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Electronic Supplementary Information for

Spontaneous wormlike micelles formed in a single-tailed zwitterionic surface active ionic liquid aqueous solution

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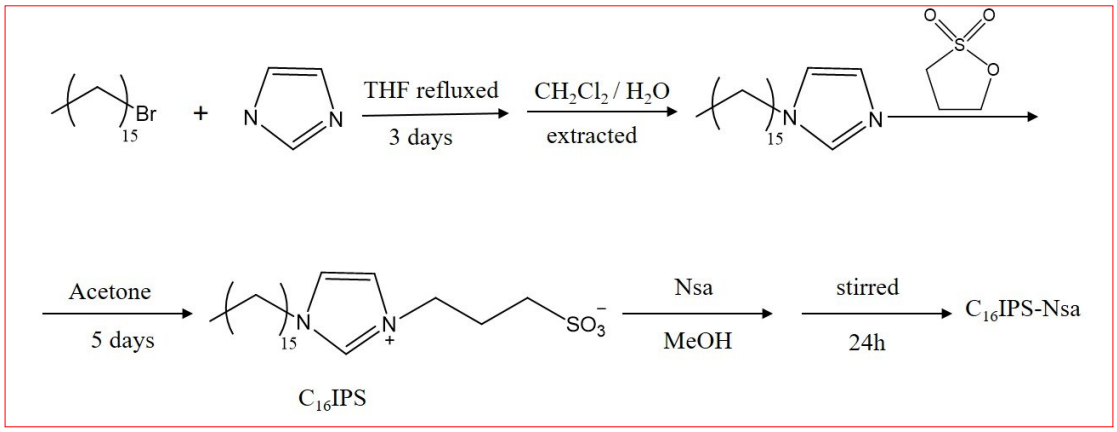
Additional results



Scheme S1 The route of the synthesis of C_{16}IPS-Nsa.

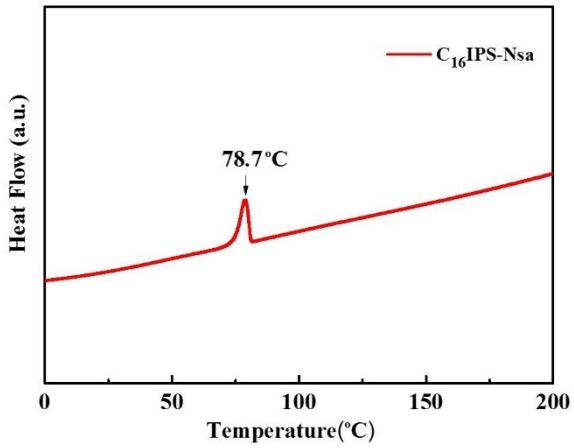


Fig. **S1** DSC curve of C_{16}IPS-Nsa.

The melting temperatures of C_{16}IPS and Nsa are 82.3 and 172-173°C.[1] The obtained melting point of C_{16}IPS-Nsa is 78.7 °C.

Surface Properties and Micellization Parameters.

Surface tension measurements were carried out to evaluate the aggregation behavior of zwitterionic SAILs in aqueous solutions. Fig.S2 demonstrates the surface tension (γ) versus concentration (C) plots for the aqueous solutions of C_{16}IPS-Nsa at 25°C. The surface tension gradually decreases with increasing IL concentrations until to a plateau region, indicating that the formation of micelle. From the distinct break point we can obtain the critical micelle concentration (CMC) and the corresponding γ_{cmc} (surface tension at CMC) (the value listed the Table S1). DLS was utilized to further investigate the size distributions of the aggregates formed by zwitterionic SAILs. As can be seen from the Fig. S3, the micelle size of 0.64wt% C_{16}IPS-Nsa aqueous solution is approximately 2.8 nm.

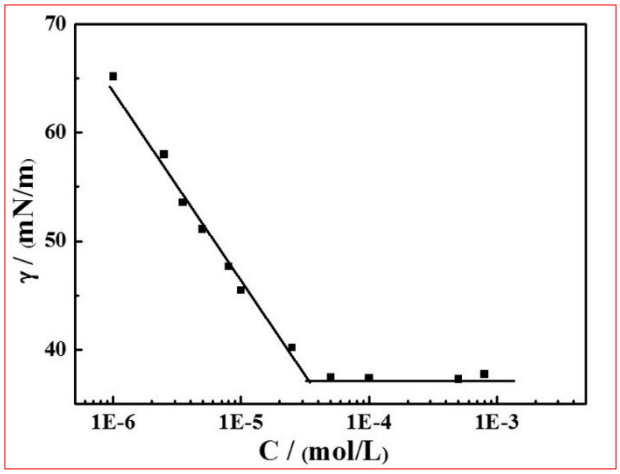


Fig. **S2** Surface tension as a function of concentration of C_{16}IPS-Nsa in aqueous solutions at 25°C.

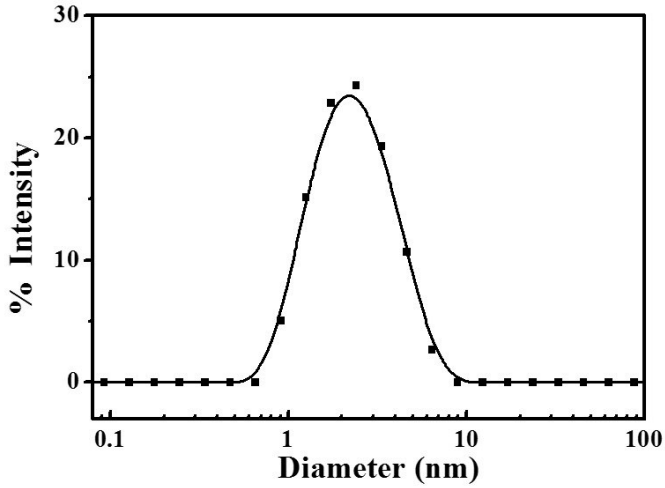


Fig. **S3** Size and size distributions of the aggregations formed by 10mM C_{16}IPS-Nsa at 25°C.

Table S1. Surface properties and micellization parameters of zwitterionic SAILs (C_{16}IPS-Nsa).

	CMC mM	γ_{CMC} *mN/m*	Γ_{max} 10^{-3}mmol/m^2	A_{min} Å^2	*P*
C_{16}IPS-Nsa	0.032	37.5	3.15	47.4	0.44

The amount of adsorbed surfactant (Γ) at the air-water interface can be calculated using the Gibbs adsorption isotherm:[2]

$$\Gamma = -\frac{1}{nRT}\left(\frac{\partial\gamma}{\partial \ln C}\right)_T \text{ (mmol/m}^2\text{)} \qquad [1]$$

where the value of n stands for the number of species at the interface, *R* is the gas constant (8.314 $J \cdot mol^{-1} \cdot K^{-1}$), *T* is the absolute temperature (K), C is the surfactant concentration ($mol \cdot L^{-1}$), and $\partial\gamma/\partial \ln C$ refers to the slope below the CMC in the surface tension plots. The minimum area occupied (*A*) by a surfactant molecule at the air-solution interface was obtained from the saturated adsorption as follows:

$$A_{\min} = \frac{1}{N_A \cdot \Gamma_{\max}} (\times 10^{23} \text{Å}^2) \qquad [2]$$

where N is Avogadro's number (6.022×10^{23} mol^{-1}), and Γ_{max} is the maximum surface excess concentration.

The packing parameter P is determined as $P=v/al$ by Israelachvili *et al*, which is an important parameter to interpret the self-assembled structure for amphiphile. where v is the effective hydrophobic chain volume, a is the effective head group area of the surfactant molecules, and l is the surfactant alkyl chain length.[3] Surfactants with $P<1/3$ tend to form spherical micelles, while $1/3 \leq P < 1/2$ prefer to form cylindrical aggregates and $1/2 \leq P < 1$ prefer to form bilayers. Surfactants with even higher values of P ($P > 1$) tend to form reverse structures.

The hydrocarbon chain length l can be calculated from the following Tanforde quation:[3]

$$l = 1.5 + 1.265N \qquad [3]$$

Here N is the number of carbon atoms in one hydrocarbon chain. The obtained value of l is21.74 Å. The effective volume of the hydrocarbon chains v has been calculated from the equation. The value of the v_l is 457.8 Å^3.

$$v_l\ (\text{Å}^3) = 27.4 + 26.9N [4]$$

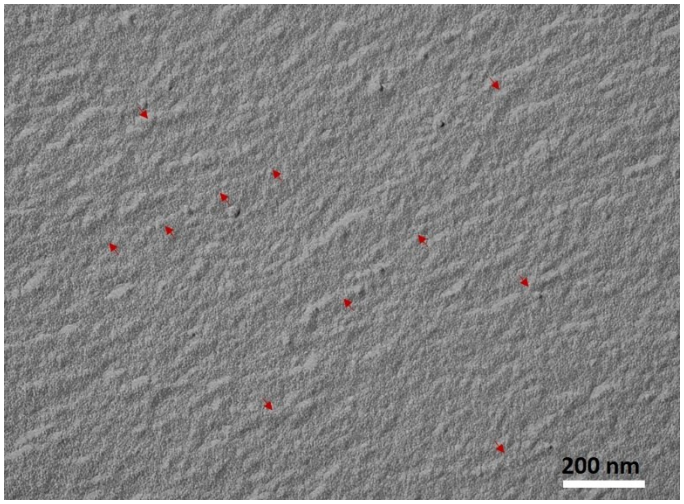


Fig S4. FF-TEM image of the C_{16}IPS-Nsa aqueous solutions at 13.96 wt%.

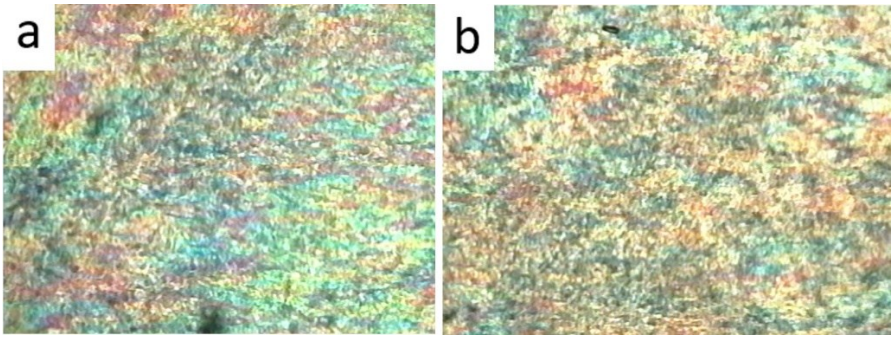


Fig S5. POM pictures of the C_{16}IPS-Nsa aqueous solutions at different concentrations.

a (49.76 wt%); b (60.11 wt%)

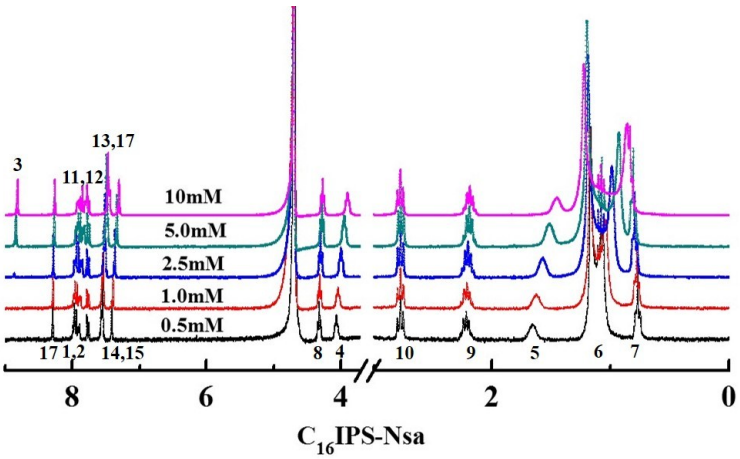


Fig S6. Proton assignments and ^{1}H NMR spectra of at different C_{16}IPS-Nsa

concentrations in D_2O at 25°C.

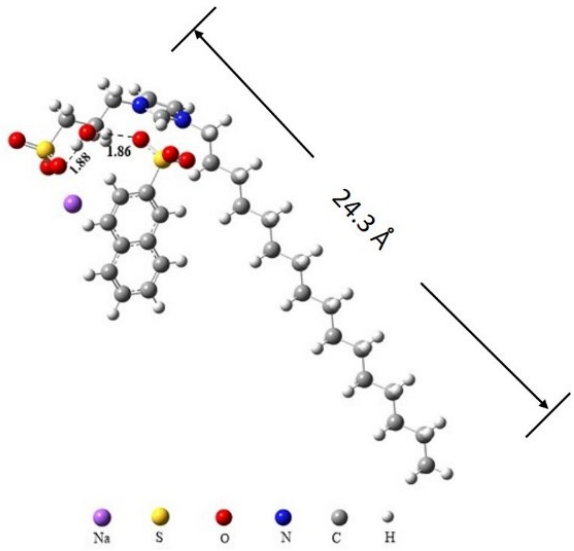


Fig S7. Geometries optimized at the B3LYP/6-31G (d, p) level of C_{16}IPS-Nsa.

The calculation of structural parameters of H_1 phase is according to the theory as follows.

The lattice parameters (a_0) of the hexagonal liquid crystalline phase (distance between the centers of adjacent cylinders) were obtained according to equation.[4]

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

where h, k are Miller indexes; q(h,k) is the scattering vector corresponding to the scattering peaks observed in the SAXS spectra for the hexagonal phase; 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:

$$a_0 = 4\pi/\sqrt{3}q \quad [2]$$

the radius of the cylinder unit (d_H) can be obtained using equation [3]:

$$d_H = a_0\sqrt{\frac{\sqrt{3}}{2\pi}\Phi_L} \quad [3]$$

Where Φ_L is the volume fraction of surfactant (C_{16}IPS-Nsa). The volume fraction of the hydrophobic long alkyl chain part in C_{16}IPS-Nsa/H_2O mixture system Φ_L is calculated by equation [4]:[5]

$$\Phi_L = \frac{\frac{W_C}{\rho_C} \times \frac{V_{CL}}{V_C}}{(\frac{W_C}{\rho_C} + \frac{W_W}{\rho_W} + \frac{W_N}{\rho_N})} = \frac{\frac{W_C}{M_C} \times V_{CL}}{(\frac{W_C}{\rho_C} + \frac{W_W}{\rho_W} + \frac{W_N}{\rho_N})} \quad [4]$$

where W_C ,W_N and W_w are the weight fraction of C_{16}IPS, Nsa and water, respectively, and ρ_C, ρ_N and ρ_w are the densities of C_{16}IPS, Nsa and water, respectively. The density of C_{16}IPS and Nsa are obtained using a pycnometer as reported previously. The densities of C_{16}IPS, Nsa and water are 1.1595, 1.420 and 0.997g/cm^{-3}, respectively. V_C, V_{CL} and M_C are molecule volume of C_{16}IPS, molar volume of alkyl chain and the molecular weight of C_{16}IPS. V_{CL} is calculated by equation [5]:[6]

$$V_{CL} = N_A \times 10^{-21}[0.027(m-1) + 0.055] \quad [5]$$

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

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