

Supporting Information

Synthesis, Properties, and FET Performance of Rectangular Oligothiophene

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Synthetic Procedure

Compound 3

THF (67 mL) and *n*-BuLi (1.6 M hexane solution, 21.2 mL, 33.9 mmol) was placed in a 500 mL three-necked round-bottomed flask. To the mixture was added a solution of compound **2** (6.03 g, 28.3 mmol) in THF (100 mL) at -78 °C. After stirring for 0.5 h at -78 °C, I₂ (10.8 g, 42.4 mmol) was added. The mixture was gradually warmed up to room temperature. After stirring for 12 h, the reaction was quenched by addition of sat. Na₂S₂O₃ aq., and the organic layer was separated. The aqueous layer was extracted with hexane, and the combined organic layer was washed with brine and dried over Na₂SO₄. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane) to give **3** (7.36 g, 99%).

Colorless oil; ¹H NMR (CDCl₃) δ 7.12 (t, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 5.5 Hz, 1H), 7.58 (d, *J* = 5.5 Hz, 1H), 7.70 (d, *J* = 7.4 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H); ¹³C NMR (CDCl₃) δ 87.4, 123.4, 125.3, 125.5, 126.6, 133.7, 139.1, 146.3; MS (EI) *m/z* 260 (M⁺); Anal. Calcd for C₈H₅IS: C, 36.94; H, 1.94; Found: C, 36.91; H, 1.91.

Compound 4

Compound **3** (4.08 g, 15.7 mmol) was placed in a 100 mL round-bottomed flask and dissolved with chloroform (16 mL) and acetic acid (16 mL). To the mixture was added NBS (3.49 g, 19.6 mmol) at 0 °C. The mixture was gradually warmed up to room temperature. After stirring for 12 h, to the mixture was added chloroform and washed with sat. Na₂S₂O₃ aq., sat. Na₂CO₃ aq. and water and dried over Na₂SO₄. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane) to give **4** (4.42 g, 83%).

White solid; Mp 77–79 °C; ¹H NMR (CDCl₃) δ 7.23 (t, *J* = 8.0 Hz, 1H), 7.54 (s, 1H), 7.78 (d, *J* = 7.5 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H); ¹³C NMR (CDCl₃) δ 87.9, 108.9, 122.9, 124.3, 126.2, 134.5, 137.4, 144.8; MS (EI) *m/z* 340 (M⁺); Anal. Calcd for C₈H₄BrIS: C, 28.34; H, 1.19; Found: C, 28.09; H, 0.94.

Compound 5

Compound **4** (6.57 g, 19.4 mmol), PdCl₂(PPh₃)₂ (408 mg, 0.582 mmol), and CuI (111 mg,

0.582 mmol) were placed in a 500 mL round-bottomed flask and dissolved with triethylamine (200 mL). To the mixture was added triisopropylsilylacetylene (8.61 mL, 28.8 mmol) at 0 °C. The mixture was gradually warmed up to room temperature. After stirring for 12 h, the reaction mixture was filtered through celite, which was washed with hexane. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane) to give **5** (7.62 g, 99%).

Colorless oil; ^1H NMR (CDCl_3) δ 1.18 (s, 21H) 7.43 (dd, $J = 7.5$ Hz, 8.0 Hz, 1H), 7.49 (s, 1H), 7.54–7.56 (m, 1H), 7.79 (dd, $J = 1.0$ Hz, 8.0 Hz, 1H); ^{13}C NMR (CDCl_3) δ 11.3, 18.7, 97.1, 103.1, 107.7, 118.2, 123.0, 124.3, 124.9, 128.6, 137.3, 141.7; MS (EI) m/z 394 (M^+); Anal. Calcd for $\text{C}_{19}\text{H}_{25}\text{BrSSi}$: C, 58.00; H, 6.40; Found: C, 57.72; H, 6.33.

Compound 6

Compound **5** (1.69 g, 4.31 mmol) and $\text{NiCl}_2(\text{dppp})$ (234 mg, 0.431 mmol) were placed in a 100 mL three-necked round-bottomed flask and dissolved with ether (20 mL). To the mixture was added the Grignard reagent freshly prepared from 1-bromodecane (4.44 mL, 21.6 mmol) and magnesium (576 mg, 23.7 mmol) in ether (15 mL) at 0 °C then gradually warmed up to reflux. After stirring for 12 h, the reaction mixture was cooled to 0 °C and added ice. The reaction mixture was filtered through celite, which was washed with hexane, and the organic layer was separated. The aqueous layer was extracted with hexane, and the combined organic layer was washed with brine and dried over Na_2SO_4 . After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane) to give **6** (1.68 g, 85%).

Colorless oil; ^1H NMR (CDCl_3) δ 0.88 (t, $J = 6.6$ Hz, 3H), 1.18 (s, 21H), 1.26–1.37 (m, 14H), 1.70–1.74 (m, 2H), 2.81 (t, $J = 7.6$ Hz, 2H), 7.11 (s, 1H), 7.33 (t, $J = 7.5$ Hz, 1H), 7.48 (d, $J = 7.3$ Hz, 1H), 7.70 (d, $J = 8.1$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 11.3, 14.1, 18.7, 22.7, 28.7, 29.3, 29.4, 29.5, 29.5, 29.6, 31.9, 95.7, 104.4, 118.2, 121.6, 121.9, 123.7, 127.5, 137.6, 138.9, 143.8; MS (EI) m/z 454 (M^+); Anal. Calcd for $\text{C}_{29}\text{H}_{46}\text{SSi}$: C, 76.58; H, 10.19; Found: C, 76.72; H, 10.29.

Compound 7

Compound **6** (1.58 g, 3.47 mmol) was placed in a 100 mL two-necked round-bottomed flask and dissolved with THF (35 mL). To the mixture was added *n*-BuLi (1.6 M hexane solution,

2.60 mL, 4.16 mmol) at $-78\text{ }^{\circ}\text{C}$. After stirring for 0.5 h at $-78\text{ }^{\circ}\text{C}$, I_2 (1.32 g, 5.20 mmol) was added. The mixture was gradually warmed up to room temperature. After stirring for 12 h, the reaction was quenched by addition of sat. $\text{Na}_2\text{S}_2\text{O}_3$ aq., and the organic layer was separated. The aqueous layer was extracted with hexane, and the combined organic layer was washed with brine and dried over Na_2SO_4 . After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane) to give **7** (2.00 g, 99%).

Colorless oil; ^1H NMR (CDCl_3) δ 0.88 (t, $J = 6.8$ Hz, 3H), 1.17 (s, 21H), 1.26–1.40 (m, 14H), 1.57–1.61 (m, 2H), 2.81 (t, $J = 7.6$ Hz, 2H), 7.27 (t, $J = 7.3$ Hz, 1H), 7.40 (dd, $J = 1.0$ Hz, 7.2 Hz, 1H), 7.63 (dd, $J = 0.9$ Hz, 8.2 Hz, 1H); ^{13}C NMR (CDCl_3) δ 11.3, 14.1, 18.7, 22.7, 29.3, 29.4, 29.5, 29.5, 29.6, 29.6, 30.7, 31.9, 80.9, 96.5, 103.8, 117.2, 121.5, 124.2, 127.7, 137.7, 142.2, 147.0; MS (EI) m/z 580 (M^+); Anal. Calcd for $\text{C}_{29}\text{H}_{45}\text{SSi}$: C, 59.98; H, 7.81; Found: C, 60.19; H, 7.74.

Compound 9

Compound **8** (2.34 g, 4.47 mmol), 2-tributylstannylthiophene (5.00 g, 13.4 mmol), and tetrakis(triphenylphosphine)palladium(0) (103 mg, 0.089 mmol) were placed in a 200 mL three-necked round-bottomed flask and dissolved with toluene (50 mL). The reaction mixture was stirred at $120\text{ }^{\circ}\text{C}$ for 12 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane) to give **9** (1.85 g, 78%).

Yellow oil; ^1H NMR (CDCl_3) δ 0.88 (t, $J = 6.8$ Hz, 6H), 1.26–1.43 (m, 28H), 1.54–1.60 (m, 4H), 2.68 (t, $J = 8.6$ Hz, 4H), 7.06 (dd, $J = 3.6$ Hz, 5.1 Hz, 2H), 7.13 (dd, $J = 1.2$ Hz, 3.6 Hz, 2H), 7.30 (dd, $J = 1.2$ Hz, 5.1 Hz, 2H); ^{13}C NMR (CDCl_3) δ 14.1, 22.7, 28.1, 29.3, 29.4, 29.6, 29.6, 29.9, 30.7, 31.9, 125.2, 125.8, 127.3, 129.8, 136.2, 140.0; MS (MALDI-TOF, 1,8,9-trihydroxyanthracene matrix) m/z 528.84 (M^+ , calcd 528.29); Anal. Calcd for $\text{C}_{32}\text{H}_{48}\text{S}_3$: C, 72.67; H, 9.15; N, 0.00; Found: C, 72.38; H, 8.87; N, 0.05.

Compounds 10 and 11

Compound **9** (1.28 g, 2.42 mmol) was placed in a 100 mL two-necked round-bottomed flask and dissolved with THF (30 mL). To the mixture was added $n\text{-BuLi}$ (1.6 M hexane solution, 1.51 mL, 2.42 mmol) at $-78\text{ }^{\circ}\text{C}$. After stirring for 0.5 h at $-78\text{ }^{\circ}\text{C}$, Me_3SnCl (1.0 M THF solution, 2.90 mL, 2.90 mmol) was added. The mixture was gradually warmed up to room

temperature. After stirring for 12 h, the reaction was quenched by addition of water, and the organic layer was separated. The aqueous layer was extracted with hexane, and the combined organic layer was washed with brine and dried over Na₂SO₄. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on alumina (hexane) followed by further purification with GPC (CHCl₃) to give **10** (1.11 g, 67%) and **11** (102 mg, 5%).

Compound **10**

Yellow oil; ¹H NMR (CDCl₃) δ 0.39 (s, 9H), 0.88 (t, *J* = 6.6 Hz, 6H), 1.23–1.45 (m, 28H), 1.52–1.63 (m, 4H), 2.65–2.72 (m, 4H), 7.06 (dd, *J* = 3.6 Hz, 5.1 Hz, 1H), 7.11–7.14 (m, 2H), 7.24 (d, *J* = 3.4 Hz, 1H), 7.30 (dd, *J* = 1.3 Hz, 5.1 Hz, 1H); ¹³C NMR (CDCl₃) δ –8.2, 14.1, 22.7, 28.1, 28.2, 29.3, 29.3, 29.4, 29.6, 29.6, 29.9, 30.7, 30.7, 31.9, 125.1, 125.6, 126.8, 127.3, 129.5, 130.1, 135.4, 136.3, 137.9, 139.6, 140.0, 141.9; MS (MALDI-TOF, 1,8,9-trihydroxyanthracene matrix) *m/z* 692.86 (M⁺, calcd 692.26).

Compound **11**

Yellow oil; ¹H NMR (CDCl₃) δ 0.39 (s, 9H), 0.88 (t, *J* = 6.6 Hz, 6H), 1.21–1.45 (m, 28H), 1.52–1.61 (m, 4H), 2.70 (t, *J* = 8.3 Hz, 4H), 7.13 (d, *J* = 3.4 Hz, 2H), 7.23 (d, *J* = 3.4 Hz, 2H); ¹³C NMR (CDCl₃) δ –8.2, 14.1, 22.7, 28.2, 29.3, 29.4, 29.6, 29.9, 30.7, 31.9, 126.7, 129.9, 135.4, 137.8, 139.6, 142.1; MS (MALDI-TOF, 1,8,9-trihydroxyanthracene matrix) *m/z* 854.83 (M⁺, calcd 854.22).

Compound **12**

Compound **7** (513 mg, 0.884 mmol), compound **10** (510 mg, 0.737 mmol), and tetrakis(triphenylphosphine)palladium(0) (85 mg, 0.074 mmol) were placed in a test tube and dissolved with toluene (10 mL). The reaction mixture was stirred at 120 °C for 12 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane) to give **12** (687 mg, 95%).

Yellow oil; ¹H NMR (CDCl₃) δ 0.82–0.91 (m, 9H), 1.19 (s, 21H), 1.21–1.50 (m, 42H), 1.55–1.73 (m, 6H), 2.68–2.77 (m, 4H), 3.04 (t, *J* = 7.6 Hz, 2H), 7.07 (dd, *J* = 3.7 Hz, 5.3 Hz, 1H), 7.13 (d, *J* = 3.8 Hz, 1H), 7.15 (dd, *J* = 1.2 Hz, 3.6 Hz, 1H), 7.24 (d, *J* = 3.8 Hz, 1H), 7.31–7.35 (m, 2H), 7.46 (dd, *J* = 1.2 Hz, 7.5 Hz, 1H), 7.66 (dd, *J* = 1.2 Hz, 7.9 Hz, 1H); ¹³C NMR (CDCl₃) δ 11.3, 14.1, 14.1, 18.7, 22.7, 22.7, 27.6, 28.1, 28.3, 29.3, 29.4, 29.4, 29.4, 29.5, 29.6, 29.6, 29.7, 29.7, 29.9, 30.0, 30.1, 30.8, 30.8, 31.9, 31.9, 96.1, 104.2, 117.5, 122.2, 124.3,

125.4, 125.9, 127.3, 128.0, 129.5, 130.2, 131.6, 133.7, 135.6, 136.1, 137.2, 140.2, 140.3, 140.5, 142.1; MS (MALDI-TOF, 1,8,9-trihydroxyanthracene matrix) m/z 981.23 (M^+ , calcd 980.59); Anal. Calcd for $C_{61}H_{92}S_4Si$: C, 74.63; H, 9.45; Found: C, 74.78; H, 9.39.

Compound 13

Compound **12** (933 mg, 0.950 mmol) was placed in a 50 mL two-necked round-bottomed flask and dissolved with THF (20 mL). To the mixture was added *n*-BuLi (1.6 M hexane solution, 0.89 mL, 1.43 mmol) at -78 °C. After stirring for 0.5 h at -78 °C, Me_3SnCl (1.0 M THF solution, 1.90 mL, 1.90 mmol) was added. The mixture was gradually warmed up to room temperature. After stirring for 12 h, the reaction was quenched by addition of water, and the organic layer was separated. The aqueous layer was extracted with hexane, and the combined organic layer was washed with brine and dried over Na_2SO_4 . After removal of the solvent under reduced pressure, the residue was purified by column chromatography on alumina (hexane) to give **13** (1.02 g, 94%).

Yellow oil; 1H NMR ($CDCl_3$) δ 0.40 (s, 9H), 0.83–0.90 (m, 9H), 1.15–1.50 (m, 63H), 1.55–1.75 (m, 6H), 2.66–2.80 (m, 4H), 3.04 (t, $J = 7.6$ Hz, 2H), 7.13 (d, $J = 3.6$ Hz, 1H), 7.14 (d, $J = 3.3$ Hz, 1H), 7.23 (d, $J = 3.6$ Hz, 1H), 7.26 (d, $J = 3.3$ Hz, 1H), 7.33 (t, $J = 7.7$ Hz, 1H), 7.45 (d, $J = 7.3$ Hz, 1H), 7.65 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ –8.2, 11.3, 14.1, 14.1, 18.7, 22.7, 27.6, 28.2, 28.4, 29.3, 29.4, 29.4, 29.5, 29.6, 29.7, 29.9, 30.0, 30.1, 30.7, 31.9, 96.1, 104.2, 117.5, 122.2, 124.3, 125.8, 126.9, 127.3, 127.9, 129.2, 130.6, 131.7, 133.6, 135.4, 135.5, 137.4, 138.2, 139.8, 140.4, 140.5, 141.8, 142.1; MS (MALDI-TOF, 1,8,9-trihydroxyanthracene matrix) m/z 1144.96 (M^+ , calcd 1144.55).

Compound 14

Compound **7** (486 mg, 0.806 mmol) was placed in a 50 mL round-bottomed flask and dissolved with THF (10 mL). To the mixture was added TBAF (1.0 M THF solution, 1.30 mL, 1.30 mmol), and the mixture was stirred at room temperature for 30 min. The reaction was quenched by addition of sat. $NaHCO_3$ aq, and the organic layer was separated. The aqueous layer was extracted with hexane, and the combined organic layer was washed with brine and dried over Na_2SO_4 . After removal of the solvent under reduced pressure, the residue was used for the next reaction without further purification.

The residue, Cu(OAc)₂ (1.37 g, 7.52 mmol) and TMEDA (1.13 mL, 7.52 mmol) were placed in a 50 mL round-bottom flask and dissolved with THF (10 mL). The reaction mixture was stirred at 80 °C for 12 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane) to give **14** (177 mg, 52%).

White solid; Mp 138–140 °C; ¹H NMR (CDCl₃) δ 0.88 (t, *J* = 7.1 Hz, 6H), 1.22–1.50 (m, 28H), 1.56–1.68 (m, 4H), 2.83 (t, *J* = 7.8 Hz, 4H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.51 (d, *J* = 7.6 Hz, 2H), 7.71 (d, *J* = 8.3 Hz, 2H); ¹³C NMR (CDCl₃) δ 14.0, 22.7, 29.3, 29.3, 29.5, 29.6, 29.6, 30.8, 31.9, 78.7, 80.4, 80.9, 115.5, 122.5, 124.4, 128.9, 138.2, 142.3, 147.6; MS (EI) *m/z* 846 (M⁺); Anal. Calcd for C₄₀H₄₈I₂S₂: C, 56.74; H, 5.71; Found: C, 57.12; H, 5.60.

Compound 15

Compound **13** (182 mg, 0.159 mmol), Compound **14** (56 mg, 0.066 mmol), and tetrakis(triphenylphosphine)palladium(0) (15 mg, 0.013 mmol) were placed in a test tube and dissolved with toluene (5 mL). The reaction mixture was stirred at 120 °C for 12 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (19:1 hexane/CH₂Cl₂) to give **15** (152 mg, 90%).

Orange oil; ¹H NMR (CDCl₃) δ 0.83–0.87 (m, 24H), 1.19–1.55 (m, 154H), 1.57–1.80 (m, 16H), 2.71–2.80 (m, 8H), 3.02–3.11 (m, 8H), 7.15–7.17 (m, 4H), 7.24 (d, *J* = 3.7 Hz, 2H), 7.30 (d, *J* = 3.7 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 2H), 7.39 (t, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 7.3 Hz, 2H), 7.58 (d, *J* = 7.3 Hz, 2H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 8.1 Hz, 2H); ¹³C NMR (CDCl₃) δ 11.3, 11.4, 14.1, 18.7, 18.9, 22.7, 27.6, 27.7, 28.3, 29.4, 29.5, 29.7, 29.9, 30.0, 30.1, 30.1, 30.8, 30.8, 31.9, 78.4, 80.6, 96.1, 104.2, 115.6, 117.5, 122.2, 123.1, 124.3, 124.5, 126.1, 126.1, 127.4, 127.5, 128.0, 129.2, 129.8, 129.9, 131.6, 132.0, 133.5, 133.7, 135.5, 135.8, 137.1, 137.3, 140.4, 140.5, 140.6, 140.8, 142.1, 142.3; MS (MALDI-TOF, 1,8,9-trihydroxyanthracene matrix) *m/z* 2554.14 (M⁺, calcd 2553.48); Anal. Calcd for C₁₆₂H₂₃₀S₁₀Si₂: C, 76.17; H, 9.08; Found: C, 76.10; H, 9.03.

Compound 17

Compound **16** (407 mg, 1.48 mmol) was placed in a 50 mL two-necked round-bottomed flask and dissolved with THF (15 mL). To the mixture was added *n*-BuLi (1.6 M hexane solution, 1.11 mL, 1.78 mmol) at –78 °C. After stirring for 0.5 h at –78 °C, I₂ (563 mg, 2.22 mmol) was

added. The mixture was gradually warmed up to room temperature. After stirring for 12 h, the reaction was quenched by addition of sat. Na₂S₂O₃ aq., and the organic layer was separated. The aqueous layer was extracted with hexane, and the combined organic layer was washed with brine and dried over Na₂SO₄. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane) to give **17** (531 mg, 90%).

Colorless oil; ¹H NMR (CDCl₃) δ 0.88 (t, *J* = 6.6 Hz, 3H), 1.22–1.45 (m, 14H), 1.50–1.63 (m, 2H), 2.83 (t, *J* = 7.8 Hz, 2H), 7.24–7.34 (m, 2H), 7.69 (d, *J* = 7.2 Hz, 1H), 7.74 (d, *J* = 7.2 Hz, 1H); ¹³C NMR (CDCl₃) δ 14.1, 22.7, 29.2, 29.3, 29.5, 29.6, 29.6, 30.5, 31.9, 79.7, 121.5, 121.6, 124.1, 124.2, 137.9, 141.7, 143.9; MS (EI) *m/z* 400 (M⁺); Anal. Calcd for C₁₈H₂₅IS: C, 54.00; H, 6.29; Found: C, 54.03; H, 6.28.

Compound 18

Compound **17** (297 mg, 0.741 mmol), compound **11** (211 mg, 0.247 mmol), and tetrakis(triphenylphosphine)palladium(0) (57 mg, 0.049 mmol) were placed in a test tube and dissolved with toluene (5 mL). The reaction mixture was stirred at 120 °C for 12 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane) to give **18** (166 mg, 63%).

Orange solid; Mp 107–109 °C; ¹H NMR (CDCl₃) δ 0.80–0.89 (m, 12H), 1.18–1.40 (m, 48H), 1.40–1.48 (m, 8H), 1.55–1.63 (m, 4H), 1.63–1.76 (m, 4H), 2.76 (t, *J* = 8.0 Hz, 4H), 3.05 (t, *J* = 8.1 Hz, 4H), 7.13 (d, *J* = 3.9 Hz, 2H), 7.20 (d, *J* = 3.9 Hz, 2H), 7.28–7.38 (m, 4H), 7.69 (d, *J* = 7.7 Hz, 2H), 7.76 (d, *J* = 7.2 Hz, 2H); ¹³C NMR (CDCl₃) δ 14.1, 22.7, 27.6, 28.3, 29.4, 29.4, 29.5, 29.7, 30.0, 30.8, 31.9, 31.9, 122.0, 122.1, 124.2, 124.6, 126.0, 127.0, 129.9, 130.8, 133.4, 136.0, 136.9, 138.8, 140.4, 140.8; MS (MALDI-TOF, 1,8,9-trihydroxyanthracene matrix) *m/z* 1073.51 (M⁺, calcd 1072.61); Anal. Calcd for C₆₈H₉₆S₅: C, 76.06; H, 9.01; Found: C, 76.01; H, 9.16.

Compound 19

Compound **6** (511 mg, 1.12 mmol) was placed in a 100 mL round-bottomed flask and dissolved with THF (20 mL). To the mixture was added TBAF (1.0 M THF solution, 2.24 mL, 2.24 mmol), and the mixture was stirred at room temperature for 30 min. The reaction was quenched by addition of sat. NaHCO₃ aq, and the organic layer was separated. The aqueous layer was

extracted with hexane, and the combined organic layer was washed with brine and dried over Na_2SO_4 . After removal of the solvent under reduced pressure, the residue was used for the next reaction without further purification.

The residue and $\text{Cu}(\text{OAc})_2$ (2.03 g, 11.2 mmol) were placed in a 100 mL round-bottom flask and dissolved with pyridine (20 mL). The reaction mixture was stirred at 80 °C for 12 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane) to give **19** (290 mg, 87%).

White solid; Mp 63–64 °C; ^1H NMR (CDCl_3) δ 0.88 (t, $J = 7.1$ Hz, 6H), 1.23–1.48 (m, 28H), 1.72–1.80 (m, 4H), 2.83 (t, $J = 7.8$ Hz, 4H), 7.16 (s, 2H), 7.38 (t, $J = 7.3$ Hz, 2H), 7.59 (d, $J = 7.2$ Hz, 2H), 7.77 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 14.1, 22.7, 28.6, 29.1, 29.3, 29.5, 29.5, 29.6, 31.9, 78.2, 80.6, 116.3, 121.7, 122.8, 123.8, 128.9, 137.6, 139.2, 143.9; MS (EI) m/z 594 (M^+); Anal. Calcd for $\text{C}_{40}\text{H}_{50}\text{S}_2$: C, 80.75; H, 8.47; Found: C, 80.60; H, 8.58.

DSC Thermograms

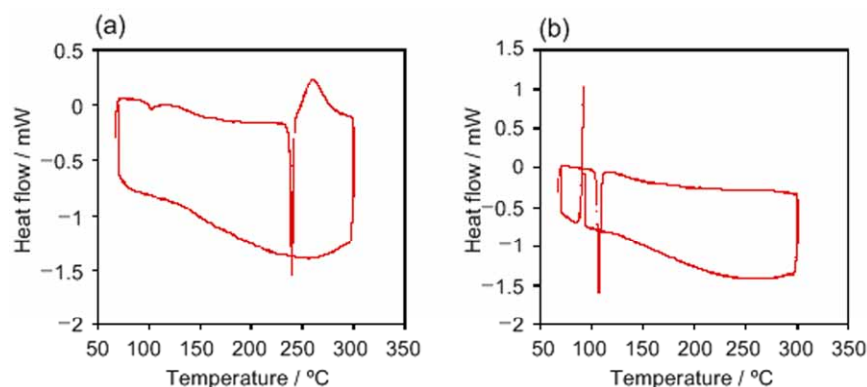


Fig. S1 DSCs of **1** (a) and **18** (b).

X-ray Diffractograms

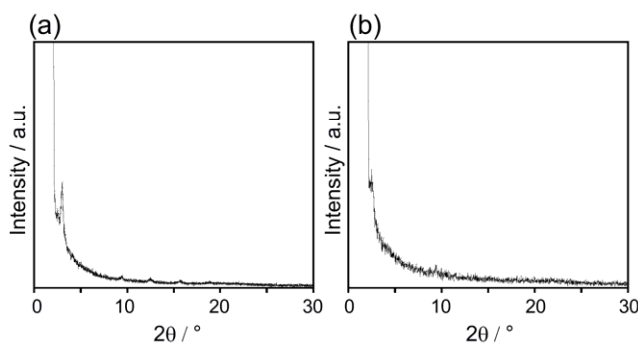


Fig. S2 X-ray diffractions of the **1(a)** and **18 (b)** films for FET device before annealing.