

Supporting Information for

Designing Thiophene-fused Benzotriazole Unit as New Electron Acceptor to Build D-A Copolymer for BJH Polymer Solar Cells

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Instruments and measurements

¹H-NMR and ¹³C-NMR were measured on a Varian Mercury 300 spectrometer in CDCl₃ or DMSO using tetramethylsilane (TMS, $\delta = 0$ ppm) as internal standard. ESI-MS analysis was performed on a Finnigan-LCQ advantage mass spectrometer, EI-MS analysis was performed on a Varian 320-MS. The molecular weights of these polymers were performed on an Agilent 1100 series HPLC system equipped with a G1326A refractive index detector, wherein polystyrene was used as a standard by using THF as eluent. Elemental analyses were carried out on a 73 CARLOERBA-1106 microelemental analyzer. The thermo-gravimetric analysis (TGA) was performed on NETZSCH STA449C

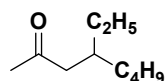
thermal analyzer at a heating rate of 10 °C/min in nitrogen with a flow rate of 20 cm³/min. The cyclic voltammetry (CV) was conducted on a CHI voltammetric analyzer at room temperature in CH₃CN containing 0.10 M tetrabutylammonium hexafluorophosphate (TBAPF₆) at a scan rate of 100 mV/s, using a platinum disc as working electrode and a silver wire as quasi-referenced electrode. The potentials were determined using ferrocene as a reference. The UV-vis absorption spectra of the polymers were measured by a Shimadzu UV-2550 spectrometer and the fluorescence spectra were recorded in a Hitachi F-4500 spectrofluorimeter. The film morphology was measured using an atomic force microscope (SPA-400) using the tapping mode.

Materials and Synthesis

Materials. Unless otherwise stated, all of the chemicals are purchased from commercial source and used as received unless otherwise specified. 2,6-bis(trimethyltin)-4,8-di(5-(2-ethylhexyl)thiophen-2-yl)-benzo[1,2-b:4,5-b']dithiophene (BDTT) was prepared following literature procedure.¹

Synthesis

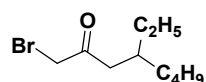
4-Ethylheptan-2-one (VIII-1):



To a 250 mL of three-necked round-bottomed flask, magnesium (2.6 g, 110 mmol) and anhydrous THF were added under Ar. Then, 3-(bromomethyl)heptane (19.3 g, 100 mmol) in constant pressure funnel was added to the solution dropwise. After addition, the solution was stirred for 1.5 h at refluxing temperature. After cooling to room temperature, the obtained Grignard reagent was added to another Schlenk flask

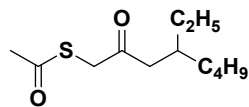
containing Iron (III) acetylacetonate (1 g, 2.8 mmol), anhydrous lithium chloride (4.2 g, 100mmol) and 100 mL anhydrous THF under Ar. And then, acetyl chloride (7.9 g, 100 mmol) was added to the mixed solution slowly and the solution was stirred for another 30 min. After reaction, the mixture was poured into the ice water and extracted with ethyl acetate. The organic layer was dried over anhydrous Na₂SO₄. The solvent was removed under vacuum. The mixture was purified by column chromatography over silica gel with petroleum ether-ethyl acetate mixtures as the eluent to give 1 as colorless oil (8.9 g, 56.5%). ¹H-NMR (300 MHz, CDCl₃, δ ppm): 2.34(d, *J* = 6.9 Hz, 2H), 2.14(s, 3H), 1.85(m, 1H), 1.36-1.24 (m, 8H), 0.91-0.83 (m, 6H). ¹³C-NMR (75 MHz, CDCl₃, δ): 209.42, 48.34, 35.24, 33.18, 30.40, 28.88, 26.38, 23.00, 14.11, 10.84. EI-MS: Calcd. for [C₁₀H₂₀O+H]⁺: 156.15; Found: 156.12.

1-Bromo-4-ethyloctan-2-one (VIII-2):



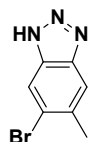
Br₂ (6.4 g, 40 mmol) was added to VIII-1 (5.9 g, 37.8 mmol) in 50 mL methanol at 0 °C. The solution was stirred for 2 h. The mixture was poured into ice water and extracted with ethyl acetate. The organic layer was dried over anhydrous Na₂SO₄. The solvent was removed under vacuum. The mixture was purified by column chromatography over silica gel with petroleum ether-ethyl acetate mixtures as the eluent to give VIII-2 as colorless oil (8.3 g, 93.6%). ¹H-NMR (300 MHz, CDCl₃, δ ppm): 3.89(s, 2H), 2.57(d, *J* = 6.6 Hz, 2H), 1.90(m, 1H), 1.36-1.26 (m, 8H), 0.91-0.84 (m, 6H). ¹³C-NMR (75 MHz, CDCl₃, δ): 201.97, 44.24, 35.21, 32.99, 29.33, 28.80, 26.23, 22.91, 14.05, 10.82. EI-MS: Calcd. for [C₁₀H₁₉BrO+H]⁺: 235.06; Found: 235.12.

S-(4-ethyl-2-oxooctyl) ethanethioate (VIII-3):



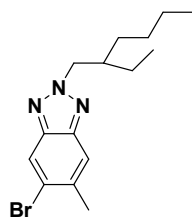
VIII-2 (4.7 g, 20 mmol) in 10 mL THF was added slowly to potassium thioacetate (2.97 g, 26 mmol) in 100 mL THF. The solution was stirred at room temperature for 13 h. After reaction, the mixture was poured into the ice water and extracted with ethyl acetate and the organic layer was dried over anhydrous Na_2SO_4 . The solvent was removed under vacuum. The mixture was purified by column chromatography over silica gel with petroleum ether-ethyl acetate mixtures as the eluent to give VIII-3 as light yellow oil (2.19 g, 47.6%). $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ ppm): 3.75(s, 3H), 2.47(s, $J = 6.9$ Hz, 2H), 2.39(s, 3H), 2.26(s, 2H), 1.98(m, 1H), 1.32-1.24 (m, 8H), 0.94-0.83(m, 6H). EI-MS: Calcd. for $[\text{C}_{12}\text{H}_{22}\text{O}_2\text{S}]^+$:230.13; Found:230.10.

6-Bromo-5-methyl-1H-benzo[d][1,2,3]triazole (VIII-4):



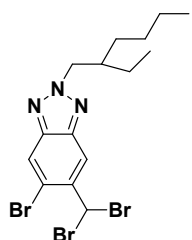
4-Bromo-5-methyl-1, 2-o-phenylenediamine (8.04 g, 40 mmol) and acetic acid (4.8 mL, 80 mmol) were dissolved in H_2O (100mL). After cooling to 0 °C, sodium nitrite (3.2 g, 44 mmol) was added to the solution. The mixture was stirred at room temperature for 2h. After reaction, the crude product was filtered, washed with water and then dried to give VIII-4. $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ ppm): 8.21(s, 1H), 7.89(s, 1H), 2.70(s, 1H), 2.55(s, 3H). $^{13}\text{C-NMR}$ (75 MHz, DMSO, δ): 135.34, 127.37, 118.88, 117.86, 115.15, 23.08. EI-MS: Calcd. for $[\text{C}_7\text{H}_6 \text{ BrN}_3]^+$:210.97; Found:210.97.

5-Bromo-2-(2-ethylhexyl)-6-methyl-2H-benzo[d][1,2,3]triazole (VIII-5):



VIII-4 (5.41 g, 25.5 mmol), bromo-2-ethylhexane (9.8 g, 51 mmol), and potassium tert-butoxide (3.7 g, 51 mmol), were added to 100 mL anhydrous methanol under Ar. The reaction solution was heated to reflux for 48 h. After reaction, the mixture was poured into the ice water and extracted with ethyl acetate and the organic layer was dried over anhydrous Na_2SO_4 . The solvent was removed under vacuum. The mixture was purified by column chromatography over silica gel with petroleum ether-ethyl acetate mixtures as the eluent to give VIII-5 as colorless oil (1.18 g, 14.3%). $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ ppm): 8.11(s, 1H), 7.72(s, 1H), 4.58(d, $J = 7.2$ Hz, 2H), 3.32(s, 3H), 2.20(m, 1H), 1.38-1.31(m, 8H), 0.93-0.85(m, 6H). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3 , δ): 144.08, 143.90, 135.98, 124.07, 121.05, 118.06, 60.12, 40.66, 30.64, 28.63, 24.23, 24.00, 23.06, 14.21, 10.66. EI-MS: Calcd. for $[\text{C}_{15}\text{H}_{22}\text{BrN}_3]^+$: 323.10; Found: 323.18.

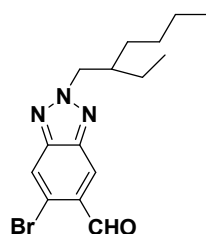
5-Bromo-6-(dibromomethyl)-2-(2-ethylhexyl)-2H-benzo[d][1,2,3]triazole (VIII-6):



VIII-5 (3.24 g, 10 mmol), NBS (5.4 g, 30 mmol) and AIBN (330 mg, 2 mmol) were dissolved in 50 mL chlorobenzene. The reaction mixture was heated to 80 °C for 4h. After cooling to the room temperature, the reaction solution was poured into ice water, The aqueous phase was extracted with CHCl_3 and the organic layer was washed

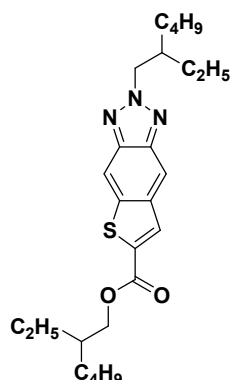
with deionized water and $\text{NaHCO}_3(\text{aq})$. The solvent was removed under vacuum. The crude product was purified by column chromatography over silica gel with petroleum ether-ethyl acetate mixtures as the eluent to give VIII-6 as colorless oil (4.24 g, 88.0%). $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ ppm): 8.67(s, 1H), 8.10(s, 1H), 7.19(s, 1H), 4.64(d, $J = 7.2$ Hz, 2H), 2.21(m, 1H), 1.33-1.26(m, 8H), 0.96-0.89(m, 6H).. $^{13}\text{C-NMR}$ (75 MHz, CDCl_3 , δ): 145.32, 143.63, 138.17, 122.01, 121.68, 118.01, 60.51, 40.74, 40.46, 30.69, 28.69, 24.05, 23.08, 14.26, 10.69. EI-MS: Calcd. for $[\text{C}_{15}\text{H}_{20}\text{Br}_3\text{N}_3]^+$:480.92; Found:480.83.

6-Bromo-2-(2-ethylhexyl)-2H-benzo[d][1,2,3]triazole-5-carbaldehyde (VIII-7):



1 M AgNO_3 (3.73 g, 22 mmol) solution was added to VIII-6 (4.24 g, 8.8 mmol) in 50 mL acetonitrile. The solution was heated to reflux for 3 h. After cooling, the reaction solution was poured into water and extracted with CHCl_3 and the organic layer was washed with deionized water (100 mL), saturated salt water (100 mL) and then dried over anhydrous Na_2SO_4 . The solvent was removed under vacuum. The mixture was purified by column chromatography over silica gel with petroleum ether-ethyl acetate mixtures as the eluent to give 7 as light yellow oil (2.57 g, 86.3%). $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ ppm): 10.51(s, 1H), 8.54(s, 1H), 8.19(s, 1H), 4.66(d, $J = 7.5$ Hz, 2H), 2.20(m, 1H), 1.60(br, 3H), 1.36-1.31(m, 6H), 0.95-0.87(m, 5H). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3 , δ): 191.82, 147.37, 143.12, 131.16, 122.94, 122.44, 121.06, 60.79, 40.73, 30.66, 28.58, 24.02, 23.01, 14.17, 10.63. EI-MS: Calcd. for $[\text{C}_{15}\text{H}_{20}\text{Br}_3\text{N}_3]^+$:337.08; Found: 337.08.

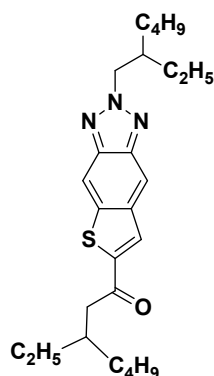
2-Ethylhexyl-2-(2-ethylhexyl)-2H-thieno[2',3':4,5]benzo[1,2-d][1,2,3]triazole-6-carboxylate (VIII-8):



VIII-7 (406 mg, 1.2 mmol), isooctyl thioglycolate (319 mg, 1.6 mmol), K_2CO_3 (300 mg, 2.2 mmol), DMSO (10 mL) were added to a 20 mL microwave tube sealed with a teflon cap. The sealed microwave tube was putted in a Biotage microwave reactor, the reaction mixture was heated to 80°C for 1.5 h under the power of 10 W and a pressure of 1 atm. After reaction, the mixture was poured into ice water and extracted with ethyl acetate and the organic layer was dried over anhydrous Na_2SO_4 . The solvent was removed under vacuum. The mixture was purified by column chromatography over silica gel with petroleum ether and ethyl acetate mixtures as the eluent to give VIII-8 as a light yellow oil (193 mg, 36.2%). 1H -NMR (300 MHz, $CDCl_3$, δ ppm): 8.42 (s, 1H), 8.34 (s, 1H), 8.09 (s, 1H), 4.71 (d, $J = 7.2$ Hz, 2H), 4.29 (d, $J = 3.3$ Hz, 2H), 2.28 (m, 1H), 1.74 (m, 1H), 1.36-1.34 (m, 16H), 1.00-0.87 (m, 12H). ^{13}C -NMR (75 MHz, $CDCl_3$, δ): 162.64, 144.30, 143.26, 140.22, 138.84, 135.69, 130.23, 114.28, 110.68, 68.22, 60.68, 40.76, 39.04, 30.69, 29.14, 28.61, 24.13, 24.05, 23.18, 23.04, 14.26, 14.14, 11.27, 10.63. EI-MS: Calcd. For $[C_{25}H_{37}N_3O_2S]^+$: 443.26; Found: 443.26.

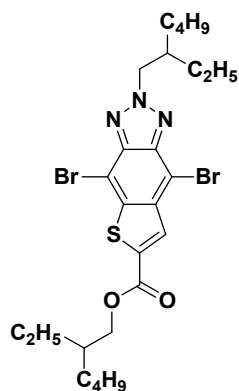
3-Ethyl-1-(2-(2-ethylhexyl)-2H-thieno[2',3':4,5]benzo[1,2-d][1,2,3]triazol-6-yl)heptan-

1-one (VIII-9):



A 20 mL microwave tube was charged with VIII-7 (854 mg, 2.5 mmol), VIII-3 (756 mg, 3.3 mmol), K_2CO_3 (593 mg, 4.3 mmol), DMSO (10 mL) and sealed with a Teflon cap. The sealed microwave tube was putted in a Biotage microwave reactor, the reaction mixture was heated to 80°C for 1.5 h under the power of 10 W and a pressure of 1 atm. After reaction, the mixture was poured into ice water and extracted with ethyl acetate and the organic layer was dried over anhydrous Na_2SO_4 . The solvent was removed under vacuum. The mixture was purified by column chromatography over silica gel with petroleum ether and ethyl acetate mixtures as the eluent to give VIII-9 as a light yellow oil (354 mg, 33.1%). 1H -NMR (300 MHz, $CDCl_3$, δ ppm): 8.45 (s, 1H), 8.34 (s, 1H), 8.00(s, 1H), 4.71 (d, $J = 7.2$ Hz, 2H), 2.93 (d, $J = 6.9$ Hz, 2H), 2.31 (m, 1H), 2.10 (m, 1H), 1.46-1.32 (m, 16H), 0.96-0.87 (m, 12H). ^{13}C -NMR (75 MHz, $CDCl_3$, δ): 195.44, 146.20, 144.66, 143.36, 140.30, 139.62, 128.90, 114.97, 111.01, 60.90, 43.90, 40.87, 36.53, 33.49, 30.74, 29.13, 28.68, 26.71, 24.12, 23.20, 23.08, 14.36, 14.25, 11.18, 10.70. EI-MS: Calcd. For $[C_{25}H_{37}N_3OS]^+$:427.27; Found: 427.35.

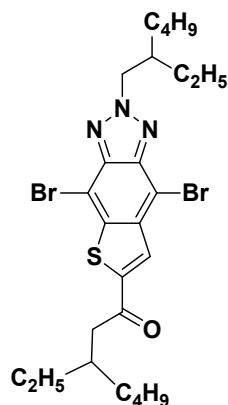
4,8-Dibromo-2-(2-ethylhexyl)-2H-thieno[2',3':4,5]benzo[1,2-d][1,2,3]triazole-6-carboxylate (VIII-10):



Br₂ (325 mg, 2.3 mmol) was added to VIII-8 (300 mg, 0.68 mmol) in 30 mL CHCl₃. The reaction mixture was stirred at room temperature for 12 h. After reaction, the mixture was poured into ice water and extracted with CH₂Cl₂ and the organic layer was dried over anhydrous Na₂SO₄. The solvent was removed under vacuum. The mixture was purified by column chromatography over silica gel with petroleum ether and ethyl acetate mixtures as the eluent to give VIII-10 as a light yellow solid (364 mg, 88.9%).

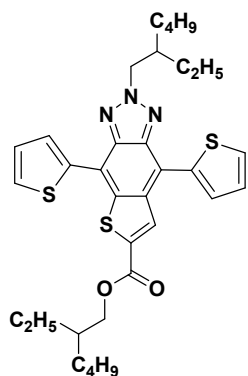
¹H-NMR (300 MHz, CDCl₃, δ ppm): 8.31(s, 1H), 4.76(d, *J* = 7.2 Hz, 2H), 4.31(d, *J* = 5.7 Hz, 2H), 2.38(m, 1H), 1.78(m, 1H), 1.41-1.28(m, 16H), 1.00-0.88(m, 12H). ¹³C-NMR (75 MHz, CDCl₃, δ): 162.11, 142.86, 142.64, 141.71, 138.22, 136.66, 130.29, 106.32, 102.038, 68.76, 61.51, 40.61, 39.06, 30.70, 30.49, 29.21, 28.47, 24.15, 23.98, 23.21, 23.06, 14.30, 14.19, 11.30, 10.60. EI-MS: Calcd. For [C₂₅H₃₅Br₂N₃O₂S]⁺: 601.08; Found: 601.03.

1-(4,8-Dibromo-2-(2-ethylhexyl)-2H-thieno[2',3':4,5]benzo[1,2-d][1,2,3]triazol-6-yl)-3-ethylheptan-1-one (VIII-11):



Br₂ (320 mg, 2 mmol) was added to VIII-9 (285 mg, 0.67 mmol) in 30 mL CHCl₃. The reaction mixture was stirred at room temperature for 12 h. After reaction, the mixture was poured into ice water and extracted with CH₂Cl₂ and the organic layer was dried over anhydrous Na₂SO₄. The solvent was removed under vacuum. The mixture was purified by column chromatography over silica gel with petroleum ether and ethyl acetate mixtures as the eluent to give VIII-11as a light yellow solid (336 mg, 86.3%).
¹H-NMR (300 MHz, CDCl₃, δ ppm): 8.17(s, 1H), 4.76(d, *J* = 7.2 Hz, 2H), 2.91(d, *J* = 6.9 Hz, 2H), 2.37(m, 1H), 2.11(m, 1H), 1.47-1.33(m, 16H), 0.96-0.88(m, 12H). EI-MS: Calcd. For[C₂₅H₃₅Br₂N₃O₂S]⁺: 585.08; Found: 585.07.

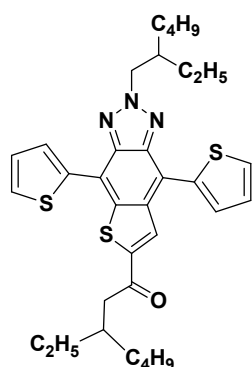
2-(2-Ethylhexyl)-4,8-di(thiophen-2-yl)-2H-thieno[2',3':4,5]benzo[1,2-d][1,2,3]triazole-6-carboxylate (VIII-12):



VIII-10 (365 mg, 0.6 mmol), 2-(tributylstannyl)thiophene (679 g, 1.8 mmol) and Pd(PPh₃)₄ (105 mg, 0.09 mmol) were dissolved in toluene (30 mL) under argon

atmosphere. The reaction mixture was heated to reflux for 48 h. After cooling to the room temperature, the solvent was removed under vacuum. The mixture was purified by column chromatography over silica gel with petroleum ether and ethyl acetate mixtures as the eluent to give VIII-12 as an orange-yellow solid (294 mg, 80.7%). ¹H-NMR (300 MHz, CDCl₃, δ ppm): 8.67(s, 1H), 8.19(br, 1H), 7.82(br, 1H), 7.61(br, 2H), 7.26(br, 2H), 4.79(d, *J* = 6.3 Hz, 2H), 4.30(d, *J* = 5.1 Hz, 2H), 2.32(m, 1H), 1.75(m, 1H), 1.38(m, 16H), 0.97-0.89(m, 12H). ¹³C-NMR (75 MHz, CDCl₃, δ): 162.85, 142.35, 137.97, 137.72, 137.05, 136.61, 135.26, 130.73, 129.91, 129.20, 127.92, 127.83, 127.72, 127.48, 120.78, 117.69, 68.55, 60.55, 40.70, 39.09, 30.79, 28.64, 24.21, 23.20, 14.29, 11.35, 10.80. EI-MS: Calcd. For [C₃₃H₄₁N₃O₂S₃]⁺: 607.24; Found: 607.16.

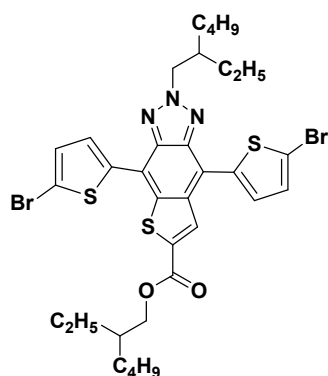
3-Ethyl-1-(2-(2-ethylhexyl)-4,8-di(thiophen-2-yl)-2H-thieno[2',3':4,5]benzo[1,2-d][1,2,3]triazol-6-yl)heptan-1-one (VIII-13):



VIII-11 (256 mg, 0.44 mmol), 2-(tributylstannyl)thiophene (489 g, 1.3 mmol) and Pd(PPh₃)₄ (47 mg, 0.04 mmol) were dissolved in toluene (30 mL) under argon atmosphere. The reaction mixture was heated to reflux for 48 h. After cooling to the room temperature, the solvent was removed under vacuum. The mixture was purified by column chromatography over silica gel with petroleum ether and ethyl acetate mixtures as the eluent to give VIII-13 as an orange-yellow solid (250 mg, 96.7%). ¹H-

NMR (300 MHz, CDCl₃, δ ppm): ¹H-NMR (300 MHz, CDCl₃, δ ppm): 8.58(s, 1H), 8.22(d, *J*=3.6 Hz, 1H), 7.84(d, *J*=2.4 Hz, 1H), 7.63(d, *J*=5.1 Hz, 1H), 7.59(d, *J*=5.1 Hz, 1H), 7.35-7.324(m, 2H), 4.79(d, *J*=6.9 Hz, 2H), 2.93(d, *J*=6.96 Hz, 2H), 2.32(m, 1H), 2.08(m, 1H), 1.46-1.32(m, 16H), 1.01-0.87(m, 12H). EI-MS: Calcd. For [C₃₃H₄₁N₃OS₃]⁺: 591.24; Found: 591.13.

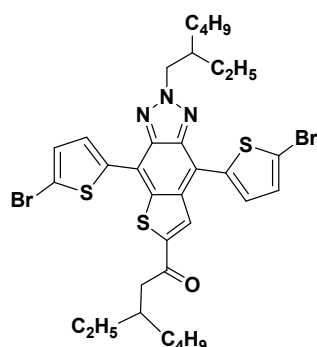
2-Ethylhexyl-4,8-bis(5-bromothiophen-2-yl)-2-(2-ethylhexyl)-2H-thieno[2',3':4,5]benzo[1,2-d][1,2,3]triazole-6-carboxylate (VIII-14):



NBS (277 mg, 1.6 mmol) was added to VIII-12 (430 mg, 0.71 mmol) in 25 mL CH₂Cl₂. After stirring at room temperature for 12 h, the solution was poured into water and extracted with CH₂Cl₂ and the organic layer was dried over anhydrous Na₂SO₄. The solvent was removed under vacuum. The mixture was purified by column chromatography over silica gel with petroleum ether and chloroform mixtures as the eluent to give VIII-14 as an orange-yellow solid (473 mg, 87.3%). ¹H-NMR (300 MHz, CDCl₃, δ ppm): 8.58 (s, 1H), 7.91(d, *J*=3.6 Hz, 1H), 7.54 (d, *J*=3.6 Hz, 1H), 7.26 (m, 2H), 4.78 (d, *J*=3.6 Hz, 2H), 4.31 (d, *J*=6.0 Hz, 2H), 2.30 (m, 1H), 1.77 (m, 1H), 1.38 (m, 16H), 1.01-0.91(m, 12H). ¹³C-NMR (75 MHz, CDCl₃, δ): 162.56, 141.78, 139.16, 138.58, 137.36, 136.27, 135.46, 133.55, 130.69, 130.49, 130.08, 129.22, 119.80, 116.88, 115.55, 115.03, 110.04, 68.75, 60.52, 57.89, 40.73, 39.06, 30.76, 29.98, 29.20, 28.63,

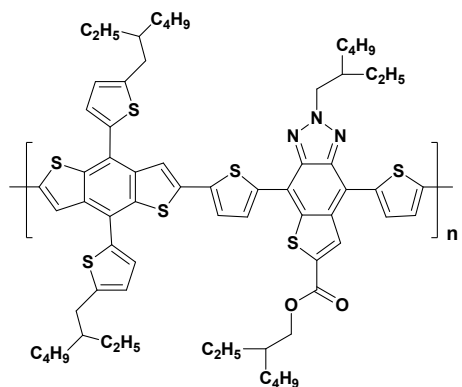
24.21, 23.28, 14.41, 11.41, 10.83. EI-MS: Calcd. For $[C_{33}H_{39}Br_2N_3O_2S_3]^+$: 765.06; Found: 765.32. Anal. Calcd for $C_{33}H_{39}Br_2N_3O_2S_3$: C, 51.77; H, 5.13; N, 5.49. Found: C, 51.58; H, 5.27; N, 5.70.

1-(4,8-Bis(5-bromothiophen-2-yl)-2-(2-ethylhexyl)-2H-thieno[2',3':4,5]benzo[1,2-d][1,2,3]triazol-6-yl)-3-ethylheptan-1-one (VIII-15):



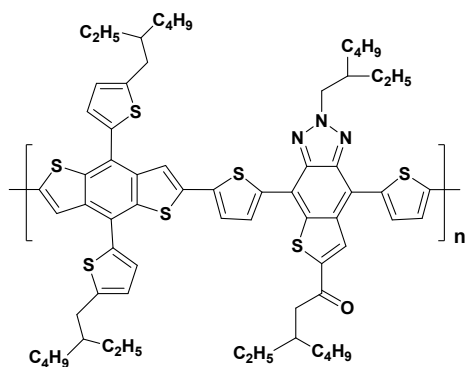
NBS (178 mg, 1 mmol) was added to VIII-13 (256 mg, 0.43 mmol) in 25 mL CH_2Cl_2 . After stirring at room temperature for 12 h, the solution was poured into water and extracted with CH_2Cl_2 and the organic layer was dried over anhydrous Na_2SO_4 . The solvent was removed under vacuum. The mixture was purified by column chromatography over silica gel with petroleum ether and chloroform mixtures as the eluent to give VIII-15 as an orange-yellow solid (289 mg, 89.6%). 1H -NMR (300 MHz, $CDCl_3$, δ ppm): 8.46(s, 1H), 7.94(d, $J=3.9$ Hz, 1H), 7.55(d, $J=3.9$ Hz, 1H), 7.28-7.24(m, 2H), 4.78(d, $J=3.6$ Hz, 2H), 2.93(d, $J=6.9$ Hz, 2H), 2.30(m, 1H), 2.10(m, 1H), 1.47-1.25(m, 16H), 1.01-0.89(m, 12H). EI-MS: Calcd. For $[C_{33}H_{39}Br_2N_3OS_3]^+$: 749.06; Found: 749.06. Anal. Calcd for $C_{33}H_{39}Br_2N_3OS_3$: C, 52.87; H, 5.24; N, 5.61. Found: C, 52.91; H, 4.98; N, 5.90.

PBDTT-BTAZT-1:



VIII-14(107 mg, 0.14 mmol), BDTT (127 mg, 0.14 mmol) and Pd(PPh₃)₄ (4.2 mg) were added to a Schlenk flask. Then the flask was purged by Ar for three times. Anhydrous toluene was added to the flask. The mixture was heated to 110 °C for 48 h. After cooling, the mixture was precipitated into MeOH. The crude polymer was put in Soxhlet extraction, and extracted with acetone and hexane respectively to remove some impurity and oligomers, and finally extracted with chloroform. The resulted chloroform fraction was precipitated in methanol. Then the precipitate was collected to give PBDTT-BTAZT-1 as a purple black solid (138 mg, yield 83.2%). ¹H-NMR (300 MHz, CDCl₃, δ ppm): 8.59-6.91(m, 11H), 4.83(br, 2H), 2.97(br, 6H), 2.32-1.00(m, 60H). Anal. Calcd for C₆₇H₇₉N₃O₂S₇: C, 68.04; H, 6.73; N, 3.55. Found: C, 67.76; H, 6.84; N, 3.55. GPC: Mn=32 kDa, PDI=2.1.

PBDTT-BTAZT-2:



It was synthesized by following a similar procedure as described above for PBDTT-

BTAZT-1. Yield: 86.8%. $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ ppm): 8.73-6.99(m, 11H), 4.85(br, 2H), 4.34(br, 2H), 2.93(br, 4H), 2.31-0.99(m, 60H). Anal. Calcd For $\text{C}_{67}\text{H}_{79}\text{N}_3\text{OS}_7$: C, 68.97; H, 6.82; N, 3.60. Found: C, 69.23; H, 6.95; N, 3.71. GPC: $M_n = 31$ kDa, PDI = 2.3.

Device fabrication

BHJ solar cells were fabricated with the structure of ITO/PEDOT:PSS/polymer:PC₇₁BM/Ca/Al and ITO/PEDOT:PSS/polymer:PC₇₁BM/ PDINO or PDIN/Al, respectively. The patterned indium tin oxide (ITO) glass (sheet resistance=10 U/sq) was pre-cleaned in an ultrasonic bath of deionized water, acetone and isopropanol, followed by oxygen plasma treatment (30 min) in an ultraviolet-ozone chamber (Jelight Company, USA). A thin layer (36 nm) of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, Baytron PVP Al 4083, Germany) was spin-coated onto the ITO glass at 3000 rpm and baked subsequently at 150 °C for 20 min. The mixture of polymer:PC₇₁BM in *o*-dichlorobenzene solvent with or without additive (DIO or NMP) was spin-coated on a PEDOT:PSS layer to form an active layer. Calcium (ca. 20 nm) and aluminium (ca. 60 nm) layers were deposited onto the active layer in a vacuum at a pressure of *ca.* 5.0×10^{-5} Pa to form the negative electrode. For another structure PSCs, the methanol solution of PDIN or PDINO at a concentrations of $1.5 \text{ mg} \cdot \text{mL}^{-1}$ was then deposited at the active layer at 3000 rpm for 30 s. Finally, aluminium (ca. 60 nm) layers were deposited onto the active layer in a vacuum at a pressure of *ca.* 5.0×10^{-5} Pa to form the negative electrode. The active area of the device was 5 mm^2 . The current density-voltage (*J-V*) characteristics were measured on a computer-controlled Keithley 2450 Source-Measure Unit. A xenon

lamp coupled with AM 1.5 solar spectrum filter was used as the light source, and the optical power at the sample was 100 mW/cm². The thickness of polymer:PC₇₁BM blend films were measured by profiler of BRUKER DEKTAKXT. The hole mobility was measured using the structure: ITO/PEDOT:PSS/polymer:PC₇₁BM/Au. And the mobility was extracted by fitting the dark *J-V* curves using the Mott-Gurney relationship (space charge limited current).

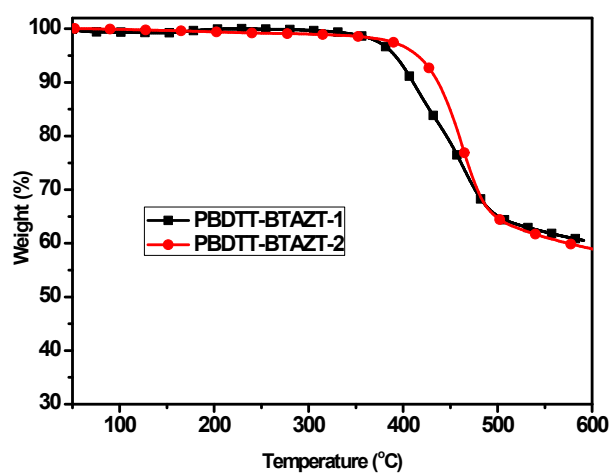


Figure S1. TGA of PBDTT-BTAZT-1 and PBDTT-BTAZT-2

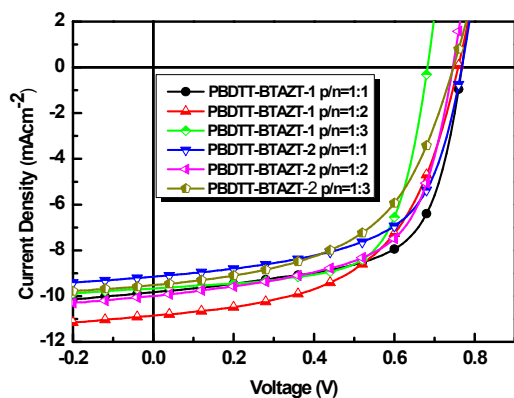


Figure S2. The J - V curves of the PSCs based on the structure of ITO/PEDOT:PSS/polymer:PC₇₁BM/Ca/Al with different p/n ratio. The concentration of the polymers is 10 mg/mL in *o*-dichlorobenzene.

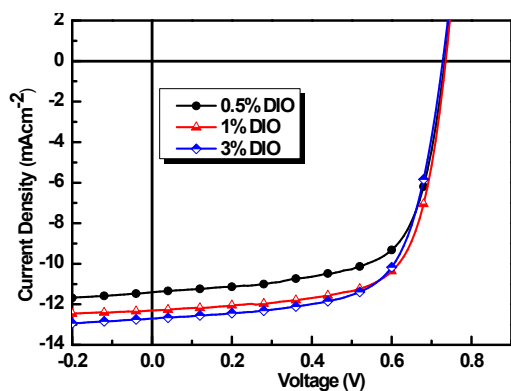


Figure S3. The J - V curves of the PSCs based on the structure of ITO/PEDOT:PSS/PBDTT-BTAZT-1/PC₇₁BM/Ca/Al with different volume of DIO. The concentration of PBDTT-BTAZT-1 is 10 mg/mL in *o*-dichlorobenzene.

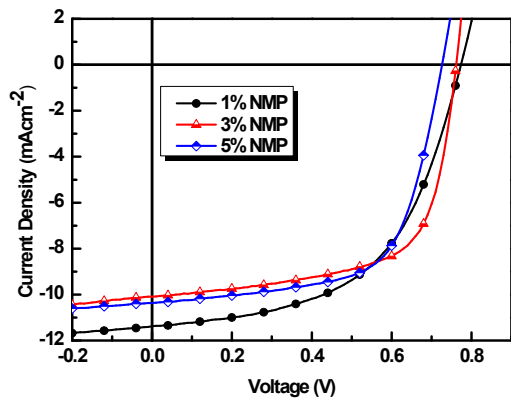


Figure S4. The J - V curves of the PSCs based on the structure of ITO/PEDOT: PSS/PBDTT-BTAZT-2/PC₇₁BM/Ca/Al with different volume of NMP.

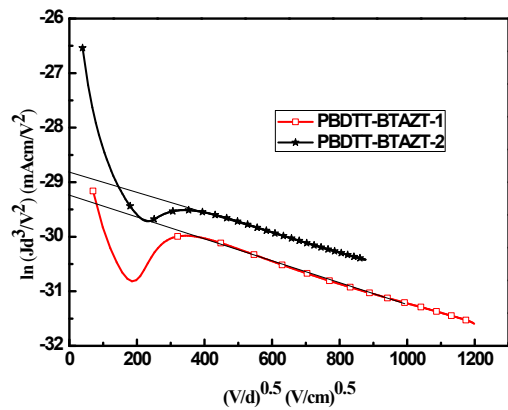


Figure S5. $\ln(JL^3/V^2)$ vs $(V/L)^{0.5}$ of plots for measurement of the hole mobility of PBDTT-BTAZT-1 and PBDTT-BTAZT-2.

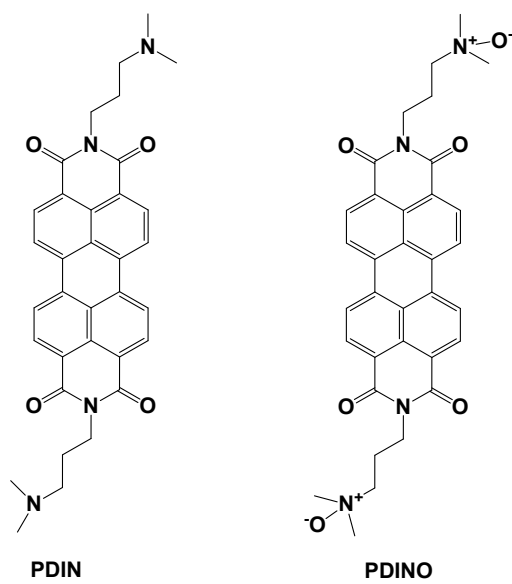


Figure S6. The molecular structure of PDIN and PDINO

Table S1. Photovoltaic performances of PSCs based on PBDTT-BTAZT polymers with

different p/n ratio

Polymer	p/n	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE _{max} (%)
PBDTT-BTAZT-1	1:1	0.77	9.84	63.1	4.78
	1:2	0.76	10.86	54.6	4.50
	1:3	0.69	9.24	68.9	4.40
PBDTT-BTAZT-2	1:1	0.77	9.15	59.2	4.16
	1:2	0.75	10.00	60.5	4.51
	1:3	0.75	9.52	53.0	3.77

Table S2. Photovoltaic performances of PSCs based on PBDTT-BTAZT polymers with different volume of additive

Polymer	additive (v/v)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE _{max} (%)
PBDTT-BTAZT-1	0.5% DIO	0.73	12.37	67.2	5.59
	1% DIO	0.74	12.30	68.4	6.22
	3% DIO	0.73	12.70	66.5	6.16
PBDTT-BTAZT-2	1% NMP	0.77	11.38	54.5	4.79
	3% NMP	0.76	10.09	65.6	5.04
	5% NMP	0.73	10.37	64.3	4.84

Table S3. Photovoltaic performances of PSCs based on PBDTT-BTAZT-1/PC₇₁BM ratio = 1:1 at with different concentration of PBDTT-BTAZT-1.

polymer	Concentration	additive	V_{oc}	J_{sc}	FF	PCE _{max}
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	(mg/mL)		(V)	(mA cm ⁻²)	(%)	(%)
PBDTT-BTAZT-1	10	NO	0.77	9.84	63.1	4.78
	10	1% DIO	0.74	12.30	68.4	6.22
	15	NO	0.72	13.74	58.2	5.79
	15	1% DIO	0.72	13.56	64.3	6.32

Table S4. Photovoltaic performances of PSCs based on PBDTT-BTAZT polymers using different electron extraction layers

polymer	p:n (w/w)	additive	cathode	Voc (V)	Jsc (mA cm ⁻²)	FF (%)	PCE (PCEmax)(%)
PBDTT-BTAZT-1	1:1	1% DIO	Ca/Al	0.72	13.56	64.3	6.32
	1:1	1% DIO	PDIN/Al	0.75	14.41	64.3	6.95
	1:1	1% DIO	PDINO/Al	0.73	13.37	58.2	5.68
PBDTT-BTAZT-2	1:2	3%NMP	Ca/Al	0.76	10.09	65.6	5.04
	1:2	3%NMP	PDIN/Al	0.71	11.16	55.17	4.37
	1:2	3%NMP	PDINO/Al	0.75	12.53	65.8	6.16

Reference

1. J. H. Kim, H. U. Kim, I. N. Kang, S. K. Lee, S. J. Moon, W. S. Shin and D. H. Hwang, *Macromolecules*, 2012, 45, 8628.