

Supplementary Materials for

Design of Ionic Liquid Crystals Forming Normal-Type Bicontinuous Cubic Phases with a 3D Continuous Ion Conductive Pathway

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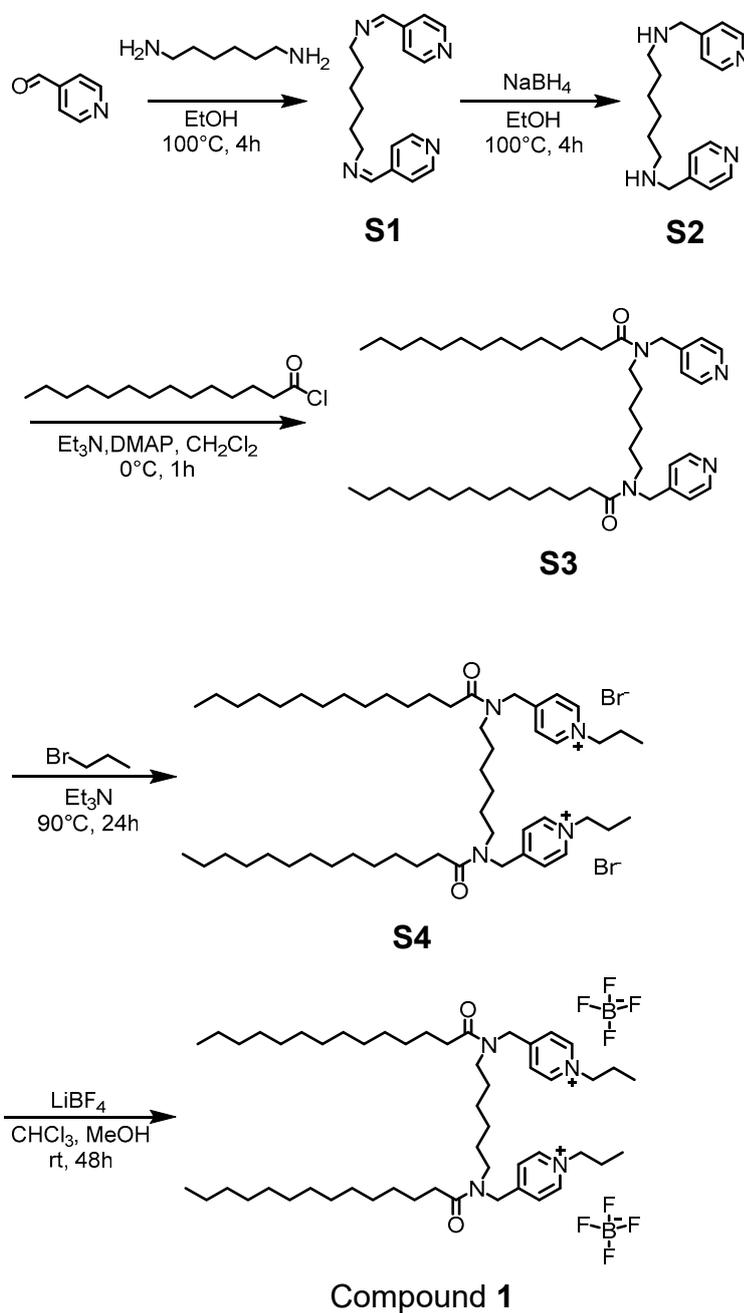
1. General Procedures and Materials

General procedures. ^1H NMR and ^{13}C NMR spectra were obtained on a JEOL JNMECX400 at 400 MHz and 500 MHz in CDCl_3 , CD_3OD , and $\text{DMSO}-d_6$. Chemical shifts of ^1H and ^{13}C NMR signals were quoted to $(\text{CH}_3)_4\text{Si}$ ($\delta = 0.00$), $\text{DMSO}-d_6$ ($\delta = 2.50$), CDCl_3 ($\delta = 77.0$) as internal standards, respectively. Elemental analyses were carried out on an Elementar Analytical vario EL3. The thermal properties of the compounds were examined by using a differential scanning calorimeter (DSC-6220, Seiko Instruments). The heating and cooling rates were $10\text{ }^\circ\text{C min}^{-1}$. A polarizing optical microscope Olympus BX51 equipped with a Linkam LK-600 hot stage was used for visual observation. Wide-angle X-ray diffraction (WAXD) patterns were obtained using a Rigaku Smart Lab.

Materials. All chemical reagents and solvents were obtained from commercial sources and used without purification. All reactions were carried out under an argon atmosphere.

2. Synthesis of compound 1-5

2. 1. Synthetic scheme for compound 1



Compound **S3** was synthesized according to the literature.¹ Compound **1** was synthesized from compound **S3** through two steps.

Synthesis of compound S2

1,6-Hexanediamine (2.70 g, 23.3 mmol) was added to a solution of 4-pyridinecarboxaldehyde (**S1**) (5.00 g, 46.7 mmol) in ethanol and then heated to reflux for 4 h. The reacted solution was cooled to room temperature. NaBH₄ (2.16 g, 57.7 mmol) in ethanol (50ml) was gradually added to this solution and then the mixture was heated to reflux for 4 h. Excess amount of NaOH aq. (3M, 20 mL) and CHCl₃ was added to the reaction solution and the organic layer was collected and evaporated. The obtained reactant was washed with diethyl ether repeatedly and collected by filtration. White powder was obtained in 83 %. The ¹H NMR data were in accordance with the literature: Saeed, H. K., et al., *Angew. Chem. Int. Ed.* 56, 12628 (2017).

Synthesis of compound S3

Myristoyl chloride (2.07 g, 8.38 mmol) was added to a solution of **S2** (1.00 g, 3.35 mmol), triethylamine (1.69 g, 16.8 mmol) and a small amount of 4-dimethylaminopyridine in CH₂Cl₂ (100 ml) at 0 °C for 1 h. Then water and CHCl₃ were added. The organic layer was separated and evaporated. The crude product was purified by flash column chromatography (silica gel, eluent: CHCl₃/methanol = 9/1). Compound **S3** was obtained as a viscous liquid (1.77 g, 76% yield).

¹H NMR (400 MHz, CDCl₃): δ = 8.56 (m, 4H), 7.08 (m, 4H), 4.51 (m, 4H), 3.33 (m, 2H), 3.21 (m, 2H), 2.38-2.22 (m, 4H), 1.69-1.52 (m, 12H), 1.33-1.18 (m, 40H), 0.88 (t, 6H).

Synthesis of compound S4

An excess amount of 1-bromopropane was added to a solution of crude compound of **S3** (1.77 g, 2.46 mmol) in acetonitrile. The mixture was heated to reflux for 8 h. Through recrystallization from acetone mixed solvent repeatedly, compound **S4** was obtained as a yellowish powder (1.43 g, 60% yield).

¹H NMR (400MHz, CDCl₃): δ = 9.11 (d, 4H), 7.97 (d, 4H), 4.95 (s, 4H), 4.85-4.81 (m, 4H), 3.44 (m, 4H), 2.41 (t, 4H), 2.11-2.00 (m, 4H), 1.70-1.56 (m, 8H), 1.44-1.20 (m, 44H), 1.00 (t, 6H), 0.89 (t, 6H).

Synthesis of compound 1

To a solution of **S4** (1.00 g, 1.04 mmol) in CHCl₃/MeOH (20 ml/5 ml) was added a solution of LiBF₄ (1.25 g, 13.3 mmol) in MeOH (2 mL) with stirring at room temperature. The mixture was stirred at room temperature for 2 h. The reaction mixture was extracted with CHCl₃. The crude product was purified by flash-column chromatography on silica gel (silica gel, eluent: CHCl₃/MeOH = 10 : 1) to give 0.82 g (81 %) of the pure product as a white solid.

¹H NMR (400MHz, CDCl₃): δ = 8.57 (d, 4H), 7.80 (d, 4H), 4.77 (s, 4H), 4.49 (m, 4H), 3.35 (m, 4H), 2.41 (t, 4H), 2.08-1.94 (m, 4H), 1.66 (m, 8H), 1.40-1.19 (m, 44H), 0.98 (6H), 0.88 (t, 6H).

2. 2. Synthesis of compound 2-5

Compound 2-5 were synthesized in the same way.

Compound 2

^1H NMR (400MHz, CDCl_3): δ = 8.66 (d, 4H), 7.83 (d, 4H), 4.78 (s, 4H), 4.52 (t, 4H), 3.35 (m, 4H), 2.41 (t, 4H), 2.07-1.96 (m, 4H), 1.73-1.52 (m, 8H), 1.42-1.15 (m, 44H), 0.99 (t, 6H), 0.88 (t, 6H).

Compound 3

^1H NMR (400MHz, CDCl_3): δ = 8.55 (d, 4H), 7.79 (d, 4H), 4.77 (s, 4H), 4.49 (t, 4H), 3.35 (t, 4H), 2.41 (t, 4H), 2.03-1.94 (m, 4H), 1.73-1.51 (m, 8H), 1.39-1.17 (m, 52H), 0.98 (6H), 0.88 (t, 6H).

Compound 4

^1H NMR (400MHz, CDCl_3): δ = 8.55 (d, 4H), 7.79 (d, 4H), 4.74 (s, 4H), 4.45 (m, 4H), 3.35 (m, 4H), 2.42 (t, 4H), 2.04-1.94 (m, 4H), 1.70-1.55 (m, 8H), 1.38-1.16 (m, 52H), 0.98 (t, 6H), 0.88 (t, 6H).

Compound 5

^1H NMR (400MHz, CDCl_3): δ = 8.63 (d, 2H), 7.81 (d, 2H), 4.73 (s, 2H), 4.52 (m, 2H), 3.49 (m, 2H), 2.45 (t, 2H), 2.04-1.94 (m, 2H), 1.69-1.60 (q, 3H), 1.39-1.19 (m, 24H), 0.98 (t, 3H), 0.88 (t, 3H).

Elemental analysis

Compound 1: Calcd for $\text{C}_{52}\text{H}_{92}\text{N}_4\text{O}_2\text{B}_2\text{F}_8\text{S}_2$: C, 63.80; N, 5.72. Found: C, 63.45; N, 5.25. Compound 2: Calcd for $\text{C}_{54}\text{H}_{92}\text{N}_4\text{O}_8\text{F}_6\text{S}_2$: C, 58.77; N, 5.07. Found: C, 58.77; N, 5.21. Compound 3: Calcd for $\text{C}_{56}\text{H}_{100}\text{B}_2\text{F}_8\text{N}_4\text{O}_2$: C, 64.98; N, 5.41. Found: C, 65.28; N, 5.59. Compound 4: Calcd for $\text{C}_{60}\text{H}_{100}\text{F}_{12}\text{N}_6\text{O}_{10}\text{S}_4$: C, 50.69; N, 5.91. Found: C, 50.70; N, 6.14.

3. Liquid-Crystalline Behavior of compound 1-4

3.1. Liquid-crystalline behavior of compound 1

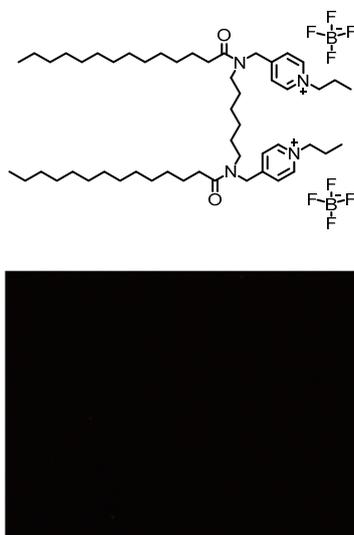


Figure S1. Polarizing optical image of compound 1 in a Cub_{bi} phase at 30 °C.

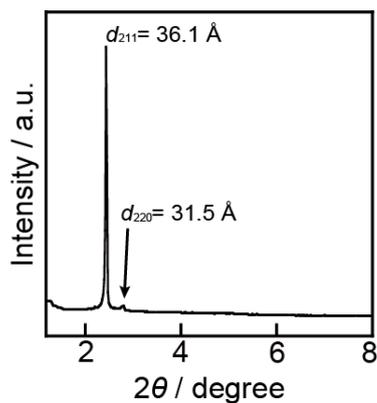


Figure S2. X-ray diffraction pattern of compound 1 in a Cub_{bi} phase at 30 °C.

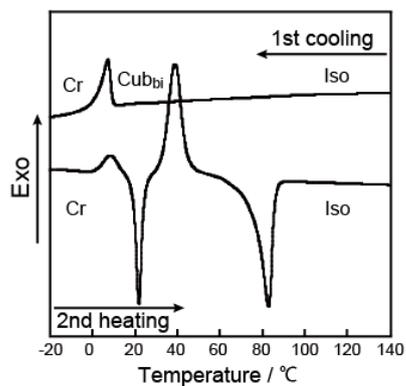


Figure S3. Differential scanning calorimetry thermograms of compound 1.

3.2. Liquid-crystalline behavior of compound 2

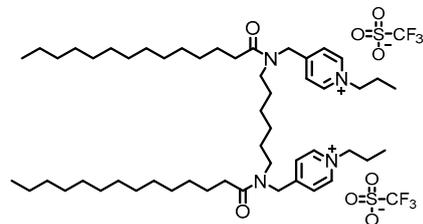


Figure S4. Polarizing optical image of compound 2 in an Iso phase at 30 °C.

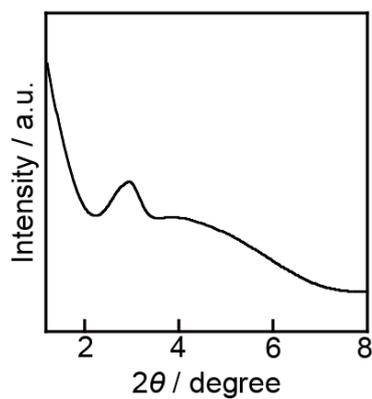


Figure S5. X-ray diffraction pattern of compound 2 in an Iso phase at 30 °C.

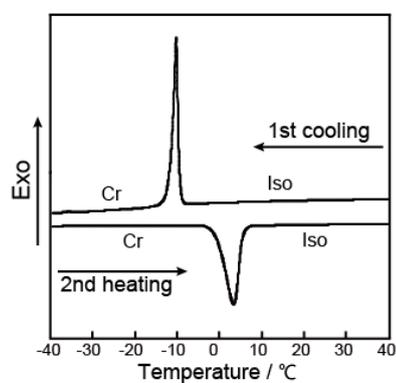


Figure S6. Differential scanning calorimetry thermograms of compound 2.

3.3. Liquid-crystalline behavior of compound 3

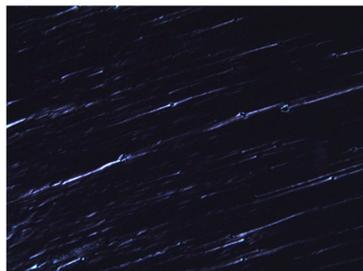
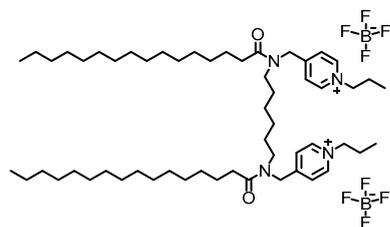


Figure S7. Polarizing optical image of compound 3 in a Sm phase at 50 °C.

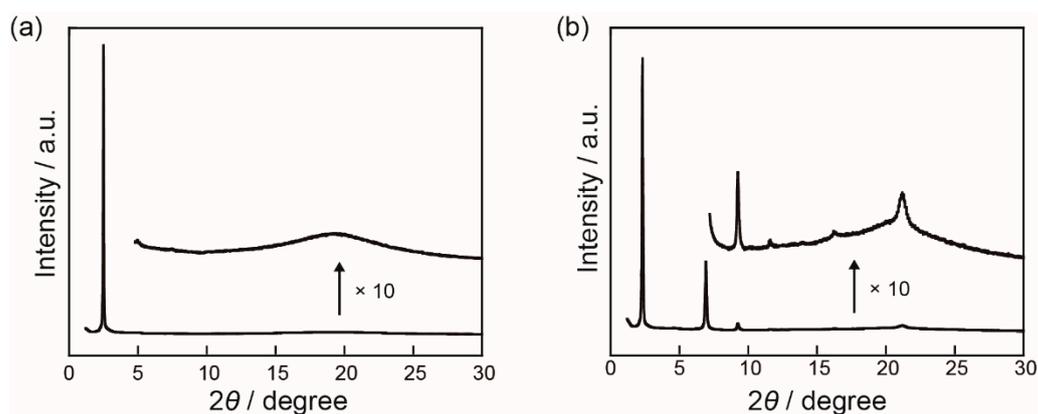


Figure S8. X-ray diffraction pattern of compound 3: (a) in a Sm phase at 105 °C; (b) in a crystalline phase at 25 °C

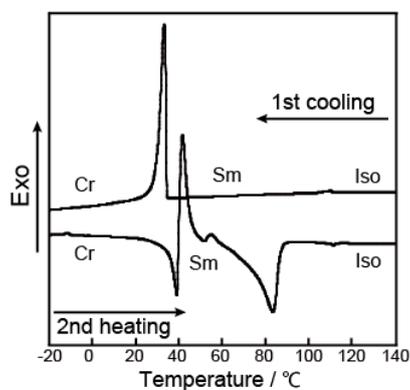


Figure S9. Differential scanning calorimetry thermograms of compound 3.

3.4. Liquid-crystalline behavior of compound 4

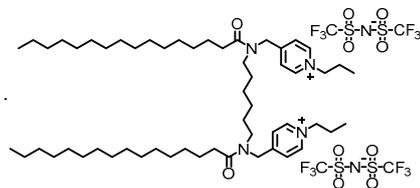


Figure S10. Polarizing optical image of compound 4 in an Iso phase at 30 °C.

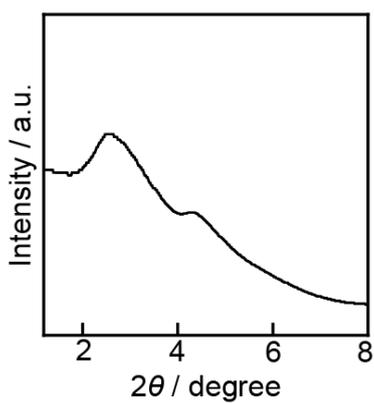


Figure S11. X-ray diffraction pattern of compound 4 in an Iso phase at 30 °C.

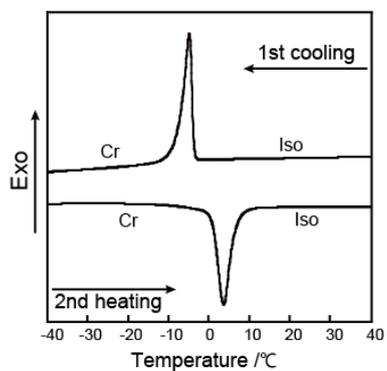


Figure S12. Differential scanning calorimetry thermograms of compound 4.

4. Liquid-crystalline behavior of the mixtures of 1 and LiBF₄

4.1. In the molar ratio of 10:1

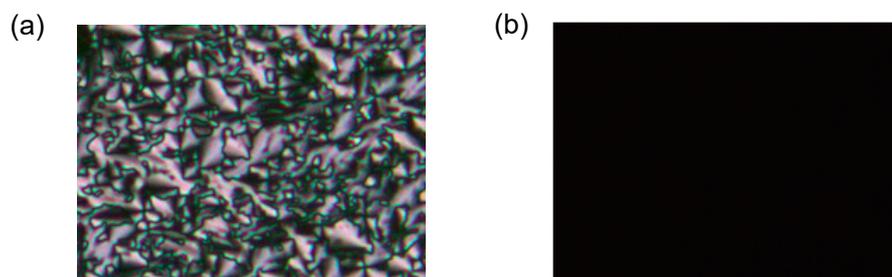


Figure S13. Polarizing optical image of the mixture of compound **1** and LiBF₄ in a 10:1 molar ratio: (a) in Col phase at 42 °C; (b) in Cub_{bi} phase at 40 °C.

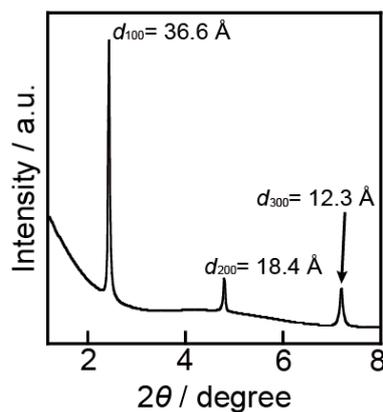


Figure S14. X-ray diffraction pattern of the mixture of compound **1** and LiBF₄ in a 10:1 molar ratio in Col phase at 42 °C.

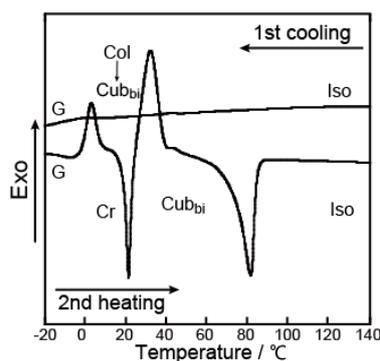


Figure S15. Differential scanning calorimetry thermograms of the mixture of compound **1** and LiBF₄ in a 10:1 molar ratio.

4. 2. In the molar ratio of 4:1

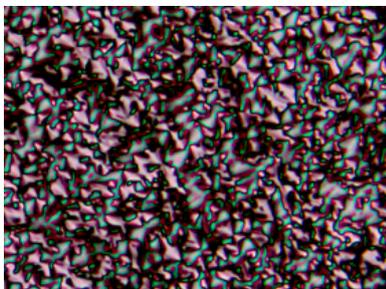


Figure S16. Polarizing optical image of the mixture of compound **1** and LiBF₄ in a 4:1 molar ratio in Col phase at 55 °C.

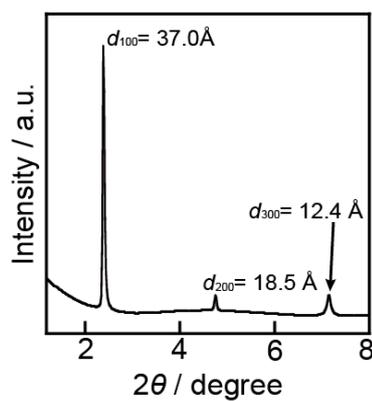


Figure S17. X-ray diffraction pattern of the mixture of compound **1** and LiBF₄ in a 4:1 molar ratio in Col phase at 55 °C.

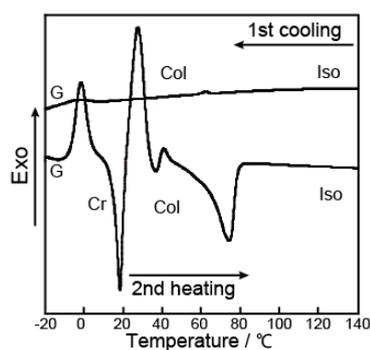


Figure S18. Differential scanning calorimetry thermograms of the mixture of compound **1** and LiBF₄ in a 4:1 molar ratio.

4.3. In the molar ratio of 2:1

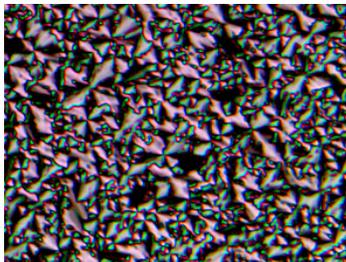


Figure S19. Polarizing optical image of the mixture of compound **1** and LiBF₄ in a 2:1 molar ratio in Col phase at 60 °C.

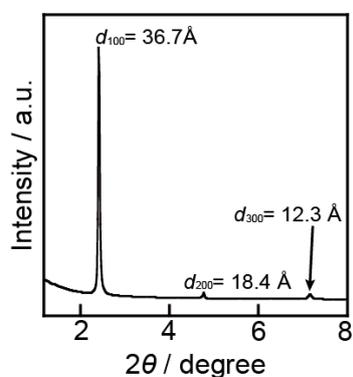


Figure S20. X-ray diffraction pattern of the mixture of compound **1** and LiBF₄ in a 2:1 molar ratio in Col phase at 60 °C.

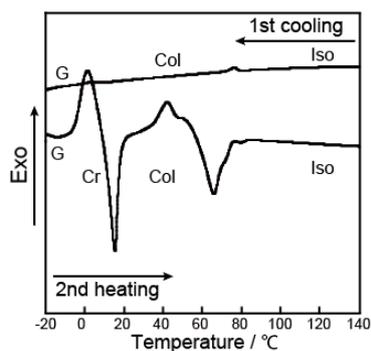


Figure S21. Differential scanning calorimetry thermograms of the mixture of compound **1** and LiBF₄ in a 2:1 molar ratio.

4. 4. In the molar ratio of 1:1

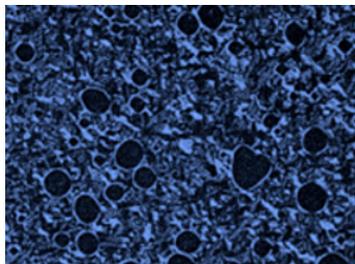


Figure S22. Polarizing optical image of the mixture of compound **1** and LiBF₄ in a 1:1 molar ratio in Col phase at 85 °C.

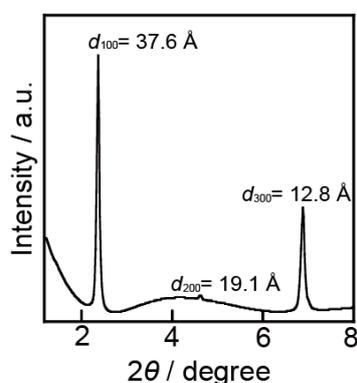


Figure S23. X-ray diffraction pattern of the mixture of compound **1** and LiBF₄ in a 1:1 molar ratio in Col phase at 85 °C.

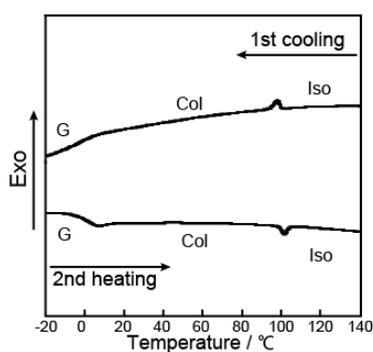


Figure S24. Differential scanning calorimetry thermograms of the mixture of compound **1** and LiBF₄ in a 1:1 molar ratio.