

Supporting Information for

Temperature-Responsive Proton-Conductive Liquid Crystals Formed by the Self-Assembly of Zwitterionic Ionic Liquids

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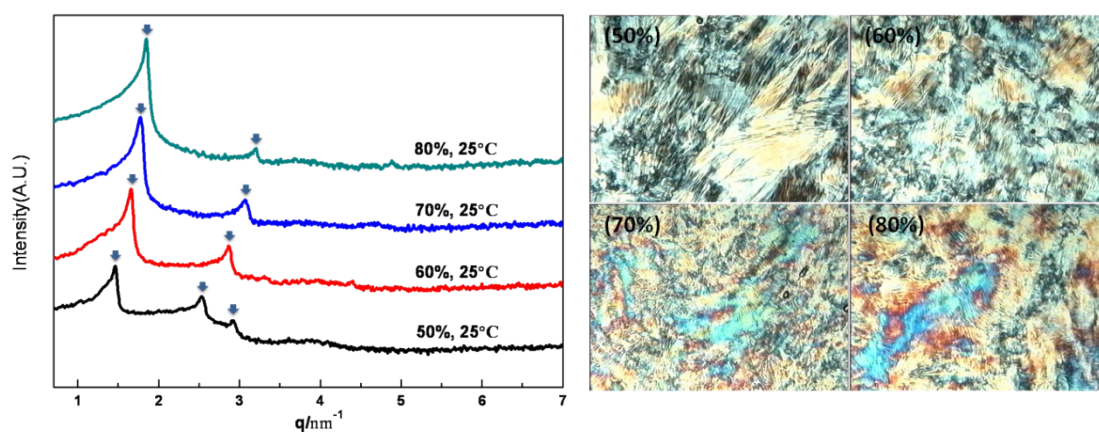


Figure S1. (a) SAXS patterns of $[\text{C}_{12}\text{IPS}][\text{C}_6\text{H}_5\text{SO}_3\text{H}]$ aqueous mixture system with increasing IL content collected at 25 °C; (b) Corresponding POM images collected at 25 °C.

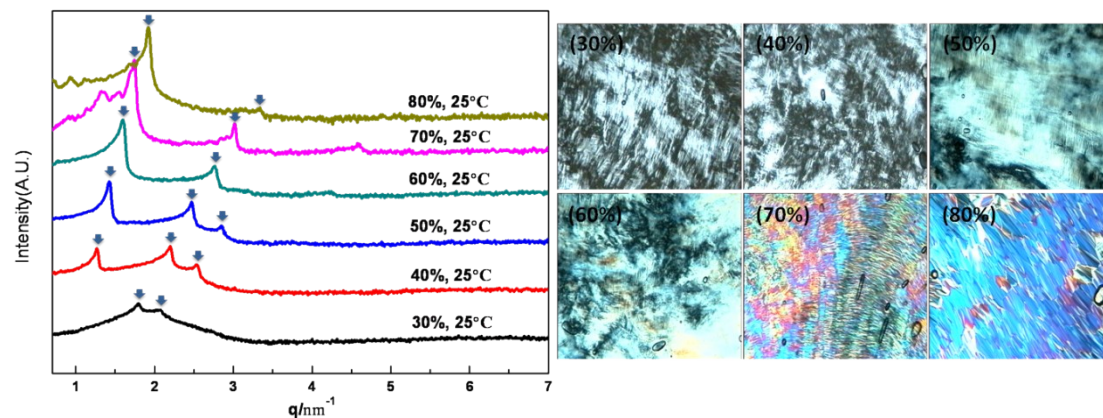


Figure S2. (a) SAXS patterns of $[\text{C}_{12}\text{IPS}][\text{CF}_3\text{SO}_3\text{H}]$ aqueous mixture system with increasing IL content collected at 25 °C; (b) Corresponding POM images collected at 25 °C.

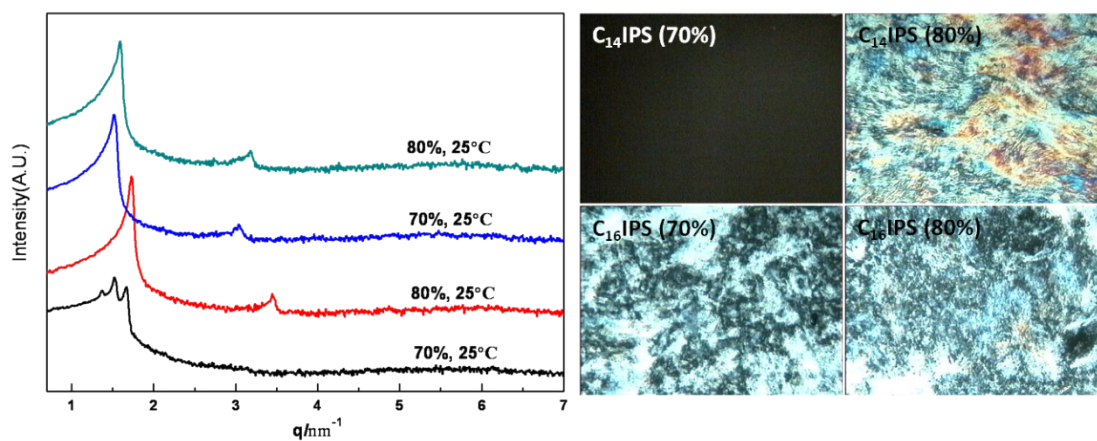


Figure S3. (a) SAXS patterns of [C₁₄IPS][CH₃SO₃H] and [C₁₆IPS][CH₃SO₃H] aqueous mixture systems with increasing IL content collected at 25 °C; (b) Corresponding POM images collected at 25 °C.

Table S1. Structural parameters for the liquid crystalline phases of $[C_n\text{IPS}][R\text{-SO}_3\text{H}]$ aqueous mixture systems.

	Sample (wt%)	ϕ_L	a_0 (nm)	r_H (nm)	r_p (nm)	d_W (nm)	a_s (nm ²)
$C_{16}\text{IPS}/\text{CH}_3\text{SO}_3\text{H}$ (H_1)	70	0.3492	4.7978	1.4885		1.8209	0.6181
	80	0.3420	4.5587	1.3997		1.7594	0.6572
$C_{14}\text{IPS}/\text{CH}_3\text{SO}_3\text{H}$ ($\text{Pm}3n, H_1$)	70	0.3237	9.2797		1.9767		0.6162
	80	0.3148	4.1935	1.2354		1.7227	0.6573
$C_{12}\text{IPS}/\text{CH}_3\text{SO}_3\text{H}$ ($\text{Pm}3n, H_1$)	60	0.2588	8.0574		1.5930		0.6629
	70	0.2785	7.8690		1.5942		0.6624
	80	0.2608	3.2146	0.8619		1.4908	0.8168
$C_{12}\text{IPS}/\text{C}_6\text{H}_6\text{SO}_3\text{H}$ (H_1)	50	0.2144	4.9490	1.2033		2.5425	0.5851
	60	0.2602	4.3598	1.1676		2.0247	0.6030
	70	0.3060	4.0844	1.1863		1.7119	0.5935
	80	0.3530	3.9239	1.2240		1.4758	0.5752
$C_{12}\text{IPS}/\text{CF}_3\text{SO}_3\text{H}$ (H_1)	30	0.1288	6.9977	1.3184		4.3609	0.5340
	40	0.1718	5.7222	1.2453		3.2316	0.5653
	50	0.2174	5.0863	1.2450		2.5962	0.5654
	60	0.2608	4.5399	1.2173		2.1054	0.5783
	70	0.3121	4.1618	1.2208		1.7202	0.5767
	80	0.3552	3.7627	1.1774		1.4079	0.5979

ϕ_L is the volume fraction of the hydrophobic long alkyl chain part; a_0 is the lattice parameters of the liquid crystalline phases; r_H is the radius of cylinder unit in the hexagonal structure; r_p is the radius of the micelle unit in the $\text{Pm}3n$ cubic structure; d_W is the thickness of the water channel of the liquid crystalline phases; a_s is the effective cross-sectional area.

Theory for calculation of structural parameters of liquid crystalline phase

The lattice parameters a_0 of the hexagonal (distance between the centers of adjacent cylinders) and Pm3n micellar cubic (cubic lattice parameter) liquid crystalline phases were obtained according to Eq. (1) and (2), respectively.^[1]

$$q_{(h,k)} = \frac{4\pi}{\sqrt{3}a_0} \cdot (h^2 + k^2 + hk)^{1/2} \quad (1)$$

$$q_{(h,k,l)} = \frac{2\pi}{a_0} \cdot (h^2 + k^2 + l^2)^{1/2} \quad (2)$$

where $q(h,k)$ and $q(h,k,l)$ are the scattering vectors corresponding to the scattering peaks observed in the SAXS spectra for the hexagonal and Pm3n micellar cubic phase, respectively, h , k , l are Miller indexes, and a_0 is the lattice parameter. From the results of SAXS, several structural parameters characterizing the structure of the liquid crystalline phase could be calculated as follows.

The volume fraction of the hydrophobic long alkyl chain part in $[C_n\text{IPS}][\text{R-SO}_3\text{H}]$ aqueous mixture system φ_L is calculated by Eq. (3)^[2]:

$$\varphi_L = \frac{\frac{W_C}{\rho_C} \times \frac{V_{C,L}}{V_C}}{\left(\frac{W_C}{\rho_C} + \frac{W_H}{\rho_H} + \frac{W_W}{\rho_W}\right)} = \frac{\frac{W_C}{M_C} \times V_{C,L}}{\left(\frac{W_C}{\rho_C} + \frac{W_H}{\rho_H} + \frac{W_W}{\rho_W}\right)} \quad (3)$$

where W_C , W_H and W_W are the weight fraction of $C_n\text{IPS}$, $\text{R-SO}_3\text{H}$ and water, respectively, and ρ_C , ρ_H and ρ_W are the densities of $C_n\text{IPS}$, $\text{R-SO}_3\text{H}$ and water, respectively. The density of $C_n\text{IPS}$ is obtained using a pycnometer as reported previously,^[3] and the reference solvent is ethyl acetate ($\rho = 0.8944 \text{ g}\cdot\text{cm}^{-3}$). The densities of $C_{12}\text{IPS}$, $C_{14}\text{IPS}$, $C_{16}\text{IPS}$, $\text{CH}_3\text{SO}_3\text{H}$, $\text{C}_6\text{H}_5\text{SO}_3\text{H}$, $\text{CF}_3\text{SO}_3\text{H}$ and water are 1.0227, 1.1098, 1.1595, 1.48, 1.32, 1.69 and $0.997 \text{ g}\cdot\text{cm}^{-3}$, respectively. V_C , $V_{C,L}$ and M_C are molecular volume of $C_n\text{IPS}$, molar volume of alkyl chain and the molecular weight of $C_n\text{IPS}$. $V_{C,L}$ is calculated by Eq. (4)^[4]:

$$V_{C,L} = N_A \times 10^{-21} [0.027(m - 1) + 0.055] \quad (4)$$

where N_A is Avogadro's number and m is the number of methylene in alkyl chain.

For hexagonal liquid crystalline, the radius of cylinder unit (r_H), the thickness of the water channel (d_W) and the effective cross-sectional area (a_s) could be obtained using Eq. (5), (6) and (7), respectively. [5]

$$r_H = a_0 \sqrt{\frac{\sqrt{3}\phi_L}{2\pi}} \quad (5)$$

$$d_W = a_0 - 2r_H \quad (6)$$

$$a_s = \frac{2V_{C,L}}{r_H \cdot N_A} \quad (7)$$

For calculation of Pm3n micellar cubic liquid crystalline structural parameters, it is generally assume that the two kinds of micelles to be spherical with the same radius. [6] The radius of the micelle unit (r_P) and the effective cross-sectional area (a_s) could be obtained using Eq. (8) and (9), respectively. [6]

$$r_P = \frac{a_0 \sqrt{3}\phi_L}{2\sqrt{4\pi}} \quad (8)$$

$$a_s = \frac{3V_{C,L}}{r_P \cdot N_A} \quad (9)$$

References

- [1] F. Nilsson, O. Söderman, *Langmuir*. **1996**, *12*, 902.
- [2] J. A. Riddick, W. B. Bunger, T. K. Sakano, in *Organic Solvents, Physical Properties and Methods of Purification*, Wiley–Interscience, New York, fourth edn., **1986**, pp. 45.
- [3] W. W. Russell, *Ind. Eng. Chem. Anal. Ed.* **1937**, *9*, 592.
- [4] Y. Yamashita, H. Kunieda, E. Oshimura, K. Sakamoto, *Langmuir*. **2003**, *19*, 4070.
- [5] Y. Yamashita, H. Kunieda, E. Oshimura, K. Sakamoto, *J. Colloid Interface Sci.* **2007**, *312*, 172.
- [6] X. Li, H. Kunieda, *Langmuir*. **200**, *16*, 10092

