Supporting Information

Self-assembly of the Imidazolium Surfactant in the Aprotic Ionic Liquid. 1. Comparison in Aprotic and Protic Ionic Liquids.

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Experimental section

Materials

The cationic surfactant C_{16}mimBr was synthesized according to the procedure previously. The 1-methylimidazole (Aladdin, 99%) and an excess amount (1.2 molar equiv.) of 1-bromohexadecane (Aladdin, 97%) were refluxed in ethanol for 24 h. The mixture was cooled to room temperature with the solvent removed by rotary evaporation. The product was recrystallized in tetrahydrofuran for at least three times and then dried in vacuum drying oven. The purity was confirmed by ^{1}H NMR. The APIL [Emim]BF_4 (99.0%, water content lower than 1000 ppm) was purchased from Lanzhou Greenchem ILs and used after further freezing drying. The PIL EAN was synthesized according to our previous researches in Ref 12.

^{1}H NMR

C_{16}mimBr (DMSO, 600 MHz) 0.87-0.91 (3H), 1.20-1.340 (26H), 1.96-2.00 (2H), 4.12-4.16 (3H), 4.31-4.35 (2H), 7.27-7.30 (1H), 7.37-7.43 (1H), 10.49-10.57 (1H).

Sample preparation and phase diagram mapping

All samples were prepared by mixing the C_{16}mimBr and [Emim]BF_4 at designed compositions (in weight percentage (%), thereinafter). These mixtures were homogenized by repeatedly mixing and centrifugation. Then they were equilibrated for at least one month before further investigations. The composition interval was first selected as 5 % for a rough phase mapping and then 1 % for the determination of the phase boundaries.

Characterizations

Small angle X-ray scattering (SAXS) The X-ray scattering measurements were performed by small angle X-ray scattering instruments (Anton Paar, Austria, Cu-Kα, λ = 0.154 nm), equipped with a Kratky block-collimation system and a mythen detector. The X-ray generator was operated at 40 kV and 50 mA. A standard temperature control unit (Anton-Paar TCS 150) was used to control the temperature at a desired value. The LLC samples were transferred to the paste cell (SAXSpace) while solution samples to the standard quartz capillary with a diameter of 1 mm (SAXSpoint). The scattering curves of solvents filled in the same capillary were recorded as the background. The solution data were corrected for background scattering from the capillary and solvent.

Polarized optical microscopy (POM) Photographs of samples were taken by a DYP-990 polarized optical microscope (Dianying, Shanghai China) with a DYE-400 thermal stage (± 1 ^{o}C) and a CMOS camera (DYS-1000).

Freeze-fracture transmission electron microscopy (FF-TEM) A small amount of solution was mounted on a specimen holder. The sample was frozen by quickly plunging the holder into the liquid ethane cooled by liquid nitrogen. Fracturing and replication were carried out on a freeze-fracture

apparatus (EM BAF060, Leica, Germany) at a temperature of -150 °C. Pt/carbon was deposited at an angle of 45 ° to shadow the replicas and carbon was deposited at an angle of 90 ° to consolidate the replicas. The resulting replicas were transferred onto copper grids and then observed using a JEOL JEM-1400 TEM operated at 120 kV.

Surface tension A tensiometer BZY-2 (Fangrui, China) was used with a Wilhelmy platinum plate to measure the critical micelle concentration (CMC). The plate was cleaned well and heated briefly in an alcoholic flame until it glowed before each measurement. All measurements were repeated at least twice until the values were reproducible. The surface parameters, such as the effectiveness of γ reduction (Π_{CMC}), the surface excess at the air/IL interface (Γ_{max}), the minimum area per surfactant molecule adsorbed at the air/IL interface (A_{min}) and the standard Gibbs free energy of micellization (ΔG_m), can be calculated according to equations (1)-(4) below, where γ_0 and γ_{CMC} are surface tensions of the pure solvent and the solution at CMC, respectively.

$$\Pi_{CMC} = \gamma_0 - \gamma_{CMC} \quad (1)$$

$$\Gamma_{max} = -\frac{1}{RT}\left(\frac{d\gamma}{d\ln C}\right) \quad (2)$$

$$A_{min} = \frac{1}{N_A \Gamma_{max}} \quad (3)$$

$$\Delta G_m = RT \ln X_{CMC} \quad (4)$$

SAXS analysis

Micelles

The SAXS curves of micelles were fitted with the SASfit software (version 0.94.7). Several models like sphere, ellipsoid and cylinder have been tried and the ellipsoid model give the best fitting results.

The scattering of ellipsoid could be expressed as equation (5),

$$I(q,a,\varepsilon) = \left(\frac{4}{3}\pi a^3 \Delta\eta\right)^2 \int_0^{\frac{\pi}{2}} K^2\left(q,a\sqrt{\varepsilon^2 cos^2\theta + sin^2\theta}\right) sin\theta d\theta \quad (5)$$

where a is the radius of the rotational axis, ε is ratio between radius of the semi-principle axes and equatorial axis.

The hard sphere structure factor with Percus-Yevick closure relation was adopted for the interaction between micelles. The structure factor of hard sphere could be expressed as equation (6),

$$S\left(q,R_{HS},f_q\right) = \frac{1}{1 + 24 f_q \frac{G\left(f_q,R_{HS}q\right)}{R_{HS}q}} \quad (6)$$

where R_{HS} is the hard sphere repulsive radius; f_p is the volume fraction.

A constant was added in the background. More details could be found in the manual of SASfit.

The L_α phase

The lattice parameter (D) of the lamellar liquid crystalline phase is obtained according to the equations (7-10), where d_s and d_a are thickness of the solvent and solvophobic layer.

$$D = \frac{2\pi}{q_1} \quad (7)$$

$$d_s = D(1 - \Phi_a) \quad (8)$$

$$d_a = \frac{D - d_s}{2} \quad (9)$$

$$S = \frac{V_a}{2d_a} \quad (10)$$

Figures and tables

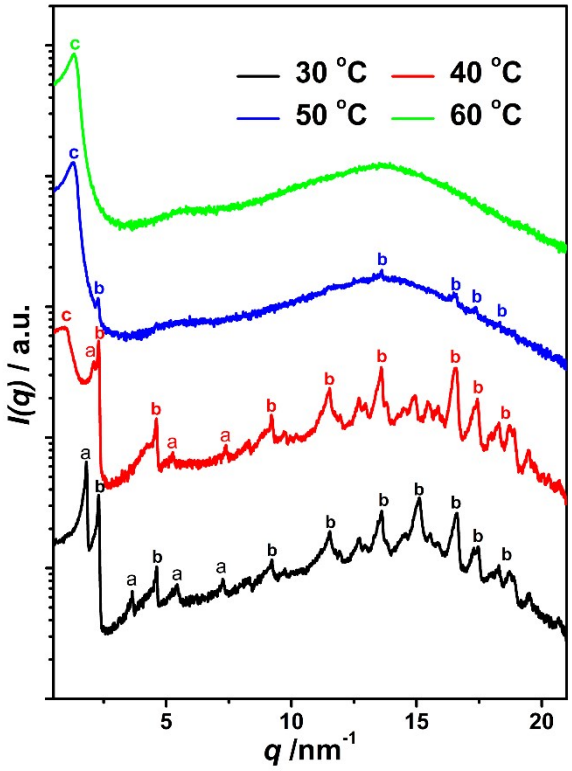

Fig. S1 SWAXS results of the 60 % C_{16}mimBr/[Emim]BF_4 sample at different temperatures. a, b, c corresponds to the scattering of the L_β, L_c, L_1 phases.

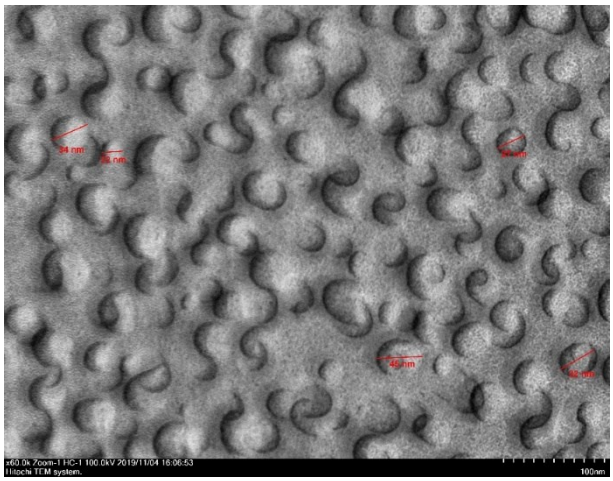

Fig. S2 The magnified FF-TEM image of the 5 % C_{16}mimBr/[Emim]BF_4 sample. The principle axis is noted by red line.

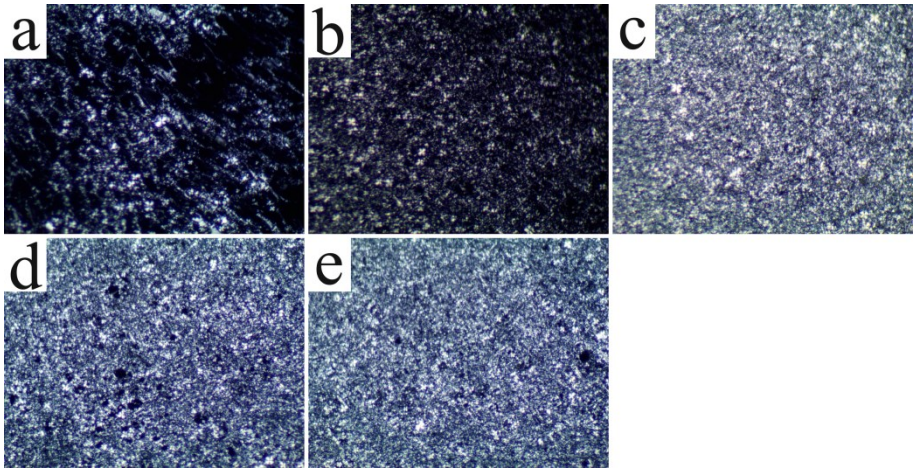

Fig. S3 POM images of the L_α phases in the C_{16}mimBr/[Emim]BF_4 system at 60 °C. (a) 70 %; (b) 75 %; (c) 80 %; (d) 85 %; (e) 90 %.

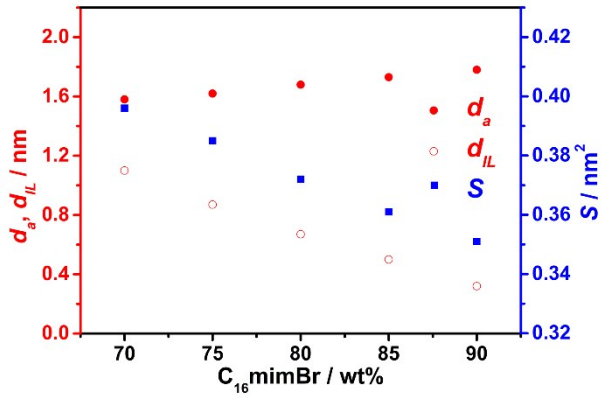

Fig. S4 Structure parameters of the L_α phases in the C_{16}mimBr/[Emim]BF_4 system at 60 °C.

Table S1 Structure parameters of the L_α phase in the C_{16}mimBr/[Emim]BF_4 system at 60 °C.

C / wt %	D / nm	d_a / nm	d_{IL} /nm	S / nm^2
70	4.25	1.58	1.10	0.396
75	4.12	1.62	0.87	0.385
80	4.03	1.68	0.67	0.372
85	3.96	1.73	0.50	0.361
90	3.88	1.78	0.32	0.351

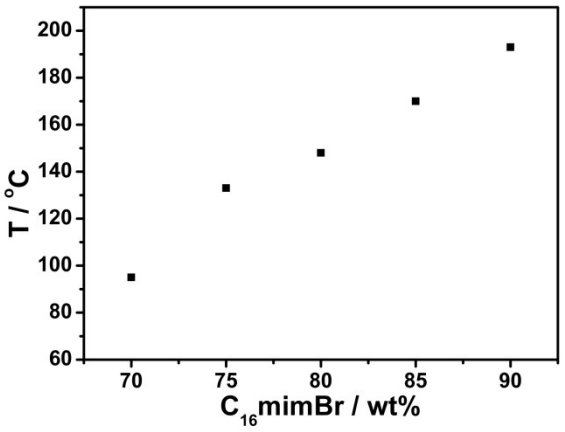

Fig. S5 The L_α to L_1 phase transition temperature in the C_{16}mimBr/[Emim]BF_4 system at different concentrations.

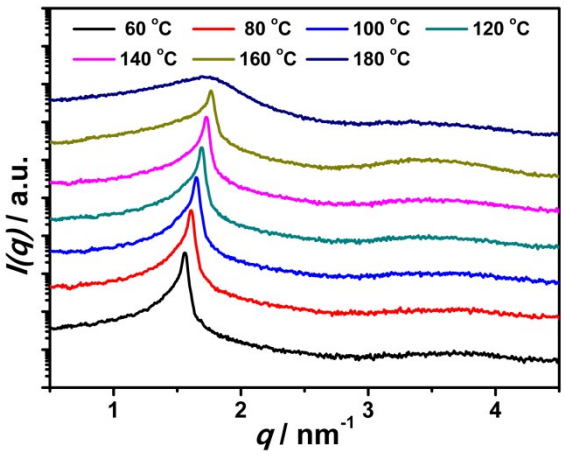

Fig. S6 The SAXS curves of the 85 % C_{16}mimBr/[Emim]BF_4 sample at different temperatures. The broad peak around 3.5 nm^{-1} results from the scattering of Kapton film made of polyimide.

Table S2 Structure parameters of the 85 % C_{16}mimBr/[Emim]BF_4 L_α phase at different temperatures.

T / °C	D / nm	d_a / nm	d_{IL} /nm	S / nm^2
60	3.96	1.73	0.50	0.361
80	3.90	1.71	0.49	0.366
100	3.81	1.66	0.48	0.375
120	3.72	1.62	0.47	0.385
140	3.63	1.59	0.46	0.394
160	3.57	1.56	0.45	0.400

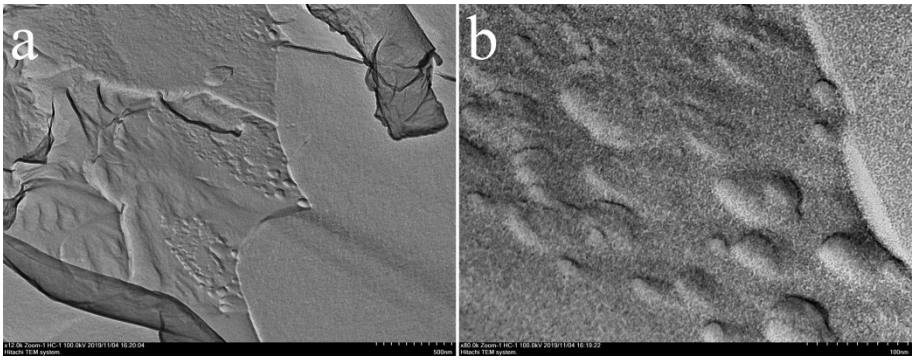

Fig. S7 FF-TEM images of the 5 % C_{16}mimBr/EAN sample at 60 °C.

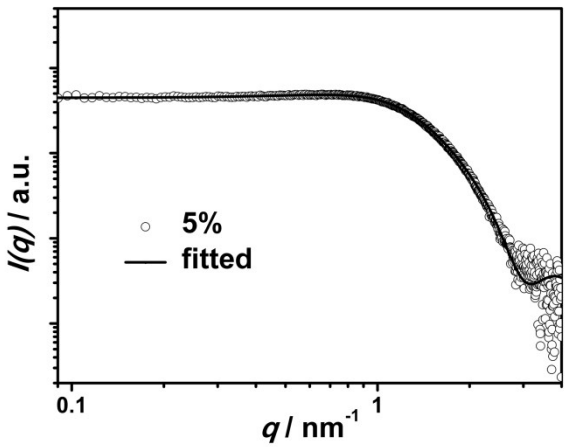

Fig. S8 SAXS results of the 5 % C_{16}mimBr/EAN sample at 60 °C.

Fig. S9 POM images of different LLC phases in the C_{16}mimBr/EAN system at 60 °C. (a) The H_1 phase, 75 %; (b) the V_1 phase, 80 %; (c) the L_α phase, 90 %.

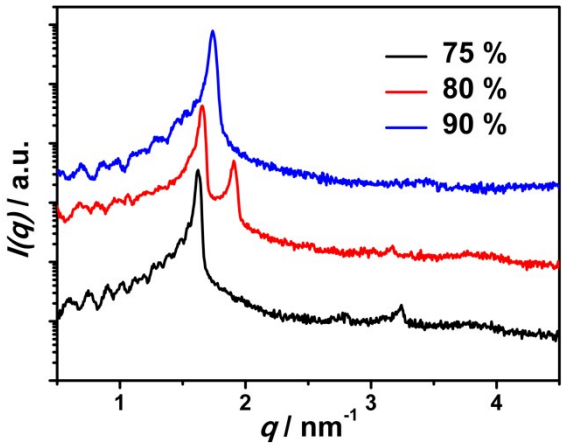

Fig. S10 SAXS curves of different LLC phases in the C_{16}mimBr/EAN system at 60 °C.

Table S3 Gordon parameters of ILs.

IL	γ / mN·m^{-1}	V_m / cm^3·mol^{-1}	G / J·m^{-3}
[Emim]BF_4	54.1[a]	155[a]	1.01
EAN	48.6[a]	83.0[a]	1.11

γ, the air/IL surface tension; V_m , molar volume; G, Gordon parameter.
a, parameters measured at 25 °C.

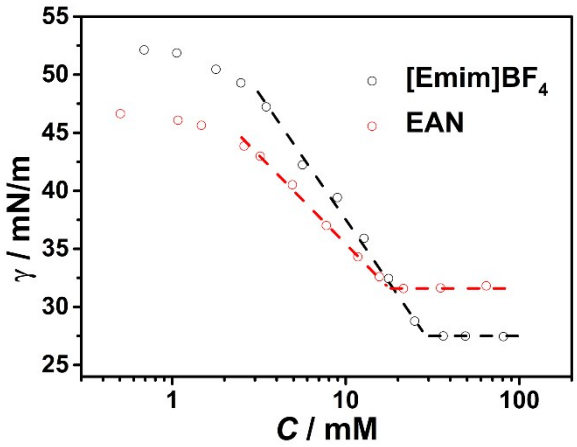

Fig. S11 Surface tension curves of C_{16}mimBr in [Emim]BF_4 and EAN at 60 °C.

Table S4 Surface parameters of C_{16}mimBr in [Emim]BF_4 and EAN at 60 °C.

IL	CMC	γ_{CMC} / mN/m	Π_{CMC} / mN/m	Γ_{max} / μmol/m^2	A_{min} / nm^2	ΔG_m / kJ/mol
[Emim]BF_4	0.911 % (30.3 mM)	27.5	25.2	3.30	0.503	-14.9
EAN	0.574 % (18.2 mM)	31.6	15.3	2.34	0.710	-17.8

Table S5 The *S* values (nm^2) of C_{16}mimBr in [Emim]BF_4 and EAN at 60 °C.

C / %	[Emim]BF_4	EAN
75	0.385 (L_α)	0.602 (H_1)
80	0.372 (L_α)	0.395 (V_1)
90	0.351 (L_α)	0.378 (L_α)