Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Induction of bicontinuous cubic liquid-crystalline assemblies for polymerizable amphiphiles via tailor-made design of ionic liquids

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1. General procedures and materials

General procedures. ^{1}H NMR and ^{13}C NMR spectra were obtained on a JEOL JNM-ECX400 at 400 and 100 MHz in *d*$_6$-DMSO, respectively. Chemical shifts of ^{1}H and ^{13}C NMR signals were quoted to $(CH_3)_4Si$ (δ = 0.00) and $CDCl_3$ (δ = 77.0) as internal standards, respectively. Elemental analyses were carried out on an Elementar Analytical vario EL3. The viscosity of amino acid ionic liquids was measured by a cone/plate viscometer (LVDV-1+, Brookfield). The thermal properties of amino acid ionic liquids were measured using a differential scanning calorimeter (DSC-6220, Seiko Instruments). The heating and cooling rates were 10 °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 in anhydrous solvents.

2. Synthesis of $[C_4mim][Asp]_x$ and AM_{12}

Amino acid ionic liquid $[C_4mim][Asp]_x$ (X = 0.50, 0.60, 0.80 and 1.0) were prepared through the neutralization of 1-butyl-3-methylimidazolium hydroxide with requisite amounts of aspartic acid according to the literature.[1] Amphiphile $\mathbf{AM_{12}}$ was also synthesized according to the literature.[2]

3. Characterization of [C$_4$mim][Asp]$_x$

[C$_4$mim][Asp]$_{0.50}$

^{1}H-NMR (400MHz, DMSO-d_6, δ/ppm relative to TMS): 0.81 (3H, t, J = 7.3 Hz), 1.18 (2H, m),1.69 (2.5H, m), 2.28 (0.5H, m), 3.04 (0.5H, q), 3.76 (2H, s), 3.85 (3H, s), 4.17 (2H, t, J = 7.1 Hz), 7.80 (1H, d, J = 1.7 Hz), 7.86 (1H, d, J = 1.9 Hz), 10.16 (1H, s).

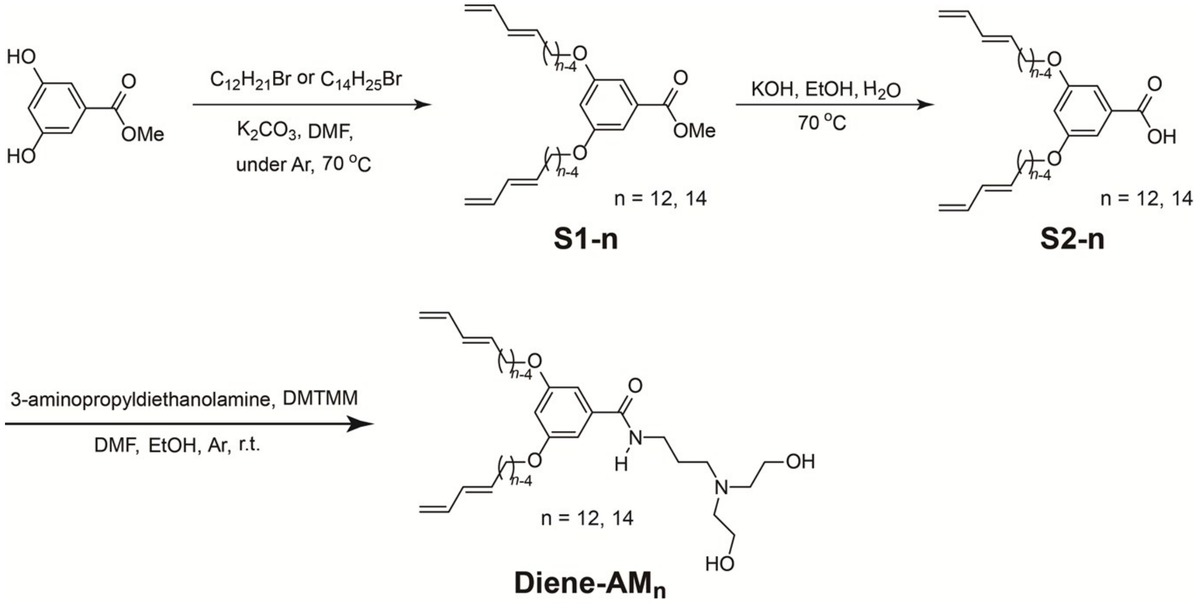
Elemental analysis calcd (%) for [C$_4$mim]$_2$[Asp]: C, 58.66; H, 8.61; N, 17.10. Found: C, 58.67; H, 8.56.; N, 17.11.

[C$_4$mim][Asp]$_{1.0}$

^{1}H-NMR (400MHz, DMSO-d_6, δ/ppm relative to TMS): 0.82 (3H, t, J = 7.3 Hz), 1.18 (2H, m), 1.70 (2H, m), 2.19 (2H, m), 3.21 (1H, q), 3.83 (3H, s), 4.14 (2H, t, J = 7.3 Hz), 7.74 (1H, s), 7.5 (3H,s), 7.79 (1H, s), 9.54(1H, s).

Elemental analysis calcd (%) for [C$_4$mim][Asp]: C, 53.12; H, 7.80; N, 15.49. Found: C, 53.14; H, 7.75.; N, 15.50.

4. Synthesis of Diene-AM$_{12}$ and Diene-AM$_{14}$



Scheme S1. Synthesis of Diene-AM$_{12}$ and Diene-AM$_{14}$.

Synthesis of S1-14: A mixture of methyl-3,5-dihydroxybenzoate (0.993 g, 5.90 mmol), $C_{14}H_{25}Br$ (8.25 g, 30.2 mmol) and potassium carbonate (4.73 g, 34.2 mmol) in DMF (100ml) was heated at 70 °C for 8 h under Ar. The mixture was diluted with ethyl acetate and poured into water. The organic phase was separated, and the aqueous phase was extracted three times with ethyl acetate. The combined organic phase was washed with sat. NH_4Cl aq., dried over $MgSO_4$, filtered and the solvent was removed in vacuo. The crude product was purified by flash column chromatography (silica gel, eluent: ethyl acetate/hexane= 1:4) to give **S1-14** (3.0 g, 89 %) as a white solid.

^{1}H-NMR (400MHz, $CDCl_3$, δ/ppm relative to TMS): 1.24-1.45 (28H, m), 1.77 (4H,m), 2.07 (4H, q), 3.50 (4H, d, *J* = 4.8 Hz), 3.90 (3H, s), 3.96 (4H, t, 5.4 Hz), 4.95 (2H, d, *J* = 8.4 Hz), 5.08 (2H, d, *J* = 14 Hz), 6.05 (2H, q), 6.63 (1H, t, *J* = 1.8 Hz), 7.16 (2H, d, *J* =2.4 Hz).

Synthesis of Diene-AM$_{14}$: Compound **S1-14** (3.0 g, 5.29 mmol) was dissolved in a mixture of EtOH and H_2O (99:1 vol/vol, 100 ml) containing potassium hydroxide (1.63 g, 29.05 mmol). After stirring at 70 ^{o}C for 3h, the solution was neutralized with 35 % HCl aq. and extracted with $CHCl_3$ twice. The combined organic phase was dried under vacuum to give 2.8 g (96% yield) of crude compound of **S2-14** as a white solid. To a solution of **S2-14** (2.8 g, 5.06 mmol) in a mixture of EtOH and DMF was added 3-aminopropyldiethanolamine (5.70 g, 38.5 mmol) and 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMT-MM) (8.00 g, 28.9 mmol). After stirring at r.t. for 24h, the solution was extracted with $CHCl_3$ and the organic phase was dried over anhydrous $MgSO_4$, filtered and concentrated. The crude product was purified by silica column chromatography (eluent: $CHCl_3$/methanol = 9:1) to give 1.06 g (30% yield) of **Diene-AM$_{14}$** as a colorless liquid.

^{1}H-NMR (400MHz, $CDCl_3$, δ/ppm relative to TMS): 1.20-1.45 (32H, m), 1.62 (2H, m), 1.69 (4H, m), 2.05 (4H, q), 3.24 (2H, q), 3.41 (4H, q), 3.97 (4H, t, *J* = 5.0Hz), 4.35 (2H, t, *J* = 4.6 Hz), 5.06 (2H, d, 11 Hz), 5.09 (2H, d, *J* = 14 Hz), 5.71 (2H, m), 6.037 (2H, q), 6.29 (2H, m), 6.58 (1H, t, *J* = 1.8Hz), 6.95 (2H, d, *J* = 2.0 Hz), 8.39 (1H, t, *J* = 4.6Hz)

Elemental analysis calcd (%) for $[C_4mim]_2[Asp]$: C, 73.86; H, 10.33; N, 4.10. Found: C, 74.12; H, 10.55.; N, 3.77.

5. NMR spectra of [C$_4$mim][Asp]$_X$ (X = 0.50, 0.60, 0.80 and 1.0)

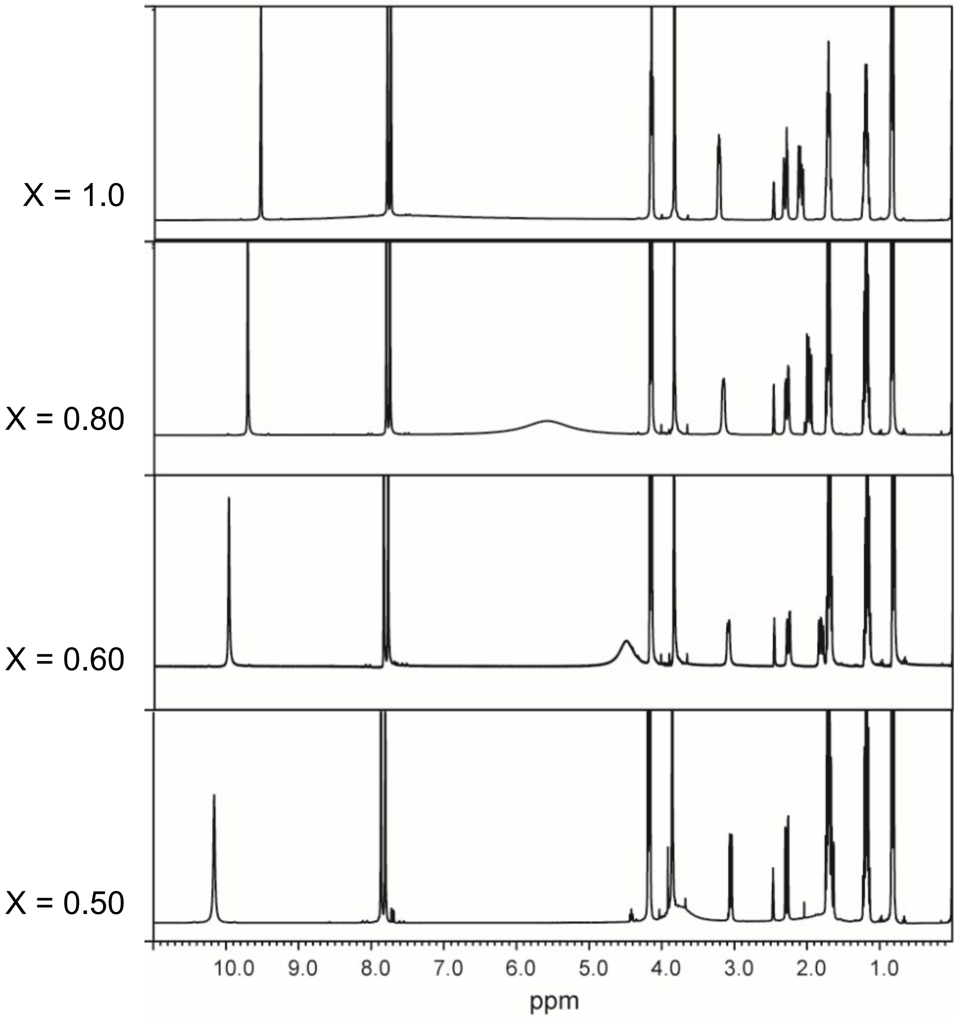


Fig. S1 NMR spectra of [C$_4$mim][Asp]$_x$ (0.1133g/ml in DMSO-d_6).

6. IR spectra of film, amphiphile and [C$_4$mim][Asp]$_{0.50}$

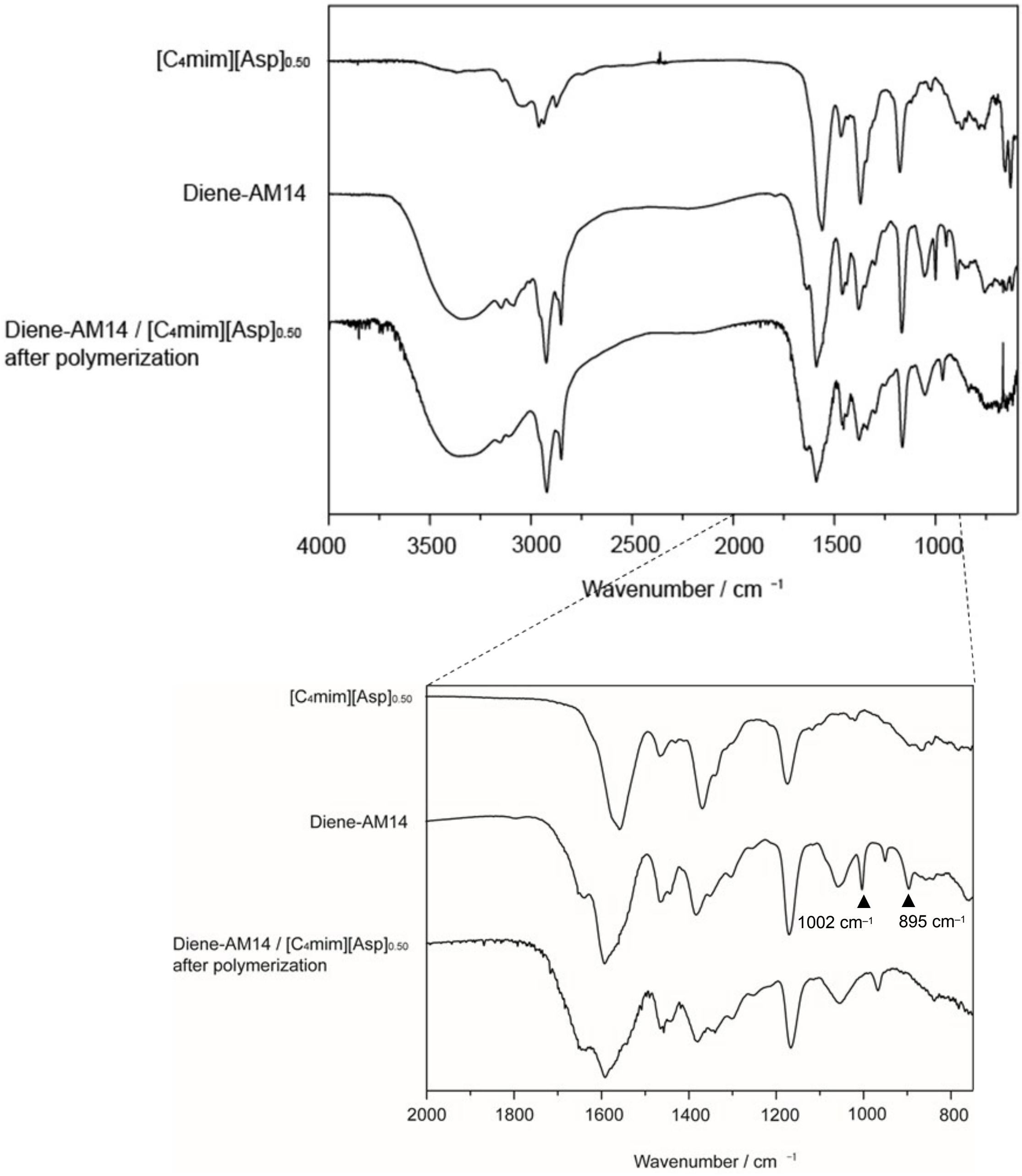


Fig. S2 IR spectra of **Diene-AM$_{14}$**, [C$_4$mim][Asp]$_{0.50}$, and the polymer film obtained by the polymerization of the **Diene-AM$_{14}$**/**AM'$_{12}$**/[C4mim][Asp]$_{0.5}$ (65/5/30 wt%) mixture

7. Liquid-crystalline property of the $\mathbf{AM_{12}}$/[C_4mim][Asp]$_x$ mixture

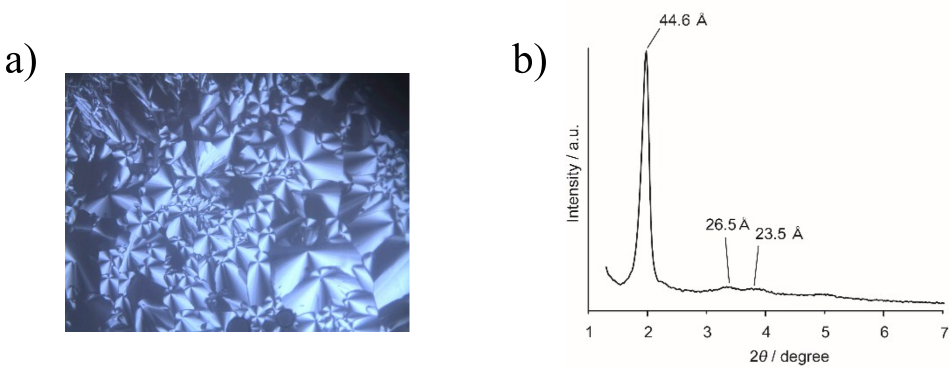


Fig. S3. (a) POM image of $\mathbf{AM_{12}}$/[C_4mim][Asp]$_{1.0}$ (74/26 wt%) in the Col phase at 85 °C. (b) WAXD pattern of $\mathbf{AM_{12}}$/[C_4mim][Asp]$_{1.0}$ (74/26 wt%) in the Col_h phase.

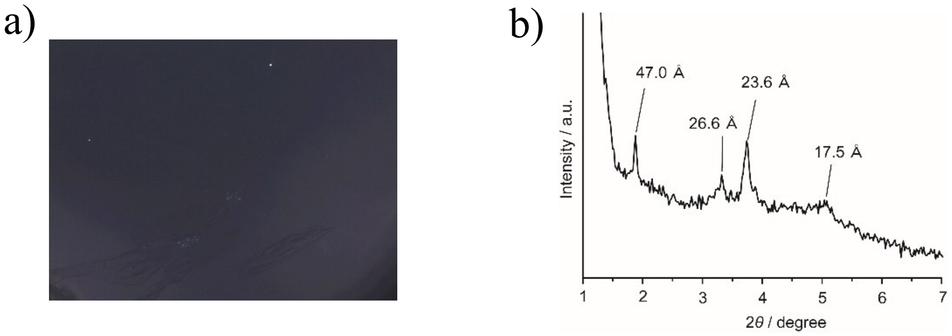


Fig. S4. POM image of $\mathbf{AM_{12}}$/[C_4mim][Asp]$_{1.0}$ (70/30 wt%) in the Cub_{bi} phase at 60 °C. (b) WAXD pattern of $\mathbf{AM_{12}}$/[C_4mim][Asp]$_{1.0}$ (70/30 wt%) in the Cub_{bi} phase.

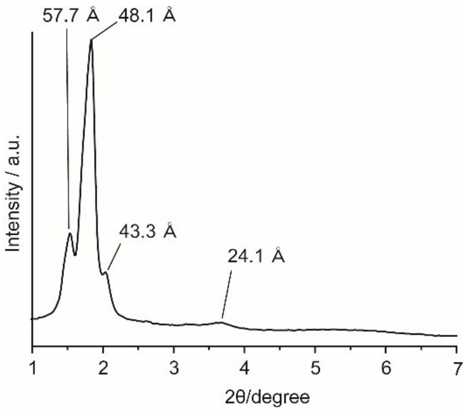


Fig. S5. Small-angle X-ray scattering pattern of $\mathbf{AM_{12}}$/[C_4mim][Asp]$_{1.0}$ (60/40 wt%) in the Cub_{bi} phase at 60 °C.

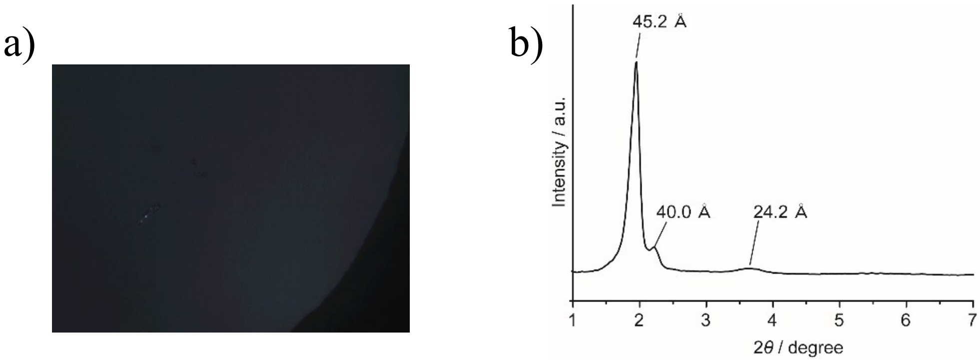


Fig. S6 (a) POM image of **AM_{12}**/[C_4mim][Asp]$_{0.50}$ (75/25 wt%) in the Cub_{bi} phase at 53 °C. (b) Small-angle X-ray scattering pattern of **AM_{12}**/[C_4mim][Asp]$_{0.50}$ (75/25 wt%) in the Cub_{bi} phase at 60 °C.

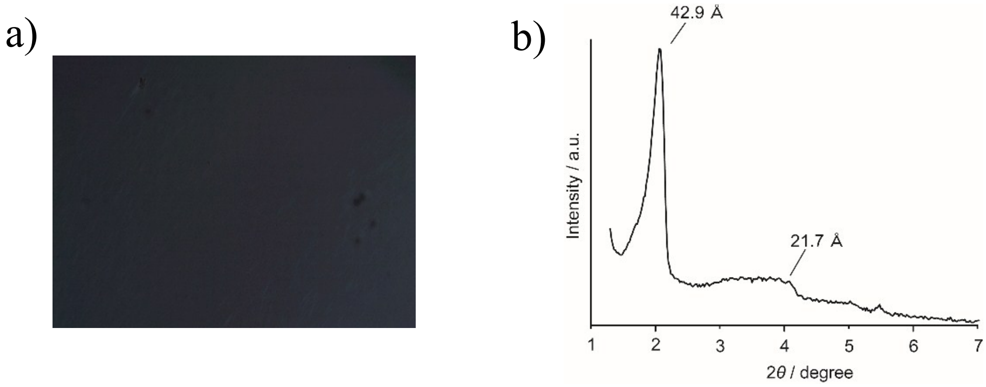


Fig. S7 (a) POM image of **AM_{12}**/[C_4mim][Asp]$_{0.50}$ (60/40 wt%) in the Sm phase at 58 °C. (b) WAXD pattern of **AM_{12}**/[C_4mim][Asp]$_{0.50}$ (60/40 wt%) in the Sm phase.

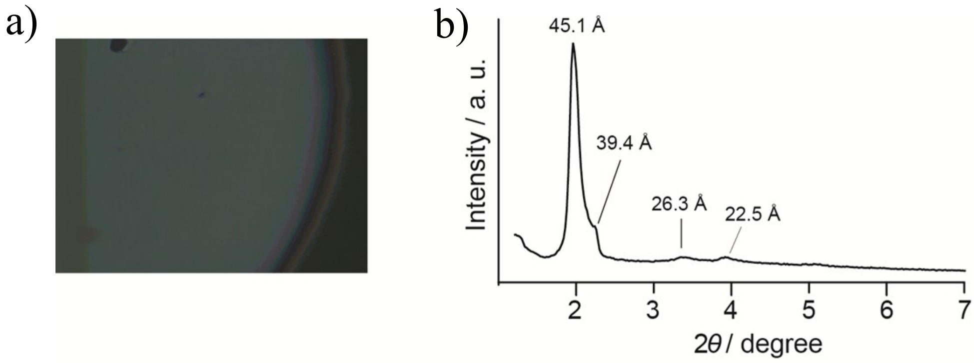


Fig. S8 (a) POM image of **AM$_{12}$**/[C$_4$mim][Asp]$_{0.75}$ (80/20 wt%) in the Cub$_{bi}$ phase at 65 ^{o}C. (b) WAXD pattern of **AM$_{12}$**/[C$_4$mim][Asp]$_{0.75}$ (80/20 wt%) in the Cub$_{bi}$ phase.

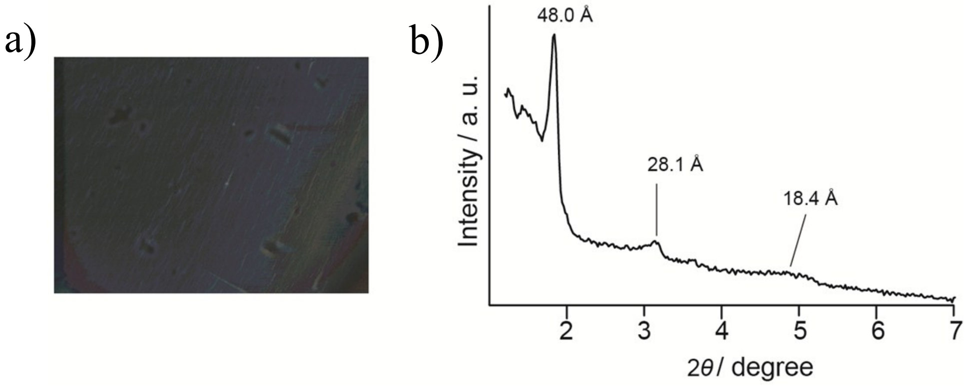


Fig. S9 (a) POM image of **AM$_{12}$**/[C$_4$mim][Asp]$_{0.75}$ (60/40 wt%) in the Sm phase at 100 ^{o}C. (b) WAXD pattern of **AM$_{12}$**/[C$_4$mim][Asp]$_{0.75}$ (60/40 wt%) in the Sm phase.

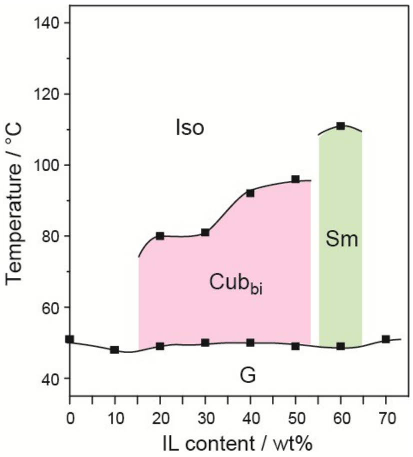


Fig. S10 Phase diagram of the **AM$_{12}$**/[C$_4$mim][Asp]$_{0.75}$ mixtures.

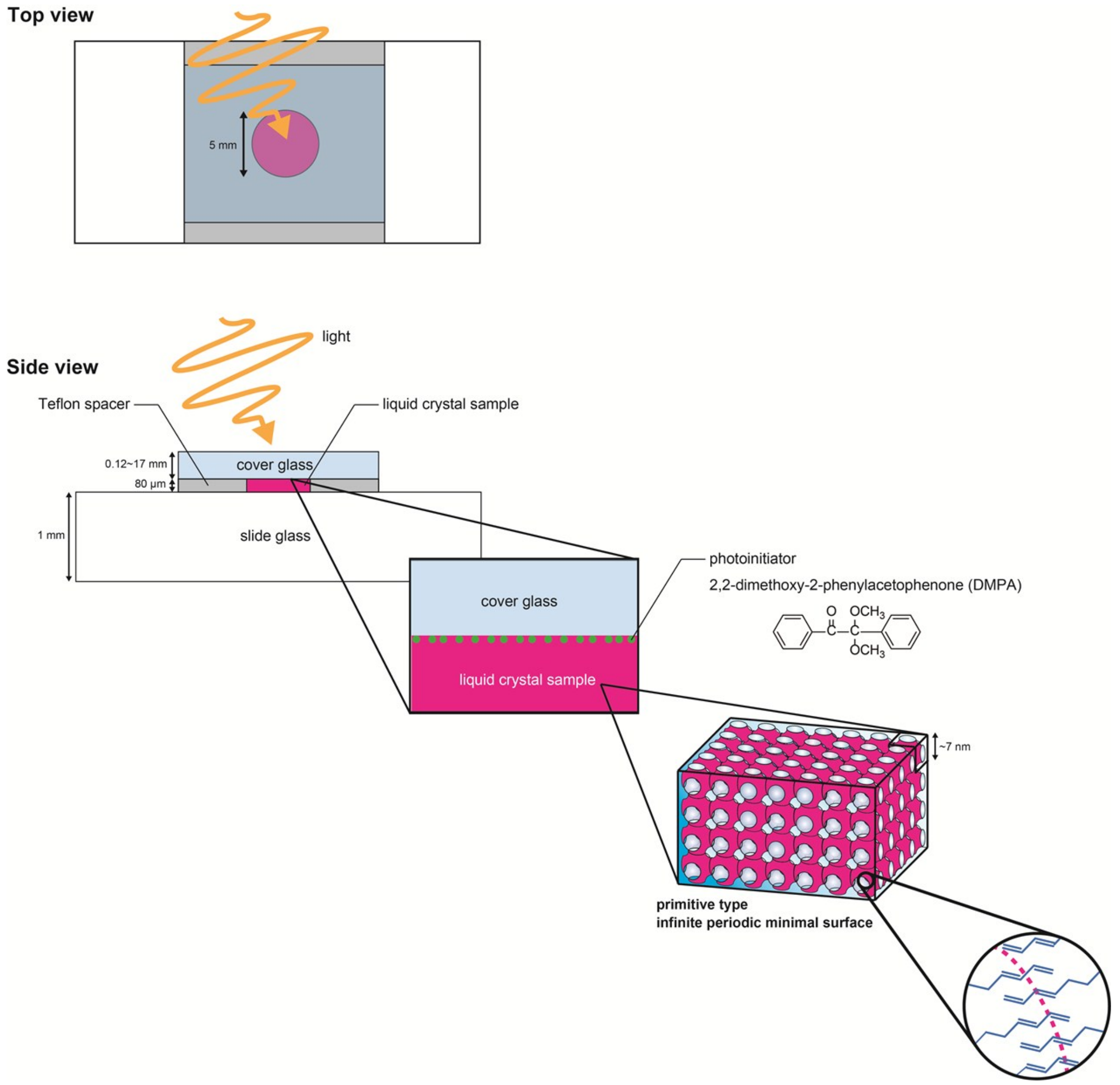


Fig. S11 Experiment of photo-polymerization of the liquid crystal sample. The sample is sandwiched by a cover glass and a slide glass. A Teflon spacer with a hole is placed between the two glasses. A photo-initiator is coated on the cover glass surface. The polymerization proceeds not only on the cover glass surface but also throughout the sample. There is a possibility that the photo-initiator migrate into the sample before the photo-irradiation. However, we believe that the radicals occurring at the cover glass induce the polymerization of the diene groups aligning along an infinite periodic minimal surface and the polymerization reaction proceeds throughout the sample owing to the 3D continuity of the periodic minimal surface.

8. Reference

1) K. Fukumoto, M. Yoshizawa and H. Ohno, *J. Am. Chem. Soc.,* 2005, **127**, 2398.

2) T. Ichikawa, M. Yoshio, S. Taguchi, J. Kagimoto, H. Ohno and T. Kato, *Chem. Sci*., 2012, **3**, 2001.