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$_3$)$_4$Si ($\delta = 0.00$) and CDCl$_3$ ($\delta = 77.0$) 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$_4$mim][Asp]$_x$ and AM$_{12}$

Amino acid ionic liquid [C$_4$mim][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 AM$_{12}$ was also synthesized according to the literature.$^2$
3. Characterization of $[\text{C}_4\text{mim}][\text{Asp}]_x$

$[\text{C}_4\text{mim}][\text{Asp}]_{0.50}$
$^1$H-NMR (400MHz, DMSO-$d_6$, $\delta$/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 $[\text{C}_4\text{mim}][\text{Asp}]$: C, 58.66; H, 8.61; N, 17.10. Found: C, 58.67; H, 8.56; N, 17.11.

$[\text{C}_4\text{mim}][\text{Asp}]_{1.0}$
$^1$H-NMR (400MHz, DMSO-$d_6$, $\delta$/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 $[\text{C}_4\text{mim}][\text{Asp}]$: 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$_{14}$.](image)
**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 (100 ml) 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_{4}Cl 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.

^1H-NMR (400MHz, CDCl₃, 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 H₂O (99:1 vol/vol, 100 ml) containing potassium hydroxide (1.63 g, 29.05 mmol). After stirring at 70 °C for 3 h, the solution was neutralized with 35 % HCl aq. and extracted with CHCl₃ 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 24 h, the solution was extracted with CHCl₃ and the organic phase was dried over anhydrous MgSO₄, filtered and concentrated. The crude product was purified by silica column chromatography (eluent: CHCl₃/methanol = 9:1) to give 1.06 g (30% yield) of Diene-AM_{14} as a colorless liquid.

^1H-NMR (400MHz, CDCl₃, 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 = 5.0 Hz), 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 = 1.8 Hz), 6.95 (2H, d, J = 2.0 Hz), 8.39 (1H, t, J = 4.6 Hz)

Elemental analysis calcd (%) for [C₄mim]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 \([\text{C}_4\text{mim}][\text{Asp}]_x\) (\(x = 0.50, 0.60, 0.80\) and 1.0)

![NMR spectra](image)

**Fig. S1** NMR spectra of \([\text{C}_4\text{mim}][\text{Asp}]_x\) (0.1133 g/ml in DMSO-\(d_6\)).
6. IR spectra of film, amphiphile and [C₄mim][Asp]₀.₅₀

![IR spectra](image)

**Fig. S2** IR spectra of Diene-AM₁₄, [C₄mim][Asp]₀.₅₀, and the polymer film obtained by the polymerization of the Diene-AM₁₄/AM'₁₂/[C₄mim][Asp]₀.₅ (65/5/30 wt%) mixture
7. Liquid-crystalline property of the AM$_{12}$/[C$_4$mim][Asp]$_x$ mixture

Fig. S3. (a) POM image of AM$_{12}$/[C$_4$mim][Asp]$_{1.0}$ (74/26 wt%) in the Col phase at 85 °C. (b) WAXD pattern of AM$_{12}$/[C$_4$mim][Asp]$_{1.0}$ (74/26 wt%) in the Col$_h$ phase.

Fig. S4. POM image of AM$_{12}$/[C$_4$mim][Asp]$_{1.0}$ (70/30 wt%) in the Cub$_{bi}$ phase at 60 °C. (b) WAXD pattern of AM$_{12}$/[C$_4$mim][Asp]$_{1.0}$ (70/30 wt%) in the Cub$_{bi}$ phase.

Fig. S5. Small-angle X-ray scattering pattern of AM$_{12}$/[C$_4$mim][Asp]$_{1.0}$ (60/40 wt%) in the Cub$_{bi}$ phase at 60 °C.
Fig. S6 (a) POM image of $\text{AM}_{12}/[\text{C}_4\text{mim}][\text{Asp}]_{0.50}$ (75/25 wt%) in the Cub$_{bi}$ phase at 53 °C. 
(b) Small-angle X-ray scattering pattern of $\text{AM}_{12}/[\text{C}_4\text{mim}][\text{Asp}]_{0.50}$ (75/25 wt%) in the Cub$_{bi}$ phase at 60 °C.

Fig. S7 (a) POM image of $\text{AM}_{12}/[\text{C}_4\text{mim}][\text{Asp}]_{0.50}$ (60/40 wt%) in the Sm phase at 58 °C. 
(b) WAXD pattern of $\text{AM}_{12}/[\text{C}_4\text{mim}][\text{Asp}]_{0.50}$ (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 °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 °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