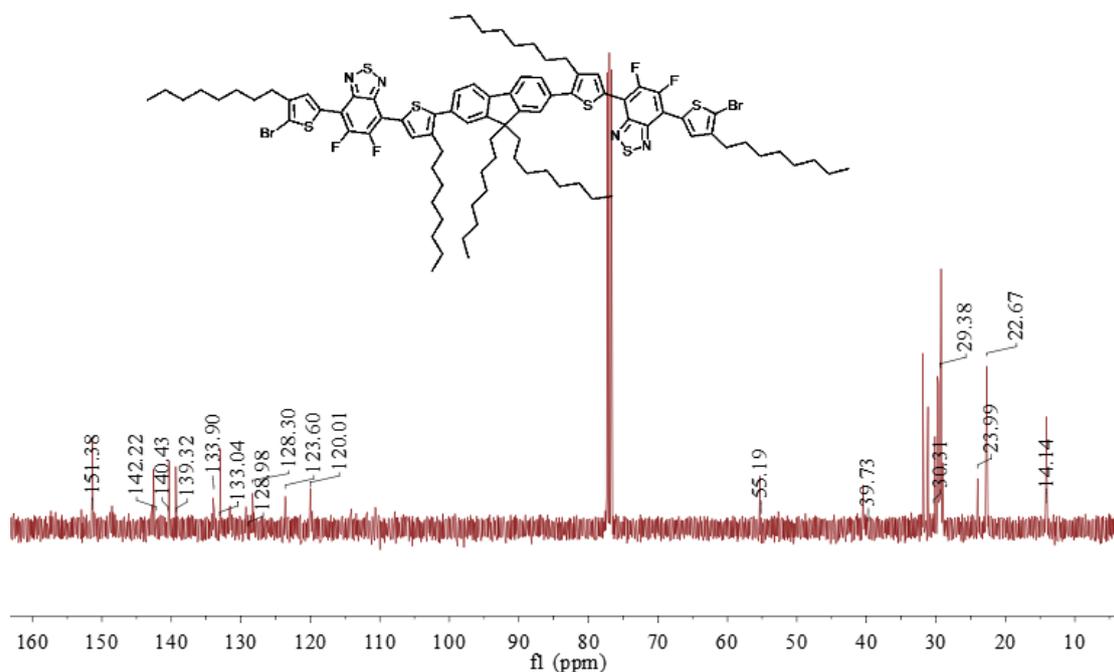


Figure SI 10. ^{13}C NMR spectra of (5).

General Measurement and Characterization ^1H NMR spectra were recorded in deuterated solvents on a Bruker ADVANCE 400 NMR Spectrometer. ^1H NMR chemical shifts were reported in ppm downfield from tetramethylsilane (TMS) reference using the residual protonated solvent as an internal standard. Molecular weights of the polymers were determined using a Waters 2410 gel permeation chromatograph (GPC) with a refractive index detector in tetrahydrofuran (THF) using a calibration curve of polystyrene standards. Thermo gravimetric analysis (TGA) was performed on a TA-600 for thermal analysis at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ under nitrogen with a sample weight of 5-8 mg. UV-vis absorption spectra were measured with Perkin Elmer Lambda 750 UV-Vis spectrophotometer. Cyclic voltammetry (CV) was performed with a Zahner IM6e electrochemical workstation. The X-ray diffraction (XRD) study of the samples was carried out on a Bruker D8 Focus X-ray diffractometer operating at 30 kV and 20 mA with a copper target ($\lambda = 1.54\text{ \AA}$) and at a scanning rate of $1^\circ/\text{min}$. Atomic force microscopic (AFM) images were measured on a Nanoscope III A (Digital Instruments) scanning probe microscope using the tapping mode. Current-voltage (J-V) characteristics were

recorded using a Keithley 2400 Source Meter in the dark and under 100 mW/cm² simulated AM 1.5 G irradiation (Abet Solar Simulator Sun2000).

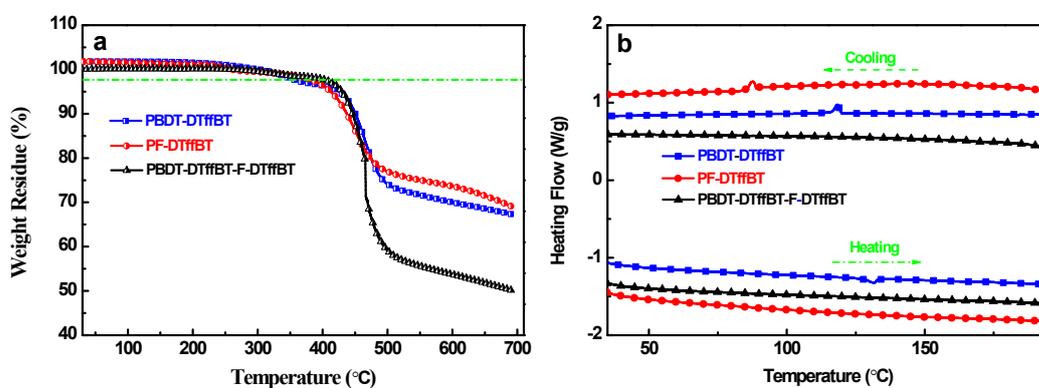


Figure SI 11. Thermogravimetry analysis (a) and differential scanning calorimetry (b) curves of copolymers.

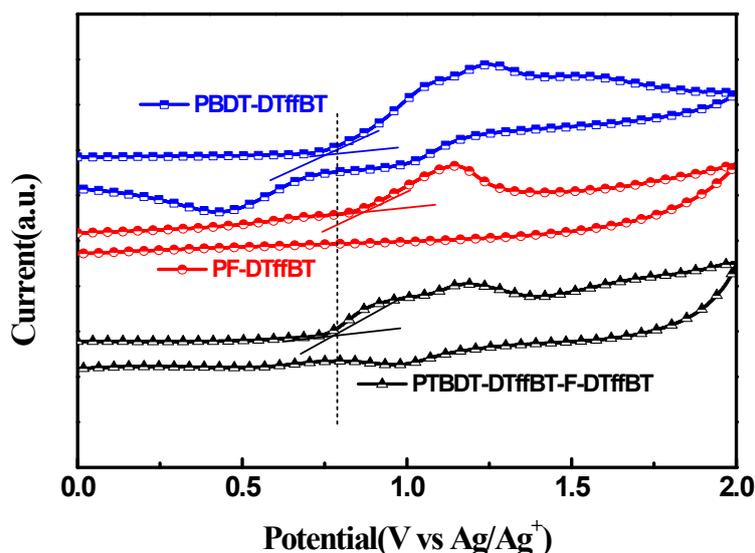


Figure SI 12. Cyclic voltammograms of copolymers.

Device Fabrication

Power conversion efficiencies (PCEs) were measured under an AM1.5G solar simulator (Sciencetech SS-0.5K Solar Simulator) and EQE under dark. The current density-voltage (J-V) characteristics were recorded with a Keithley 2400 source meter. The spectral response was measured with a commercial photo modulation spectroscopic setup (Oriel). A calibrated Si photodiode was used to determine the photosensitivity. Patterned ITO-glass substrates were used as the anode in the polymer solar cells. The ITO coated glass substrates were cleaned by sonication in

detergent, deionized water, acetone, and isopropyl alcohol and dried in a nitrogen stream, followed by an oxygen plasma treatment. Then the surface of the ITO substrate was modified by spin-coating the conducting PEDOT:PSS layer, followed by baking at 140 °C for 15 minutes under ambient conditions. The substrates were then transferred into an argon-filled glove box. The polymers were blended with PC₇₁BM and dissolved in chlorobenzene (CB), with a concentration of 10~12 mg mL⁻¹. All blended ratios of polymer/PC₇₁BM were by weight. The solutions were then spin-coated onto the PEDOT:PSS layer at 1000 rpm/min for 45 s. The thicknesses of the active layer were about 90-100 nm. Subsequently, LiF (0.8 nm) and Al (100 nm) electrodes were deposited via thermal evaporation in vacuum (<10⁻⁶ Torr) in a thickness of approximately. The effective area was measured to be 0.04 cm².

Space Charge Limited Current (SCLC) measurement

The mobility was determined by fitting the dark current to the model of a single carrier SCLC, described by the equation:

$$J = \frac{9}{8} \epsilon_0 \epsilon_r \mu_h \frac{V^2}{d^3}$$

where J is the current density, μ_h is the mobility under zero field, ϵ_0 is the permittivity of free space, ϵ_r is the material relative permittivity, d is the active layer thickness, and V is the effective voltage. The effective voltage can be obtained by subtracting the built-in voltage (V_{bi}) and the voltage drop (V_s) from the substrate's series resistance from the applied voltage (V_{appl}), $V = V_{appl} - V_{bi} - V_s$. The hole-mobility can be calculated from the slope of the $J^{1/2} \sim V$ curves.

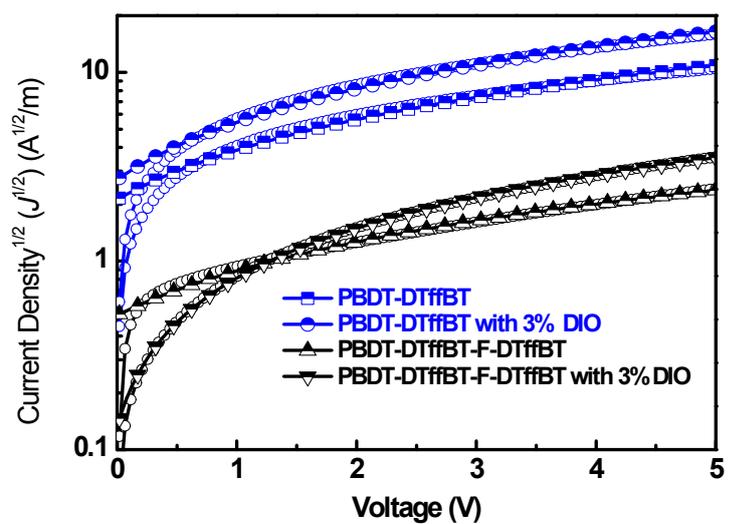


Figure SI 13. $J^{1/2} \sim V$ curves of the hole-only devices based on these random copolymers.

Table SI 1. Photovoltaic performance of polymers: PC₇₁BM in standard BHJ devices with different blending ratio.

Polymer	Polymer:PC71BM(w/w)	V_{oc} (V)	J_{sc} (mA · cm ⁻²)	FF (%)	PCE (%)
PBDT-DTffBT	1:1	0.761	5.75	40.8	1.7
	1:1.5	0.742	7.71	39.5	2.3
	1:2	0.760	6.89	38.8	2.0
PBDT-DTffBT-F-DTffBT	1:1	0.791	5.81	35.9	1.7
	1:1.5	0.853	7.60	37.9	2.5
	1:2	0.863	7.43	35.0	2.2

Table SI 2. Photovoltaic performance of polymers: PC₇₁BM in standard BHJ devices with DIO.

Polymer	Polymer:PC71BM(w/w)	DIO ratio (v/v)	V_{oc} (V)	J_{sc} (mA \cdot cm ⁻²)	FF (%)	PCE (%)
PBDT-DTffBT	1:1.5	1%	0.770	6.78	42.4	2.2
	1:1.5	3%	0.733	7.33	55.8	3.0
	1:1.5	5%	0.776	7.28	47.6	2.7
PBDT-DTffBT-F-DTffBT	1:1.5	1%	0.846	6.91	36.5	2.1
	1:1.5	3%	0.865	7.48	39.8	2.6
	1:1.5	5%	0.784	5.83	35.6	1.6

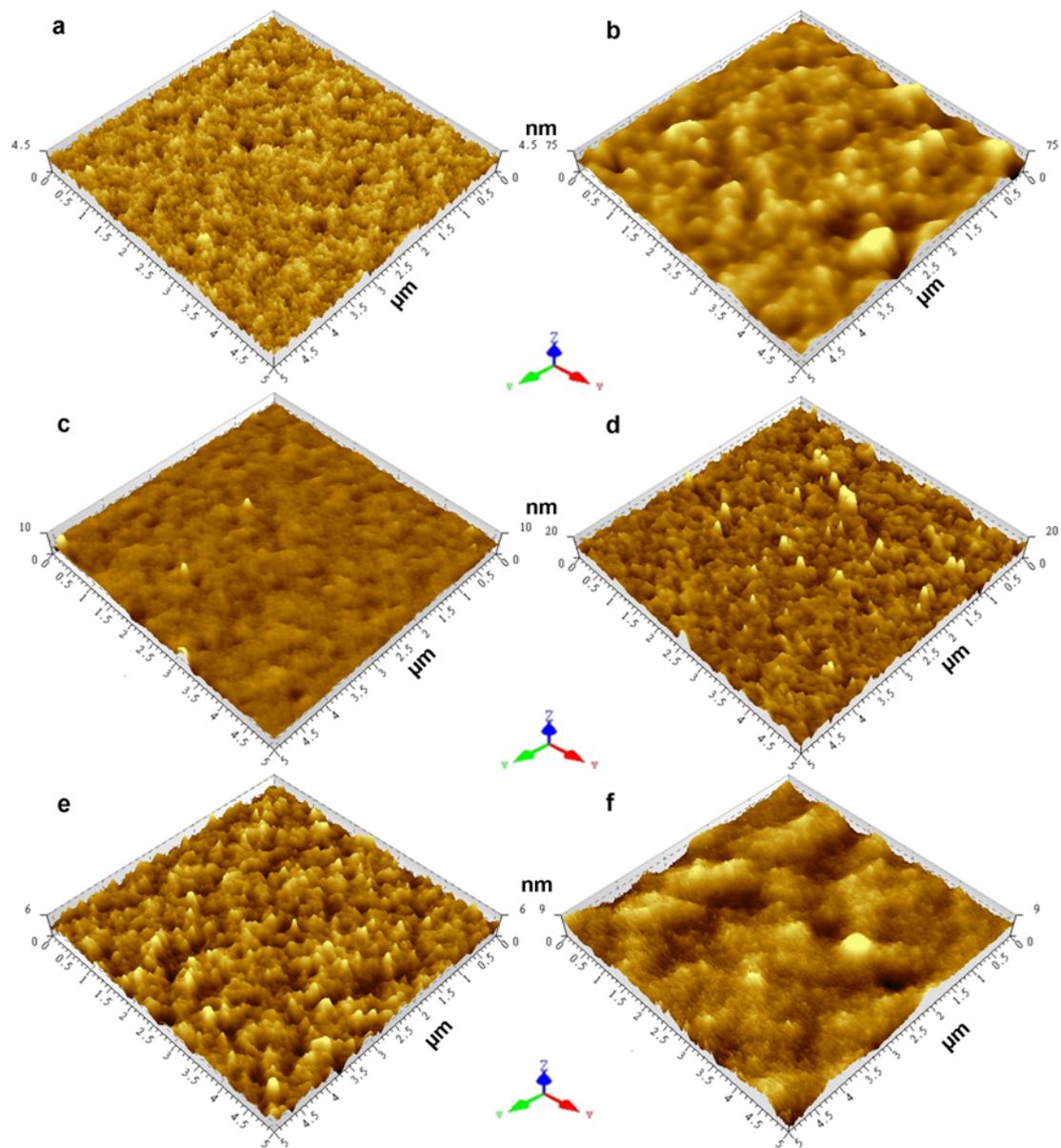


Figure SI 14. Topography in 3D images by AFM of blend films of Polymer: PC₇₁BM with or without 3% DIO: a, b for PBDT-DTffBT, c, d for PF-DTffBT, and e, f for PBDT-DTffBT-F-DTffBT.

References

- [1] F. Y. Wu, D. J. Zha, L. Chen, Y.W. Chen, *Journal of Polymer Science, Part A: Polymer Chemistry* **2013**, 51, 1506-1511.