Supporting Information
Self-assembly of the Imidazolium Surfactant in the Aprotic Ionic Liquids.
2. More than Solvents.

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¹H NMR results

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).

Calculation of surface adsorption parameters

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 (S1)-(S4) below, where γ_0 and γ_{CMC} are surface tensions of the pure solvent and the solution at CMC, respectively.

$$\Pi_{CMC} = \gamma_0 - \gamma_{CMC} \quad \text{(S1)}$$

$$\Gamma_{max} = -\frac{1}{RT}\left(\frac{d\gamma}{d\ln C}\right) \quad \text{(S2)}$$

$$A_{min} = \frac{1}{N_A \Gamma_{max}} \quad \text{(S3)}$$

$$\Delta G_m = RT\ln X_{CMC} \quad \text{(S4)}$$

SAXS analysis of 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,

$$I(q,a,\varepsilon) = \left(\frac{4}{3}\pi a^3 \Delta\eta\right)^2 \int_0^{\frac{\pi}{2}} K^2\left(q,a\sqrt{\varepsilon^2\cos^2\theta + \sin^2\theta}\right)\sin\theta d\theta \quad \text{(S5)}$$

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 and decoupling approach was adopted for the interaction between micelles. The structure factor of hard sphere could expressed as,

$$S(q,R_{HS},f_q) = \frac{1}{1 + 24f_q\dfrac{G(f_q,R_{HS}q)}{R_{HS}q}} \quad \text{(S6)}$$

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.

Calculation of the structural parameters of LLCs

The H₁ phase

The lattice parameter (*D*) of the normal hexagonal liquid crystalline phase is obtained according to the equation S7.

$$D = \frac{4\pi}{\sqrt{3}q_1} \quad \text{(S7)}$$

The V₁ phase

The lattice parameter (*D*) of the normal bicontinuous cubic liquid crystalline phase is obtained according to the equation S8.

$$D = \frac{2\pi\sqrt{h^2 + l^2 + k^2}}{q} \quad \text{(S8)}$$

The Lα phase

The lattice parameter (*D*) of the lamellar liquid crystalline phase is obtained according to the equation S9.

$$D = \frac{2\pi}{q_1} \quad \text{(S9)}$$

Structure parameters of the ternary system

The volume percentage (*Φ*) of each component are calculated by equation (S10-S14), where the subscript S, O, IL represent the surfactant, oil and IL respectively, *W* and *ρ* are the weight percentage and density.

$$\Phi_S = \frac{W_s/\rho_s}{W_s/\rho_s + W_o/\rho_o + W_{IL}/\rho_{IL}} \quad \text{(S10)}$$

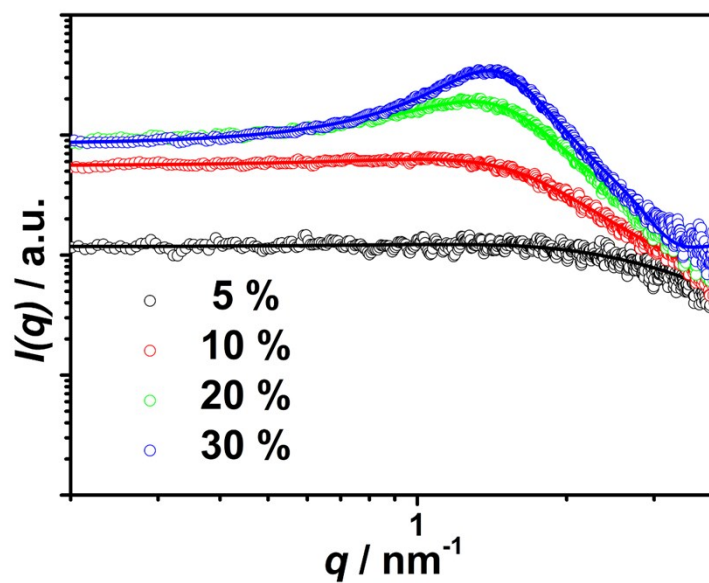$$\Phi_O = \frac{W_o/\rho_o}{W_s/\rho_s + W_o/\rho_o + W_{IL}/\rho_{IL}} \quad \text{(S11)}$$

$$\Phi_{IL} = \frac{W_{IL}/\rho_{IL}}{W_s/\rho_s + W_o/\rho_o + W_{IL}/\rho_{IL}} \quad \text{(S12)}$$

The solvophobic domain thickness of the Lα phase d_a and the area occupied by the surfactant molecule at the solvophilic/solvophobic interface *S* are expressed by equation S13&S14, where V_S is the molar volume of the surfactant.

$$d_a = D(\Phi_s + \Phi_o)/2 \quad \text{(S13)}$$

$$S = \frac{V_S(\Phi_S + \Phi_O)}{d_a \Phi_S} \quad \text{(S14)}$$

Figures and Tables

Fig. S1 SAXS results of micelles in the $C_{16}mimBr/[Bmim]BF_4$ system at different surfactant concentrations. Open symbols for experimental and lines for fitting curves.

Table S1 Parameters of micelles in the $C_{16}mimBr/[Bmim]BF_4$.

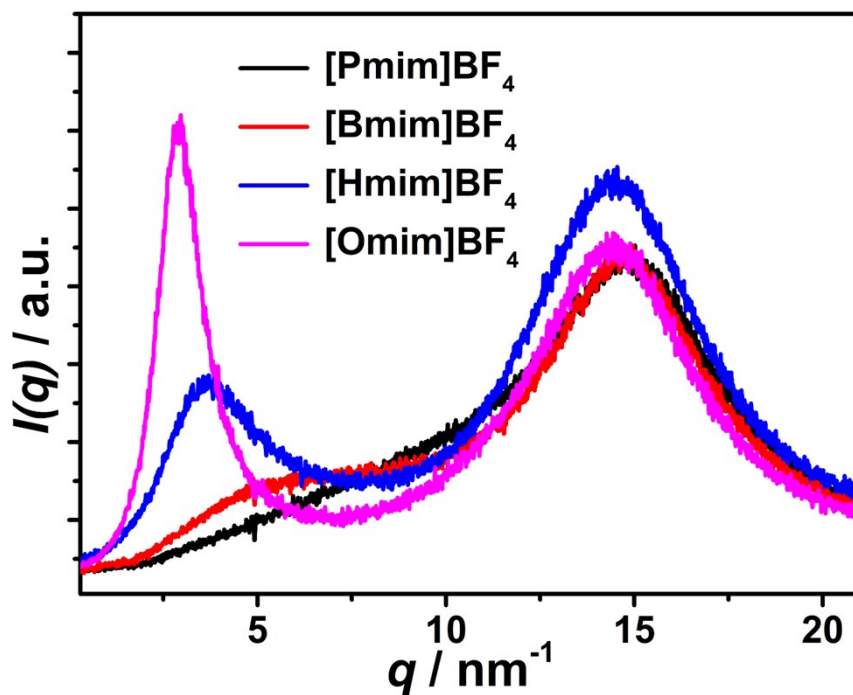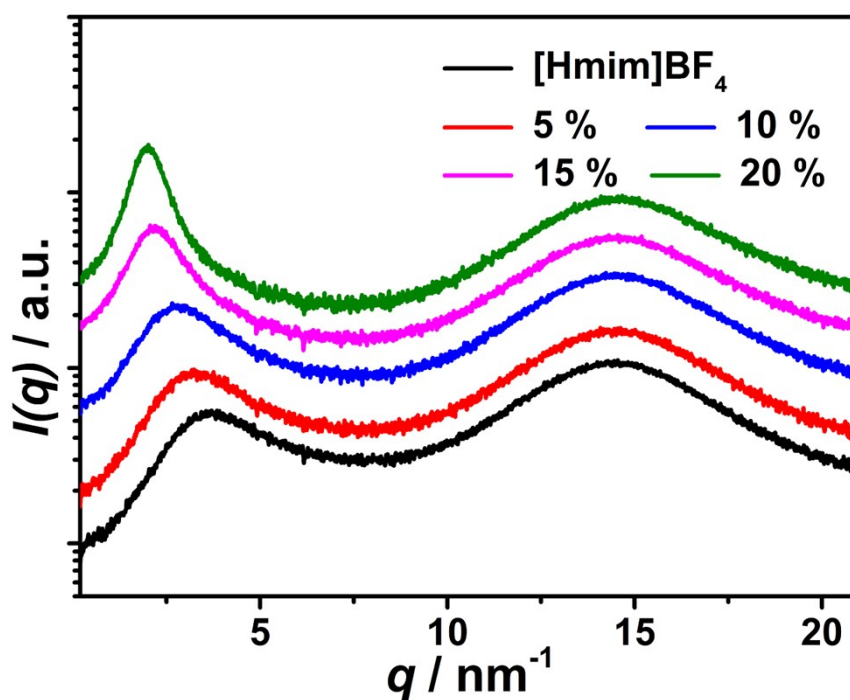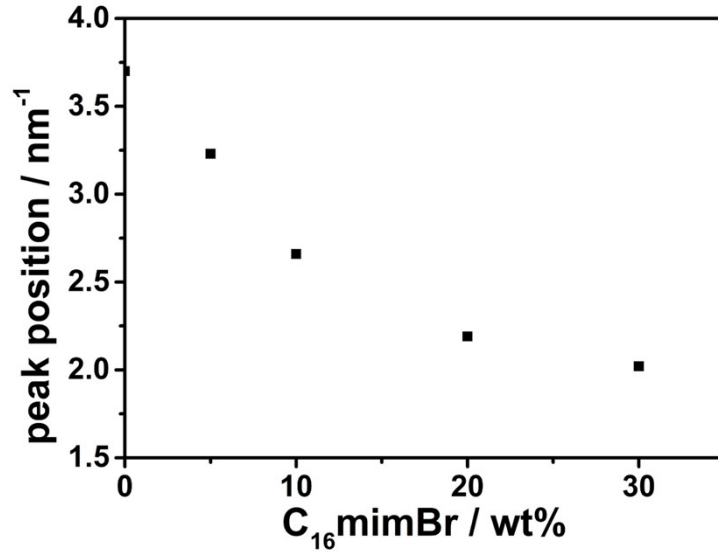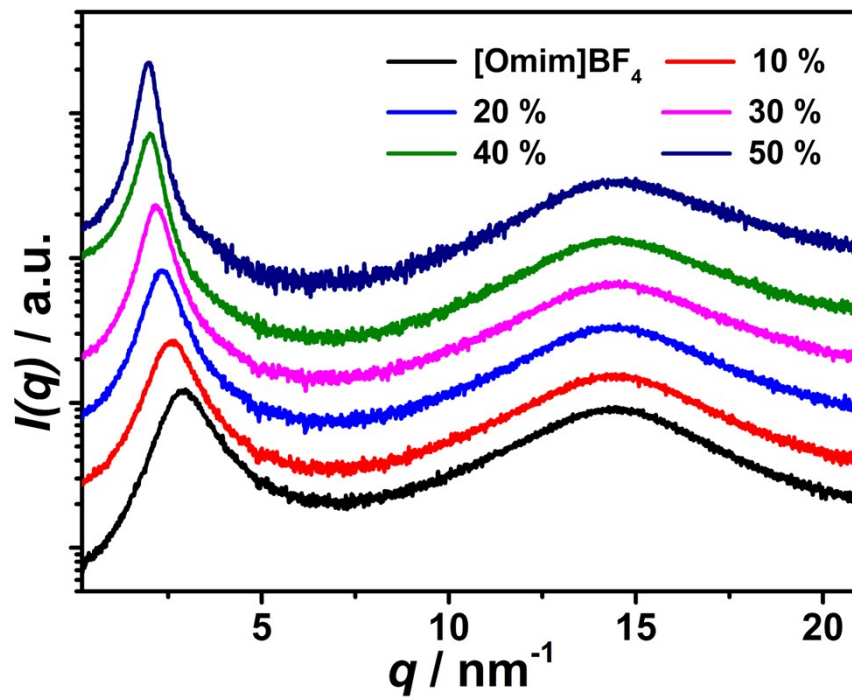| C / %	a / nm	b / nm	ε	N
5	0.549	0.560	1.00	-
10	0.893	2.01	2.25	15
20	1.10	1.79	1.63	20
30	1.18	1.77	1.50	23

Fig. S2 SWAXS curves of APILs.

Fig. S3 SWAXS results of the $C_{16}mimBr$/[Hmim]BF_4 solutions at different surfactant concentrations.

Fig. S4 Correlation peak position of [Hmim]BF$_4$ at different surfactant concentrations.
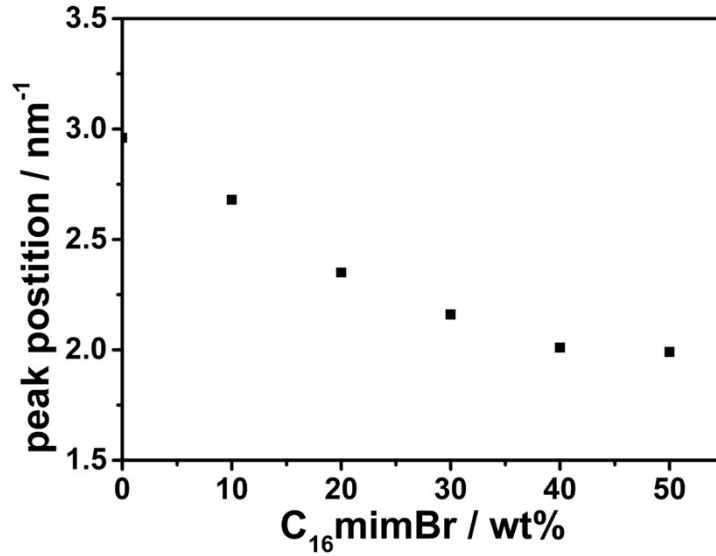

Fig. S5 SWAXS results of the C$_{16}$mimBr/[Omim]BF$_4$ solutions at different surfactant concentrations.

Fig. S6 Correlation peak position of [Omim]BF$_4$ at different surfactant concentrations.

Table S2 Gordon parameter of APILs at 25 °C.

APIL	γ / mN·m^{-1}	V_m / cm^3·mol^{-1}	G / J·m^{-3}
[Emim]BF$_4$	54.1	156	1.01
[Pmim]BF$_4$	46.6	171	0.840
[Bmim]BF$_4$	44.7	188	0.780
[Hmim]BF$_4$	37.8	221	0.625
[Omim]BF$_4$	32.8	256	0.516

Table S3 Structure parameters of the LLC phases in the C$_{16}$mimBr/[Emim]BF$_4$/1-octanol system.

Sample	D / nm	d_a /nm	d_{IL} /nm	S / nm^2
b1	4.33	1.60	1.14	0.420
b2	4.13	1.65	0.83	0.454
b3	3.90	1.63	0.65	0.489
b4	3.55	1.59	0.37	0.556
c0	3.96	1.74	0.49	0.360
c1	3.83	1.74	0.35	0.378
c2	3.75	1.77	0.21	0.394
c3	3.73	1.79	0.15	0.399