Supporting Information for

Nanostructured Liquid Crystals Combining Ionic and Electronic Functions

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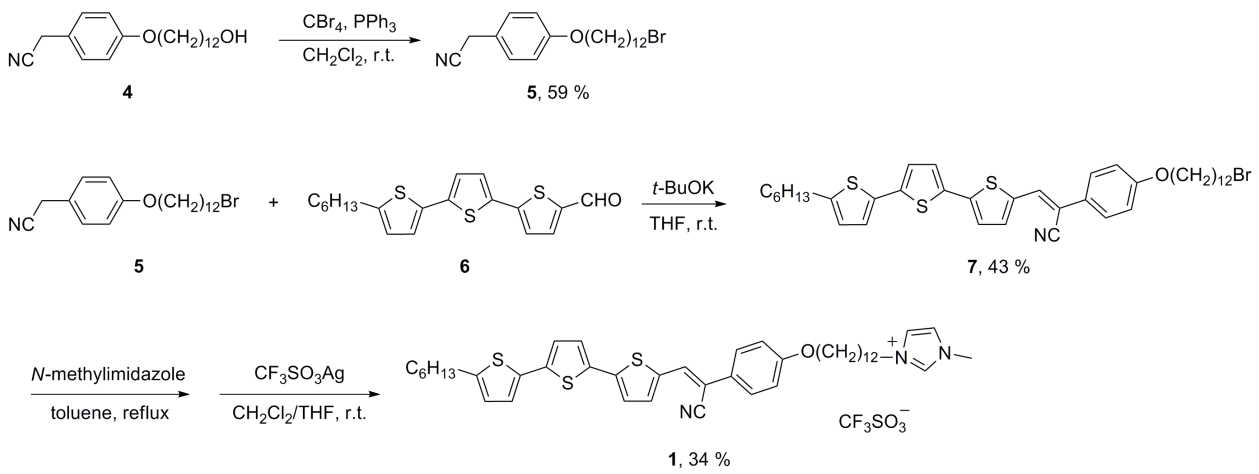
General. All ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer. FT-IR measurements were conducted on a JASCO FT/IR-660 Plus spectrometer. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were recorded on an Applied Biosystems Voyager-DE STR spectrometer using 1,8,9-trihydroxyanthracene or 3-indoleacrylic acid as the matrix. Elemental analyses were carried out with a Yanaco MT-6 CHN autocorder. Differential scanning calorimetry (DSC) measurements were conducted with a NETZSCH DSC 204 Phoenix.

Materials and Syntheses. All reagents and solvents were purchased from Aldrich, Tokyo Kasei, Kanto, or Wako, and used as received. All of the reactions were carried out under an Ar atmosphere. 5-Hexyl-2,2':5',2''-terthiophene-5''-carbaldehyde (**6**) and 4-(12-hydroxydodecyloxyphenyl)acetonitrile (**4**) were synthesized according to the literature.[1,2] 2-(12-Bromododecyloxy)tetrahydro-*2H*-pyran (**8**) and terthiophene derivative (**10**) were obtained according to the procedure reported previously.[3]



Scheme 1. Synthesis of compound **1**.

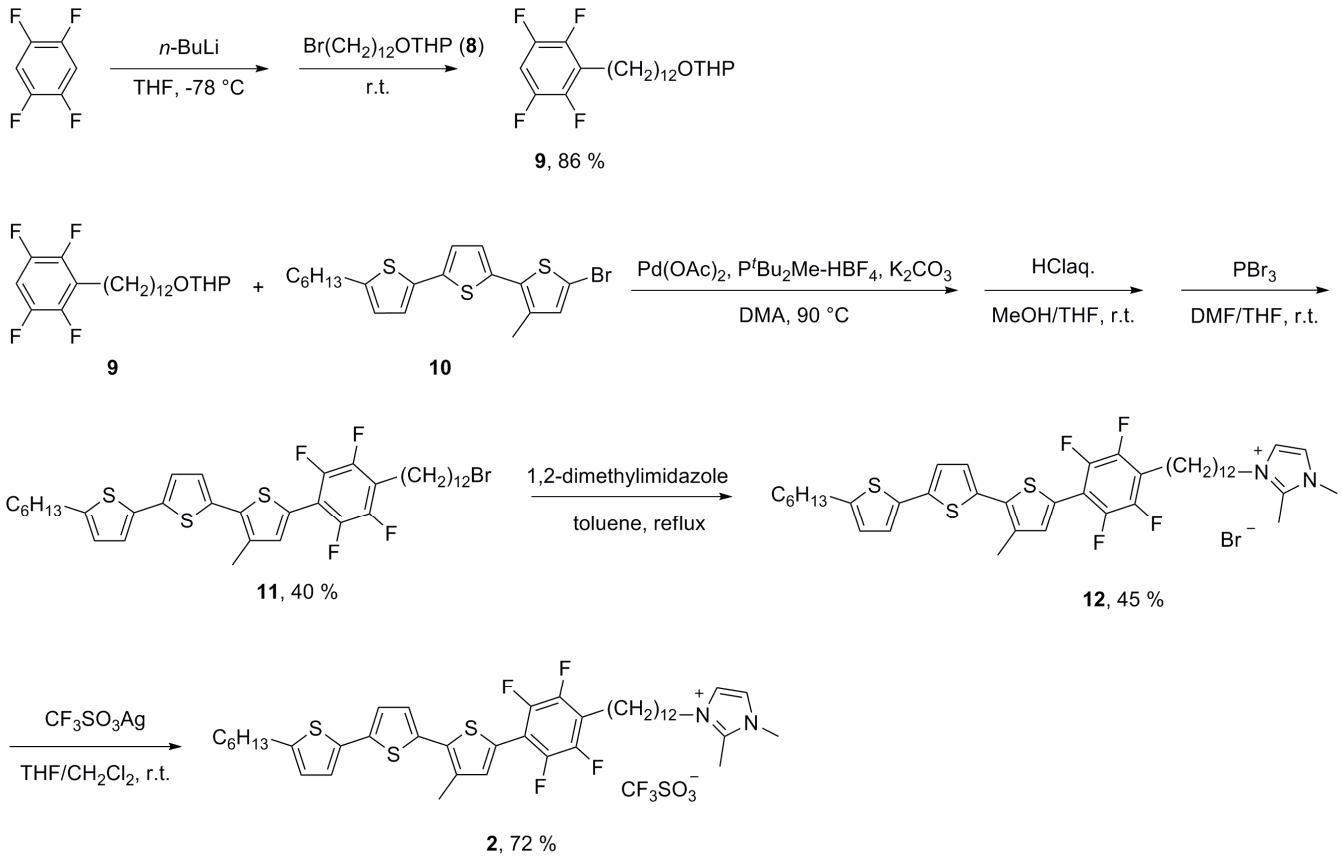
4-(12-Bromododecyloxyphenyl)acetonitrile (5). To a solution of **4** (2.00 g, 6.30 mmol) in CH_2Cl_2 (100 mL) at 0 °C were added CBr_4 (3.13 g, 9.45 mmol) slowly and subsequently a solution of PPh_3 (2.48 g, 9.45 mmol) in CH_2Cl_2. The mixture was stirred for 6 h at room temperature. The reaction mixture was evaporated and purified by column chromatography (silica, eluent: $CHCl_3$). The obtained crude product was recrystallized from hexane, and dried under vacuum to provide **5** as a white solid (yield = 1.41 g, 59 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (d, J = 8.0 Hz, 2H), 6.89 (d, J = 8.0 Hz, 2H), 3.95 (t, J = 6.6 Hz, 2H), 3.68 (s, 2H), 3.41 (t, J = 6.8 Hz, 2H), 1.86 (m, 2H), 1.78 (m, 2H), 1.55-1.28 (m, 16H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.9, 129.0, 121.5, 115.1, 68.1, 34.1, 32.8, 29.5, 29.5, 29.5, 29.4, 29.3, 29.2, 28.7, 28.2, 26.0, 22.9. IR (KBr pellet): 3064, 3042, 3006, 2933, 2917, 2849, 2246, 1614, 1586, 1518, 1256, 811 cm^{-1}. MS (MALDI-TOF): m/z 458.97 $[M+Br]^+$; calcd. 458.07. Elemental analysis calcd. for $C_{20}H_{30}BrNO$: C, 63.15; H, 7.95; N, 3.68 %. Found: C, 63.04; H, 8.06; N, 3.42 %.

1-[4-(12-Bromododecyloxy)phenyl]-2-(5-hexyl-2,2':5',2''-terthienyl)-1-carbonitrile (7). To a solution of **5** (733 mg, 1.93 mmol) and **6** (579 mg, 1.61 mmol) in THF (20 mL) was added slowly a solution of *t*-BuOK (234 mg, 2.09 mmol) in THF (10 mL) at room temperature. The mixture was stirred for 12 h at room temperature. The reaction mixture was concentrated and poured into an aqueous solution of NH_4Cl. The mixture was extracted with $CHCl_3$ three times. The combined organic layers

were dried over anhydrous Na_2SO_4. After filtration and evaporation, the product was purified by column chromatography (silica, eluent: $CHCl_3$). The obtained crude product was further purified by column chromatography (silica, eluent: gradient $CHCl_3$/hexane 1:1, v/v followed by $CHCl_3$). The obtained crude product was recrystallized from hexane/$CHCl_3$, and dried under vacuum to provide **7** as an orange solid (yield = 497 mg, 43 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 8.4 Hz, 2H), 7.47 (s, 1H), 7.45 (d, J = 3.2 Hz, 1H), 7.20 (d, J = 4.0 Hz, 1H), 7.15 (d, J = 3.2 Hz, 1H), 7.03 (d, J = 4.0 Hz, 1H), 7.02 (d, J = 4.0 Hz, 1H), 6.93 (d, J = 8.8 Hz, 2H), 6.70 (d, J = 3.2 Hz, 1H), 3.99 (t, J = 6.4 Hz, 2H), 3.41 (t, J = 6.6 Hz, 2H), 2.80 (t, J = 7.6 Hz, 2H), 1.86 (m, 2H), 1.80 (m, 2H), 1.69 (m, 2H), 1.48-1.29 (m, 22H), 0.90 (t, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 146.3, 141.2, 138.5, 136.8, 134.5, 134.2, 133.1, 131.7, 127.0, 126.4, 125.7, 125.0, 123.9, 123.8, 123.6, 118.4, 115.1, 107.3, 68.3, 33.9, 32.9, 31.6, 31.5, 30.2, 29.5, 29.5, 29.4, 29.4, 29.2, 28.8, 28.7, 28.2, 26.0, 22.5, 14.0. IR (KBr pellet): 3062, 2918, 2850, 2210, 1604, 1572, 1511, 1259, 830 cm^{-1}. MS (MALDI-TOF): m/z 723.47 $[M]^+$; calcd. 723.21. Elemental analysis calcd. for $C_{39}H_{48}BrNOS_3$: C, 64.80; H, 6.69; N, 1.94 %. Found: C, 64.70; H, 6.72; N, 1.79 %.

Compound 1. To a solution of **7** (260 mg, 0.360 mmol) in toluene was added *N*-methylimidazole (1.20 mL, 15.1 mmol). The mixture was refluxed for 5 h. The reaction mixture was concentrated and purified by column chromatography (silica, eluent: gradient CH_2Cl_2 followed by CH_2Cl_2/MeOH = 7:1, v/v). The obtained crude product was recrystallized from hexane/$CHCl_3$, and dried under vacuum to provide an orange solid. This compound was used in the next step without further purification. To a solution of the obtained solid in CH_2Cl_2 (30 mL) was added a solution of silver trifluoromethanesulfonate (120 mg, 0.467 mmol) in THF (2 mL). The mixture was stirred for 1 h at room temperature. The reaction mixture was concentrated and purified by column chromatography (silica, eluent: CH_2Cl_2/MeOH = 7:1, v/v). The obtained crude product was recrystallized from $CHCl_3$/hexane, and dried under vacuum to provide **1** as an orange solid (yield = 106 mg, 34 %). ^{1}H-

NMR (400MHz, $CDCl_3$): δ = 9.39 (s, 1H), 7.56 (d, J = 9.2 Hz, 2H), 7.48 (s, 1H), 7.44 (d, J = 4.0 Hz, 1H), 7.21-7.20 (m, 2H), 7.19 (d, J = 4.0 Hz, 1H), 7.14 (d, J = 4.0 Hz, 1H), 7.03 (d, J = 4.0 Hz, 1H), 7.01 (d, J = 3.2 Hz, 1H), 6.94 (d, J = 8.8 Hz, 2H), 6.70 (d, J = 4.0 Hz, 1H), 4.20 (t, J = 7.6 Hz, 2H), 4.01 (s, 3H), 3.99 (t, J = 6.8 Hz, 2H), 2.80 (t, J = 7.8 Hz, 2H), 1.89 (m, 2H), 1.80 (m 2H), 1.69 (m, 2H), 1.48-1.27 (m, 22H), 0.90 (t, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 146.2, 141.1, 138.4, 137.1, 136.6, 134.4, 134.1, 133.4, 131.8, 126.9, 126.1, 125.6, 124.9, 123.8, 123.7, 123.5, 123.4, 121.8, 118.5, 115.0, 106.9, 68.2, 50.2, 36.4, 31.5, 31.5, 30.2, 30.0, 29.4, 29.4, 29.4, 29.3, 29.1, 28.9, 28.7, 26.2, 25.9, 22.5, 14.1. IR (KBr pellet): 3150, 3112, 3072, 2917, 2852, 2209, 1603, 1570, 1513, 1261, 1034, 1164, 832 cm^{-1}. MS (MALDI-TOF): m/z 724.04 $[M-CF_3SO_3]^+$; calcd. 724.34. Elemental analysis calcd. for $C_{44}H_{54}F_3N_3O_4S_4$: C, 60.45; H, 6.23; N, 4.81 %. Found: C, 60.21; H, 6.39; N, 4.66 %.



Scheme 2. Synthesis of compound **2**.

2-[12-(2,3,5,6-Tetrafluorophenyl)dodecyloxy]-2*H*-pyran (9). To a solution of 1,2,4,5-tetrafluorobenzene (2.15 g, 14.3 mmol) in THF (120 mL) was added dropwise a solution of *n*-BuLi (*ca*. 1.59 M in hexane, 5.40 mL, 8.59 mmol) at – 78 °C. The mixture was stirred for 30 min at – 78 °C, then 2-(12-bromododecyloxy)tetrahydro-*2H*-pyran (**8**, 2.50 g, 7.16 mmol) was added. The reaction mixture was allowed to reach room temperature and stirred for 24 h, and quenched by the addition of water. The reaction mixture was poured into water and extracted with EtOAc three times. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvent, the product was purified by column chromatography (silica, eluent: hexane/EtOAc 10:1, v/v). The obtained product was dried under vacuum to provide **9** as a colorless oil (yield = 2.58 g, 86 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.89 (m, 1H), 4.59-4.57 (m, 1H), 3.87 (m, 1H), 3.73 (m, 1H), 3.50 (m, 1H), 3.38 (m, 1H), 2.72 (t, J = 7.6 Hz, 2H), 1.82 (m, 2H), 1.75-1.69 (m, 2H), 1.64-1.26 (m, 22H). IR (KBr pellet): 3082, 3057, 2928, 2855, 1649, 1611, 1508, 1252, 1034 cm^{-1}. MS (MALDI-TOF): m/z 441.43 $[M+Na]^+$; calcd. 441.24. Elemental analysis calcd. for $C_{23}H_{34}F_4O_2$: C, 66.01; H, 8.19 %. Found: C, 65.86; H, 8.37 %.

5-[4-(12-Bromododecyl)-2,3,5,6-tetrafluorophenyl]-5''-hexyl-3-methyl-2,2':5',2''-terthiophene (11). To a solution of **9** (4.43 g, 10.6 mmol) and **10** (2.50 g, 5.88 mmol) in dry DMA (20 mL) were added P^{t}Bu$_2$Me-HBF$_4$ (0.292 g, 1.18 mmol), K_2CO_3 (3.09 g, 22.3 mmol), and $Pd(OAc)_2$ (0.106 g, 0.472 mmol). The mixture was stirred for 24 h at 90 °C. After cooling to room temperature, the reaction mixture was poured into water, and extracted with EtOAc three times. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvent, the product was purified by column chromatography (silica, eluent: hexane/EtOAc 10:1, v/v). The obtained orange solid was used in the next step without further purification. To a solution of the obtained solid in THF (300 mL)/MeOH (100 mL) was added an aqueous solution of HCl (1 M, 50 mL). The mixture was stirred for 20 h at room temperature. The reaction mixture was concentrated, poured into an aqueous solution of $NaHCO_3$, and extracted with EtOAc three times. The combined organic layers were dried over

anhydrous Na_2SO_4. After filtration and evaporation of the solvent, the product was purified by column chromatography (silica, eluent: gradient CH_2Cl_2/MeOH = 10:1 followed by CH_2Cl_2/MeOH = 2:1, v/v). The obtained crude product was used in the next step without further purification. PBr_3 (1.0 M in CH_2Cl_2, 9.35 mL, 9.35 mmol) was slowly added to dry DMF (30 mL) at 0 °C and the solution was stirred for 15 min at room temperature. To this solution was added a solution of the crude product in THF. The mixture was stirred for 20 h at room temperature, and neutralized with an aqueous solution of $NaHCO_3$. The mixture was extracted with EtOAc three times. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration and evaporation, the product was purified by column chromatography (silica, eluent: hexane/EtOAc 40:1, v/v). The crude product was recrystallized from hexane, and dried under vacuum to provide **11** as an yellow solid (yield = 1.75 g, 40 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (s, 1H), 7.10 (d, J = 4.0 Hz, 1H), 7.07 (d, J = 4.0 Hz, 1H), 7.01 (d, J = 3.2 Hz, 1H), 6.70 (d, J = 3.2 Hz, 1H), 3.41 (t, J = 6.8 Hz, 2H), 2.80 (t, J = 7.8 Hz, 2H), 2.74 (t, J = 7.6 Hz, 2H), 2.46 (s, 3H), 1.85 (m, 2H), 1.69 (m, 2H), 1.62 (m, 2H), 1.44-1.28 (m, 22H), 0.90 (t, J = 6.8 Hz, 3H). IR (KBr pellet): 3062, 2954, 2920, 2850, 1650, 1544, 1477, 1143, 1132 cm^{-1}. MS (MALDI-TOF): m/z 742.15 $[M]^+$; calcd. 742.18. Elemental analysis calcd. for $C_{37}H_{45}BrF_4S_3$: C, 59.90; H, 6.11 %. Found: C, 59.78; H, 6.13 %.

Compound 12. To a solution of **11** (800 mg, 1.08 mmol) in toluene was added 1,2-dimethylimidazole (1.04 g, 10.8 mmol). The mixture was refluxed for 12 h. The reaction mixture was concentrated and purified by column chromatography (silica, eluent: gradient $CHCl_3$ followed by $CHCl_3$/MeOH = 7:1, v/v). The obtained crude product was recrystallized from EtOH/EtOAc and dried under vacuum to provide **12** as an yellow solid (yield = 406 mg, 45 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (d, J = 1.6 Hz, 1H), 7.37 (s, 1H), 7.25 (d, J = 1.6 Hz, 1H), 7.10 (d, J = 4.0 Hz, 1H), 7.07 (d, J = 4.0 Hz, 1H), 7.02 (d, J = 4.0 Hz, 1H), 6.70 (d, J = 3.6 Hz, 1H), 4.15 (t, J = 7.6 Hz, 2H), 3.40 (s, 3H), 2.82 (s, 3H), 2.80 (t, J = 8.0 Hz, 2H), 2.74 (t, J = 7.6 Hz, 2H), 2.46 (s, 3H), 1.84 (m, 2H), 1.69 (m, 2H), 1.64-1.58 (m, 2H),

1.41-1.27 (m, 22H), 0.90 (t, J = 7.0 Hz, 3H). IR (KBr pellet): 3103, 3043, 3016, 2923, 2852, 1648, 1540, 1474, 1144, 1134 cm^{-1}. MS (MALDI-TOF): m/z 757.11 $[M-Br]^+$; calcd. 757.33. Elemental analysis calcd. for $C_{42}H_{53}BrF_4N_2S_3$: C, 60.20; H, 6.37; N, 3.34 %. Found: C, 59.96; H, 6.38; N, 3.09 %.

Compound 2. To a solution of **12** (350 mg, 0.418 mmol) in CH_2Cl_2 (30 mL) was added a solution of silver trifluoromethanesulfonate in THF (5 mL)/CH_2Cl_2 (5 mL). The mixture was stirred for 1 h at room temperature. After filtration, the mixture was poured into water and extracted with $CHCl_3$ three times. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration and evaporation, the product was purified by column chromatography (silica, eluent: gradient $CHCl_3$ followed by $CHCl_3$/MeOH = 10:1, v/v). The obtained crude product was recrystallized from EtOAc, and dried under vacuum to provide **2** as an yellow solid (yield = 273 mg, 72 %). ^1H NMR (400 MHz, $CDCl_3$): δ 7.37 (s, 1H), 7.24 (d, J = 2.0 Hz, 1H), 7.16 (d, J = 2.0 Hz, 1H), 7.10 (d, J = 4.0 Hz, 1H), 7.07 (d, J = 3.2 Hz, 1H), 7.01 (d, J = 3.2 Hz, 1H), 6.70 (d, J = 3.2 Hz, 1H), 4.08 (t, J = 7.6 Hz, 2H), 3.87 (s, 3H), 2.80 (t, J = 7.6 Hz, 2H), 2.74 (t, J = 7.6 Hz, 2H), 2.67 (s, 3H), 2.46 (s, 3H), 1.82 (m, 2H), 1.69 (m, 2H), 1.62 (m, 2H), 1.40-1.26 (m, 22H), 0.90 (t, J = 7.0 Hz, 3H). IR (KBr pellet): 3186, 3142, 3119, 3070, 2923, 2850, 1651, 1544, 1477, 1258, 1160, 1034 cm^{-1}. MS (MALDI-TOF): m/z 757.37 $[M-CF_3SO_3]^+$; calcd. 757.33. Elemental analysis calcd. for $C_{43}H_{53}F_7N_2O_3S_4$: C, 56.93; H, 5.89; N, 3.09 %. Found: C, 56.80; H, 6.06; N, 2.89 %.

DSC thermograms for Compounds 1 and 2. The phase transition temperatures and enthalpies for **1** and **2** were determined by the DSC measurements (Figure S1).

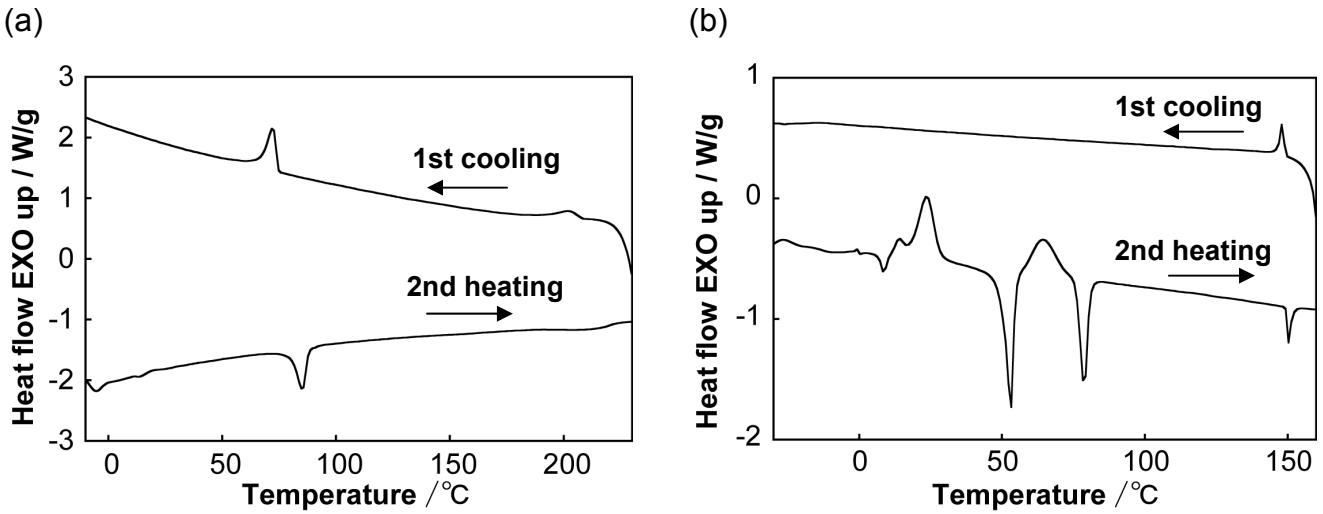


Figure S1. DSC thermograms for **1** (a) and **2** (b) at a scanning rate of 10 °C min^{-1}.

Evaluation of the HOMO-LUMO Energy Gaps for Compounds 1–3 by the UV-Vis Absorption Spectra. The values of the HOMO-LUMO energy gaps for compounds **1**–**3** have been estimated from the onset positions of their absorption spectra (Figure S2). The onset positions of 518 nm for **1**, 448 nm for **2**, and 446 nm for **3** indicate the values of the HOMO-LUMO energy gap of 2.4 eV for **1**, 2.8 eV for **2**, and 2.8 eV for **3**, respectively.

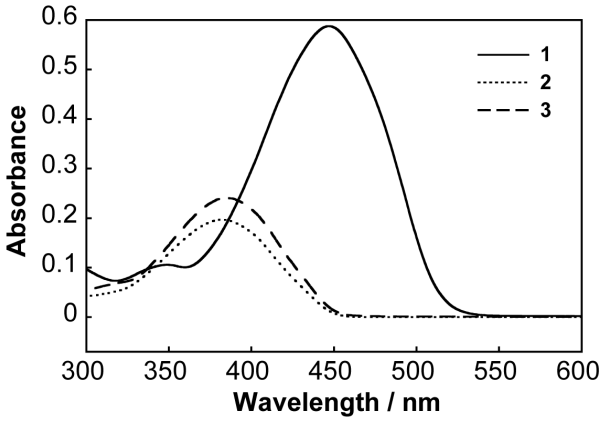


Figure S2. Absorption spectra for **1**–**3** in chloroform solutions (1×10^{-7} M).

Electrochromism in the Solution States for Compounds 1 and 2. In the oxidized state of compound **1**, the peaks at 634, 714, 1057, and 1254 nm are observed (Figure S3a), indicating the existence of monocations and their dimeric aggregates of the π-conjugated moieties.[4] On the electrochemical reduction, three peaks appear at 575, 681, 1062 nm, which are assigned to the formation of anion radicals[4] of compound **1** (Figure S3a). For compound **2**, absorption bands centered at 610 and 940 nm are obtained in the oxidized state, indicative of the formation of monocations (Figure S3b).[4]

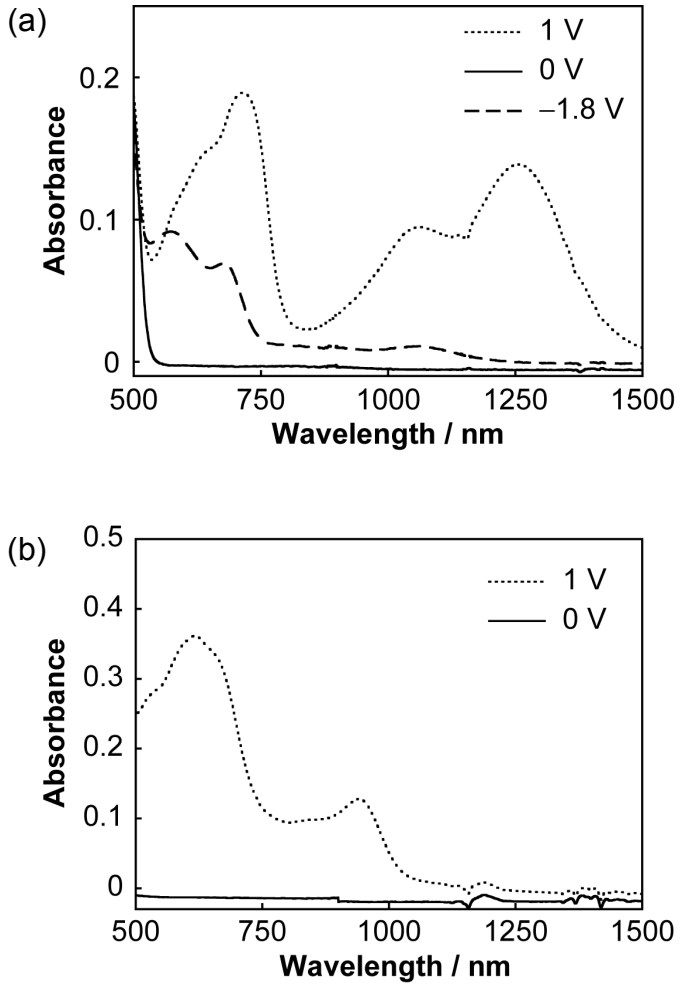


Figure S3. UV–vis–NIR spectra of compounds **1** (a) and **2** (b) in CH_2Cl_2 solutions (1.0 mM) observed under the application of the oxidation and reduction potentials using a Pt mesh working electrode. The supporting electrolyte is Bu_4NClO_4 (0.10 M).

Wide-Angle X-ray Diffraction Pattern for Compound 2 and Small-Angle X-ray Diffraction Pattern for Compounds 1 and 2. The wide-angle X-ray diffraction pattern of compound **2** (Figure S4) is similar to that of compound **1** as shown in Figure 4 in the main text. This result indicates that compound **2** forms the layered nanosegregated structure as illustrated in Figure 5 in the main text.

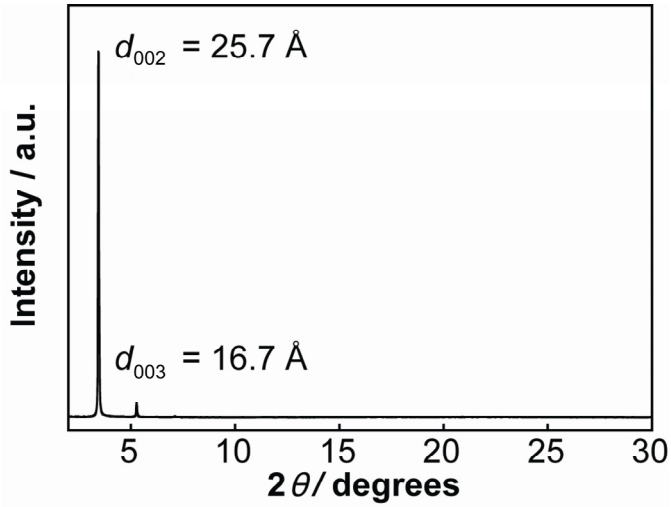


Figure S4. X-ray diffraction pattern for **2** in the SmA phase at 120 °C.

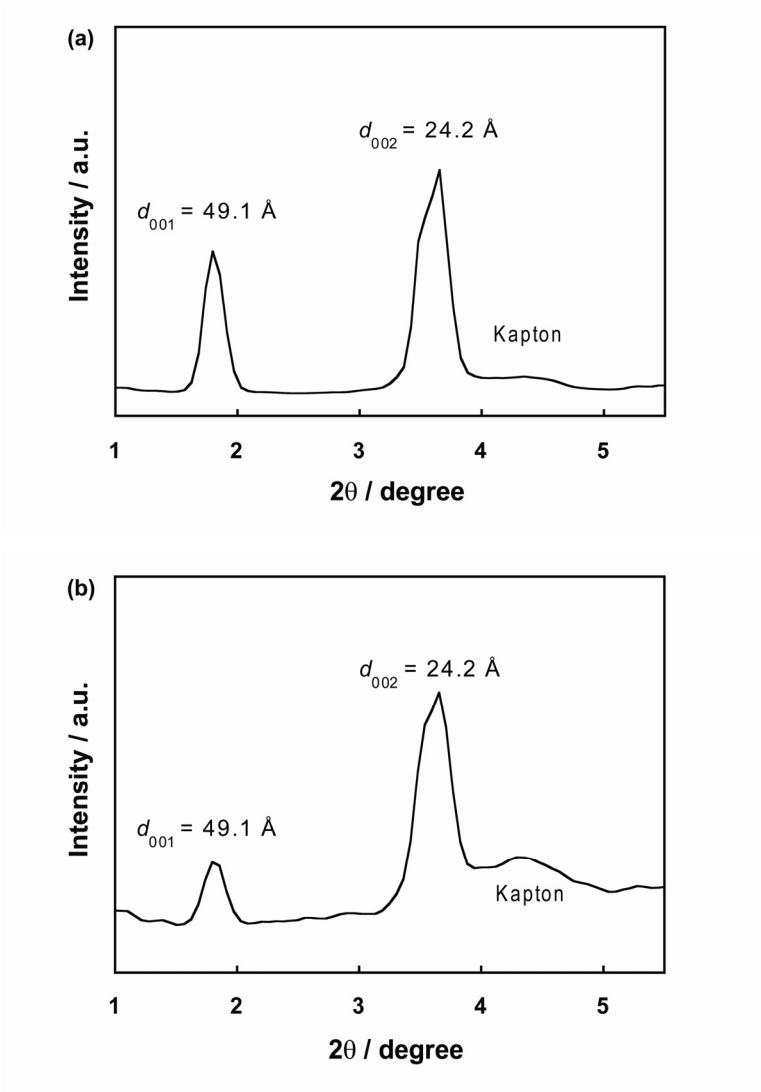


Figure S5. Small-angle X-ray scattering patterns for **1** at 160 °C (a) and for **2** at 120 °C (b). The shoulders at 4.4 degrees in the small-angle X-ray scattering patterns are attributed to the Kapton film placed between the sample and the X-ray detector.

In the wide-angle X-ray diffraction patterns, the diffractions indexed as (001) are weak and ambiguous in the SmA phases for compounds **1** and **2**. The small-angle X-ray scattering measurements reveal the peaks corresponding to (001) and (002) diffractions in the SmA phases for compounds **1** and **2** (Figure S5). The diffraction angles in Figure S5 are slightly different from those in the wide-angle diffraction patterns (Figure 4 and Figure S4) because of the differences in the preparation methods of the samples and in the alignments of the setups.

References

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