

Supporting Information

Self-healing and shape memory functions exhibited by supramolecular liquid-crystalline networks formed by combination of hydrogen bonding interactions and coordination bonding

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1. Synthesis

Synthesis of ligand 1

Ligand **1** was synthesized according to a reported procedure.^[1]

2. Alignment control of supramolecular LC networks

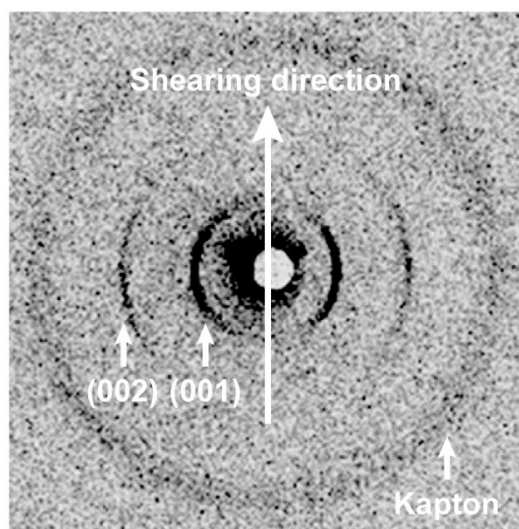


Fig. S1. The 2D small-angle X-ray diffraction pattern of supramolecular hydrogen-bonded LC network $1/2(3 : 2)$ at 70 °C in the film state.

The film of supramolecular hydrogen-bonded LC network $1/2(3 : 2)$ were aligned by applying shear force in the LC phase. The 2D small-angle X-ray diffraction pattern of $1/2(3 : 2)$ showed the split diffraction pattern (Fig. S1), which indicates that the uniaxial orientation of the LC assembly in the film state was obtained by mechanical shearing.

3. Macroscopic self-healing and shape memory effects of supramolecular LC networks

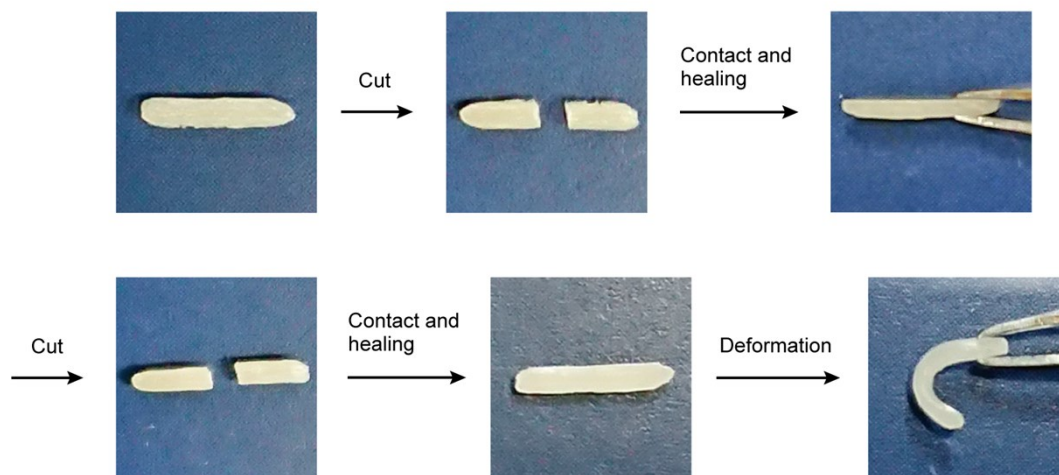


Fig. S2. Recycling of self-healing properties for supramolecular hydrogen-bonded LC network $1/2(3 : 2)$.

Recycling of self-healing properties was demonstrated for hydrogen-bonded LC network $1/2(3 : 2)$ (Fig. S2). The supramolecular LC materials showed adhesive and flexible properties even after multiple cycles of the self-healing.

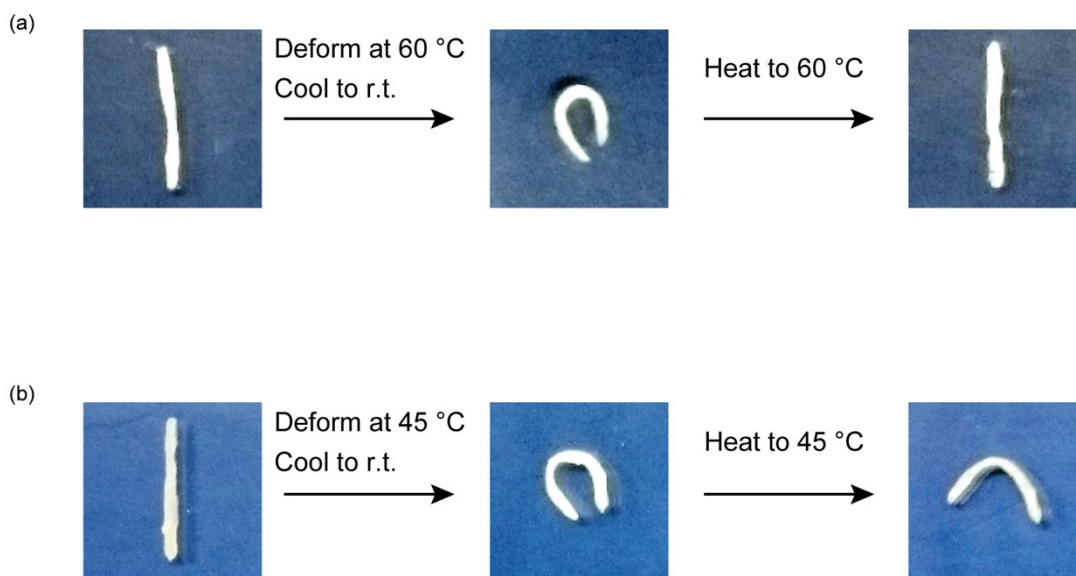


Fig. S3. (a) Photographs showing shape memory effects of supramolecular hybrid LC network $1/2/AgCF_3SO_3(3 : 1.2 : 1.2)$. (b) Photographs showing insufficient shape recovery of supramolecular hydrogen-bonded LC network $1/2(3 : 2)$.

Supramolecular hybrid LC network $1/2/AgCF_3SO_3(3 : 1.2 : 1.2)$ showed shape memory effects (Fig. S23a), while supramolecular hydrogen-bonded LC network $1/2(3 : 2)$ did not exhibit sufficient shape recovery (Fig. S3b). The recovery temperature was optimized for each LC materials. The difference in the behavior of shape recovery can be explained from the viewpoint of strength of intermolecular interactions, as discussed in the main text.

4. Characterization of supramolecular LC polymers and networks

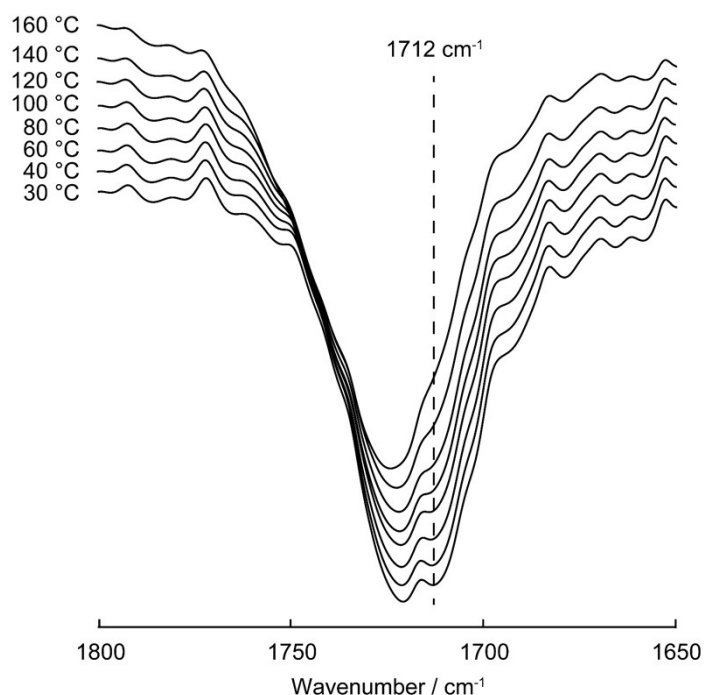


Fig. S4. Temperature-dependent IR spectra of supramolecular hydrogen-bonded LC network **1/2**(3 : 2).

A peak at 1700 cm^{-1} , which can be attributed to C=O stretching for **2** in the solid state (Fig. 6), was not observed for complex **1/2** (Fig. S4). These results suggest that aggregation of the single component of **2** was not induced for LC complex **1/2** by thermal treatment. Fig. S4 also shows a peak around 1712 cm^{-1} and its intensity gradually decreases on heating. We reported that C=O bands of the carboxylic acid forming hydrogen bonds with pyridine appeared between C=O bands of monomeric and dimeric carboxylic acids in IR spectra.^[2] Based on these observations, the peak around 1712 cm^{-1} for **1/2** can be ascribed to a C=O band of **2** forming hydrogen bonds with **1**.

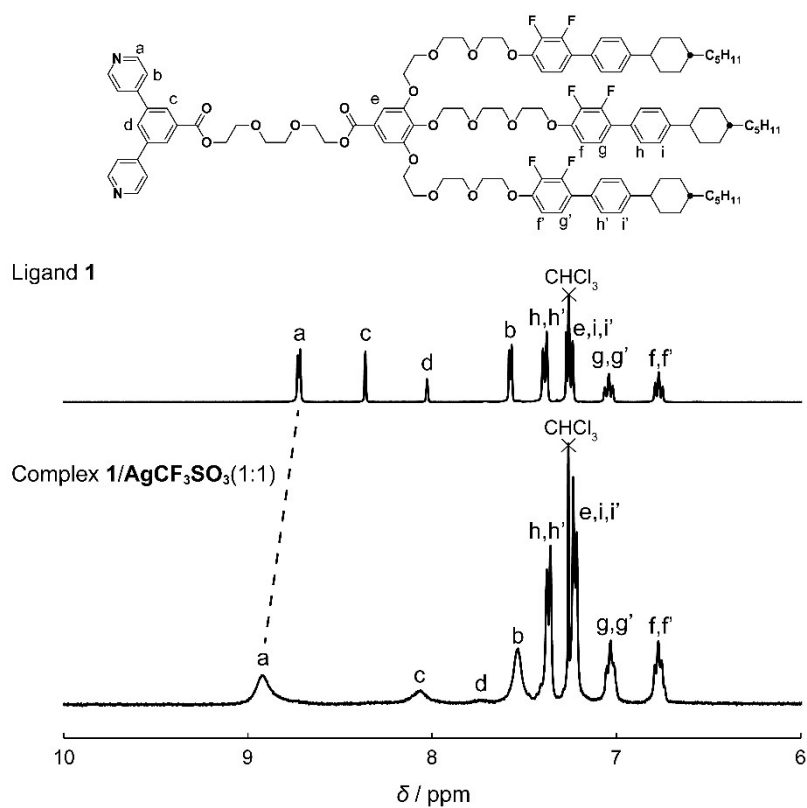


Fig. S5. ^1H NMR spectra (400 MHz) of ligand **1** and supramolecular coordination LC polymer $1/\text{AgCF}_3\text{SO}_3(1 : 1)$ in CDCl_3 .

The signal of pyridine α protons showed downfield shift after complexation of ligand **1** with AgCF_3SO_3 (Fig. S5). Moreover, the signals for $1/\text{AgCF}_3\text{SO}_3(1 : 1)$ were broader than those for **1**. These results indicate that large supramolecular structures with slow molecular motion were formed through complexation between pyridine moieties and Ag^+ ions.

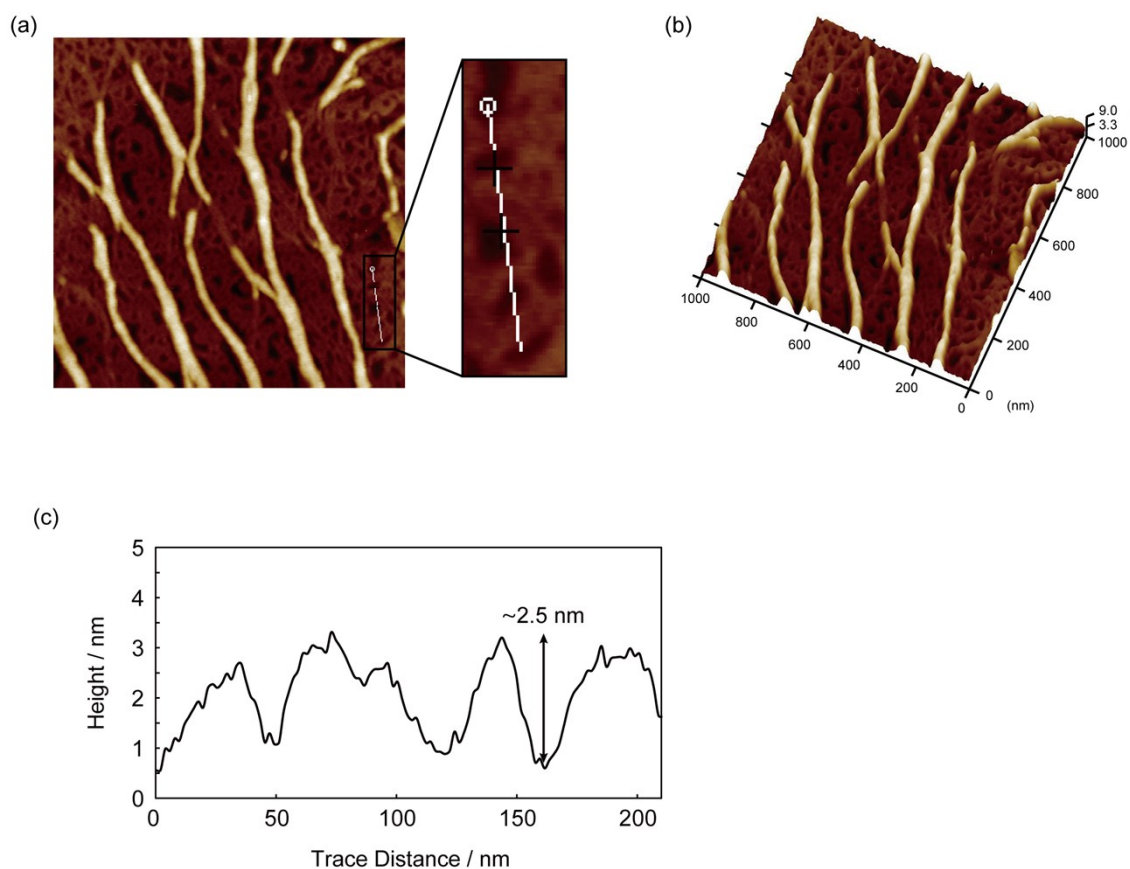


Fig. S6. (a) 2D and (b) 3D AFM images of supramolecular coordination LC polymer **1/AgCF₃SO₃(1 : 1)**. (c) Height profile along the white line in Fig. S6a.

The formation of fibrous aggregates was examined by AFM observation for **1/AgCF₃SO₃(1 : 1)** (Fig. S6a,b). Height profile of **1/AgCF₃SO₃(1 : 1)** showed that the diameter of thinner fibers was 2-3 nm (Fig. S6c).

5. Thermal and mesomorphic properties of supramolecular LC polymers and networks

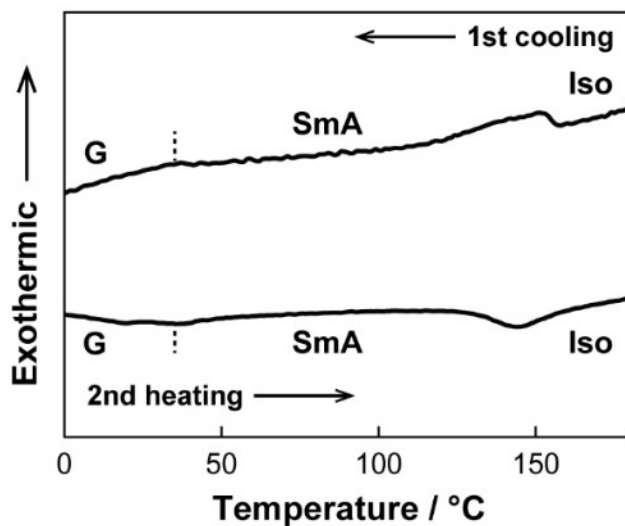


Fig. S7. Differential scanning calorimetry of supramolecular hydrogen-bonded LC network $1/2(3 : 2)$ at the scanning rate of $10\text{ }^{\circ}\text{C}/\text{min}$ (G: glassy, SmA: smectic A, Iso: isotropic).

The supramolecular hydrogen-bonded LC network of $1/2(3 : 2)$ showed reversible thermotropic phase transitions (Fig. S7). The exothermic peak was observed at $151\text{ }^{\circ}\text{C}$ on the first cooling from the isotropic state, indicating that the phase transition between isotropic and LC states occurred. The glass transition also appeared for $1/2(3 : 2)$ at $34\text{ }^{\circ}\text{C}$.

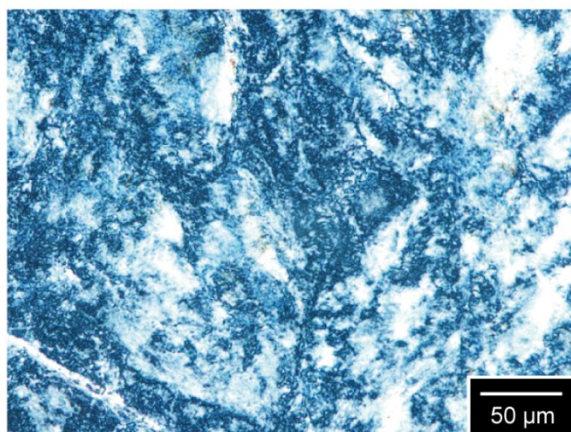


Fig. S8. Polarizing optical micrograph of supramolecular coordination LC polymer **1/AgCF₃SO₃(1 : 1)** at 100 °C.

Polarizing optical micrograph of **1/AgCF₃SO₃(1 : 1)** showed a polydomain texture in a viscous fluid state at 100 °C on heating (Fig. S8).

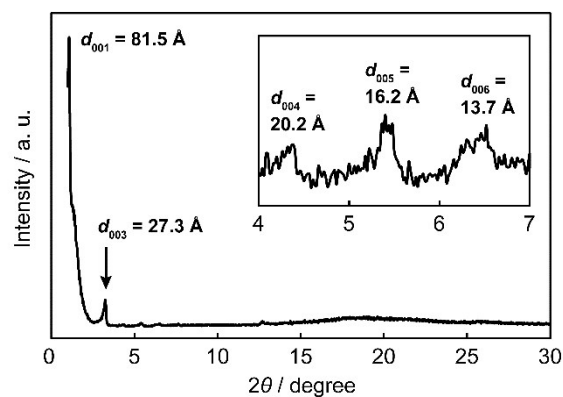


Fig. S9. X-ray diffraction pattern of supramolecular coordination LC polymer **1/AgCF₃SO₃(1 : 1)** at 100 °C.

XRD pattern of complex **1/AgCF₃SO₃(1 : 1)** at 100 °C gave several periodic peaks at 81.5, 27.3, 20.2, 16.2, and 13.7 Å (Fig. S9). These peaks were assigned to the (001), (003), (004), (005), and (006) diffractions of a smectic A phase with the average spacing of 81 Å.

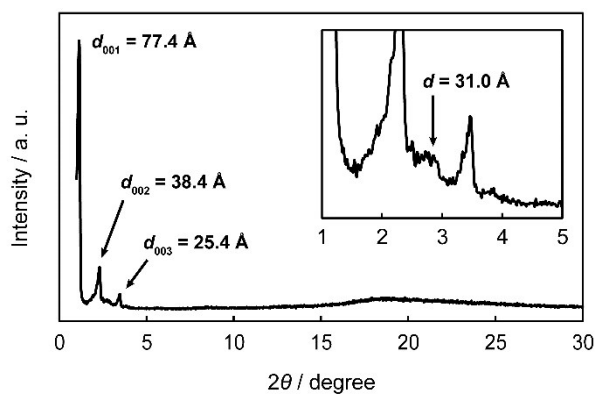


Fig. S10. X-ray diffraction pattern of supramolecular hybrid LC network $1/2/\text{AgCF}_3\text{SO}_3(3 : 1.2 : 1.2)$ at $100\text{ }^\circ\text{C}$.

XRD pattern of supramolecular hybrid LC network $1/2/\text{AgCF}_3\text{SO}_3(3 : 1.2 : 1.2)$ showed several periodic peaks at 77.4, 38.4, and 25.4 Å, which were ascribed to the (001), (002), and (003) diffractions of a smectic structure with the spacing of 77 Å (Fig. S10). In addition, a weak diffraction peak with a periodicity of 31 Å was observed. This might be due to the formation of local order of network structures in a smectic LC phase.

6. References

- [1] J. Uchida, M. Yoshio, S. Sato, H. Yokoyama, M. Fujita and T. Kato, *Angew. Chem. Int. Ed.*, 2017, **56**, 14085.
- [2] (a) T. Kato, J. M. J. Fréchet, P. G. Wilson, T. Saito, T. Uryu, A. Fujishima, C. Jin and F. Kaneuchi, *Chem. Mater.*, 1993, **5**, 1094; (b) T. Kato, T. Uryu, F. Kaneuchi, C. Jin and J. M. J. Fréchet, *Liq. Cryst.*, 1993, **14**, 1311; (c) T. Kato, C. Jin, F. Kaneuchi and T. Uryu, *Bull. Chem. Soc. Jpn.* 1993, **66**, 3581.