Supporting Information for ***New Journal of Chemistry***

2D Assemblies of Ionic Liquid Crystals Based on Imidazolium Moieties: Formation of Ion-Conductive Layers

Junji Sakuda,[a] Masafumi Yoshio,[a] Takahiro Ichikawa,[b] Hiroyuki Ohno[b] and Takashi Kato*[a,c]

[a]*Department of Chemistry and Biotechnology, School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan.*

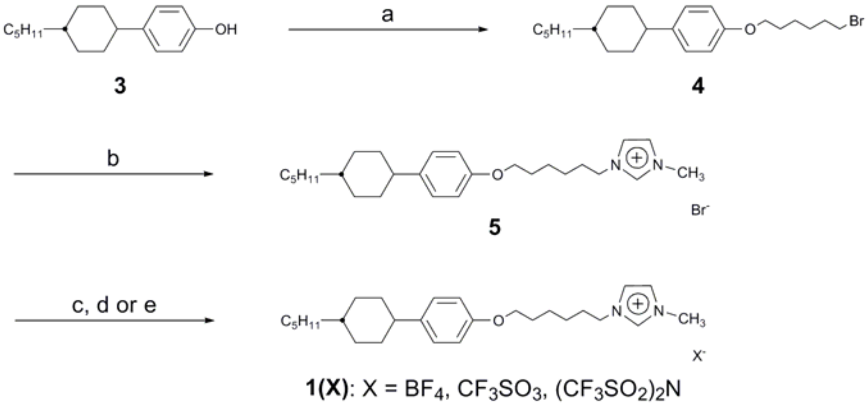
E-mail: kato@chiral.t.u-tokyo.ac.jp

[b]*Department of Biotechnology, Tokyo University of Agriculture and Technology, Nakacho, Koganei, Tokyo 184-8588, Japan*

[c]*CREST, JST, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan.*

1. Materials

Ionic liquid crystals **1(X)** were synthesized by following Scheme S1. All chemical reagents and solvents were obtained from commercial sources and used without purification. Ionic liquids **2(X)** and lithium salts were purchased from Tokyo Kasei.



Scheme S1 Synthetic routes of **1(X)**. Reagents and conditions: (a) 6-bromohexanol, PPh_3, diethyl azodicarboxylate, toluene, room temperature; (b) 1-methylimidazole, 80 °C; (c) $AgBF_4$, methanol, room temperature; (d) $AgOSO_2CF_3$, methanol, room temperature; (e) $LiN(SO_2CF_3)_2$, methanol, room temperature.

1.1 Syntheses of 1(X)

4-(*trans*-4-Pentylcyclohexyl)-1-(6-bromohexyloxy)benzene (4)

4-(*trans*-4-Pentylcyclohexyl)phenol (**3**) (6.00 g, 24.4 mmol), 6-bromohexanol (4.42 g, 24.4 mmol), and triphenylphosphine (7.69 g, 29.3 mmol) were dissolved in dry toluene (40 mL). Diethyl azodicarboxylate (DEAD, 2.2 M toluene solution, 13.4 mL, 29.5 mmol) was added dropwise to the stirred mixture at room temperature. The solution was stirred under an argon atmosphere for 17 h at room temperature. After addition of methanol and evaporation of the solvent by a rotary evaporator, the residue was dissolved in hexane/diethyl ether = 3/1 (v/v). An insoluble solid was filtered off and the filtrate was concentrated by a rotary evaporator. The residue was purified by flash column chromatography on silica gel (eluent: hexane followed by hexane/ethyl acetate = 10/1) twice and recrystallized from methanol/ethyl acetate to give **4** (5.57 g, 13.6 mmol, 56%) as a white solid. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.11 (d, J = 8.8 Hz, 2H), 6.82 (d, J = 8.8 Hz, 2H), 3.93 (t, J = 6.4 Hz, 2H), 3.42 (t, J = 6.8 Hz, 2H), 2.40 (tt, J = 3.2, 12 Hz, 1H), 1.94–1.73 (m, 8H), 1.53–1.15 (m, 15H), 1.03 (m, 2H), 0.89 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.09, 140.00, 127.57, 114.18, 67.62, 43.70, 37.38, 37.29, 34.57, 33.79, 33.64, 32.68, 32.20, 29.15, 27.91, 26.65, 25.31, 22.71, 14.11. IR (KBr): 3034, 2954, 2918, 2850, 1612, 1581, 1513, 1475, 1466, 1446, 1396, 1306, 1284, 1245, 1228, 1176, 1109, 1049, 1037, 1012, 944, 827, 811, 730 cm^{-1}. MS (MALDI-TOF): calcd. for $[M + K]^+$, 448.54; found, 448.94. Elemental analysis: calcd. (%) for $C_{23}H_{37}BrO$: C, 67.47; H, 9.11. Found: C, 67.58; H, 9.32.

1-Methyl-3-{6-[4-(*trans*-4-pentylcyclohexyl)phenoxy]hexyl}imidazolium bromide (5)

The mixture of compound **4** (4.95 g, 12.1 mmol) and 1-methylimidazole (3.00 g, 36.5 mmol) was stirred at 80 ºC for 5 h. The reaction mixture was purified by flash column chromatography on silica gel (eluent: $CHCl_3$/methanol = 10/1) and recrystallized from acetone to give **5** (3.61 g, 7.33 mmol, 61%) as a white solid. ^1H NMR (400 MHz, $CDCl_3$): δ = 10.56 (s, 1H), 7.36 (t, J = 1.8 Hz, 1H), 7.30 (t, J = 1.8 Hz, 1H), 7.11 (d, J = 8.8 Hz, 2H), 6.80 (d, J = 8.8 Hz, 2H), 4.34 (t, J = 7.4 Hz, 2H), 4.10 (s, 3H), 3.92 (t, J = 6.0 Hz, 2H), 2.40 (tt, J = 3.0, 12 Hz, 1H), 1.96–1.73 (m, 8H), 1.57–1.18 (m, 15H), 1.04 (m, 2H), 0.89 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.67, 139.76, 136.83, 127.30, 123.45, 121.91, 113.90, 67.20, 49.59, 43.36, 37.04, 36.95, 36.35, 34.26, 33.29, 31.87, 29.91, 28.71, 26.31, 25.58, 25.18, 22.37, 13.80. IR (KBr): 3437, 3141, 3052, 2921, 2851, 1610, 1578, 1560, 1513, 1467, 1248, 1175, 1109, 1015, 828, 761 cm^{-1}. MS (MALDI-TOF): calcd. for $[M - Br]^+$, 411.64; found, 411.23. Elemental analysis: calcd. (%) for $C_{27}H_{43}BrN_2O$: C, 65.97; H, 8.82; N, 5.70. Found: C, 65.72; H, 9.10; N, 5.41.

1-Methyl-3-{6-[4-(*trans*-4-pentylcyclohexyl)phenoxy]hexyl}imidazolium tetrafluoroborate (1(BF_4))

To a solution of compound **5** (0.390 g, 0.793 mmol) in methanol (20 mL) was added a solution of $AgBF_4$ (0.217 g, 1.11 mmol) in methanol (5 mL) with stirring at room temperature. The mixture was stirred for 14 h at room temperature. Insoluble AgBr was filtered off and the filtrate was concentrated by a rotary evaporator. The crude product was purified by flash column chromatography on silica gel (eluent: $CHCl_3$/methanol = 5/1) to give **1(BF_4)** (0.320 g, 0.642 mmol, 81%) as a white solid. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.97 (s, 1H), 7.19 (m, 2H), 7.11 (d, J = 8.8 Hz, 2H), 6.80 (d, J = 8.8 Hz, 2H), 4.20 (t, J = 7.4 Hz, 2H), 3.96 (s, 3H), 3.92 (t, J = 6.2 Hz, 2H), 2.40 (tt, J = 3.0, 12 Hz, 1H), 1.96–1.73 (m, 8H), 1.57–1.20 (m, 15H), 1.02 (m, 2H), 0.89 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.99, 140.06, 136.33, 127.60, 123.59, 122.02, 114.16, 67.45, 49.88, 43.66, 37.34, 37.25, 36.19, 34.55, 33.59, 32.18, 29.86, 28.94, 26.63, 25.76, 25.37, 22.68, 14.09. IR (KBr): 3437, 3141, 3052, 2921, 2851, 1611, 1578, 1559, 1513, 1467, 1248, 1175, 1109, 1084, 1038, 828 cm^{-1}. MS (MALDI-TOF): calcd. for $[M - BF_4]^+$, 411.64; found, 411.32. Elemental analysis: calcd. (%) for $C_{27}H_{43}BF_4N_2O$: C, 65.06; H, 8.70; N, 5.62. Found: C, 64.94; H, 8.74; N, 5.72.

1-Methyl-3-{6-[4-(*trans*-4-pentylcyclohexyl)phenoxy]hexyl}imidazolium trifluoromethanesulfonate (1(CF_3SO_3))

To a solution of compound **5** (0.800 g, 1.63 mmol) in methanol (10 mL) was added a solution of $AgOSO_2CF_3$ (0.505 g, 1.97 mmol) in methanol (10 mL) with stirring at room temperature. The mixture was stirred for 16 h at room temperature. Insoluble AgBr was filtered off and the filtrate was concentrated by a rotary evaporator. The crude product was purified by flash column chromatography on silica gel (eluent: $CHCl_3$/methanol = 10/1) and recrystallized from hexane/ethyl acetate to give **1(CF_3SO_3)** (0.675 g, 1.21 mmol, 74%) as a white solid. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.33 (s, 1H), 7.20 (m, 2H), 7.11 (d, J = 8.0 Hz, 2H), 6.80 (d, J = 8.8 Hz, 2H), 4.22 (t, J = 7.2 Hz, 2H), 3.98 (s, 3H), 3.92 (t, J = 6.0 Hz, 2H), 2.40 (tt, J = 3.0, 12 Hz, 1H), 1.96–1.75 (m, 8H), 1.55–1.20 (m, 15H), 1.03 (m, 2H), 0.89 (t, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.01, 140.14, 136.99, 127.65, 123.47, 121.98, 120.65 (q), 114.19, 67.42, 50.02, 43.71, 37.39, 37.29, 36.41, 34.59, 33.63, 32.22, 29.96, 28.93, 26.67, 25.78, 25.41, 22.73, 14.14. IR (KBr): 3156, 3113, 3087, 2921, 2852, 1611, 1577, 1562, 1511, 1474, 1275, 1264, 1247, 1226, 1150, 1030, 831, 756, 635, 625 cm^{-1}. MS (MALDI-TOF): calcd. for $[M - CF_3SO_3]^+$, 411.64; found, 411.40. Elemental analysis: calcd. (%) for $C_{28}H_{43}F_3N_2O_4S$: C, 59.98; H, 7.73; N, 5.00. Found: C, 59.88; H, 7.65; N, 5.03.

1-Methyl-3-{6-[4-(*trans*-4-pentylcyclohexyl)phenoxy]hexyl}imidazolium bis(trifluoromethanesulfonyl)imide (1(($CF_3SO_2)_2N$))

To a solution of compound **5** (0.218 g, 0.443 mmol) in methanol (5 mL) was added a solution of $LiN(SO_2CF_3)_2$ (0.640 g, 2.23 mmol) in methanol (15 mL) with stirring at room temperature. The mixture was stirred for 10 h at room temperature. The reaction mixture was extracted with $CHCl_3$. The resulting organic phase was dried over anhydrous $MgSO_4$. $MgSO_4$ was filtered off and the filtrate was concentrated by a rotary evaporator. The crude product was purified by flash column chromatography on silica gel (eluent: $CHCl_3$ followed by $CHCl_3$/methanol = 10/1) and recrystallized from hexane/ethyl acetate to give **1(($CF_3SO_2)_2N$)** (0.191 g, 0.276 mmol, 62%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.83 (s, 1H), 7.22 (m, 2H), 7.11 (d, J = 8.4 Hz, 2H), 6.80 (d, J = 8.8 Hz, 2H), 4.19 (t, J = 7.6 Hz, 2H), 3.93 (s, 3H), 3.91 (t, J = 6.8 Hz, 2H), 2.40 (tt, J = 3.0, 12.0 Hz, 1H), 1.92–1.76 (m, 8H), 1.54–1.20 (m, 15H), 1.03 (m, 2H), 0.89 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.99, 140.11, 135.98, 127.61, 123.63, 122.17, 119.74 (q), 114.16, 67.39, 50.00, 43.67, 37.35, 37.25, 36.25, 34.56, 33.60, 32.18, 29.91, 28.87, 26.63, 25.69, 25.33, 22.68, 14.09. IR (KBr): 3174, 3127, 2927, 2855, 1614, 1571, 1512, 1460, 1352, 1337, 1246, 1209, 1192, 1176, 1139, 1055, 827, 754, 617 cm^{-1}. MS (MALDI-TOF): calcd. for $[M - (CF_3SO_2)_2N]^+$, 411.64; found, 411.38. Elemental analysis: calcd. (%) for $C_{29}H_{43}F_6N_3O_5S_2$: C, 50.35; H, 6.27; N, 6.07. Found: C, 50.43; H, 6.10; N, 6.01.

1.2 Preparation of the mixtures

The mixtures containing **2(BF_4)** were prepared by evaporation of the methanol solution at 80 °C followed by drying under reduced pressure at 80 °C. The other mixtures were prepared by using tetrahydrofuran solutions in the similar manner.

2. Liquid-crystalline properties

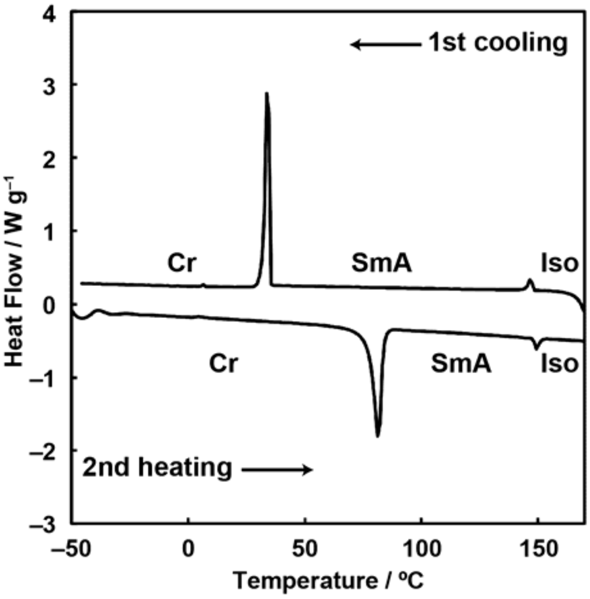


Fig. S1 Differential scanning calorimetry (DSC) thermograms of **1(CF$_3$SO$_3$)** at the scanning rate of 10 K min^{-1}. Cr: crystalline; SmA: smectic A; Iso: isotropic.

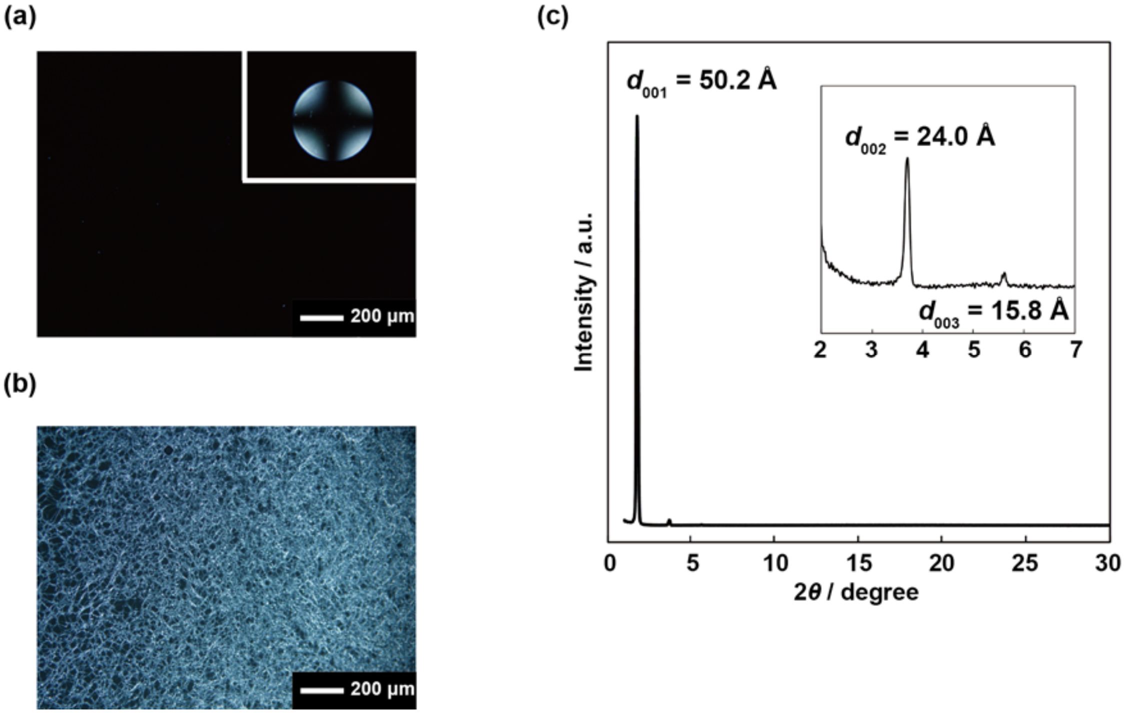


Fig. S2 (a) Polarizing optical microscopic image of a homeotropically aligned sample of **1(CF$_3$SO$_3$)** at 100 °C on cooling from the isotropic state. The inset shows the conoscopic image. (b) Polarizing optical microscopic image of a nonaligned sample of **1(CF$_3$SO$_3$)** at 100 °C on heating. (c) X-ray diffraction pattern of **1(CF$_3$SO$_3$)** at 58 °C.

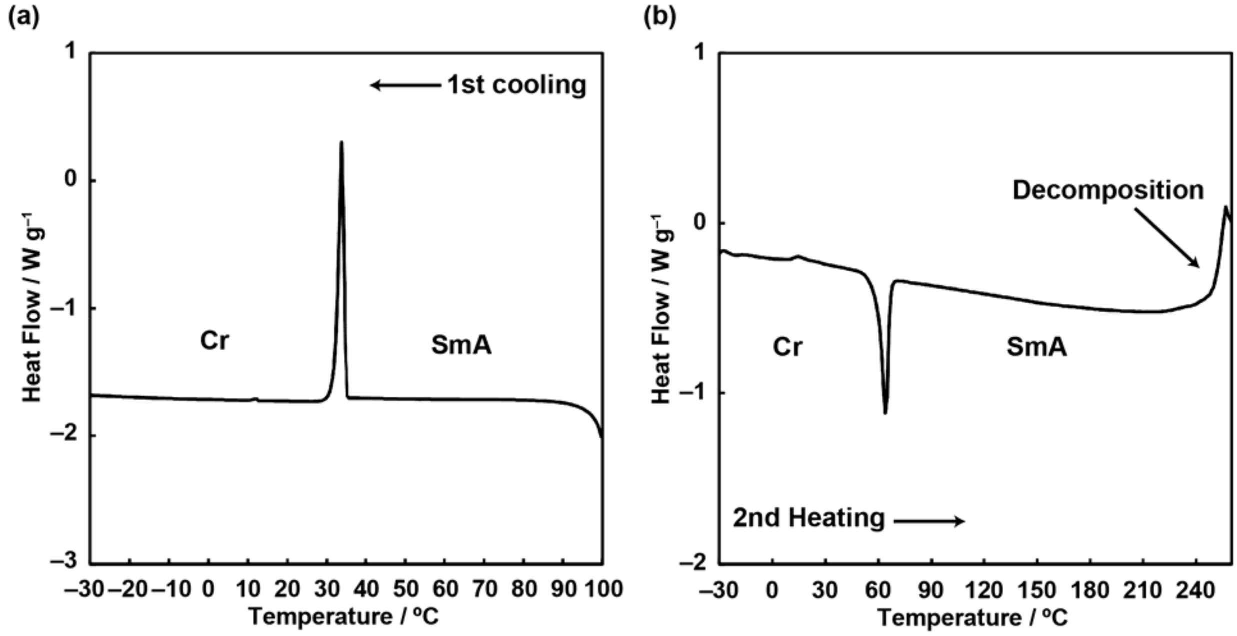


Fig. S3 DSC thermograms of **1(BF$_4$)** at the scanning rate of 10 K min^{-1}: (a) on the 1st cooling from 100 °C; (b) on the 2nd heating. Cr: crystalline; SmA: smectic A.

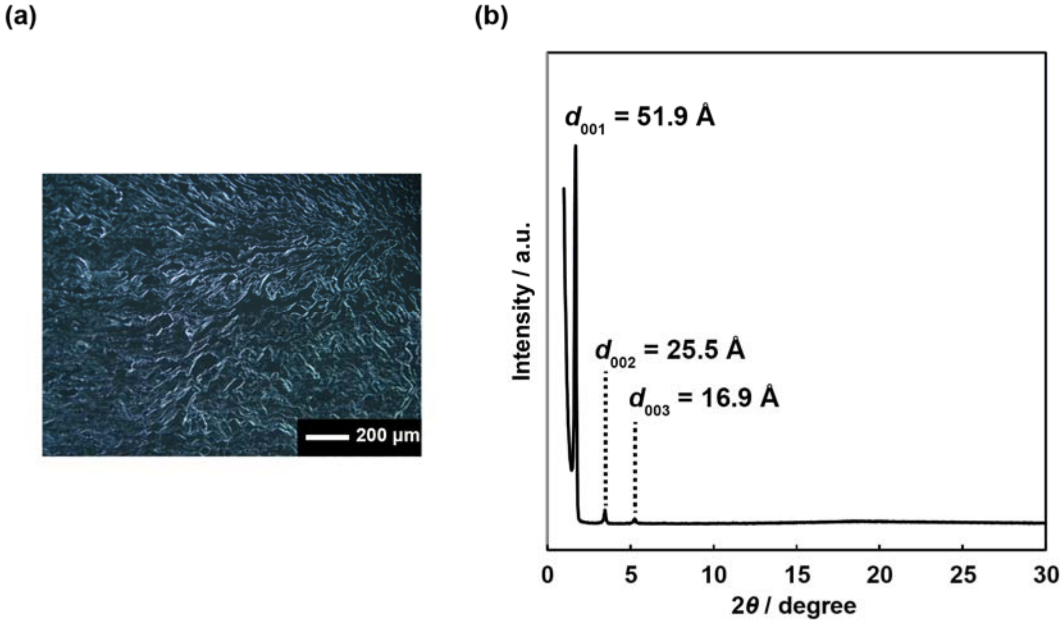


Fig. S4 (a) Polarizing optical microscopic image of a nonaligned sample of **1(BF$_4$)** at 75 °C on heating. (b) X-ray diffraction pattern of **1(BF$_4$)** at 80 °C.

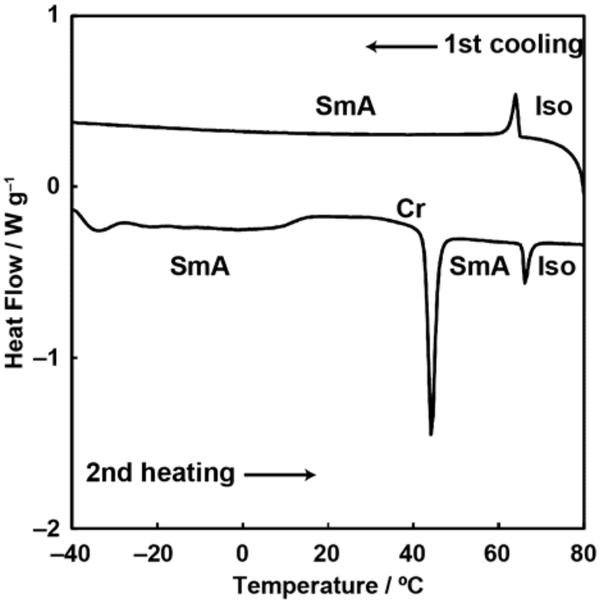


Fig. S5 DSC thermograms of **1((CF$_3$SO$_2$)$_2$N)** at the scanning rate of 10 K min^{-1}. Cr: crystalline; SmA: smectic A; Iso: isotropic.

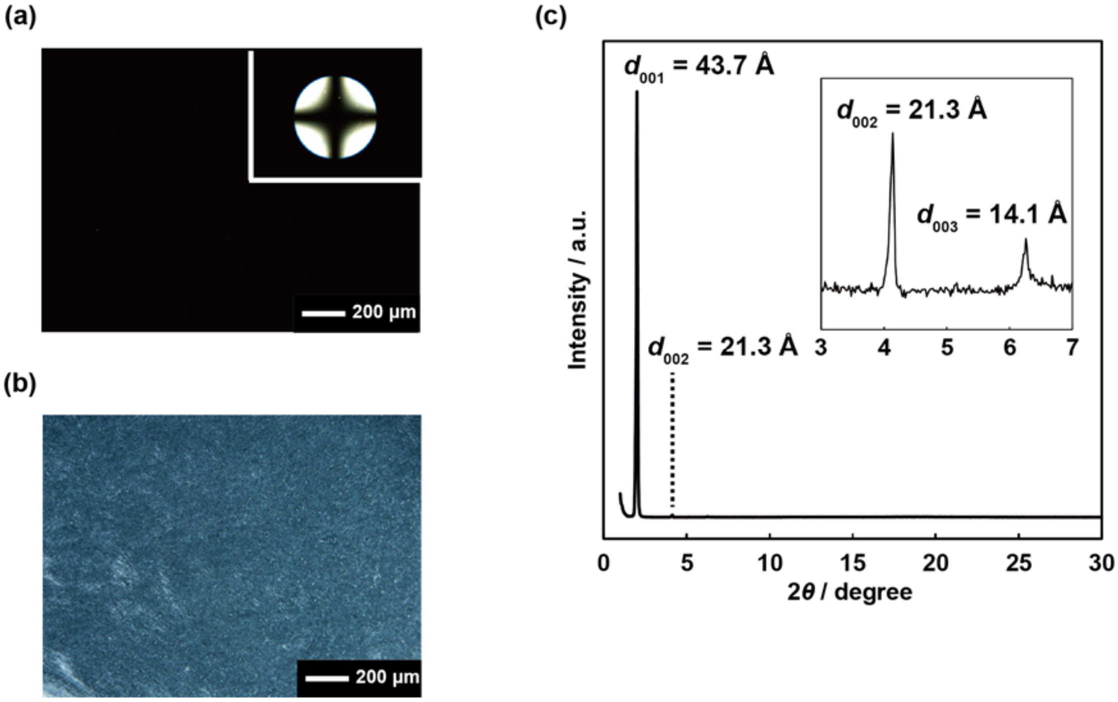


Fig. S6 (a) Polarizing optical microscopic image of a homeotropically aligned sample of **1((CF$_3$SO$_2$)$_2$N)** at 40 °C on cooling from the isotropic state. The inset shows the conoscopic image. (b) Polarizing optical microscopic image of a nonaligned sample of **1((CF$_3$SO$_2$)$_2$N)** at 40 °C on heating. (c) X-ray diffraction pattern of **1((CF$_3$SO$_2$)$_2$N)** at 30 °C.

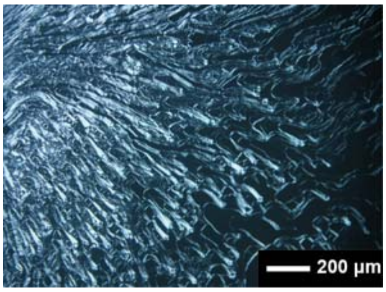


Fig. S7 Polarizing optical microscopic image of the nonaligned LC mixture of **1(CF_3SO_3)** and **2(CF_3SO_3)** in a 7:3 molar ratio at 85 °C on heating.

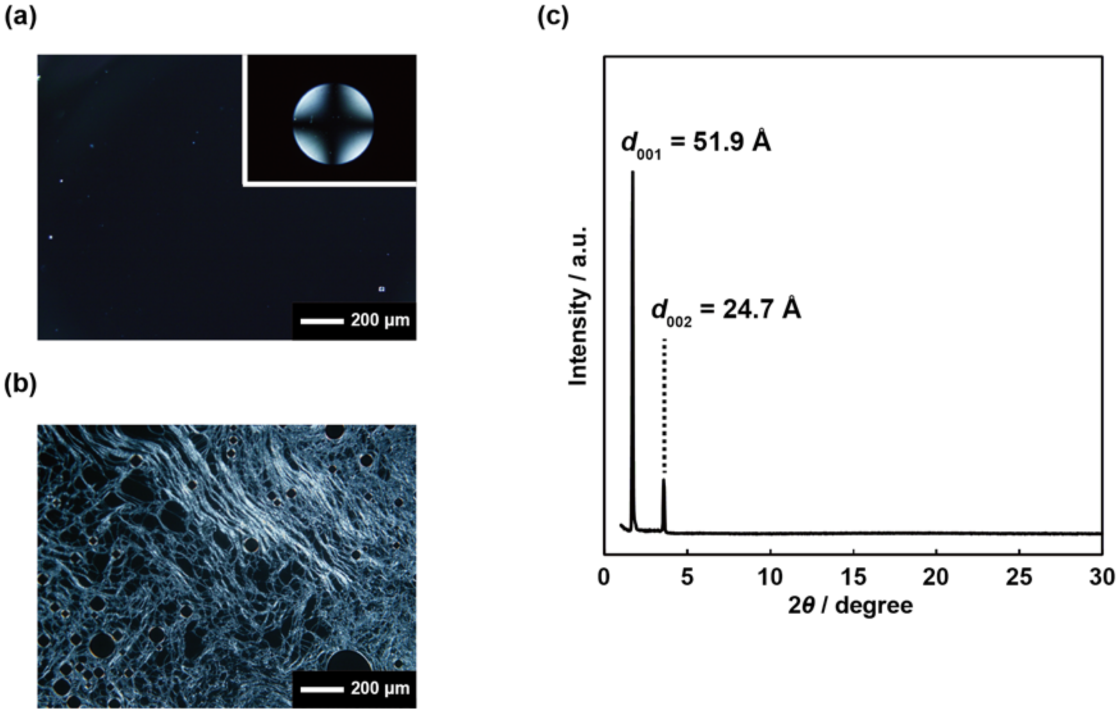


Fig. S8 (a) Polarizing optical microscopic image of the homeotropically aligned LC mixture of **1(CF_3SO_3)**, **2(CF_3SO_3)**, and **$LiCF_3SO_3$** in 7:3:1.5 molar ratios at 100 °C on cooling from the isotropic state. The inset shows the conoscopic image. (b) Polarizing optical microscopic image of the nonaligned LC mixture at 80 °C on heating. (c) X-ray diffraction pattern of the mixture at 59 °C.

3. Macroscopic phase separation of the mixtures of 1(CF_3SO_3) and 2(CF_3SO_3)

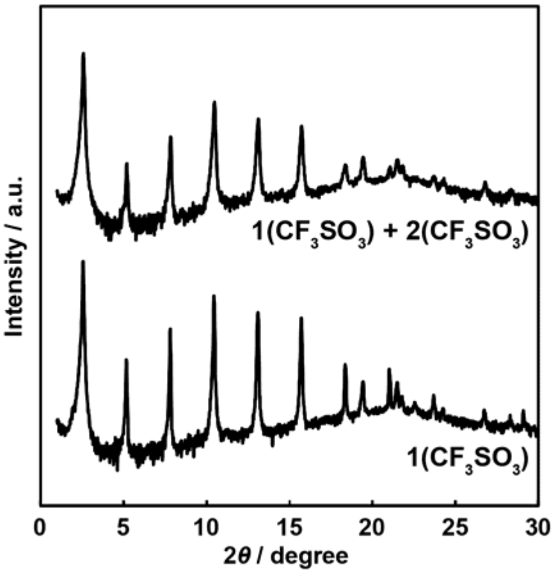


Fig. S9 X-ray diffraction patterns of the mixture of **1(CF_3SO_3)** and **2(CF_3SO_3)** in a 7:3 molar ratio in the phase separated state (top) and **1(CF_3SO_3)** in the crystalline state (bottom). The patterns were obtained at 22 °C on heating.

The optical microscopic observation of the mixture of **1(CF_3SO_3)** and **2(CF_3SO_3)** in a 7:3 molar ratio at 22 °C on heating reveals the existence of the biphasic mixtures of crystalline and isotropic liquid phases. Moreover, the X-ray diffraction pattern of the mixture at 22 °C on heating is almost the same as that of **1(CF_3SO_3)** in the crystalline state as shown in Fig. S7. These results suggest that the crystallization of **1(CF_3SO_3)** in the mixture causes the macroscopic phase separation

4. Ionic conductivities of 1(X)

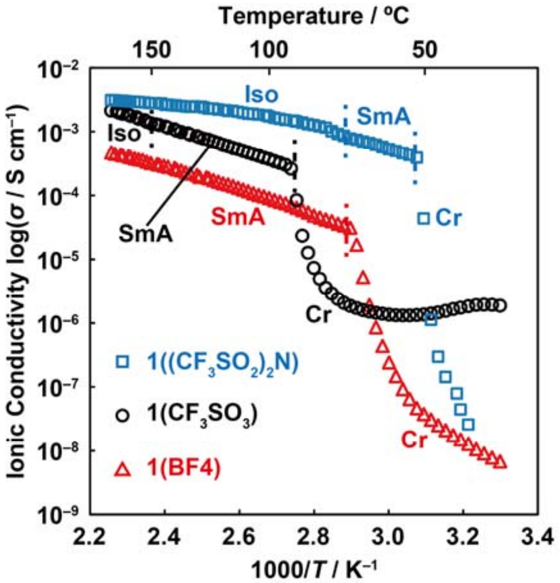


Fig. S10 Ionic conductivities of **1(BF_4)**, **1(CF_3SO_3)**, and **1((CF_3SO_2)$_2$N)** on heating. Cr: crystalline; SmA: smectic A; Iso: isotropic.

The ionic conductivity of sample was measured by using a cell consisting of a pair of indium tin oxide (ITO) electrodes. The sample thickness was fixed by a Teflon spacer to be 130 μm, where the sample in the smectic A (SmA) phase formed randomly oriented polydomain.

The ionic conductivities in the SmA phases increase in the order of **1((CF_3SO_2)$_2$N)** > **1(CF_3SO_3)** > **1(BF_4)**. It is assumed that ion-conductive pathways with higher mobility are formed for **1(X)** with larger anions.[S1]

5. Calculation of activation energy for ion conduction

Activation energies for ion conduction were calculated from the slopes of Arrhenius plots of ionic conductivities using the following Arrhenius equation (eqn (S1)) for conductivity σ:

$$\sigma = \sigma_0 \exp[-(E_a/RT)] \qquad \text{(S1)}$$

where σ_0 is the constant, E_a is the activation energy for ion conduction, R is the gas constant, and T is temperature.

This equation comes from the Arrhenius behavior[S2] of viscosity η of fluids (eqn (S2)), which inversely relates to ionic conductivity[S3]:

$$\eta = \eta_0 \exp[(E_a/RT)] \qquad \text{(S2)}$$

where η_0 is the constant.

6. Association of ions in the mixtures containing $LiCF_3SO_3$

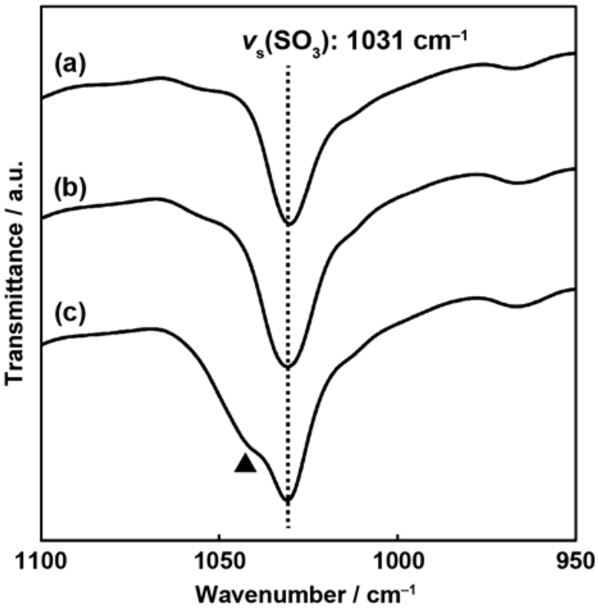


Fig. S11 IR spectra of (a) **1(CF_3SO_3)**, (b) the mixture of **1(CF_3SO_3)** and **2(CF_3SO_3)** in a 7:3 molar ratio, and (c) the mixture of **1(CF_3SO_3)**, **2(CF_3SO_3)**, and **$LiCF_3SO_3$** in 7:3:1.5 molar ratios. All spectra were taken for the samples in the SmA phases at 90 °C.

Only for the mixture containing **$LiCF_3SO_3$**, the shoulder around 1040 cm^{-1} is observed for the peak at 1031 cm^{-1} that is assigned to the symmetric stretching mode of SO_3 groups ($v_s(SO_3)$). The observation of the shoulder suggests the existence of CF_3SO_3 anions interacting with lithium cations and the association of the ions.[S4]

7. Thermal stability of the liquid-crystalline phases of the mixtures of 1(CF_3SO_3) and 2(X)

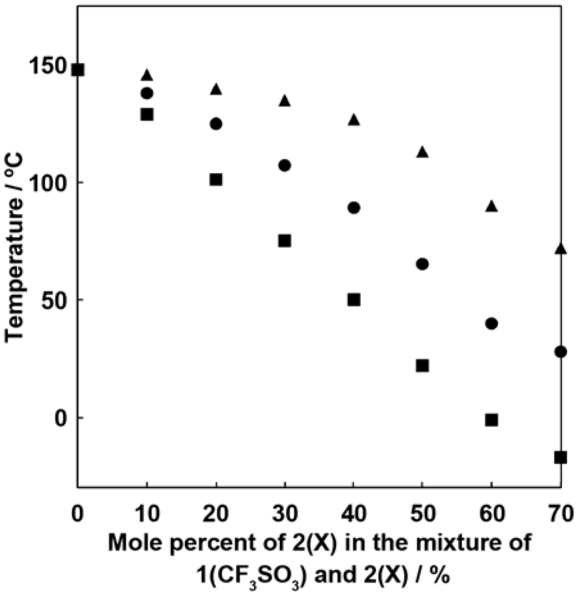


Fig. S12 Isotropization temperatures of the mixtures of **1(CF_3SO_3)** and **2(X)**. The counter anions X are BF_4 (▲), CF_3SO_3 (●), and $(CF_3SO_2)_2N$ (■).

8. References

S1 M. Ue, A. Murakami and S. Nakamura, *J. Electrochem. Soc.*, 2002, **149**, A1385–A1388.

S2 O. O. Okoturo and T. J. VanderNoot, *J. Electroanal. Chem.*, 2004, **568**, 167–181.

S3 P. Bonhôte, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram and M. Grätzel, *Inorg. Chem.*, 1996, **35**, 1168–1178.

S4 C. M. Burba, N. M. Rocher, R. Frech and D. R. Powell, *J. Phys. Chem. B*, 2008, **112**, 2991–2995; W. Huang, R. Frech and R. A. Wheeler, *J. Phys. Chem.*, 1994, **98**, 100–110; M. Deepa, N. Sharma, S. A. Agnihotry and R. Chandra, *J. Mater. Sci.*, 2002, **37**, 1759–1765.