Supporting Information

REDOX RESPONSIVE POLYMER INCORPORATED WITH MESOGENIC UNIT AND BIS(BENZODITHIOLYL)BITHIENYL SCAFFOLD

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Table of Contents

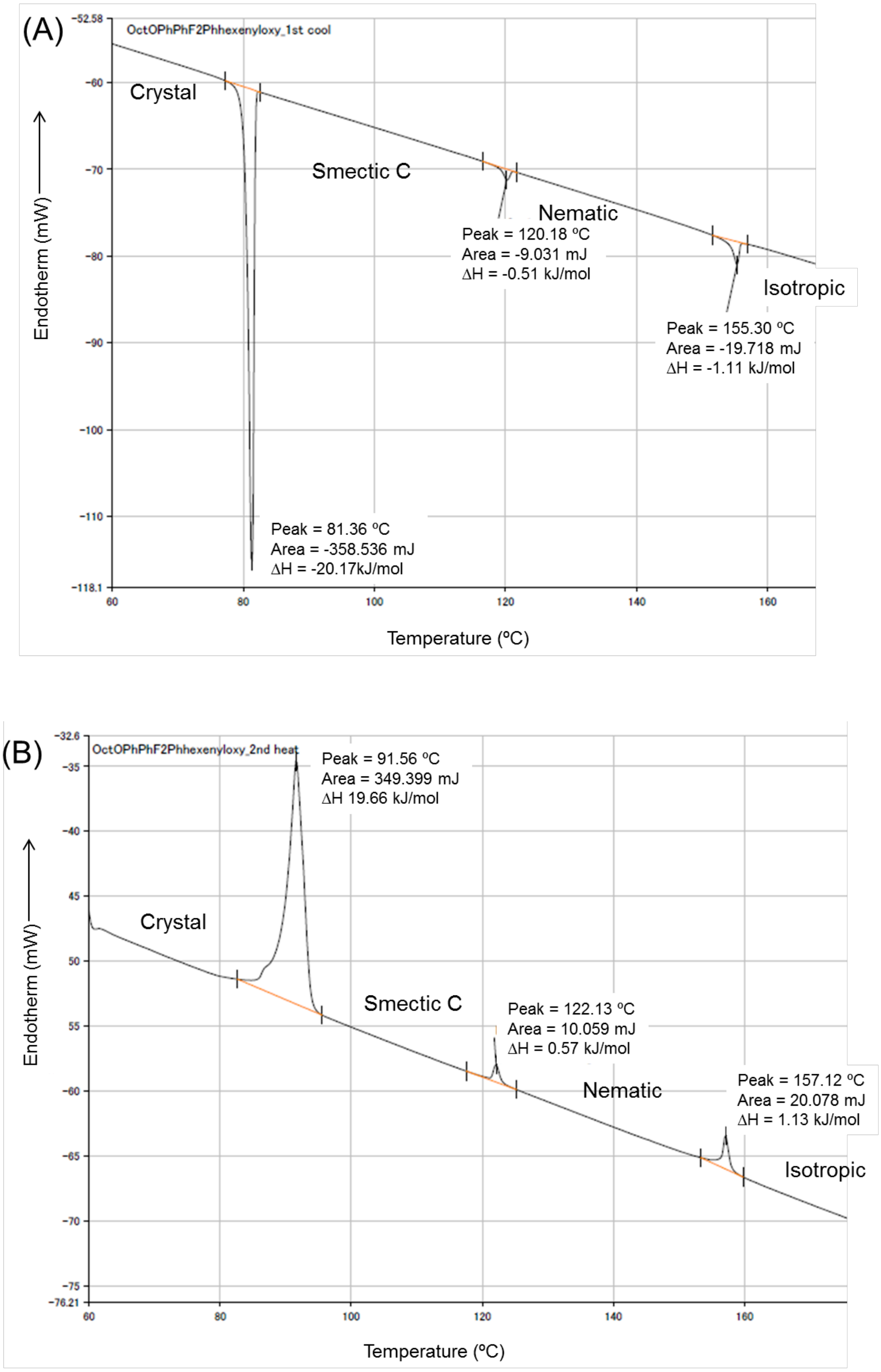


Figure S1. DSC thermograms of **1.** (A) 1st cooling and (B) 2nd heating (rate: 10 ^{o}C/min).

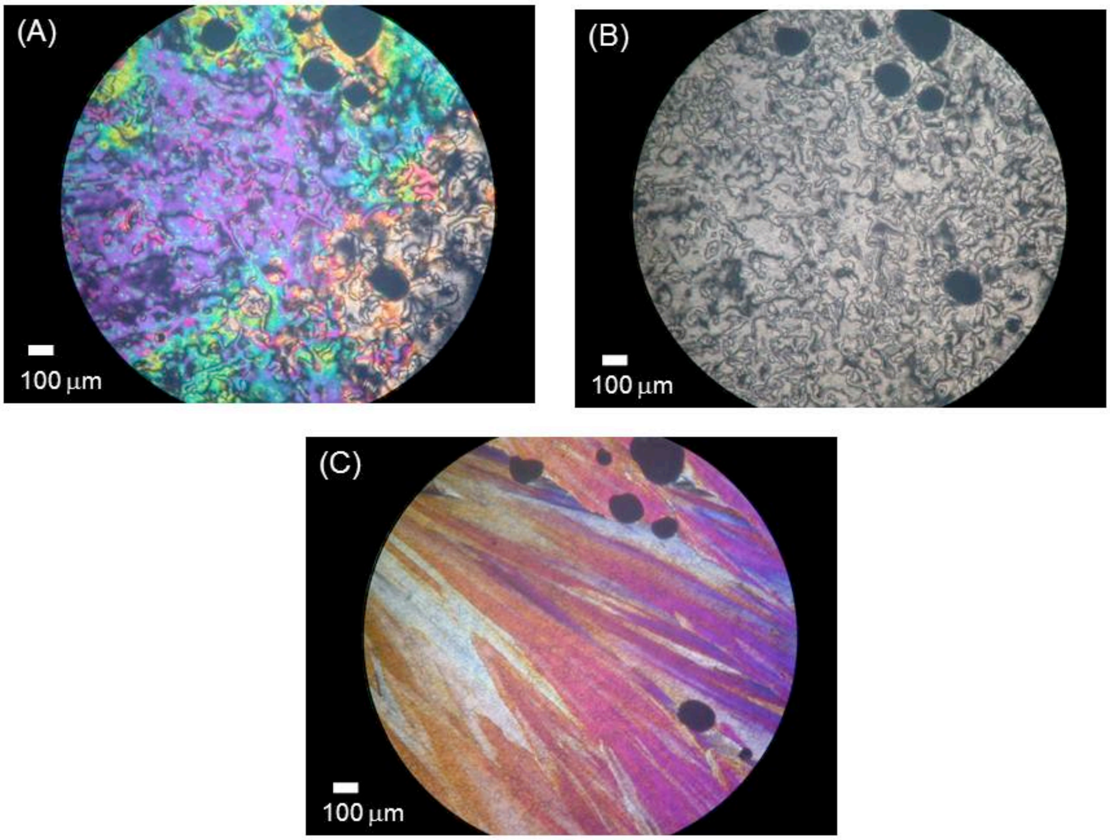


Figure S2. Polarized photomicrographs of **1** in (A) nematic phase at 145 °C, (B) smectic C phase at 115 °C, and (C) crystalline phase at 80 °C on cooling.

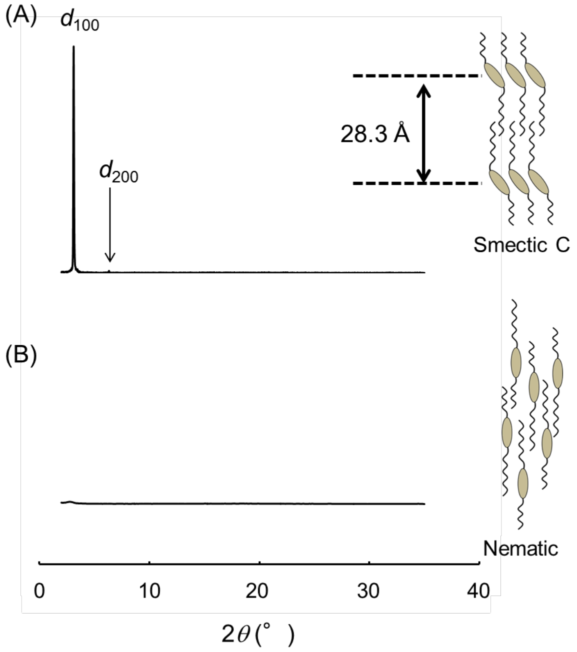


Figure S3. X-ray diffraction patterns for **1** at (A) 98 °C and (B) 142 °C during cooling. The insets illustrate the possible packing structures of each liquid-crystalline phase.

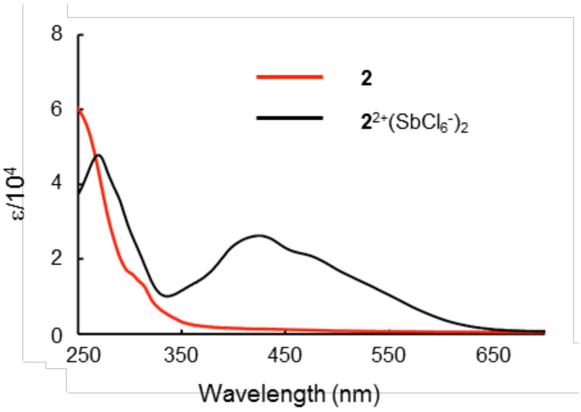


Figure S4. UV spectra of **2** and $\mathbf{2}^{2+}(\mathrm{SbCl_6^-})_2$ in CH_2Cl_2.

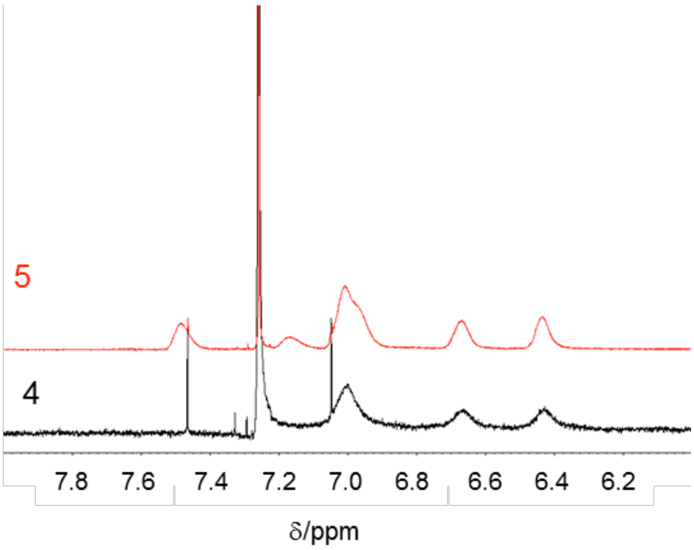


Figure S5. NMR spectra of **4** and **5**.

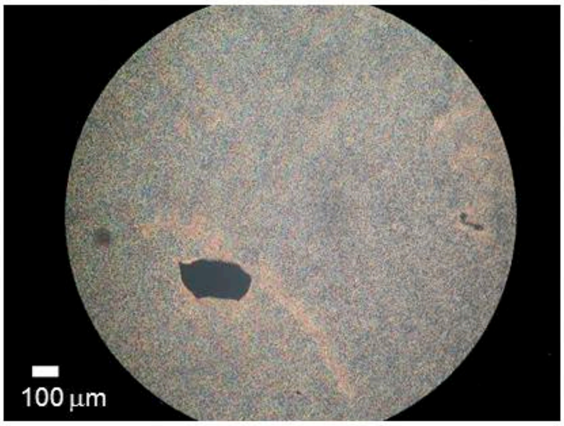
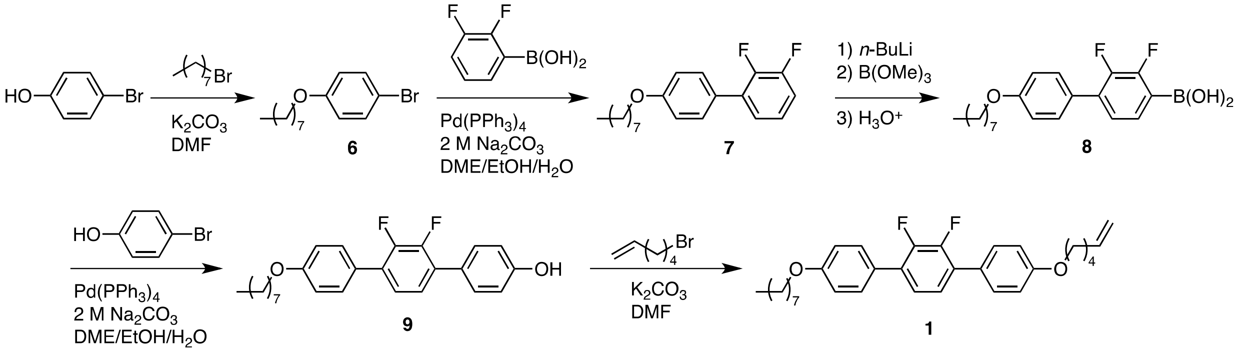


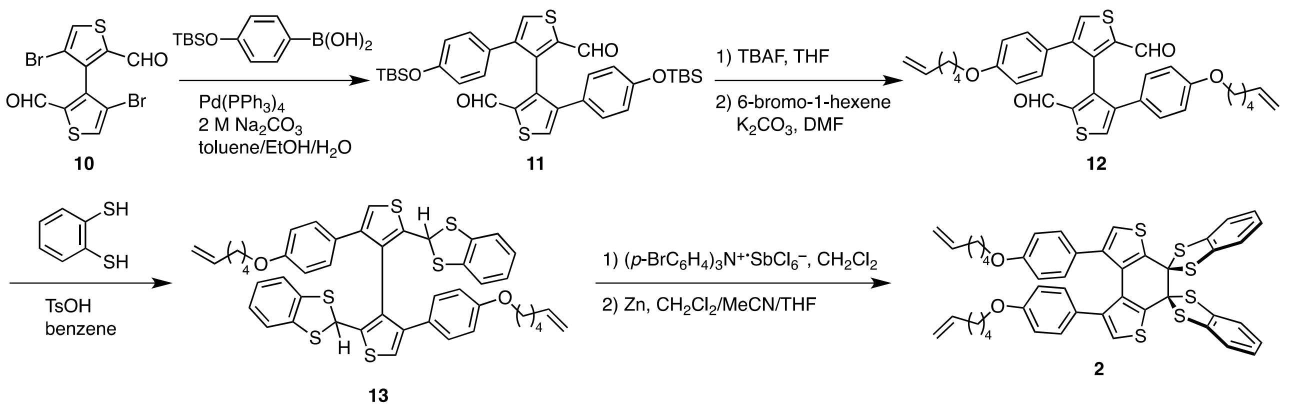
Figure S6. Polarized photomicrograph of **14** in smectic A phase at 106 °C on cooling scan.

Synthesis

General Procedures. Unless otherwise noted, all reactions were run under nitrogen atmosphere. The ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 (^{1}H: 400 MHz; ^{13}C: 100 MHz) or a JEOL ECA500 (^{1}H: 500 MHz; ^{13}C: 125 MHz) spectrometer. Chemical shifts are in parts per million (ppm) using either the solvent's residual protons or TMS employed as the internal standard. High-resolution mass spectra were measured on a Waters Xevo G2-Q Tof or a JEOL JMS-777V. Melting points were measured on a Yanagimoto hot stage melting point apparatus and are uncorrected. For mesomorphic compounds, DSC measurements were carried out on a Q1000 (TA Instruments) to determine phase transition temperatures. Heating and cooling rates were 10 °C/min. The transition temperatures were determined by the maximum of exothermic and minimum point of endothermic peaks, respectively. A polarizing microscope (Olympus BX-51) equipped with hot stage (Mettler FP82HT) and crossed polarizers were used for visual observation of mesophases. The following abbreviations are used to describe the phase transition behaviors. G: glassy; Cr: crystal; N: nematic; S_A: smectic A; S_C: smectic C; I: isotropic liquid. The syntheses of **1** and **2** were carried out as shown in Scheme S1 and S2, respectively. The morphologies of polymer gel **4** were evaluated on a scanning electron microscope (SEM) (Hitachi S-4800). UV spectra were recorded on a Shimadzu UV 2550 spectrometer. Cyclic voltammetry was carried out in a three-compartment cell and cyclic voltammograms were recorded with a BAS ALS 610D electrochemical analyzer.



Scheme S1. Synthesis of **1**.



Scheme S2. Synthesis of **2**.

Octyloxy-1-bromobenzene (6).[1] The mixture of 1-bromooctane (15.5 g, 80.1 mmol), 4-bromophenol (11.4 g, 65.6 mmol), and K_2CO_3 (20.3 g, 147 mmol) in acetone (170 mL) was stirred and heated to reflux for 19 h. To the reaction mixture added water and CH_2Cl_2. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 three times. The combined organic extracts were washed with water and brine, dried over Na_2SO_4, and filtered. The solvent was evaporated and the crude product was distilled to yield **6** (12.6 g, 44.1 mmol): yield 67%; colorless liquid; bp 144–149 °C (0.03 mmHg); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.0 Hz 3H), 1.25–1.47 (m, 10H), 1.72–1.79 (m, 2H), 3.90 (t, *J* = 6.6 Hz, 2H), 6.74–6.78 (AA'BB', 2H), 7.33–7.37 (AA'BB', 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2 (s), 22.8 (s), 26.1 (s), 29.3 (s), 29.4 (s), 29.5 (s), 32.0 (s), 68.4 (s), 112.7 (s), 116.4 (s), 132.3 (s), 158.4 (s); HR-MS (APCI) $C_{14}H_{22}BrO$ $[M+H]^+$ calcd *m/z* 285.0854, found *m/z* 285.0849.

2,3-Difluoro-4-(4-octyloxyphenyl)benzene (7). A suspension of $Pd(PPh_3)_4$ (0.35 g, 0.30 mmol) and **6** (2.87 g, 10.1 mmol) in DME (30 mL) was stirred at room temperature for 10 min. To this suspension were added subsequently a solution of 2, 3-difluorophenylboronic acid (1.74 g, 11.0 mmol) in ethanol (10 mL) and aqueous Na_2CO_3 (2 M solution, 10 mL, 20 mmol). The mixture was heated to reflux for 16 h, cooled to room temperature, and extracted with CH_2Cl_2 three times. The combined extracts were washed with water and brine, dried over Na_2SO_4, and filtered. The solvent was evaporated and the residue was purified by column chromatography (silica gel, eluent: hexane followed by hexane/ethyl acetate = 10/1) to afford **7** (2.96 g, 9.30 mmol): yield 92%; white solid; mp 31–32 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.9 Hz, 3H), 1.29–1.49 (m, 10 H), 1.77-1.82 (m, 2H), 3.98 (t, *J* = 6.6 Hz, 2H), 6.94–6.97 (AA'BB', 2H), 7.04–7.16 (m, 3H), 7.44–7.47 (AA'BB', 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.3 (s), 22.8 (s), 26.2 (s), 29.4 (s), 29.5 (s), 32.0 (s), 60.5 (s), 68.2 (s), 114.7 (s), 115.5 (d, *J* = 17 Hz), 124.0 (dd, *J* = 7.2 Hz, 4.7 Hz), 125.1 (s), 126.9 (s), 130.12 (s), 130.2 (s), 131.1 (d, *J* = 9.5 Hz), 148.0 (dd, *J* = 247 Hz, 13 Hz), 151.3 (dd, *J* = 247 Hz, 14 Hz), 159.3 (s); IR (KBr) 781, 837, 895, 1095, 1256, 1411, 1469, 1519, 1610, 2855, 2920 cm^{-1}; HR-MS (APCI) $C_{20}H_{24}F_2O$ $[M]^+$ calcd *m/z* 318.1795, found *m/z* 318.1790.

2,3-difluoro-4-(4-octyloxyphenyl)phenylboronic acid (8).[2] A solution of **7** (2.71 g, 8.51 mmol) in THF (40 mL) was stirred at –78 °C. BuLi (1.65 M in hexane, 6.2 mL, 10.2 mmol) was added dropwise to the solution. The reaction mixture was stirred at the same condition for 2.5 h, then trimethyl borate (3.00 g, 26.9 mol) was added to the mixture. The mixture was allowed to warm to room temperature overnight and quenched with 3 M HCl solution (20 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 three times. The combined organic extracts were washed with water and brine, dried over Na_2SO_4, and filtered. The solvent was evaporated and the residue was purified by column chromatography (silica gel, eluent: CH_2Cl_2 followed by CH_2Cl_2/MeOH = 10/1) to give **8** (2.64 g, 7.30 mmol): yield 86%; white solid; mp 123–124 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.9 Hz, 3H), 1.29–1.39 (m, 8H), 1.44–1.50 (m, 2H), 1.78-1.83 (m, 2H), 4.00 (t, *J* = 6.3 Hz, 2H), 6.96–6.99 (AA'BB', 2H), 7.18–7.21 (m, 1H), 7.48–7.52 (m, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 13.9 (s), 22.2 (s), 25.6 (s), 28.76 (s), 28.80 (s), 28.9 (s), 31.4 (s), 67.5 (s), 114.6 (s), 124.3 (s), 126.1 (d, *J* = 12 Hz), 129.7 (dd, *J* = 8.3 Hz, 4.7 Hz), 129.9 (d, *J* = 2 Hz), 131.1 (d, *J* = 10 Hz), 146.9 (dd, *J* = 247 Hz, 16 Hz), 153.5 (dd, *J* = 248 Hz, 13 Hz), 158.85 (s), 158.88 (s); IR (KBr) 822, 916, 1031, 1259, 1371, 1406, 1521, 1609, 2855, 2935, 3373 cm^{-1}.

1-Hydroxy-4-[2,3-difluoro-4-(4-octyloxyphenyl)phenyl]benzene (9). The experimental procedure was as described for the preparation of **7**. Quantities: **8** (1.81 g, 5.00 mmol), 4-bromophenol (0.728 g, 4.21 mmol), $Pd(PPh_3)_4$ (0.173 g, 0.15 mmol), 2 M Na_2CO_3 aq. (5 mL, 10.0 mmol), and DME (30 mL). The crude product was purified by column chromatography (silica gel, eluent: hexane/ethyl acetate = 6/1 followed by 4/1) to give **9** (1.28 g, 3.11 mmol): yield 74%; white powder; phase transition temperature /°C (DSC on 2nd heating): Cr 183 S_A 194 I; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 7.2 Hz 3H), 1.25–1.38 (m, 8H), 1.45–1.51 (m, 2H), 1.78–1.84 (m, 2H), 4.01 (t, *J* = 6.6 Hz, 2H), 4.78 (s, 1H), 6.91–6.94 (AA'BB', 2H), 6.97–7.00 (AA'BB', 2H), 7.18-7.21 (m, 2H), 7.46–7.52 (m, 4H); ^{13}C NMR (125 MHz, DMSO-d_6): δ =14.0 (s), 22.1 (s), 25.5 (s), 28.66

(s), 28.70 (s), 28.8 (s), 31.3 (s), 67.5 (s), 114.7 (s), 115.6 (s), 124.4 (s), 124.59 (s), 124.62 (s), 125.9 (s), 127.9 (d, $J = 6$ Hz), 128.6 (d, $J = 8$ Hz), 129.82 (s), 129.83 (s), 147.5 (dd, $J = 8$ Hz, 248 Hz), 147.6 (dd, $J = 8$ Hz, 248 Hz), 157.67 (s), 158.71 (s); IR (KBr) 811, 1251, 1461, 1489, 1527, 1611, 2853, 2920, 3469 cm^{-1}; HR-MS (APCI) $C_{26}H_{29}F_2O_2$ [M+H]$^+$ calcd *m/z* 411.2136, found *m/z* 411.2132.

Compound 1. The experimental procedure was as described for the preparation of **6**. Quantities: **9** (411 mg, 1.00 mmol), 1-bromo-6-hexene (195 mg, 1.20 mmol), K_2CO_3 (276 mg, 2.00 mmol). The crude product was purified by column chromatography (silica gel, eluent: hexane/ethyl acetate = 8/1) to give **1** (403 mg, 0.82 mmol): yield 82%; white waxy solid; phase transition temperature /°C (DSC on 1st cooling): I 155 N 120 S_C 81 Cr; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.89$ (t, $J = 6.9$ Hz 3H), 1.25–1.38 (m, 8H), 1.45–1.50 (m, 2H), 1.57–1.63 (m, 2H), 1.78–1.86 (m, 4H), 2.13–2.17 (m, 2H), 3.99–4.03 (m, 4H), 4.98 (dd, $^3J_{cis} = 10$ Hz, $^2J_{gem} = 1.1$ Hz, 1H), 5.05 (dd, $^3J_{trans} = 17$ Hz, $^2J_{gem} = 1.1$ Hz, 1H), 5.80–5.88 (m, 1H), 6.97–7.00 (AA'BB', 4H), 7.19-7.20 (m, 2H), 7.49–7.52 (AA'BB', 4H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 14.3$ (s), 22.8 (s), 25.5 (s), 26.2 (s), 28.9 (s), 29.4 (s), 29.5 (s), 32.0 (s), 33.6 (s), 68.0 (s), 68.2 (s), 114.7 (s), 114.9 (s), 124.41 (s), 124.43 (s), 124.5 (s), 126.97 (s), 127.04 (s), 128.96 (s), 129.04 (s), 130.1 (s), 138.6 (s), 148.6 (dd, $J = 248$ Hz, 16 Hz), 159.2 (s), 159.3 (s); IR (KBr) 813, 905, 1253, 1458, 1525, 1609, 2855, 2935 cm^{-1}; HR-MS (APCI) $C_{32}H_{38}F_2O_2$ [M]$^+$ calcd *m/z* 492.2840, found *m/z* 492.2839.

2,2'-diformyl-4,4'-bis(4- *tert*-butyldimethylsilyloxyphenyl)-3,3'-bithienyl (11). The experimental procedure was as described for the synthesis of **7** except that toluene was used as a solvent. Quantities: **10**[3,4] (2.17 g, 5.72 mmol), $Pd(PPh_3)_4$ (396 mg, 343 μmol), 4-*tert*-butyldimehylsilyloxyphenyl boronic acid (3.49 g, 13.9 mmol), K_2CO_3 (2.3 M solution, 25 mL, 57.5 mmol). The crude product was purified by column chromatography (silica gel, eluent: hexane/ethyl acetate = 8/1) to give **11** (1.41 g, 2.22 mmol): yield 39%; light yellow solid; mp 207–208 °C; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 0.18$ (s, 12H), 0.97 (s, 18H), 6.60–6.63 (AA'BB', 4H), 6.68–6.71 (AA'BB', 4H), 7.65 (d, $J = 1.2$ Hz, 2H), 9.62 (d, $J = 1.2$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = -4.3$ (s), 18.4 (s), 25.8 (s), 120.3 (s), 127.1 (s), 129.3 (s), 131.2 (s), 140.3 (s), 142.2 (s), 145.0 (s), 155.7 (s), 183.1 (s); IR (KBr) 672, 792, 840, 913, 1521, 1667, 2857, 2940 cm^{-1}; HR-MS (APCI) $C_{34}H_{43}O_4S_2Si_2$ $[M+H]^+$ calcd m/z 635.2141, found m/z 635.2131.

2,2'-diformyl-4,4'-bis(4-hexenyloxyphenyl)-3,3'-bithienyl (12). To a solution of **11** (1.24 g, 1.96 mmol) in THF (50 mL) was added tetrabutylammonium fluoride (1 M in THF, 20 mL, 20 mmol). After stirring at room temperature for 1 h, the reaction mixture was treated with 2 M HCl aq. (60 mL) and extracted with ethyl acetate. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated. Then, the crude product was dissolved in DMF (30 mL). 1-Bromo-6-hexene (756 mg, 4.64 mmol) and K_2CO_3 (1.83 g, 13.2 mmol) were added to the solution. After stirring the mixture at 85 °C for 23 h, the resulting mixture was diluted with $CHCl_3$, washed with water and brine, dried over Na_2SO_4, filtered and concentrated. The crude product was purified by column chromatography (silica gel, eluent: hexane/ethyl acetate = 8/1) to give **12**(1.05 g, 1.83 mmol): yield

93%; yellow waxy solid; mp 96–98 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.53–1.59 (m, 4H), 1.75–1.81 (m, 4H), 2.10–2.15 (m, 4H), 3.91 (t, *J* = 6.3 Hz, 4H), 4.97 (dd, *J* = 10.3 Hz, 1.7 Hz, 2H), 5.03 (dd, *J* = 17.2 Hz, 1.7 Hz, 2H), 5.78–5.86 (m, 2H), 6.67–6.70 (AA'BB', 4H), 6.79–6.82 (AA'BB', 4H), 7.68 (d, *J* = 1.2 Hz, 2H), 9.56 (d, *J* = 1.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.4 (s), 28.8 (s), 33.6 (s), 68.0 (s), 114.7 (s), 115.0 (s), 126.3 (s), 129.4 (s), 131.1 (s), 138.6 (s), 140.3 (s), 142.0 (s), 145.0 (s), 158.9 (s), 183.1 (s); IR (KBr) 1177, 1250, 1523, 1668, 2858, 2937, 3086 cm^{-1}; HR-MS (APCI) $C_{34}H_{35}O_4S_2$ $[M+H]^+$ calcd *m/z* 571.1977, found *m/z* 571.1968.

2,2'-bis(benzodithiolyl)-4,4'-bis(4-hexenyloxyphenyl)-3,3'-bithienyl (13). A solution of **12** (1.11 g, 1.94 mmol), *p*-toluenesulfonic acid monohydrate (106 mg, 0.57 mmol), 1,2-benzenedithiol (757 mg, 5.32 mmol) in benzene (4 mL) was heated to reflux for 7 h. To the solution was added sat. $NaHCO_3$ aqueous solution, and then the mixture were extracted with CH_2Cl_2 three times. The combined extracts were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography (silica gel, eluent: hexane/CH_2Cl_2 = 3/1 followed by 3/2) to give **13** (1.21 g, 1.47 mmol): yield 76%; white waxy solid; mp 45–50 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.54–1.60 (m, 4H), 1.77–1.82 (m, 4H), 2.11–2.15 (m, 4H), 3.95 (t, *J* = 6.6 Hz, 4H), 4.97 (dd, *J* = 10.3 Hz, 1.7 Hz, 2H), 5.03 (dd, *J* = 17.2 Hz, 1.7 Hz, 2H), 5.78–5.87 (m, 4H), 6.73–6.76 (AA'BB', 4H), 6.94–6.97 (AA'BB', 4H), 7.01–7.03 (m, 4H), 7.09–7.11 (m, 2H), 7.17–7.19 (m, 2H), 7.21 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.5 (s), 28.8 (s), 33.6 (s), 50.4 (s), 68.0 (s), 114.7 (s), 114.9 (s), 122.0 (s), 122.1 (s), 122.3 (s), 125.9 (s), 126.0 (s), 128.0 (s), 129.0 (s), 131.1 (s), 136.8 (s), 137.3 (s), 138.6 (s), 141.5 (s), 144.2 (s), 158.7 (s); IR (KBr) 734, 821, 902, 1168, 1239, 1433, 1514, 1600, 2853, 2933, 3072 cm^{-1}; HR-MS (APCI) $C_{46}H_{42}O_2S_6$ $[M]^+$ calcd *m/z* 818.1509, found *m/z* 818.1510.

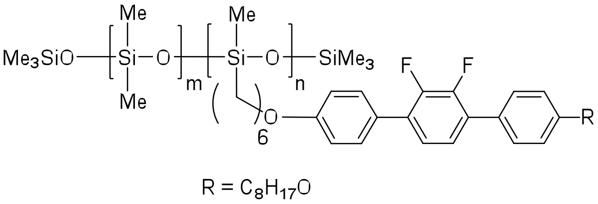
Compound 2. To a solution of **13** (813 mg, 992 μmol) dissolved in CH_2Cl_2 (150 mL) was added tris(4-bromophenyl)aminium hexachloroantimonate (3.24 g, 3.97 mmol) at room temperature, and the mixture was stirred for 4.5 h. To the reaction mixture was added ether (250 mL). The precipitate was filtered, washed and dried in vacuo. Then the precipitate was dissolved in the mixture of CH_2Cl_2 (70 mL), MeCN (70 mL), and THF (5 mL). To the solution was added Zn powder (6.48 g, 99.1 mmol). Then the mixture was stirred at room temperature for 4.5 h, and filtered to remove Zn powder. The filtrate was concentrated and the residue was purified by column chromatography (alumina, eluent: CH_2Cl_2/hexane = 1/3 followed by 2/3) to afforded **2** (318 mg, 389 μmol): yield 39%; white solid; mp 222–223 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ =1.56–1.62 (m, 4H), 1.77–1.83 (m, 4H), 2.14–2.18 (m, 4H), 3.87 (t, *J* = 6.6 Hz, 4H), 5.00 (dd, *J* = 10.3 Hz, 1.2 Hz, 2H), 5.06 (dd, *J* = 17.2 Hz, 1.7 Hz, 2H), 5.82–5.89 (m, 2H), 6.44–6.47 (AA'BB', 4H), 6.67–6.70 (AA'BB', 4H), 6.99–7.05 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.6 (s), 28.9 (s), 33.6 (s), 67.9 (s), 80.4 (s), 114.0 (s), 115.0 (s), 121.2 (s), 121.3 (s), 125.0 (s), 125.4 (s), 125.7 (s), 128.9 (s), 129.5 (s), 131.1 (s), 136.7 (s), 138.3 (s), 138.6 (s), 141.7 (s), 143.8 (s), 157.9 (s); IR (KBr) 550, 744, 1173, 1240, 1449, 1518, 1607, 2862, 2929, 3061 cm^{-1}; HR-MS (APCI) $C_{46}H_{41}O_2S_6$ $[M+H]^+$ calcd *m/z* 817.1431, found *m/z* 817.1428.

Dication salt $2^{2+}(SbCl_6^-)_2$. To a solution of **2** (57 mg, 69.7 μmol) in CH_2Cl_2 (5 mL) was added tris(4-bromophenyl)aminium hexachloroantimonate (114 mg, 140 μmol) at room temperature, and the mixture was stirred for 4 h. To the reaction mixture was added ether. The precipitate was filtered, washed and dried in vacuo to afford **2**$^{2+}$($SbCl_6^-$)$_2$ (97 mg, 64.6 μmol): yield 93%; dark brown powder; mp 149–150 °C; ^{1}H NMR (500 MHz, CD_2Cl_2):δ = 1.48–1.54 (m, 4H), 1.72–1.77 (m, 4H), 2.07–2.11 (m, 4H), 3.87–3.94 (m, 4H), 4.93–4.96 (m, 2H), 4.99–5.03 (m, 2H), 5.77–5.85 (m, 2H), 6.77–6.80 (AA'BB', 4H), 7.07–7.10 (AA'BB', 4H), 7.90–7.93 (m, 4H), 8.42–8.44 (m, 4H), 8.61 (s, 2H); ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 25.3 (s), 28.6 (s), 33.4 (s), 68.2 (s), 114.6 (s), 115.6 (s), 126.4 (s), 129.0 (s), 131.8 (s), 131.9 (s), 138.57 (s), 138.59 (s), 138.61 (s), 138.64 (s), 138.66 (s), 140.2 (s), 184.2 (s); IR (KBr) 1003, 1178, 1249, 1330, 1395, 1523, 1606, 2862, 2932, 3086 cm^{-1}; HR-MS (FAB) $C_{46}H_{40}O_2S_6SbCl_6$ [M–$SbCl_6$]$^+$ calcd *m/z* 1146.8522, found *m/z* 1146.8533.

Polymer 4. Monomeric compound **2** (26 mg, 32 μmol) and **3** (12 mg, 6 μmol) dissolved in toluene (150 μL) were placed in sample tube. A solution of (1,3-divinyl-1,1,3,3-tetramethylsiloxane)platinum (0) in xylene (Pt 2%) (40 μL) was added to the solution, which was heated at 85 °C for 4 days. The resulting gel was washed with methanol three times, and dried to give **4** as brown powder (17 mg); mp 236 °C (decomposition); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.07 (br, 168H), 1.41–1.76 (m, 30H), 3.84 (br, 4H), 6.42 (br, 4H), 6.66 (br, 4H), 7.00 (br, 8H); IR (KBr) 800, 1024, 1092, 1257, 1454, 1522, 2958 cm^{-1}.

Polymer 5. The experimental procedure was as described for the preparation of **4**. Quantities: **1** (115 mg, 233 μmol), **2** (130 mg, 159 μmol), (1,3-divinyl-1,1,3,3-tetramethylsiloxane)platinum (0) in xylene (Pt 2%) (50 μL), **3** (118 mg, 60 μmol), toluene (2 mL): yield 239 mg; light brown powder; mp 168–175 °C; ^{1}H NMR (500 MHz, CDCl$_3$): δ = 0.04–0.14 (m, 97H), 0.54 (br, 8H), 0.89 (br, 3H), 1.29–1.49 (m, 28H), 1.78 (br, 8H), 3.84 (br, 4H), 3.98 (br, 4H), 4.68 (br, 0.7H), 6.43 (br, 4H), 6.67 (br, 4H), 7.01 (br, 4H), 7.16 (br, 2H), 7.48(br, 4H); IR (KBr) 801, 1027, 1094, 1260, 2154, 2856, 2927, 2961 cm^{-1}.

Polymer 14. The experimental procedure was as described for the preparation of **4**. Quantities: **1** (29 mg, 48 μmol), (1,3-divinyl-1,1,3,3-tetramethylsiloxane)platinum (0) in xylene (Pt 2%) (20 μL), **3** (12 mg, 6 μmol), toluene (200 μL): yield 28 mg; dark brown solid; phase transition temperature /°C (DSC on 2nd heating): G 39 S$_A$ 141 I; ^{1}H NMR (500 MHz, CDCl$_3$): δ = 0.07 (br, 30H), 0.53 (br, 2H), 0.89 (br, 3H), 1.29–1.54 (m, 18H), 1.78 (br, 4H), 3.96 (br, 4H), 6.94 (brs, 4H), 7.13–7.18 (brs, 2H), 7.46 (brs, 4H); IR (KBr) 802, 1024, 1092, 1260, 1460, 1488, 1527, 1610, 2857, 2925, 2961 cm^{-1}.



14

X-ray Structure Analysis of 2. X-ray diffraction data were collected on a Rigaku MERCURY CCD with a graphite–monochromated Mo-$K\alpha$ (λ = 0.7107 Å) radiation. The structures were solved by direct methods using SIR2004.[5] All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 using SHELXL97.[6] All the H atoms were geometrically positioned and refined using a riding model. All calculations were performed using the WinGX program package.[7]

Crystal data for **2**: $C_{46}H_{40}O_2S_6$, M = 817.14, T = 173 K, monoclinic, space group $C2/c$, a = 22.2284(14), b = 18.6647(6), c = 13.5647(9) Å, β = 135.013(2), V = 3978.6(4) Å^3, Z = 4, D_{calcd} = 1.364 g cm^{-3}, 16575 reflections measured, 4922 unique, 272 parameters refined, GOF = 1.051, R_1 = 0.045 [$I > 2\sigma(I)$], wR = 0.1211 (all data).

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