

Electronic Supplementary Information

All-thiophene-substituted N-heteroacene Electron-donor Materials for Efficient Organic Solar Cells

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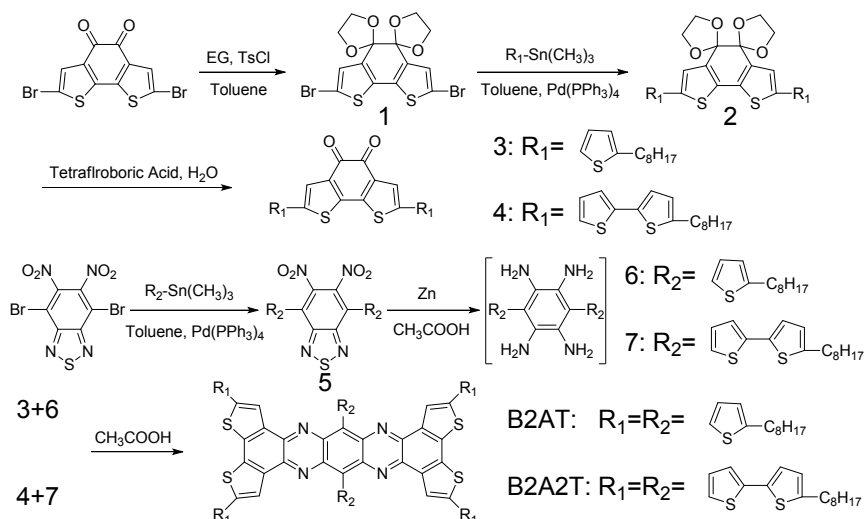
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1. Synthetic Procedures and Characterizations

1.1 General Methods

Chemicals were used as received unless otherwise indicated. Reaction solvents were distilled from Na and benzophenone under nitrogen immediately prior to use. ^1H and ^{13}C NMR spectra were recorded on Bruker 600 MHz spectrometer using CDCl_3 as the solvent and chemical shifts were reported as δ values (ppm) relative to an internal tetramethylsilane standard. Fourier transform mass spectra (FTMS) were recorded on a Bruker Apex Fourier transformation mass spectrometer.

1.2 General Procedures



Scheme S1 Synthesis of B2AT and B2A2T.

Compound 1. In a 250 mL, flame-dried, two necked, round-bottomed flask with a condenser, 2,7-dibromobenzo[1,2-b:6,5-b']dithiophene-4,5-dione (3.78 g, 10 mmol), catalytic amount of 4-toluene sulfonyl chloride, ethylene glycol (5.6 mL) and toluene (150 mL) were added. The mixture was heated to reflux for one day, then cooled to room temperature and dropped by water. The organic layer was washed successively by water and dried over anhydrous MgSO_4 . The solvent was evaporated. The bright-yellow product was purified by column chromatography (silica gel, dichloromethane) as eluent. Yield: 36.5%. ^1H NMR (600 MHz, CDCl_3): δ 7.14 (s, 2H), 4.11 (m, 4H), 3.61 (m, 4H). ^{13}C NMR (150 MHz, CDCl_3): δ 137.1, 133.9, 129.0, 111.8, 93.4, 67.2, 62.1. FTMS (APCI): found $m/z = 465.8433$, Calc. for $\text{C}_{14}\text{H}_{10}\text{Br}_2\text{O}_4\text{S}_2$: 465.84.

Compound 2 ($\text{R}_1 = \text{2-octylthiophen-2-yl}$). In a 250 mL, flame-dried, two necked, round-bottomed flask with a condenser, 1 (2.33 g, 5 mmol), trimethyl(5-octylthiophen-2-yl)stannane (5.34 g, 12.5 mmol), $\text{Pd}(\text{PPh}_3)_4$ (152 mg, 0.13 mmol), and anhydrous toluene (80 mL) were added. The mixture was purged with nitrogen gas and heated to reflux for 2 days, then cooled to room temperature. The solvent was evaporated. The orange product was purified by column chromatography (silica gel, petroleum ether : dichloromethane = 3 : 1) as eluent. Yield: 56.8%. ^1H NMR (600 MHz, CDCl_3): δ 7.16 (s, 2H), 7.02 (d, 2H), 6.72 (d, 2H), 4.18 (m, 4H), 3.68 (m, 4H), 2.82 (t, 4H), 1.69 (m, 4H), 1.4-1.3 (m, 20H), 0.93 (t, 6H). ^{13}C NMR (150 MHz, CDCl_3): δ 146.9, 137.4, 137.0, 134.6, 131.2, 125.6, 124.3, 121.7, 93.9, 62.2, 34.9, 33.2, 32.2, 32.1, 30.7, 29.3,

23.2, 14.4. FTMS (APCI): found $m/z = 696.2442$, Calc. for $C_{38}H_{48}O_4S_4$: 696.24.

Compound 2 ($R_1 = 5$ -octyl-2,2'-bithiophene). The compound has been prepared using the same synthetic process as for compound 2 ($R_1 = 2$ -octylthiophene). The yield of the orange product was 52.1%. 1H NMR (600 MHz, $CDCl_3$): δ 7.18 (s, 2H), 7.08-7.02 (m, 4H), 6.75 (m, 4H), 4.13 (m, 4H), 3.60 (m, 4H), 2.81 (t, 4H), 1.71 (m, 4H), 1.4-1.3 (m, 20H), 0.91 (t, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 146.7, 137.4, 137.0, 136.8, 134.6, 131.2, 130.6, 130.0, 129.5, 125.1, 124.1, 121.9, 93.6, 62.5, 34.5, 33.0, 32.6, 32.1, 30.6, 29.6, 23.6, 14.3. FTMS (APCI): found $m/z = 860.2198$, Calc. for $C_{46}H_{52}O_4S_6$: 860.22.

Compound 3. In a 100 mL, flame-dried, two necked, round-bottomed flask with a condenser, 2 ($R_1 = 2$ -octylthiophene) (860 mg, 1 mmol), dichloromethane (20 mL), THF (10 mL), and tetrafluoroboric acid (20 mL) were added. The mixture was stirred at room temperature for 2 days under nitrogen gas, then dropped by water. The organic layer was washed successively by water and dried over anhydrous $MgSO_4$. The solvent was evaporated. The orange product was purified by column chromatography (silica gel, dichloromethane) as eluent. Yield: 83.1%. 1H NMR (600 MHz, $CDCl_3$): δ 7.30 (s, 2H), 7.03 (d, 2H), 6.71 (d, 2H), 2.79 (t, 4H), 1.67 (m, 4H), 1.4-1.2 (m, 20H), 0.90 (t, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 174.6, 148.6, 141.5, 139.0, 136.2, 132.8, 125.8, 125.7, 122.1, 32.1, 32.0, 30.7, 30.2, 29.7, 29.3, 23.2, 14.4. FTMS (APCI): found $m/z = 608.1945$, Calc. for $C_{32}H_{40}O_4S_4$: 608.19.

Compound 4. The compound has been prepared using the same synthetic process as for compound 3. The yield of the orange product was 79.6%. 1H NMR (600 MHz, $CDCl_3$): δ 7.28 (s, 2H), 7.12-7.06 (m, 4H), 6.86 (m, 4H), 2.77 (t, 4H), 1.73 (m, 4H), 1.4-1.2 (m, 20H), 0.89 (t, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 173.8, 148.1, 141.9, 139.3, 138.6, 136.5, 136.3, 125.8, 124.5, 123.8, 122.1, 32.5, 32.2, 30.8, 30.1, 29.7, 29.2, 23.0, 14.1. FTMS (APCI): found $m/z = 772.1658$, Calc. for $C_{42}H_{44}O_2S_6$: 772.17.

Compound 5 ($R_2 = 2$ -octylthiophene). In a 250 mL, flame-dried, two necked, round-bottomed flask with a condenser, 4,7-dibromo-5,6-dinitrobenzo[*c*][1,2,5]-thiadiazole (3.82 g, 10 mmol), trimethyl(5-octylthiophen-2-yl)stannane (10.68 g, 25 mmol), $Pd(PPh_3)_4$ (305 mg, 0.26 mmol), and anhydrous toluene (150 mL) were added. The mixture was purged with nitrogen gas and heated to reflux for 2 days, then cooled to room temperature. The solvent was evaporated. The orange product was purified by column chromatography (silica gel, petroleum ether : toluene = 3 : 1) as eluent. Yield: 52.1%. 1H NMR (600 MHz, $CDCl_3$): δ 7.31 (d, 2H), 6.91 (d, 2H), 2.77 (t, 4H), 1.32-1.18 (m, 24H), 0.87(t, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 161.2, 143.1, 142.8, 135.3, 127.1, 126.4, 125.6, 39.2, 32.2, 31.7, 30.0, 29.6, 29.0, 22.7, 14.1. FTMS (APCI): found $m/z = 614.2056$, Calc. for $C_{30}H_{38}N_4O_4S_3$: 614.21.

Compound 5 ($R_2 = 5$ -octyl-2,2'-bithiophene). The compound has been prepared using the same synthetic process as for compound 5 ($R_2 = 2$ -octylthiophene). The yield of the orange product was 60.1%. 1H NMR (600 MHz, $CDCl_3$): δ 7.70-7.51 (m, 6H), 6.83 (d, 2H), 2.75 (t, 4H), 1.30-1.15 (m, 24H), 0.86(t, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 161.2, 144.3, 143.0, 138.1, 136.9, 136.1, 128.8, 125.6, 125.2, 124.1, 123.0, 39.1, 32.1, 31.1, 30.5, 29.9, 29.3, 22.5, 14.3. FTMS (APCI): found $m/z = 778.1802$, Calc. for $C_{38}H_{42}N_4O_4S_5$: 778.18.

Compound 6. In a 250 mL, flame-dried, two necked, round-bottomed flask with a condenser, compound 5 ($R_2 = 2$ -octylthiophene) (6.14 g, 10 mmol), Zn powder (500 mg), and acetic acid (150 mL) were added. The mixture was stirred at room temperature for one day under nitrogen gas, then dropped by water. The organic layer was washed successively by 5% aqueous solution of sodium bicarbonate, water and dried over anhydrous $MgSO_4$. The solvent was evaporated. The crude compound was used for next step without further purification.

Compound 7. The compound has been prepared using the same synthetic process as for Compound 6.

B2AT. In a 100 mL, flame-dried, two necked, round-bottomed flask with a condenser, 3 (121 mg, 0.2 mmol), 6 (52.6 mg, 0.1 mmol), and acetic acid (30 mL) were added. The mixture was purged with nitrogen gas and heated to reflux for 2 days, then cooled to room temperature and dropped by water. The organic layer was washed successively by 5% aqueous solution of sodium bicarbonate, water and dried over anhydrous $MgSO_4$. The solvent was evaporated. The black-red product was purified by column chromatography (silica gel, petroleum ether : dichloromethane = 1 : 1.5) as eluent. Yield: 41.1%. 1H NMR (600 MHz, $CDCl_3$): δ 7.70 (s, 4H), 7.44 (d, 4H), 7.31 (d, 2H), 6.83 (m, 6H), 2.73 (t, 12H), 1.26-1.11 (m, 72H), 0.94(t, 18H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 153.3, 143.6, 143.0, 142.3, 137.4, 137.0, 135.9, 130.1, 129.7, 126.9, 126.0, 123.4, 120.5, 39.1, 36.3, 31.7, 29.6, 29.4, 28.8, 22.2, 14.2. FTMS (APCI): found $m/z = 1670.6551$, Calc. for $C_{98}H_{118}N_4S_{10}$: 1670.66.

B2A2T. The compound has been prepared using the same synthetic process as for B2AT. The yield of the black-red product was 36.2%. 1H NMR (600 MHz, $CDCl_3$): δ 7.75-7.70 (m, 16H), 7.47 (s, 6H), 6.87 (d, 6H), 2.83 (t, 12H), 1.35-1.30 (m, 72H), 0.96(t, 18H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 151.5, 143.5, 143.0, 142.3, 138.5, 138.0, 137.1, 136.9, 130.4, 130.0, 128.8, 126.5, 125.0, 123.5, 120.8, 38.9, 36.0, 31.6, 29.7, 29.0, 26.73, 23.0, 14.2. FTMS (APCI): found $m/z = 2162.5842$, Calc. for $C_{122}H_{130}N_4S_{18}$: 2162.58.

2. Thermal Properties

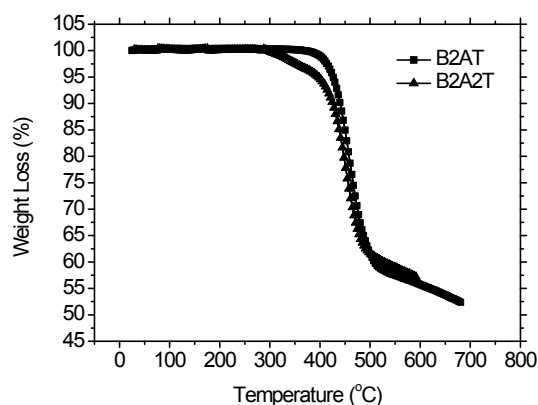


Fig. S1 TG curves of B2AT and B2A2T.

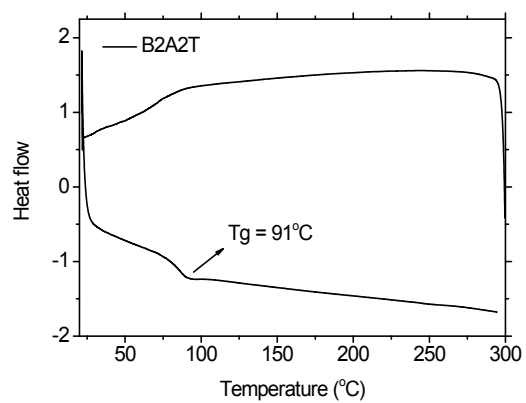
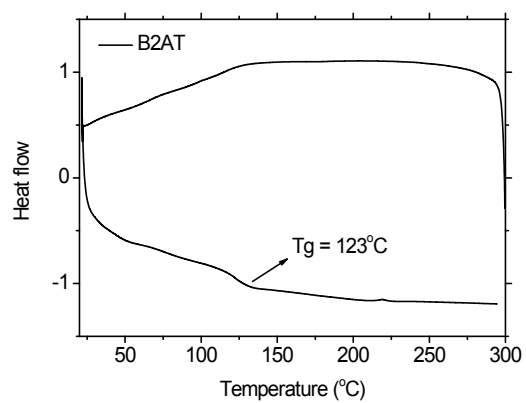


Fig. S2 DSC curves of B2AT (top) and B2A2T (bottom).