Supporting Information of

"Liquid Crystalline Mesophases Based on Symmetric Tetrathiafulvalene"

Lei Wang,† Hyunduck Cho,ζ Soo-Hyoung Lee,‡ Changhee Lee,ζ* Kwang-Un Jeong,†* Myong-Hoon Lee†*

†Deparment of Polymer/Nano Science and Technology, Chonbuk National University, Chonju, Chonbuk 561-756, Korea

‡Division of Environmental and Chemical Engineering, Chonbuk National University, Chonju, Chonbuk 561-756, Korea

ζSchool of Electrical Engineering and Computer Science, Seoul National University, Seoul 151-744, Korea

Experimental

General

All reagents and solvents were bought commercially and used without further purification. All the reactions were performed under an inert atmosphere of nitrogen. ^{1}H NMR spectra were recorded on a JNM-EX400 spectrometer in deuterated chloroform. Chemical shifts are quoted in parts per million (ppm) and referenced to tetramethylsilane. The ^{13}C NMR spectra were recorded at 100 MHz on the same spectrometer in deuterated chloroform. Chemical shifts were defined relative to the ^{13}C resonance shift of chloroform (77.0 ppm). The UV absorption was determined with a SCINCO UV-vis S-3100 spectrometer. Elementary analyses were carried out on a FISONS EA-1108 Elemental Analyzer. High-resolution mass spectrometry was taken on a SD303 spectrometer. The phase transition behavior of the materials was examined by a different scanning calorimetry (DSC) using a TA Instruments DSC 2010. The heating and cooling rate is 5 °C/min. The reported temperatures are onset temperatures of first cooling. The polarizing optical images were taken on a Nikon ECLIPSE E600POL polarizing optical microscope with a LINKAM LTS 350 hot stage. The 1D WAXD experiments were conducted in the reflection mode of a Rigaku 12 kW rotating-anode X-ray (Cu Kα radiation) generator coupled to a diffractormeter. The diffraction peak positions and widths were calibrated with silicon crystals of known crystal size in the high 2θ-angle region (>15°) and silver behenate in the low 2θ-angle region. The cyclic voltammetry measurements were performed by Versa STAT3 of Princeton Applied Research in a solution of Bu_4NBF_4 (0.1 M) in water-free dichloromethane with a scan rate of 10 mV/s at room temperature. A glass carbon electrode, a Ag/AgCl electrode and a platinum wire were used as a working electrode, a reference electrode and a counter electrode, respectively. The field-effect measurement was carried out using bottom-contact thin film transistor (TFT) geometry. TFT devices with a channel length (*L*) of 40 μm and a channel width (*W*) of 1800 μm were fabricated on thermally oxidized highly n-doped silicon substrates. The SiO_2 gate dielectric was 300 nm in thickness. Gold source/drain electrodes (60 nm) were evaporated through a shadow mask.

Materials.

Starting material **1** was prepared according to the literatures. [1]

*General procedure to compound **3**:*

The mixture of compound **1** (1.33 g, 5.0 mmol), n-alkyl acid (10.5 mmol), DMAP (0.12 g, 1.0 mmol), and DCC (2.38 g, 11.5 mmol) and dried CH_2Cl_2 (50 mL) were stirred at room temperature for 12 h. The solvent was removed by rotating evaporation. The yellow solid was obtained by column chromatography with mixture of PE and MC as the eluant.

Compound **3a**: This compound was prepared according to the general procedure and obtained as yellow solid (0.70g, 27.0 %). 1H-NMR: 7.77 (2H, q), 7.58 (2H, q), 2.75 (4H, t), 1.87 (4H, f), 1.54-1.25 (16H, m), 0.92 (6H, t). 13C-NMR: 210.49, 170.48, 136.28, 131.38, 127.68, 126.80, 121.24, 33.93, 31.63, 29.14, 28.87, 25.03, 22.60, 14.06. UV: 273.36 nm, 329.47nm, 372.65nm. HRMS calcd for $C_{27}H_{34}O_4S_3$ 518.16, found $(M + H)^+$ 519.15. Anal. Calcd for $C_{27}H_{34}O_4S_3$: C, 62.5; H, 6.6; S, 18.5. Found: 63.4%, 6.7%, 18.8%.

Compound **3b**: This compound was prepared according to the general procedure and obtained as yellow crystals (1.45g, 50.4%). 1H-NMR: 7.77 (2H, q), 7.59 (2H, q), 2.76 (4H, t), 1.87 (4H, f), 1.54-1.22 (24H, m), 0.89 (6H, t). 13C-NMR: 210.45, 170.48, 136.27, 131.38, 127.67, 126.80, 121.24, 33.93, 31.85, 29.40, 29.25, 29.21, 29.19, 25.03, 22.66, 14.10 UV: 272.39nm, 330.44nm, 373.60nm. HRMS calcd for $C_{31}H_{42}O_4S_3$ 574.22, found $(M + H)^+$ 575.24. Anal. Calcd for $C_{31}H_{42}O_4S_3$: C, 64.8; H, 7.4; S, 16.7. Found: 64.9%, 7.4%, 16.8%.

Compound **3c**: This compound was prepared according to the general procedure and obtained as yellow solid (1.75g, 55.4%). 1H-NMR: 7.76 (2H, q), 7.58 (2H, q), 2.75 (4H, t), 1.86 (4H, f), 1.54-1.20 (32H, m), 0.89 (6H, t). 13C-NMR: 210.47, 170.47, 136.27, 131.39, 127.67, 126.78, 121.25, 33.94, 31.91, 29.60, 29.45, 29.33, 29.22, 25.03, 22.69, 14.11. UV: 272.39nm, 329.47nm, 373.60nm. HRMS calcd for $C_{35}H_{50}O_4S_3$ 630.28, found $(M + H)^+$ 631.29. Anal. Calcd for $C_{35}H_{50}O_4S_3$: C, 66.6; H, 8.0; S, 15.2. Found: 66.7%, 8.0%, 15.4%.

Compound **3d**: This compound was prepared according to the general procedure and obtained as yellow solid (2.02g, 58.8%). 1H-NMR: 7.76 (2H, q), 7.57 (2H, q), 2.75 (4H, t), 1.87 (4H, f), 1.54-1.16 (40H, m), 0.88 (6H, t). 13C-NMR: 210.47, 170.48, 136.27, 131.39, 127.68, 126.81, 121.25, 33.94, 31.93, 29.68, 29.65, 29.60, 29.46, 29.36, 29.22, 29.20, 25.03, 22.69, 14.11. UV: 272.38nm, 329.47nm, 372.65nm. HRMS calcd for $C_{39}H_{58}O_4S_3$ 686.35, found $(M + H)^+$ 687.33. Anal. Calcd for $C_{39}H_{58}O_4S_3$: C, 68.2; H, 8.5; S, 14.0. Found: 68.3%, 8.6%, 14.1%.

*General procedure to compound **4**:*

Mercury (II) acetate (2.5 eq) was added to a solution of compound **3** in CH_2Cl_2. After stirring at room temperature for 1 h, the mixture became white from orange. The mixture was filtered through a celite, and the filtrate was washed with water (3 x 100 ml), dried with Na_2SO_4, the crude product was obtained after evaporating the solvent, which was purified by column chromatography.

Compound **4a**: This compound was prepared according to the general procedure and obtained as yellow solid (0.42g, 86.7%), 1H-NMR: 7.74 (2H, q), 7.57 (2H, q), 2.75 (4H, t), 1.87 (4H, f), 1.54-1.25 (16H, m), 0.92 (6H, t). 13C-NMR: 187.50, 170.57, 138.43, 127.46, 126.42, 123.88， 120.99, 33.95, 31.63, 29.14, 28.88, 25.03, 22.59, 14.05. UV: 248.04nm, 303.42nm. HRMS calcd for $C_{27}H_{34}O_5S_2$ 502.18, found $(M + H)^+$ 503.21. Anal. Calcd for $C_{27}H_{34}O_5S_2$: C, 64.5; H, 6.8; S, 12.8. Found: 64.6%, 6.7%, 12.8%.

Compound **4b**: This compound was prepared according to the general procedure and obtained as yellow solid (1.25g, 95.3%), 1H-NMR: 7.74 (2H, q), 7.56 (2H, q), 2.75 (4H, t), 1.87 (4H, f), 1.53-1.21 (24H, m), 0.89 (6H, t). 13C-NMR: 187.47, 170.55, 138.43, 127.45, 126.42, 123.89, 120.99, 33.95, 31.84, 29.40, 29.25, 29.22, 29.18, 25.03, 22.66, 14.09. UV: 249.01nm, 303.42nm. HRMS calcd for $C_{31}H_{42}O_5S_2$ 558.25, found $(M + H)^+$ 559.30. Anal. Calcd for $C_{31}H_{42}O_5S_2$: C, 66.6; H, 7.6; S, 11.5. Found: 66.7%, 7.6%, 11.6%.

Compound **4c**: This compound was prepared according to the general procedure and obtained as yellow solid (1.60g, 99.5%), 1H-NMR: 7.73 (2H, q), 7.56 (2H, q), 2.75 (4H, t), 1.86 (4H, f), 1.53-1.19 (32H, m), 0.89 (6H, t). 13C-NMR: 187.54, 170.54, 138.45, 127.45, 126.43, 123.90, 121.00, 33.96, 31.91, 29.60, 29.45, 29.33, 29.19, 25.04, 22.68, 14.10. UV: 249.01nm, 303.42nm. HRMS calcd for $C_{35}H_{50}O_5S_2$ 614.31, found $(M + H)^+$ 615.27. Anal. Calcd for $C_{35}H_{50}O_5S_2$: C, 68.4; H, 8.2; S, 10.4. Found: 68.5%, 8.3%, 10.6%.

Compound **4d:** This compound was prepared according to the general procedure and obtained as yellow solid (1.21g, 93.9%), 1H-NMR: 7.74 (2H, q), 7.57 (2H, q), 2.75 (4H, t), 1.87 (4H, f), 1.54-1.18 (40H, m), 0.88 (6H, t). 13C-NMR: 187.45, 170.54, 138.43, 127.44, 126.42, 123.88, 120.99, 33.95, 31.91, 29.67, 29.64, 29.60, 29.45, 29.34, 29.22, 29.18, 25.03, 22.68, 14.10. UV: 248.04nm, 303.42nm. HRMS calcd for $C_{39}H_{58}O_5S_2$ 670.37, found $(M + H)^+$ 671.35. Anal. Calcd for $C_{39}H_{58}O_5S_2$: C, 69.8; H, 8.7; S, 9.6. Found: 69.6%, 8.8%, 9.8%.

General procedure to compound ***5****:*

Compound **4** were added to triethyl phosphate, the mixture was heated to 120 ºC for 4 h. After the solution was cooled, the precipitate was filtered, washed with PE and methanol, respectively, and dried. Finally, organe solid was reprecipitated by drop the cholorform solution to PE, filtered and dried.

Compound **5a**: This compound was prepared according to the general procedure and obtained as dark orange solid (0.17g 58.5%). 1H-NMR: 7.60 (4H, q), 7.47 (4H, q), 2.76 (8H, t), 1.89 (8H, f), 1.56-1.26 (32H, m), 0.93 (12H, t). 13C-NMR: 170.47, 137.25, 128.85, 126.89, 126.87, 120.80, 33.98, 31.70, 29.18, 28.92, 25.03, 22.63, 14.10. UV: 247.1nm, 315.0nm, 385.1nm. (1/10: 431.6nm) HRMS calcd for $C_{54}H_{68}O_8S_4$ 972.38, found $(M + H)^+$ 972.38. Anal. Calcd for $C_{54}H_{68}O_8S_4$: C, 66.6; H, 7.0; S, 13.2. Found: 66.6%, 7.1%, 13.2%.

Compound **5b**: This compound was prepared according to the general procedure and obtained as orange solid (1.00g, 89.4%).1H-NMR: 7.59 (4H, q), 7.48 (4H, q), 2.76 (8H, t), 1.90 (8H, f), 1.59-1.23 (48H, m), 0.90 (12H, t). 13C-NMR: 170.46, 137.25, 128.84, 126.89, 126.86, 120.80, 34.00, 31.88, 29.47, 29.30, 29.28, 29.25, 25.05, 22.70, 14.11. UV: 247.1nm, 315.0nm, 383.2nm. (1/10: 432.6nm) HRMS calcd for $C_{62}H_{84}O_8S_4$ 1084.50, found $(M + H)^+$ 1084.59. Anal. Calcd for $C_{62}H_{84}O_8S_4$: C, 68.6; H, 7.8; S, 11.8. Found: 68.8%, 7.8%, 11.7%.

Compound **5c**: This compound was prepared according to the general procedure and obtained as yellow soft solid (1.26g, 85.1%). 1H-NMR: 7.60 (4H, q), 7.46 (4H, q), 2.76 (8H, t), 1.90 (8H, f), 1.60-1.21 (64H, m), 0.88 (12H, t). 13C-NMR: 170.47, 137.25, 128.80, 126.90, 126.86, 120.79, 34.00, 31.93, 29.65, 29.54, 29.37, 29.29, 29.26, 25.06, 22.69, 14.10. UV: 247.1nm, 316.0 nm, 383.7nm. (1/10: 432.6nm) HRMS calcd for $C_{70}H_{100}O_8S_4$ 1196.63, found $(M + H)^+$ 1196.73. Anal. Calcd for $C_{70}H_{100}O_8S_4$: C, 70.2; H, 8.4; S, 10.7. Found: 70.5%, 8.5%, 10.3%.

Compound **5d**: This compound was prepared according to the general procedure and obtained as soft yellow solid (0.45g, 78.1%). 1H-NMR: 7.62 (4H, q), 7.47 (4Hn q), 2.77 (8H, t), 1.91 (8H, f), 1.54-1.20 (80H, m), 0.89 (12H, t). 13C-NMR: 170.43, 137.25, 128.84, 126.90, 126.86, 120.81, 34.01, 31.93, 29.72, 29.69, 29.66, 29.54, 29.37, 29.30, 29.26, 25.06, 22.68, 14.10. UV: 247.1nm, 315.0nm, 384.5nm. (1/10: 430.6 nm) HRMS calcd for $C_{78}H_{116}O_8S_4$ 1308.76, found $(M + H)^+$ 1309.26. Anal. Calcd for $C_{78}H_{116}O_8S_4$: C, 71.5; H, 8.9; S, 9.8. Found: 71.7%, 9.0%, 9.9%.

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[1] Dumur, F.; Gautier, N.; Gallego-Planas, N.; Sahin, Y.; Levillain, E.; Mercier, N.; Hudhomme, P.; Masino, M.; Girlando, A.; Lloveras, V.; Vidal-Gancedo, J.; Veciana, J.; Rovira, C. J. Org. Chem. 2004, 69, 2164-2177.

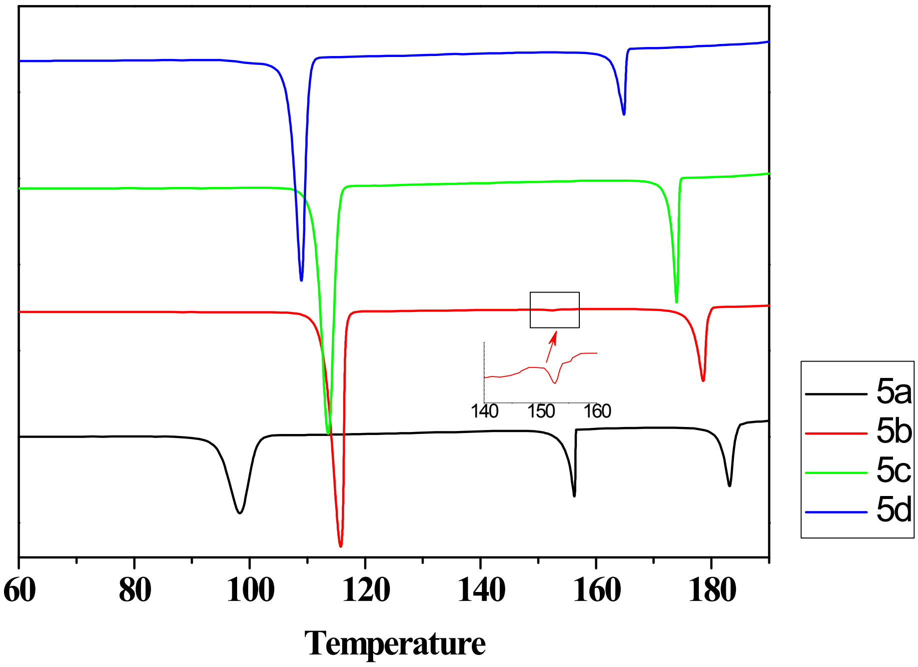


Figure S1. DSC traces of first cooling for compounds **5a-5d** (cooling rate: 5 °C/min). Black line is **5a**, red line is **5b**, green line is **5c**, and blue line is **5d**.

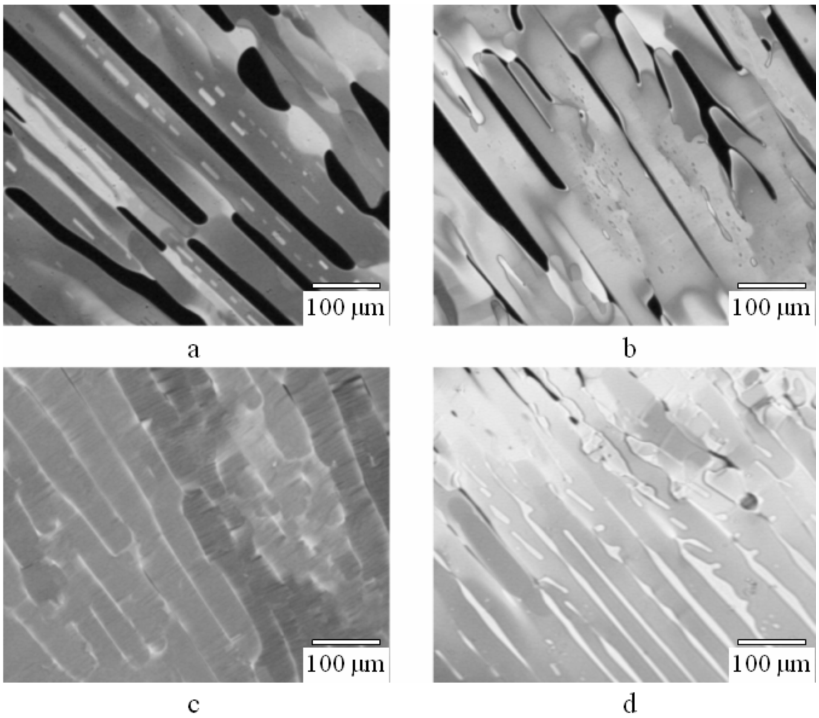


Figure S2. POM images of phase texture for compounds **5a-5d** during the first cooling with 2°C/min rate; (a) **5a** at 180°C, (b) **5b** at 175°C, (c) **5c** at 170 °C, and (d) **5d** at 160 °C.

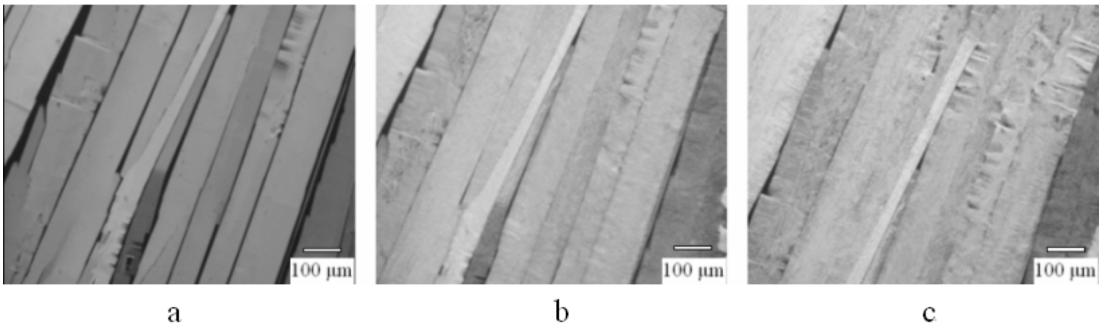


Figure S3. Well aligned 1D lamellar of **5a** during the first cooling with 2°C/min rate. At (a) 158 °C, (b) 133°C and (c) 25 °C in SmA, Cr2 and Cr1 phase, respectively.

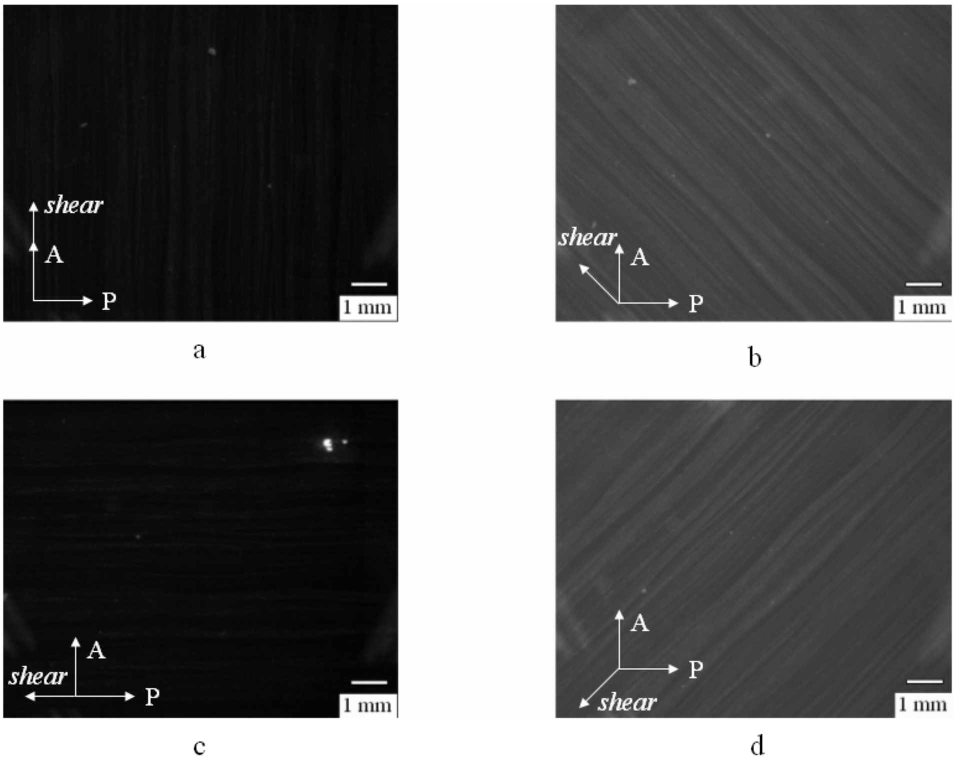


Figure S4. POM images of mechanically sheared sample of **5c** at 172 °C. Images were taken at room temperature. Arrows indicate the directions of mechanical shear, polarizer (P) and analyzer (A) axes.

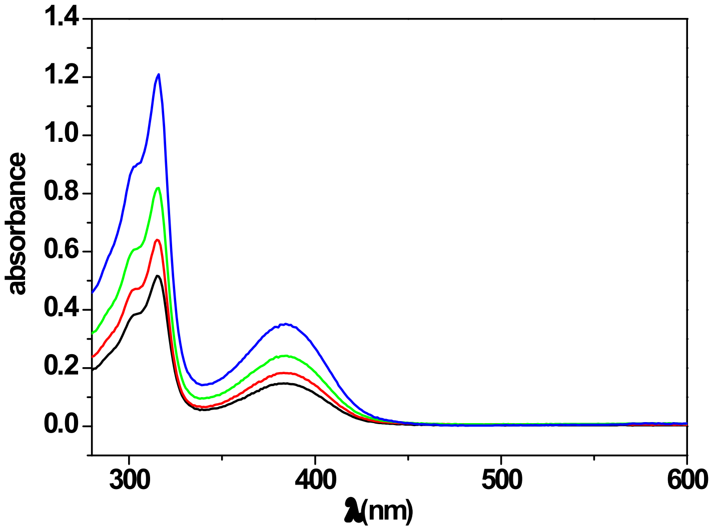


Figure S5. UV absorption spectra of compounds **5a-5d** in $CHCl_3$. Black line is **5a**, red line is **5b**, green line is **5c**, and blue line is **5d**.

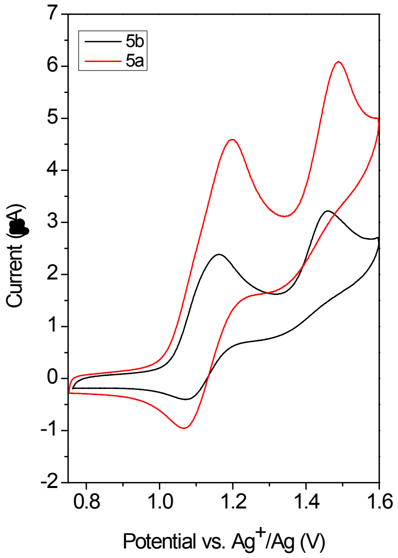


Figure S6. Cyclic voltammograms of compounds **5a** and **5b**.

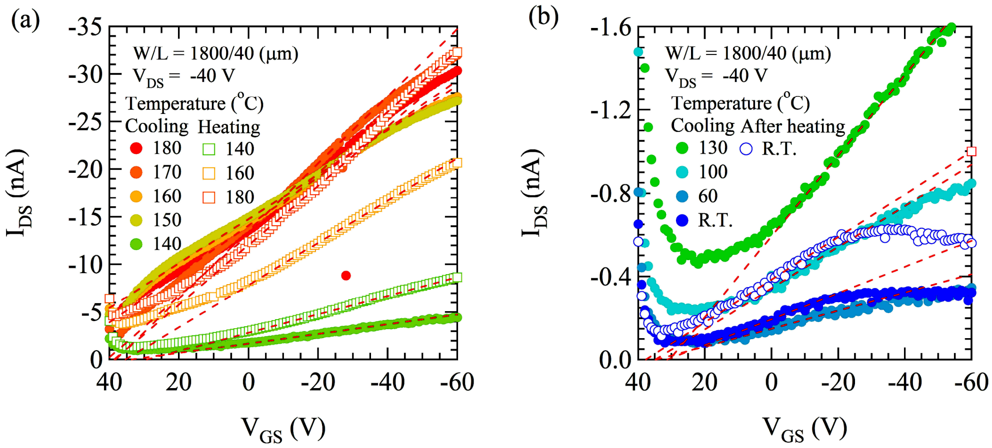
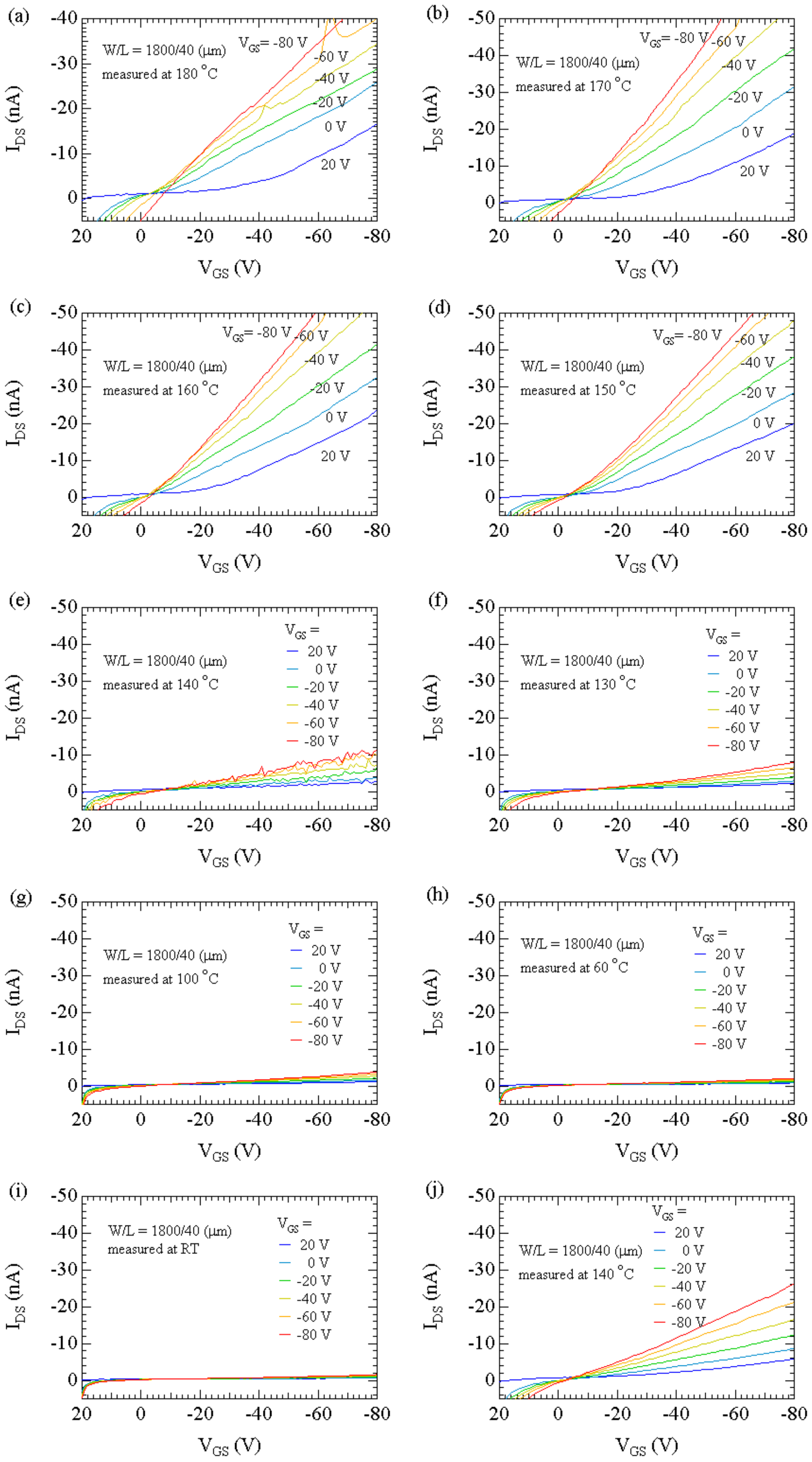


Figure S7. (a) Drain-source current (I_{DS}) vs. gate-source voltage (V_{GS}) characteristics for (●) decreasing temperature from 180 °C to room temperature and (□) increasing temperature from room temperature to 180 °C. Solid lines are fit in the linear regime. (b) Magnified I_{DS}- V_{GS} characteristics in the small I_{DS} region.


(a)
W/L = 1800/40 (μm)
measured at 180 °C
V_{GS}= -80 V
-60 V
-40 V
-20 V
0 V
20 V
(b)
W/L = 1800/40 (μm)
measured at 170 °C
V_{GS}= -80 V
-60 V
-40 V
-20 V
0 V
20 V
(c)
W/L = 1800/40 (μm)
measured at 160 °C
V_{GS}= -80 V
-60 V
-40 V
-20 V
0 V
20 V
(d)
W/L = 1800/40 (μm)
measured at 150 °C
V_{GS}= -80 V
-60 V
-40 V
-20 V
0 V
20 V
(e)
W/L = 1800/40 (μm)
measured at 140 °C
(f)
W/L = 1800/40 (μm)
measured at 130 °C
(g)
W/L = 1800/40 (μm)
measured at 100 °C
(h)
W/L = 1800/40 (μm)
measured at 60 °C
(i)
W/L = 1800/40 (μm)
measured at RT
(j)
W/L = 1800/40 (μm)
measured at 140 °C
V_{GS} =
20 V
0 V
-20 V
-40 V
-60 V
-80 V
I_{DS} (nA)
-50
-40
-30
-20
-10
0
V_{GS} (V)
20
0
-20
-40
-60
-80

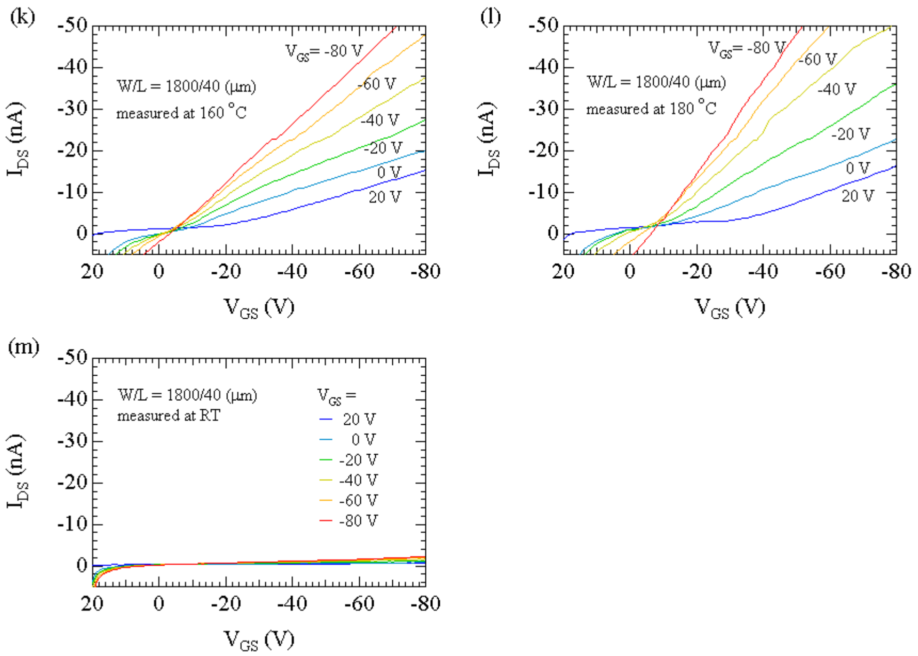


Figure S8. Drain-source current (I_{DS}) vs. drain-source voltage (V_{DS}) characteristics during the cooling cycle ((a) 180 °C, (b) 170 °C, (c) 160 °C, (d) 150 °C, (e) 140 °C, (f) 130 °C, (g) 100 °C, (h) 60 °C, and (i) room temperature), heating cycle ((j) 140 °C, (k) 160 °C, and (l) 180 °C), and (m) the second cooling from 180 °C to room temperature.