

## Electronic Supplementary Information

# Benzobisthiadiazole-*alt*-bithiazole copolymers with deep HOMO levels for good-performance field-effect transistors with air stability and high on/off ratio

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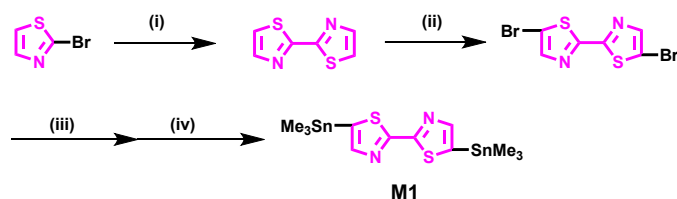
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## 1. Experimental Section

### 1.1 Materials and general methods

The dry toluene and THF were prepared by refluxing with the alloy of potassium/sodium under argon atmosphere. Other agents and reagents were obtained from commercial sources and used without further purification. <sup>1</sup>H-NMR spectra were recorded on a Varian Unity 300 MHz spectrometer using CDCl<sub>3</sub> as solvent and tetramethylsilane as internal reference. Elemental analysis of hydrogen, carbon and nitrogen was performed on Vario EL-III microanalyzer. EI-MS spectra were recorded on VJ-ZAB-3F-Mass spectrometer. Gel permeation chromatography was carried out at 150 °C using a Polymer Labs PL 220 system using a refractive index detector and 1,2,4-trichlorobenzene as the eluent. UV-vis-NIR absorption spectra were measured on polymer solutions in CHCl<sub>3</sub> and polymer films casted onto quartz glass using a Hitachi U-3010 spectrophotometer. Cyclic voltammetric measurements were carried out on a computer-controlled EG&G Potentiostat/Galvanostat model 283 using tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte in acetonitrile and conventional three-electrode cell with a Pt work electrode of 2 mm diameter, a platinum-wire counter electrode and a Ag/AgCl reference electrode was employed. The polymer was deposited on the Pt work electrode as a thin film before measured. XRD data of polymer films was obtained using an Empyrean XRD system. The polymer film samples were prepared by spin-coating CHCl<sub>3</sub> solution onto OTS-modified SiO<sub>2</sub>/Si substrates and then annealed. Polymer thin-film samples were illuminated at a constant incidence angle of 0.2° ( $\lambda = 2d\sin\theta = 1.54 \text{ \AA}$ ). Computation for the polymers was carried by DFT (B3LYP/6-31G(d)) method for three monomers, in which the side chains were replaced by methyl groups. Compound **1**, **2** and monomer **M2** was synthesized according to literatures.<sup>1-2</sup>

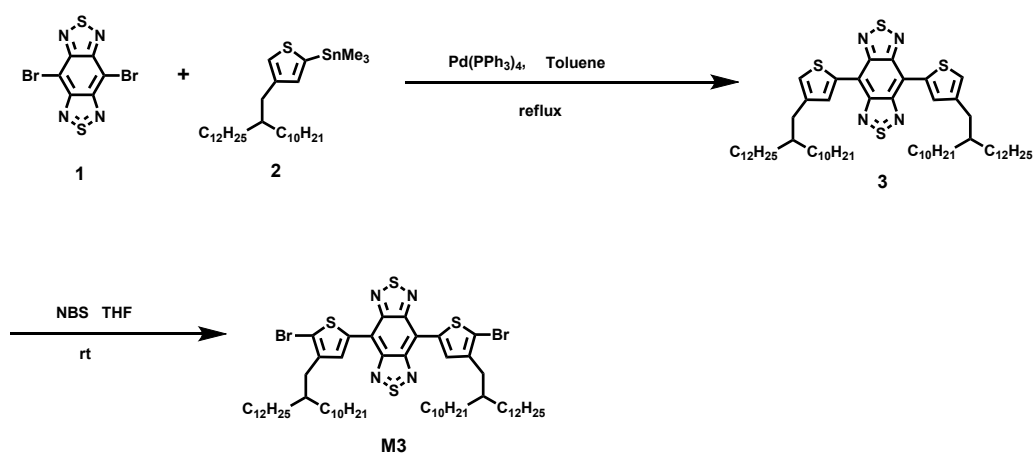


**Scheme S1.** (a) Synthesis of 5,5'-bis(trimethylstannyl)-2,2'-bithiazole. (i) Pd(OAc)<sub>2</sub>, *i*-Pr<sub>2</sub>EtN, *n*-Bu<sub>4</sub>NBr, toluene, 120 °C, 48h; (ii) NBS, DMF, 60 °C, 48h; (iii) *n*-BuLi, THF, -78 °C, 2h; (iv) Me<sub>3</sub>SnCl, 12h, rt.

**2,2'-bithiazole:** 3.3 g (20 mmol) 2-bromothiazole, 100 mg Pd(OAc)<sub>2</sub>, 2.7 mL *i*-Pr<sub>2</sub>EtN, 2.5 g *n*-Bu<sub>4</sub>NBr and 5 mL toluene were added in a Schlenk tube under Ar atmosphere. The mixture was stirred at 120 °C for 48 h. Then the mixture was poured into water, extracted by CHCl<sub>3</sub>. The crude product was purified by silicon chromatography (ethyl acetate (EA): petroleum ether (PE) (1:1), v/v) to get pure product (0.81 g, 54 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm): 7.90 (d, *J* = 3.1 Hz, 2H), 7.44 (d, *J* = 3.1 Hz, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ (ppm): 161.8, 144.0, 121.1. EI-MS (*m/z*, [M<sup>+</sup>]): 168.1

**5,5'-dibromo-2,2'-bithiazole:** 800 mg (4.8 mmol) 2,2'-bithiazole was dissolved in 40 mL dry DMF, and 1.78 g NBS was added. After stirred at 60 °C for 48 h, the mixture was poured into 200 mL water and extracted by CHCl<sub>3</sub>. The crude product was purified by silicon chromatography (EA: PE (1:1), v/v) to get pure product as white solid (1.51 g, 95 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ(ppm): 7.75 (s, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ (ppm): 162.0, 145.2, 112.0. EI-MS (*m/z*, [M<sup>+</sup>]): 323.6

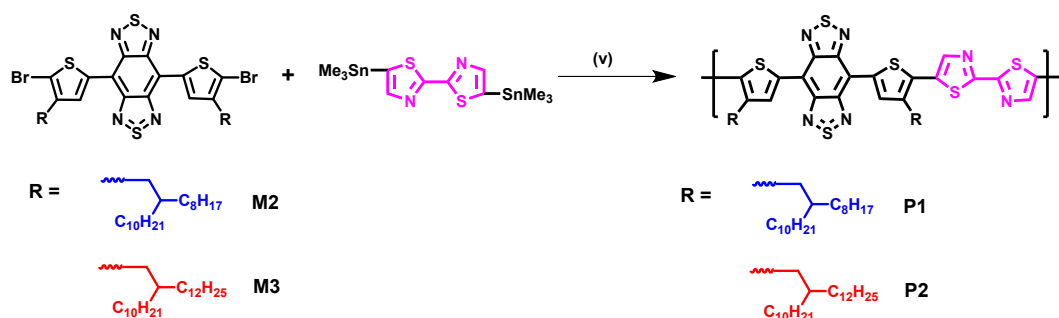
**5,5'-bis(trimethylstannyl)-2,2'-bithiazole (M1):** 200 mg (0.62 mmol) 5,5'-dibromo-2,2'-bithiazole was dissolved in 60 mL dry THF in a Schlenk flask under Ar atmosphere. At -78 °C, 0.7 mL 2 M *n*-BuLi was dropped slowly into the THF solution and the mixture was then stirred for 2 h. Then 1.7 mL Me<sub>3</sub>SnCl (1M) was injected into the solution and the mixture was stirred at room temperature for 12 h. Then, the reaction mixture was concentrated in vacuo, hexane was added, and the resulting suspension was filtered to remove the solid portion and concentrated in vacuo to yield a crude solid. The crude material was crystallized using EtOH under the temperature of -78 °C. The pure product **M1** is a pale yellow solid (220 mg, 72 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ(ppm): 7.80 (s, 2H), 0.45 (s, 18 H). EI-MS (*m/z*, [M<sup>+</sup>]): 494.0.



**Scheme S2.** Synthesis of **M3**.

**3:** 350 mg (1 mmol) **1**, 1.8 g **2** (3 mmol), 40 mg Pd(PPh<sub>3</sub>)<sub>4</sub> were dissolved in 50 mL dry toluene under Ar atmosphere and stirred at 110 °C for 24 h. The reacting mixture was concentrated into vacuo. The crude product was purified by silicon chromatography (CH<sub>2</sub>Cl<sub>2</sub>: PE (1:1), v/v) to get pure product as green solid (380 mg, 37 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm): 8.78 (s, 2H), 7.29 (s, 2H), 2.02 (d, *J* = 6.6 Hz, 4H), 1.82 (br, 2H), 1.31-1.26 (m, 80H), 0.84 (m, 12H) <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ (ppm): 186.7, 149.8, 142.1, 135.5, 133.2, 38.5, 33.3, 31.9, 30.1, 29.8, 29.5, 26.6, 22.7, 14.2. MS (MALDI, *m/z*): [M]<sup>+</sup> calcd for C<sub>62</sub>H<sub>102</sub>N<sub>4</sub>S<sub>4</sub>, 1031.8; found, 1031.3. Elemental anal. calcd for C<sub>62</sub>H<sub>102</sub>N<sub>4</sub>S<sub>4</sub>: C, 72.17; H, 9.96; N, 5.43. Found: C, 72.09; H, 10.02; N, 5.26.

**M3:** 300 mg **3** was dissolved in 40 mL THF and 280 mg NBS was added in small portions. The mixture was stirred at room temperature for 24 h and extracted by Et<sub>2</sub>O. The organic layer was washed by water, dried and concentrated by vacuum evaporation. The resulting product was purified by silicon chromatography (CH<sub>2</sub>Cl<sub>2</sub>: PE (1:3), v/v) to get pure product (200 mg, 64 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm): 8.59 (s, 2 H), 2.02 (d, *J* = 6.6 Hz, 4H), 1.82 (br, 2H), 1.31-1.26 (m, 80H), 0.84 (m, 12H) <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ (ppm): 188.8, 150.2, 142.1, 136.8, 133.8, 38.5, 33.3, 31.9, 30.1, 29.8, 29.4, 26.6, 22.7, 14.1. MS (MALDI, *m/z*): [M]<sup>+</sup> calcd for C<sub>62</sub>H<sub>100</sub>N<sub>4</sub>S<sub>4</sub>Br<sub>2</sub>, 1186.5; found, 1186.1. Elemental anal. calcd for C<sub>62</sub>H<sub>100</sub>N<sub>4</sub>S<sub>4</sub>Br<sub>2</sub>: C, 62.60; H, 8.47; N, 4.71. Found: C, 62.46; H, 8.66; N, 4.82.



**Scheme S3.** Synthesis of **P1** and **P2**. (v) Pd<sub>2</sub>(dba)<sub>3</sub>, P(*o*-tol)<sub>3</sub>, toluene, 120 °C, 72h.

**P1:** 100.0 mg **M3**, 46.0 mg **M1**, 5 mg Pd<sub>2</sub>(dba)<sub>3</sub> and 10 mg P(*o*-tol)<sub>3</sub> were mixed in a Schlenk tube under Ar atmosphere. 5 mL of toluene was added and the solution was heated at 120 °C for 3 days. After the reaction, the mixture was poured into 100 mL methanol and filtered. The precipitate was extracted by a Soxhlet extractor with methanol, acetone, hexane, and CH<sub>2</sub>Cl<sub>2</sub> subsequently. Finally, the polymer was extracted by CHCl<sub>3</sub>. The solution was concentrated and precipitated into 150 mL of methanol. The polymer was collected as a dark solid (52 mg). Yield: 53 %. GPC: M<sub>n</sub> = 44.4 kDa, M<sub>w</sub> = 77.3 kDa, PDI = 1.74. Elemental anal. calcd for (C<sub>68</sub>H<sub>102</sub>N<sub>6</sub>S<sub>6</sub>)<sub>n</sub>: C, 68.29; H, 8.60; N, 7.03. Found: C, 68.50; H, 8.78; N, 7.14.

**P2:** **P2** (65 mg) was prepared using the same procedure as **P1**. Yield: 66 %. GPC: M<sub>n</sub> = 33.4 kDa, M<sub>w</sub> = 88.4 kDa, PDI = 2.65. Elemental anal. calcd for (C<sub>60</sub>H<sub>86</sub>N<sub>6</sub>S<sub>6</sub>)<sub>n</sub>: C, 66.49; H, 8.00; N, 7.75. Found: C, 66.25; H, 8.01; N, 7.67.

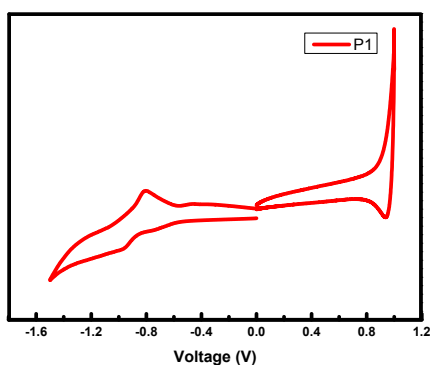
## 1.2 Devices Fabrication and Measurement

OFET devices were fabricated in a bottom-gate bottom-contact (BGBC) configuration (gold electrode on Si/SiO<sub>2</sub> substrates). Before the deposition of organic semiconductors, octadecyltrichlorosilane (OTS) treatment was performed on the gate dielectrics which were placed in a vacuum oven with OTS at a temperature of 120 °C for 3 hours to form an OTS self-assembled monolayer. Then the thin films were spin-coated on the OTS modified SiO<sub>2</sub>/Si substrates from the solutions. The OFETs devices were annealed at 80 °C, 120 °C, 160 °C, 180 °C, 200 °C, 220 °C, respectively, for 5 min in air, and measured after each annealing step at room temperature in air by using a Keithley 4200 Semiconductor Characterization System. The channel length (*L*) of the FET devices is 50 μm and the width (*W*) is 1400 μm. As contrast, the characteristics of as-prepared devices were also measured. The mobility of the devices was calculated in the saturation regime. The equation is listed as follows:

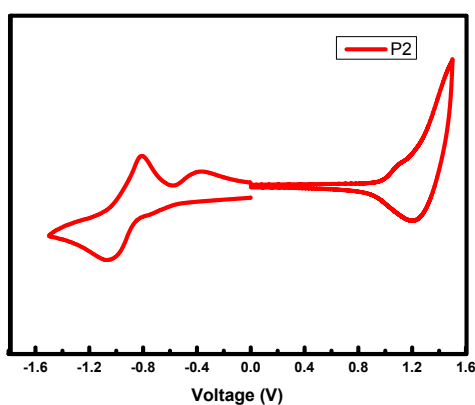
$$I_{DS} = (W / 2L) C_i \mu (V_{GS} - V_{th})^2$$

where *W/L* is the channel width / length, *C<sub>i</sub>* is the insulator capacitance per unit area, and *V<sub>GS</sub>* and *V<sub>th</sub>* are the gate voltage and threshold voltage, respectively.

## 2. Cyclic Voltammetry Curves of P1 and P2.



(a)



(b)

**Fig. S1** Cyclic voltammograms of polymers in CH<sub>3</sub>CN solution. (a) P1; (b) P2.

## References

- 1 J. D. Yuen, J. Fan, J. Seifert, B. Lim, R. Hufschmid, A. J. Heeger and F. Wudl, *J. Am. Chem. Soc.* 2011, **133**, 20799.
- 2 C. An, M. Li, T. Marszalek, D. Li, R. Berger, W. Pisula and M. Baumgarten, *Chem. Mater.* 2015, **26**, 5923