

Supporting Information for

Constructing D-A Copolymers based on Thiophenen-fused Benzotriazole Unit Containing Different Alkyl Side-Chain for Non-Fullerene Polymer Solar Cells

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Instruments and measurements

¹H-NMR and ¹³C-NMR were measured on a Varian Mercury 300 spectrometer. ESI-MS analysis was determined on a Finnigan-LCQ advantage mass spectrometer.

MALDI-TOF analysis was performed on an Applied Biosystems 4700 proteomics Analyzer 155 mass spectrometer. Gel permeation chromatography(GPC) was performed on an Agilent 1100 series HPLC system equipped with a G1326A refractive index detector using THF as eluent. The thermo-gravimetric analysis(TGA) was performed on NETZSCH STA449C thermal analyzer. Elemental analyses were carried out on a 73 CARLOERBA-1106 microelemental analyzer. The electrochemical Cyclic Voltammetry(CV) was conducted on a CHI voltammetric analyzer with glassy carbon disk, Pt wire and Ag/Ag⁺ electrode as working electrode, counter electrode and reference electrode respectively in a 0.1mol/L tetrabutylammonium hexafluorophosphat(Bu₄NPF₆) acetonitrile solution. The UV-vis absorption spectra of the polymers were measured by a Varian Cary 5000 UV-vis-NIR spectrophotometer. The morphology of active layers were observed using atomic force microscope (AFM) (Cypher ES, Asylum Research, Oxford Instruments) in contact mode and transmission electron microscope (TEM) (JEM2012--HT). The samples for the AFM measurements were prepared by spin-casting the active layer films on the Si substrates. The Si substrates with the active layers were used in the AFM measurements. TEM samples were prepared by spin-coating the active layer films on the ITO/PEDOT:PSS substrates. And then the substrates with the active layers were submerged in deionized water to make the active layers float onto the air-water interface. The TEM samples were obtained by picking up the floated films on the unsupported 200 mesh copper grids. The grazing incidence X-ray scattering measurements (GIWAXS) were carried out at 14B of Shanghai Synchrotron Radiation

Facility, Shanghai. The energy of the X-ray source was set to 10 keV (wavelength of 1.24 Å) and the incident angle was 0.15°.

Device fabrication

Bulk heterojunction solar cells were fabricated with a conventional architecture of ITO/PEDOT:PSS/polymer:ITIC/Ca/Al. The patterned indium tin oxide (ITO) glass (sheet resistance= 10 Ω sq⁻¹) was pre-cleaned in an ultrasonic bath of deionized water, acetone and isopropanol, followed by oxygen plasma treatment (25 min) in an ultraviolet–ozone chamber (Jelight Company, USA). A thin layer (30 nm) of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS, Baytron PVP AI 4083, Germany) was spin-coated onto the ITO glass at 4000 rpm and baked subsequently at 150°C for 20 min. The mixture of polymer:ITIC in *o*-dichlorobenzene solvent (20 mg mL⁻¹ in total) with or without diphenyl ether (DPE) was spin-coated on a PEDOT:PSS layer to form an active layer. Calcium (ca. 20 nm) and aluminium (ca. 80 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 4mm². The current density–voltage (*J-V*) characteristics were measured on a computer–controlled B2912A Precision Source/Measure Unit (Agilent Technologies). A XES-70S1 (SAN-EI Electric Co., Ltd) solar simulator (AAA grade, 70×70 mm² photobeam size) coupled with AM 1.5 G solar spectrum filters was used as the light source, and the optical power at the sample was 100 mW/cm². A 2×2 cm² monocrystalline silicon reference cell (SRC-1000-TC-QZ) was purchased from VLSI Standards Inc. A Solar Cell Spectral Measurement System QE-R3011 (Enlitech Co., Ltd) was used for the EQE spectrum

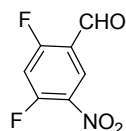
measurement. The light intensity at each wavelength was calibrated using a standard single crystal Si photovoltaic cell. The hole mobility and electron mobility were measured using the structure: ITO/PEDOT:PSS/polymer:ITIC/Au and ITO/titanium (diisopropoxide) bis(2,4-pentanedionate) (TIPD)/polymer:ITIC/Al respectively. And the mobility was extracted by fitting the current J - V curves using the Mott–Gurney relationship (space charge limited current).

Materials and Synthesis

All the chemicals were used as commercially purchased without further purification except specified stated. **M3** and **M4** were prepared according to the procedure described in the literature¹.

Synthesis of M1 and M2

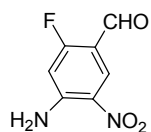
2,4-Difluoro-5-nitrobenzaldehyde (1):



To a 200mL concentrated H_2SO_4 at 0°C was slowly added KNO_3 (41.4g, 0.4mol), and the solution was stirred for 30min, then 2,4-difluorobenzaldehyde (28.4g, 0.2mol) was added. The mixture was stirred for 3 hours at room temperature. After reaction, the mixture was poured into a mass of ice water and extracted with ethyl acetate. The organic layer was washed with water for three times, and then dried over anhydrous Na_2SO_4 . The solvent was removed under vacuum to give 1 (35.5g, 95%) as a colourless oil. $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ ppm): 10.29 (s, 1H), 8.68 (d, $J=7.2\text{Hz}$, 1H), 7.21 (t, 1H). $^{13}\text{C-NMR}$ (75MHz, CDCl_3 , δ): 183.87, 183.81, 127.85, 127.79, 108.53, 108.19,

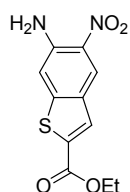
107.85. ESI-MS: Calcd. for $[C_7H_3F_2NO_3]^+$: 187.01; Found: 187.02.

4-Amino-2-fluoro-5-nitrobenzaldehyd (2):



To a solution of compound 1(30.4g, 0.16mol) in THF (100mL) at 0°C was slowly added $NH_3 \cdot H_2O$ (50mL). After addition, the mixture was kept at room temperature for 30min. A little too much concentrated hydrochloric acid was added dropwise. The mixture was extracted with ethyl acetate twice. After drying over anhydrous $MgSO_4$, the solvent was removed under vacuum to give 2(26.8g, 91%) as a yellow solid. 1H -NMR (300 MHz, $CDCl_3$, δ ppm): 10.06(s, 1H), 8.78 (d, $J=7.2$ Hz, 1H), 6.57 (s, 1H), 6.53 (s, 2H). ^{13}C -NMR (75MHz, DMSO, δ ppm): 185.75, 185.73 166.96, 164.35, 151.66, 151.51, 132.25, 132.19, 128.32, 114.01, 113.88, 104.27, 104.02. ESI-MS: Calcd. for $[C_7H_5FN_2O_3]^+$: 184.03; Found: 104.03.

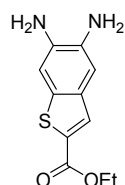
Ethyl 5-amino-6-nitrobenzo[b]thiophene-2-carboxylate (3):



Compound 2 (1.84g, 10mmol), ethyl 2-mercaptoacetate (1.44g, 12mmol) and K_2CO_3 (2.07g, 15mmol) were dissolved in DMSO (10mL). The mixture was reacted in a microwave reactor for 1.5h at 80°C. After reaction, the mixture was poured into ice water and the crude product was filtered, washed with methanol and then dried to give 3 (2.53g, 95%) as a red solid. 1H -NMR (300 MHz, $CDCl_3$, δ ppm): 8.67 (s, 1H), 7.81 (s, 1H), 7.25 (s, 1H), 5.84 (s, 2H), 4.42 (m, 2H), 1.42 (t, $J=6.9$ Hz, 3H). ^{13}C -NMR (75

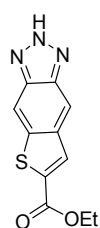
MHz, DMSO, δ ppm): 162.18, 145.35, 143.64, 140.71, 133.54, 129.57, 128.64, 121.86, 113.48, 62.50, 14.75. EI-MS: Calcd. for $[C_{11}H_{10}N_2O_4S]^+$: 266.04; Found: 265.9.

Ethyl 5,6-diaminobenzo[b]thiophene-2-carboxylate (4):



Compound 3 (9.50g, 35.7mmol) and $SnCl_2 \cdot 2H_2O$ (32.20g, 142.7mmol) were dissolved in THF (200mL) and then stirred at refluxing temperature overnight. After reaction, the mixture was poured into excessive sodium bicarbonate solution. Then the mixture was extracted with ethyl acetate for several times. The organic layer was dried over anhydrous Na_2SO_4 . The solvent was removed under vacuum. A yellow solid (6.84g, 82%) was obtained without further purification and used directly in the next-step reaction. 1H -NMR (300 MHz, DMSO, δ ppm): 7.74 (s, 1H), 6.99 (s, 1H), 6.92 (s, 1H), 5.26 (s, 2H), 4.78 (s, 2H), 4.26 (m, 2H), 1.28 (t, 3H). ^{13}C -NMR (75 MHz, DMSO, δ ppm): 162.98, 139.67, 135.67, 134.12, 130.71, 130.60, 125.99, 108.23, 104.46, 60.93, 14.72. EI-MS: Calcd. for $[C_{11}H_{12}N_2O_2S]^+$: 236.06; Found: 236.07..

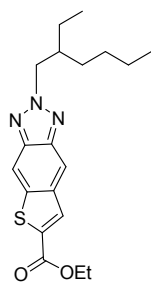
Ethyl 3H-thieno[2'3':4,5]benzo[1,2-d][1,2,3]triazole-6-carboxylate (5):



Compound 4 (7.73g, 32.7mmol) and acetic acid were dissolved in HAc (40mL) and H_2O (98mL). After cooling to $0^\circ C$, sodium nitrite (2.71g, 39.3mmol) was added to the solution. The mixture was stirred at room temperature for 2h. After reaction, the crude

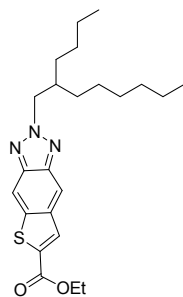
product was filtered, washed with water and then dried to give 5 (6.77g, 83%) as an orange solid. ¹H-NMR (300 MHz, DMSO, δ ppm): 15.90 (s, 1H), 8.60 (br, 2H), 4.37 (m, 2H), 1.34 (t, 3H). EI-MS: Calcd. for [C₁₁H₉N₃O₂S]⁺: 247.04; Found: 247.05.

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



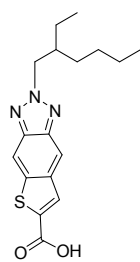
Compound 5 (3.02g, 12.2mmol), bromo-2-ethylhexane (3.54g, 18.33 mmol), and t-BuLi (2.06g, 18.3 mmol), were added to 100 mL anhydrous methanol under Ar. The reaction solution was heated to reflux for 48 h. After reaction, the mixture was poured into the ice water and extracted with ethyl acetate and the organic layer was dried over anhydrous 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 6a (1.23g, 28%) as a white solid. ¹H-NMR (300 MHz, CDCl₃, δ ppm): 8.41 (s, 1H), 8.33 (s, 1H), 8.10 (s, 1H), 4.80 (d, *J* = 6.9Hz, 2H), 4.44 (m, 2H), 2.28 (m, 1H), 1.45-1.38 (m, 3H), 1.35-1.32 (m, 8H), 0.96-0.87 (m, 6H). ¹³C-NMR (75MHz, CDCl₃, δ ppm): 162.35, 144.08, 143.03, 139.99, 138.63, 135.44, 130.11, 114.04, 110.48, 61.68, 60.53, 40.52, 30.44, 28.35, 23.81, 22.71, 14.18, 13.83, 10.35. EI-MS: Calcd. for [C₁₉H₂₅N₃O₂S]⁺: 359.17; Found: 359.18.

Ethyl 2-(2-butyloctyl)-2H-thieno[2',3':4,5]benzo[1,2-d][1,2,3]triazole-6-carboxylate(6b):



6b was prepared using the same procedure as 6a. yield, 1.51g (30.2%) ¹H-NMR (300 MHz, CDCl₃, δ ppm): 8.41 (s, 1H), 8.33 (s, 1H), 8.10 (s, 1H), 4.71 (d, *J* = 7.2Hz, 2H), 4.44 (m, 2H), 2.32(m, 1H), 1.46-1.41 (m, 4H), 1.31-1.24 (m, 15H), 0.86-0.83 (m, 6H). ¹³C-NMR (75MHz, CDCl₃, δ ppm): 162.37, 144.08, 143.03, 139.99, 138.63, 135.42, 130.14, 130.11, 114.06, 110.51, 61.69, 60.93, 39.23, 31.33, 29.39, 29.33, 28.31, 26.08, 22.73, 22.46, 14.25, 14.21, 13.95, 13.78. EI-MS: Calcd. for [C₂₃H₃₃N₃O₂S]⁺: 415.23; Found: 415.25.

2-(2-Ethylhexyl)-2H-thieno[2',3':4,5]benzo[1,2-d][1,2,3]triazole-6-carboxylic acid (7a):

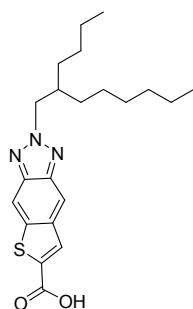


Compound 6a (2.45g, 6.8mmol) was dissolved in THF (200mL). LiOH·H₂O (2.9g, 68mmol) was dissolved in H₂O (20mL) and then added dropwise in the above solution. The mixture was stirred at 50°C overnight. After reaction, the mixture was extracted with ethyl acetate and drying over anhydrous Na₂SO₄. The solvent was removed under vacuum to give 7a (2.2g, 97%) as a white solid. ¹H-NMR (300 MHz, DMSO, δ ppm): 8.43 (s, 1H), 8.38 (s, 1H), 7.66 (s, 1H), 4.72 (d, *J* = 6.9Hz, 2H), 2.15 (m, 1H), 1.25-1.24

(m, 8H), 0.90-0.82 (m, 6H). EI-MS: Calcd. for $[C_{17}H_{21}N_3O_2S]^+$: 331.14; Found: 331.16.

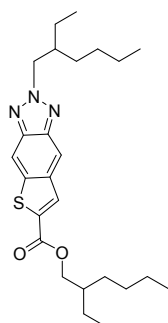
2-(2-Butyloctyl)-2H-thieno[2',3':4,5]benzo[1,2-d][1,2,3]triazole-6-carboxylic acid

(7b):



Compound 7b was prepared using the same procedure as 7a. yield, 1.34g (95%) 1H -NMR (300 MHz, DMSO, δ ppm): 8.38 (s, 1H), 8.33 (s, 1H), 7.59 (s, 1H), 4.68 (d, J = 5.1Hz, 2H), 2.18 (m, 1H), 1.22-1.17 (m, 16H), 0.79 (m, 6H). EI-MS: Calcd. for $[C_{21}H_{29}N_3O_2S]^+$: 387.20; Found: 387.22.

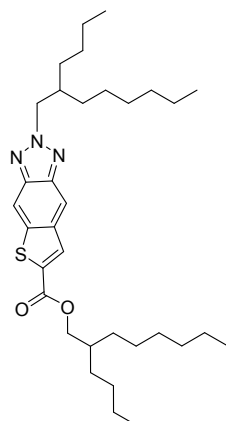
2-Ethylhexyl 2-(2-ethylhexyl)-2H-thieno[2',3':4,5]benzo[1,2-d][1,2,3]triazole-6-carboxylate (8a):



Compound 7a (1.1g, 3.3mmol), 2-ethylhexan-1-ol (0.56g, 4.3mmol), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (0.76g, 4.0mmol) and 4-dimethylaminopyridine(0.08g, 0.66mmol) were dissolved in CH_2Cl_2 . The mixture was stirred at room temperature overnight. After reaction, the mixture was extracted with

CHCl₃. The organic layer was dried over anhydrous Na₂SO₄. The solvent was removed and purified with column chromatography using petroleum ether-ethyl acetate mixture as eluent to obtain light yellow oil(0.89g, 61%). ¹H-NMR (300 MHz, CDCl₃, 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). ¹³C-NMR (75 MHz, CDCl₃, 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 [C₂₅H₃₇N₃O₂S]⁺:443.26; Found: 443.26.

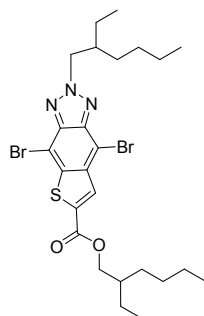
2-Butyloctyl-2-(2-butyloctyl)-2H-thieno[2',3':4,5]benzo[1,2-d][1,2,3]triazole-6-carboxylate (8b):



Compound 8b was prepared using the same procedure as 8a. yield, 1.3g (58%) ¹H-NMR (300 MHz, CDCl₃, δ ppm): 8.42 (s, 1H), 8.34 (s, 1H), 8.09 (s, 1H), 4.71 (d, *J* = 6.9Hz, 2H), 4.28 (d, *J* = 5.1Hz, 2H), 2.33 (s, 1H), 1.80 (s, 1H), 1.36-1.24 (m, 28H), 0.92-0.85 (m, 12H). ¹³C-NMR (75 MHz, CDCl₃, δ): 162.51, 144.09, 143.04, 140.04, 138.65, 135.51, 130.01, 114.06, 110.48, 68.47, 60.95, 39.22, 37.32, 31.70, 31.57, 31.40, 31.30, 30.98, 29.57, 29.50, 29.33, 28.87, 28.31, 26.64, 26.08, 22.87, 22.73, 22.60, 22.54, 22.46, 13.96, 13.96, 13.92, 13.83. EI-MS: Calcd. for [C₃₃H₅₃N₃O₂S]⁺:555.39;

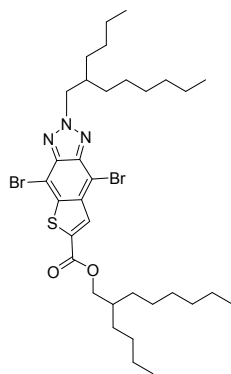
Found: 555.43.

2-Ethylhexyl-4,8-dibromo-2-(2-ethylhexyl)-2H-thieno[2',3':4,5]benzo[1,2-d][1,2,3]triazole-6-carboxylate (9a):



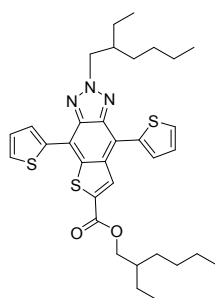
Br₂ (325 mg, 2.3 mmol) was added to 8 (300 mg, 0.68mmol) in 30mL CHCl₃. The reaction mixture was stirred at room temperature for 12 h. After reaction, the mixture was poured into ice water and extracted with CH₂Cl₂ and the organic layer was dried over anhydrous Na₂SO₄. The solvent was removed under vacuum. The mixture was purified by column chromatography over silica gel with petroleum ether-ethyl acetate mixtures as the eluent to give 10 as a light yellow solid (364 mg, 89%). 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.

2-Butyloctyl-4,8-dibromo-2-(2-butyloctyl)-2H-thieno[2',3':4,5]benzo[1,2-d][1,2,3]triazole-6-carboxylate (9b):



Compound 9b was prepared using the same procedure as 9a. yield, 0.9 g (88%) $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ ppm): 8.30 (s, 1H), 4.77 (d, $J = 7.5\text{Hz}$, 2H), 4.31 (d, $J = 2.4\text{Hz}$, 2H), 2.40 (m, 1H), 1.83 (m, 1H), 1.37-1.25 (m, 32H), 0.93-0.84 (m, 12H). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3 , δ): 161.92, 142.69, 142.48, 141.53, 138.03, 136.54, 130.08, 106.18, 101.89, 69.06, 61.66, 39.26, 37.52, 32.00, 31.83, 31.55, 31.23, 31.02, 29.79, 29.61, 29.15, 28.39, 26.91, 26.15, 23.17, 23.01, 22.84, 22.76, 14.25. EI-MS: Calcd. for $[\text{C}_{33}\text{H}_{51}\text{Br}_2\text{N}_3\text{O}_2\text{S}]^+$: 713.20; Found: 713.16.

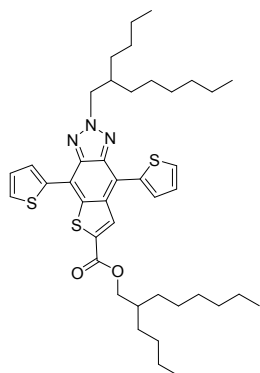
2-ethylhexyl 2-(2-Ethylhexyl)-4,8-di(thiophen-2-yl)-2H-thieno[2',3':4,5]benzo[1,2-d][1,2,3]triazole-6-carboxylate (10a):



9a (365 mg, 0.6 mmol), 2-(tributylstannyl)thiophene (679 mg, 1.8 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (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-ethyl acetate mixtures as the

eluent to give 12 as an orange-yellow solid (294 mg, 81%). 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, 29.20, 28.64, 24.21, 23.20, 14.29, 11.35, 10.80. EI-MS: Calcd. for [C₃₃H₄₁N₃O₂S₃]⁺: 607.24; Found: 607.16.

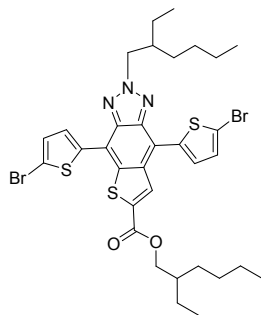
2-Butyloctyl-2-(2-butyloctyl)-4,8-di(thiophen-2-yl)-2H-thieno[2',3':4,5]benzo[1,2-d][1,2,3]triazole-6-carboxylate (10b):



Compound 10b was prepared using the same procedure as 10a. yield, 0.8g (80.8%) ¹H-NMR (300 MHz, CDCl₃, δ ppm): 8.68 (s, 1H), 8.21 (br, 1H), 7.83 (br, 1H), 7.60 (br, 2H), 7.32 (m, 2H), 4.79 (d, *J* = 6.6Hz, 2H), 4.30 (d, *J* = 3.0Hz, 2H), 2.36 (m, 1H), 1.83 (m, 1H), 1.37-1.26 (m, 32H), 0.95-0.84 (m, 12H). ¹³C-NMR (75 MHz, CDCl₃, δ): 162.51, 142.08, 137.72, 137.42, 136.76, 136.35, 135.03, 130.37, 129.54, 128.86, 127.54, 127.46, 127.35, 127.11, 120.49, 117.43, 68.67, 60.54, 39.09, 37.33, 31.70, 31.42, 31.38, 31.08, 29.54, 29.44, 28.89, 28.36, 26.66, 26.10, 22.89, 22.84, 22.56, 13.97, 13.78. EI-MS: Calcd. for [C₄₁H₅₇N₃O₂S₃]⁺: 719.36; Found: 719.32.

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 (**M1**):



NBS (277 mg, 1.6 mmol) was added to 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-chloroform mixtures as the eluent

to give 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,

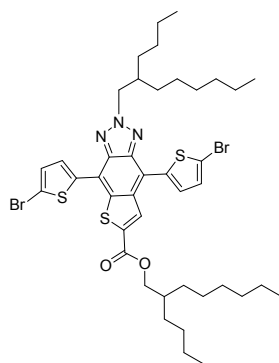
115.55, 115.03, 110.04, 68.75, 60.52, 57.89, 40.73, 39.06, 30.76, 29.98, 29.20, 28.63,

24.21, 23.28, 14.41, 11.41, 10.83. EI-MS: Calcd. For [C₃₃H₃₉Br₂N₃O₂S₃]⁺: 765.06;

Found: 765.32.

2-Butyloctyl-4,8-bis(5-bromothiophen-2-yl)-2-(2-butylthiophen-5-yl)-2H-

thieno[2',3':4,5]benzo[1,2-d][1,2,3]triazole-6-carboxylate (**M2**):



M2 was prepared using the same procedure as M1. yield, 0.9g (89.2%) $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ ppm): 8.53 (s, 1H), 7.87 (d, $J = 3.6\text{Hz}$, 2H), 7.53 (d, $J = 6.0\text{Hz}$, 2H), 7.22 (m, 2H), 4.74 (d, $J = 3.9\text{Hz}$, 2H), 4.29 (d, $J = 3.9\text{Hz}$, 2H), 2.28 (m, 1H), 1.83 (m, 1H), 1.38-1.27 (m, 32H), 0.93-0.88 (m, 12H). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3 , δ): 162.20, 141.59, 138.91, 138.31, 137.21, 136.10, 135.33, 130.34, 130.15, 129.69, 128.88, 119.56, 116.70, 115.24, 115.17, 68.88, 60.44, 39.15, 37.32, 31.72, 31.43, 31.38, 31.13, 31.08, 29.55, 29.49, 28.90, 28.38, 26.68, 26.10, 22.90, 22.57, 13.98. EI-MS: Calcd. For $[\text{C}_{41}\text{H}_{55}\text{Br}_2\text{N}_3\text{O}_2\text{S}_3]^+$: 877.18; Found: 877.09.

Synthesis of the polymers (P1-P3)

Polymerization for **P1**: **M1** (109.8mg, 0.12mmol), **M3** (89.4 mg, 0.12mmol) and $\text{Pd}(\text{PPh}_3)_4$ (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 $^\circ\text{C}$ for 48 h. After cooling, the mixture was precipitated into CH_3OH . The raw polymer was put in Soxhlet extraction and extracted with methanol, acetone, hexane and CHCl_3 . The resulted chloroform fraction was precipitated in methanol. Then the precipitate was collected to give P1 as purple black solid. Yield, 118 mg (83%). GPC: $M_n = 91$ kDa, $\text{PDI} = 2.9$. Anal. Calcd for Anal. Calcd for for $\text{C}_{67}\text{H}_{77}\text{F}_2\text{N}_3\text{O}_2\text{S}_7$ (%): C, 66.03; H, 6.37; N, 3.45. Found: C, 66.16; H, 6.58; N, 3.40.

Polymerization for **P2** and **P3**: **P2** or **P3** was prepared as the same procedure as **P1**.

P2, yield, 105 mg (80%). GPC: $M_n = 43\text{kDa}$, PDI = 2.0. Anal. Calcd for $\text{C}_{75}\text{H}_{93}\text{F}_2\text{N}_3\text{O}_2\text{S}_7$ (%): C, 67.68; H, 7.04; N, 3.16. Found: C, 67.81; H, 6.88; N, 3.23. C, 67.68; H, 7.04; N, 3.16.

P3, yield, 97mg (77%). GPC: $M_n = 39\text{ kDa}$, PDI = 1.7. Anal. Calcd $\text{C}_{75}\text{H}_{93}\text{F}_2\text{N}_3\text{O}_2\text{S}_7$ (%): C, 67.68; H, 7.04; N, 3.16. Found: C, 67.49; H, 7.16; N, 3.30.

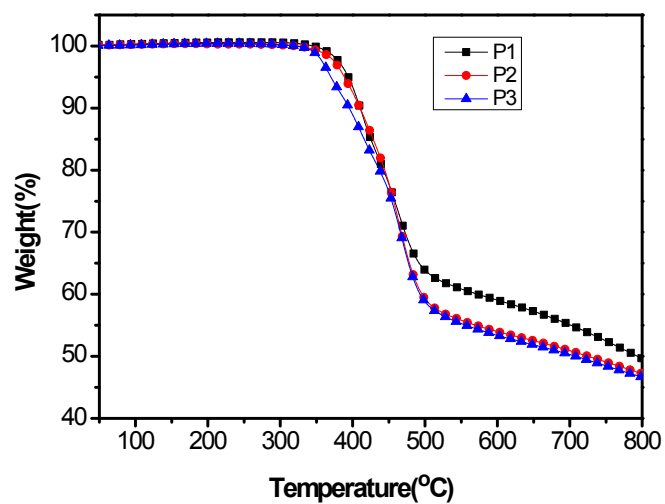


Figure S1. TGA of polymer P1, P2, and P3

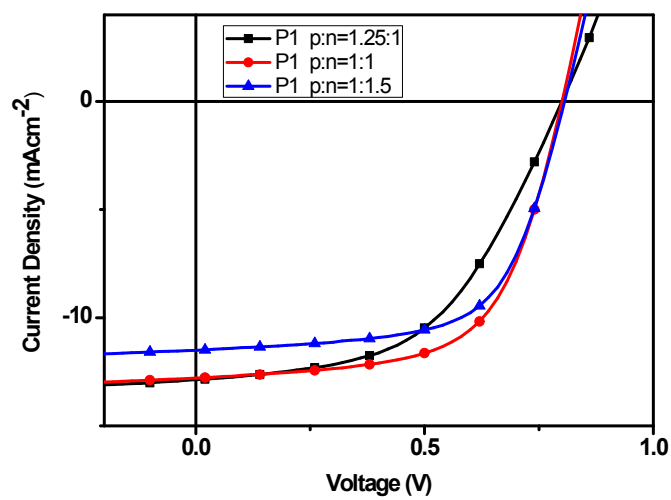


Figure S2. The J - V curves of P1/ITIC PSC devices with different p/n ratio.

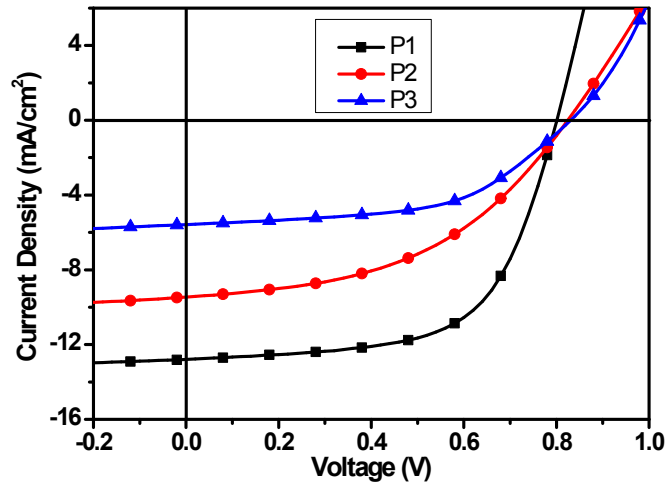


Fig. S3 The J - V curves of the solar cells based on the structure of ITO/PEDOT:PSS/polymer:ITIC/Ca/Al without DPE.

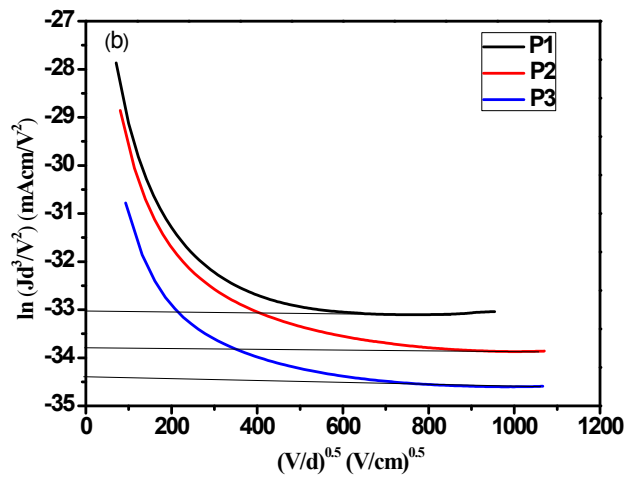
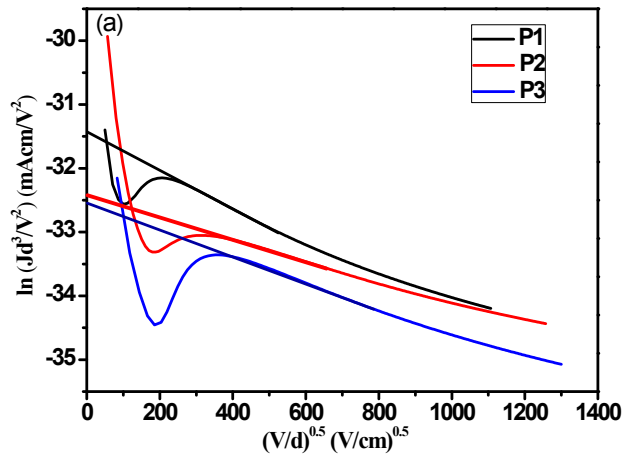


Figure S4 $\ln(JL^3/V^2)$ vs $(V/L)^{0.5}$ plots of the polymer:ITIC(1:1) with 1% DPE additive of hole mobility (a) and electron mobility (b) by the SCLC method.

Table S1. The solar cell parameters of the devices without DPE

devices	D:A	V_{oc}	J_{sc}	FF	PCE_{max}
		(V)	(mA cm ⁻²)	(%)	(%)
P1:ITIC	1:1	0.81	12.44	62.99	6.33
P2:ITIC	1:1	0.83	8.75	56.14	4.09
P3:ITIC	1:1	0.83	5.58	53.92	2.51

REFERENCES

- 1 M. Zhang, X. Guo, W. Ma, H. Ade, J. Hou, *Adv.Mater.*, 2015, **27**, 4655.