Electronic Supplementary Material (ESI) for Soft Matter.

High electric conductivity of liquid crystals formed by ordered self-assembly of nonionic surfactant N,N-bis(2-hydroxyethyl)dodecanamide in water

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ELECTRONIC SUPPLEMENTARY INFORMATION

1. Experimental

General methods

Liquid-crystalline phase transition behavior was examined with an AxioCam MRc5 optical polarizing microscope equipped with a Linkam THMSG600 heating and cooling stage at a heating rate of 1 K/2 min. Differential scanning calorimetry (DSC) measurements were conducted with a METTLER TOLEDO DSC 1 STAR system at a cooling rate of 10 K/min. Deuterium NMR spectra were recorded using a BRUKER AVANCE 400 at 61.42 MHz for ^{2}H-NMR in D_2O. Small-angle X-ray scattering (SAXS) patterns were obtained by an Anton Paar SAXSess diffractmeter with a heating stage using a Ni-filtered CuKα radiation. Fracturing and replication of liquid-crystalline sample was obtained by a freeze-fracture apparatus (LEICA EM BAF060) at a temperature of -140 ℃. The replica was examined on a JEOL JSM-7600F. The conductivities were measured by METTLER TOLEDO S975-uMix SevenExcellence, the temperature was controlled by a thermostatic water bath. A series of DDA solutions with different water contents were prepared. Measurements of the conductivity of DDA solutions were made after magneton stirring for two hours and resting for one week at 40 ± 0.1 ℃.

Material

N,N-bis(2-hydroxyethyl)dodecanamide was prepared in our laboratory. And the details of synthetic process refer to the literature.[1]

2. Simulation Method and Model of BS and DOS

Cambridge serial total energy package (CASTEP),[3] an ab initio pseudo-potential method based on DFT, was used in this paper. GGA with PBE[4] parameterization was adopted to describe the exchange–correlation interaction. Ultrasoft pseudo-potentials[5] were applied to model the electron–ion interaction. A 3 × 3 × 4 Monkhorst Pack grid of k-points was adopted for sampling the Brillouin zone. According to the result of MD simulation, a DDA molecule linking two water molecule through intermolecular hydrogen-bond were placed in an orthorhombic super-cell with spacing suitable for the formation of the long-range ordered association structure. The atoms' locations of the lowest energy and stress could be obtained by optimizing the super-cells. The BFGS algorithm[6] was chosen for the geometry optimization of the super-cells. The energy cut-off for the plane wave basis was chosen as 300 eV for the electronic structure calculation. Test calculations showed that the denser k-point grid and higher energy cut-off slightly affected the computational results. The tolerances were set as follows: 2×10^{-6} eV/atom for the total energy, 0.1 eV/nm for maximum force, and 0.0001 nm for displacement.

Band electronic structure (BS) and density of states (DOS) of pure DDA

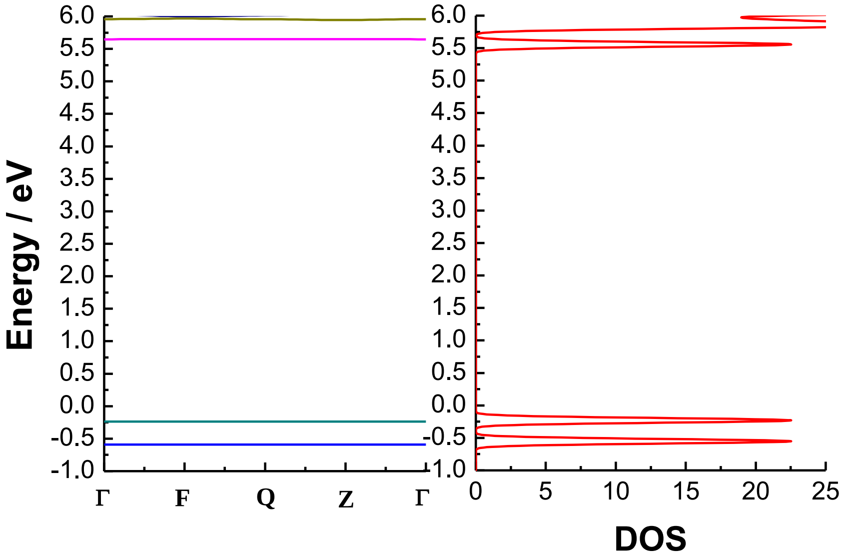


Figure S1: BS and DOS of pure DDA calculated by first principles.

3. The details of the MD simulation

DDA was represented by a bead-spring chain and the water molecule was described by the flexible SPC model. The parameters used in the simulation were calculated by COMPASS force field. In DDA-water system, 32 surfactant and 800 water molecules were prepared. To construct the configuration, 16 surfactant molecules of DDA were prepared to form a surfactant monolayer with spacing suitable for hexagonal closed packing in an orthorhombic simulation box with periodic boundary conditions applied to all three spatial directions. The initial lattice constants were chosen to satisfy the surface area/molecule of 44 Å^2, corresponding to the value for the saturated surfactant adsorption at the air/water interface at the critical micelle concentration (cmc). The dimensions of the cell parameters Lx, Ly, and Lz of the orthorhombic simulation box with the surfactant monolayer were 24.59, 28.4 and 20 Å, with hydrocarbon chains extending perpendicular to the xy plane. The water box had the same Lx and Ly dimensions as the orthorhombic surfactant simulation box, while the Lz dimension was 34.26 Å. Two surfactant monolayers were added at opposite sides of the water film, with the hydrophilic head in contact with the water interface. The Lz dimension of the water box is large enough for the two monolayers to remain effectively isolated from each other.[2] To remove the possible molecule overlap in the initial configurations, 5000 steps of minimized optimization were first run using a steepest descent algorithm. Then, molecular dynamic simulation was carried out starting with the minimized configuration. All simulations are equilibrated at constant temperature and volume (NVT) for about 1.0 ns with a time step of 1 fs. The MD simulations were run for 4ns, and the results of the last 1 ns were used to analyze and evaluate the properties.

Coordination number

The pair correlation function $g_{ij}(r)$ of particles j, which are water molecules, to the particles i, which are head groups of DDA molecules were calculated. The first peak of the $g_{ij}(r)$ curve showed the first hydration shell of i. The number of particle j in the space around the particle i, in distance from r_0, where the pair correlation function $g_{ij}(r)$ just becomes nonzero before the first peak, to r_{fp}, the last point of first peak, is calculated by integrating $g_{ij}(r)$ from r_0 up to r_{fp}, and yields a value for the first coordination number n,[7,8] where ρ was the density of simulation.

$$\mathrm{n} = 4\pi \int_{r_0}^{r_{fp}} r^2 g_{ij}(r)\rho dr$$

4. The details of dissipative particle dynamics simulation

DPD as a mesoscopic simulation technique has been described in detail elsewhere[9] and will be covered here only briefly. In the simulation, molecules are represented by a bead-and-spring type particles. The motions of beads follow Newton's equations:

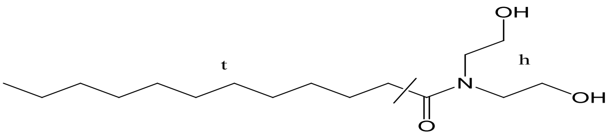
$$\frac{\mathrm{d}r_i}{\mathrm{dt}} = v_i \qquad m_i \frac{\mathrm{d}v_i}{\mathrm{dt}} = f_i \tag{1}$$

Where r_i, v_i, f_i, are the position, velocity and force of the i particle, respectively. The total force exerted on bead i includes FC_{ij}, FD_{ij} and FR_{ij}. FC_{ij} is the conservative force, FD_{ij} and FR_{ij} are the dissipative and random forces, respectively. Each of them is pairwise additive. All three forces tend to 0 when the distance between two particles is larger than the cutoff radius.[10-12]

The head group and tail group of DDA are represented as two beads, which are connected by a harmonic spring with the spring constant C = 4 (in kT units); water is represented as single bead. Water beads, head groups, and tail groups are denoted by w, h, and t, respectively. The size of the box with periodic boundary conditions is 30×30×30 DPD units in the simulation system containing 81000 beads (ρ =3). DPD units are adopted in simulation for length, energy, and time. The mass of all of the beads is 1, and k_BT (the temperature of the thermostat) is the units of energy, we set the temperature of the system as $k_BT=1.0$. As the DPD technique is based on soft sphere interactions, the repulsion parameter a_{ij} needs to be chosen while taking into account the compressibility of the system. A linear relationship for the repulsion parameters a_{ij} and the Flory–Huggins interaction parameters $\chi_{ij}(T)$ is given[13] in k_BT units:

$$\mathrm{a}_{ij} = a_{ii} + \frac{\chi_{ij}(T)}{0.306} = 25 + 3.27\chi_{ij}(T) \qquad (2)$$

Between beads of the same type, the repulsion parameters are taken as $a_{ij} = 75k_BT/\rho = 25\ k_BT$ (ρ=3). Simulations were performed for 20000 time steps, the time step was chosen as 0.05. And the simulation was performed through the Gibbs canonical ensemble. In DPD simulation, the calculated a_{ij} parameters by the above theories and methods are given in table 1 which is determined according to the liner relation with Flory-Huggins parameters χ_{ij}. The χ_{ij} between pairs of particles can be obtained from the calculation of the mixing energy with Blend module. All simulations were carried out by Materials Studio 4.3 from Accelrys in this paper.



Scheme S1 The chemical structure of N,N-bis(2-hydroxyethyl)dodecanamide (DDA).

Table 1. The interaction parameters a_{ij} of DDA-water systems (in *kT* units).

a_{ij}	**h**	**w**	**t**
h	25.0		
w	32.1	25.0	
t	117.0	79.1	25.0

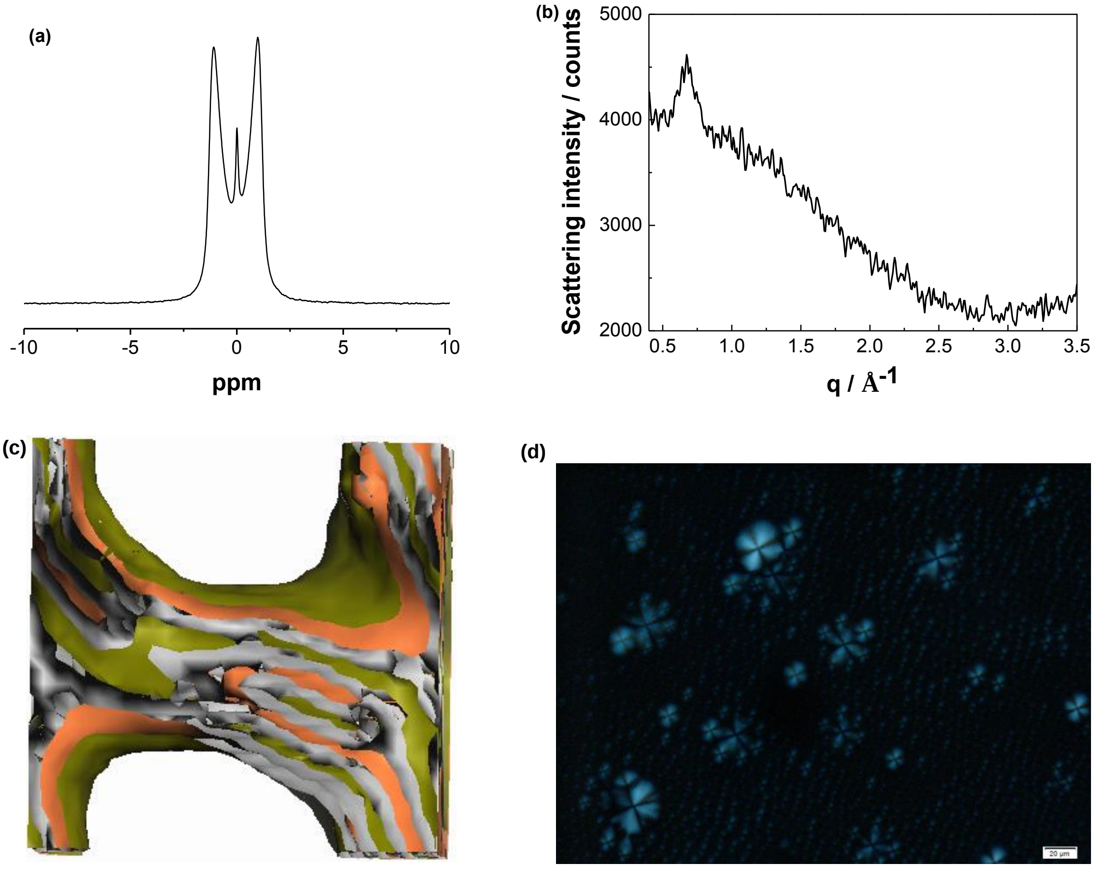


Figure S2: (a) ^{2}H-NMR spectrum; (b) SAXS diffraction pattern; (c) Isosurface image of the DPD simulation result; and (d) POM image of DDA/water binary system with 70 wt% water at 40±0.01 ℃.

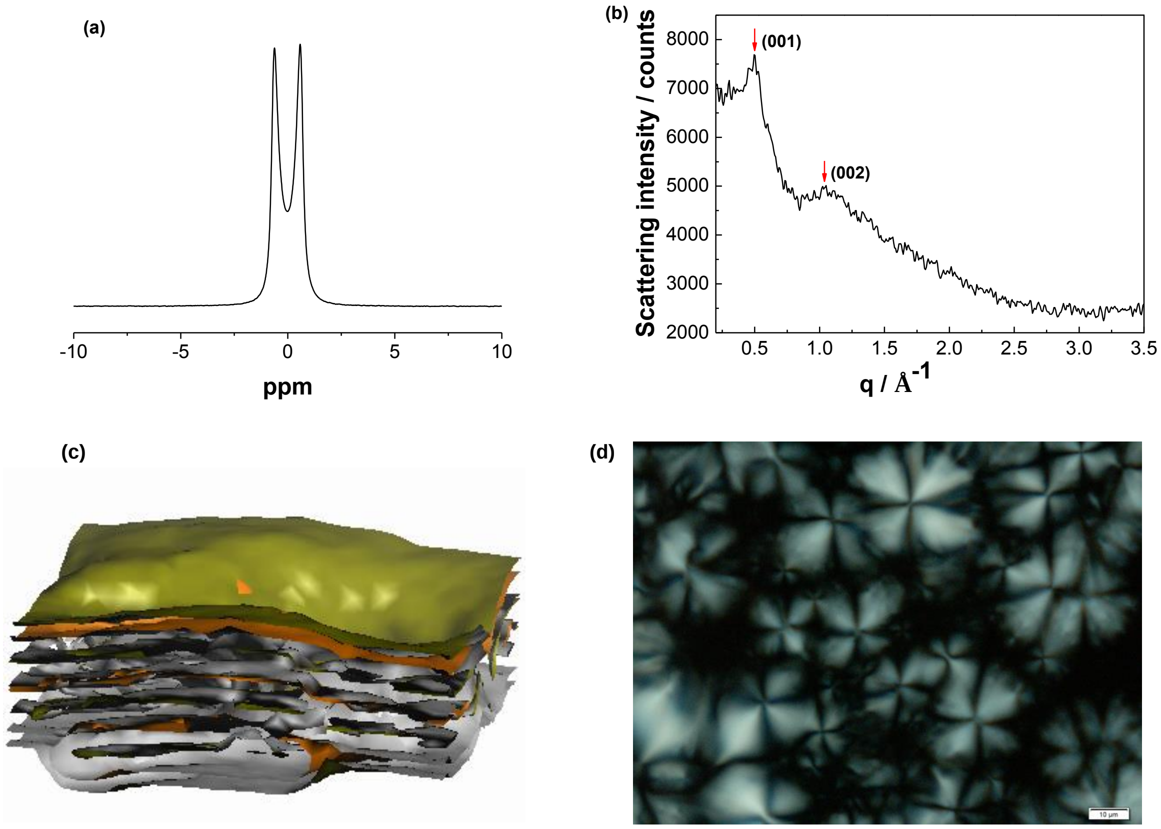


Figure S3: (a) ^{2}H-NMR spectrum; (b) SAXS diffraction pattern; (c) Isosurface image of the DPD simulation result; and (d) POM image of DDA/water binary system with 80 wt% water at 40 ±0.01 ℃.

The newly added results agreed with the previous analysis and prediction very well. The ^{2}H-NMR spectrum of DDA/water binary system with 70 wt% water content consisted of a doublet and a central singlet at 40 ±0.01 ℃, which corresponded to the lamellar crystal and the isotropous cubic respectively (Figure S2a). Namely, the phase structure transformed from Cub$_{bi}$ to lamellar phase gradually, and the two different kind of liquid crystal phase coexisted at the point. Accordingly, no classical SAXS diffraction pattern was observed for DDA liquid crystals with 70 wt% water content (Figure S2b). In Figure S3a, the result of the SAXS measurement confirmed that the phase structure of DDA liquid crystals with 80 wt% water content was lamellar (Figure S3b). The above results agreed very well with the POM, ^{2}H-NMR investigation and DPD simulation.

5. The mechanism of the conductivity deviation above 70 ℃

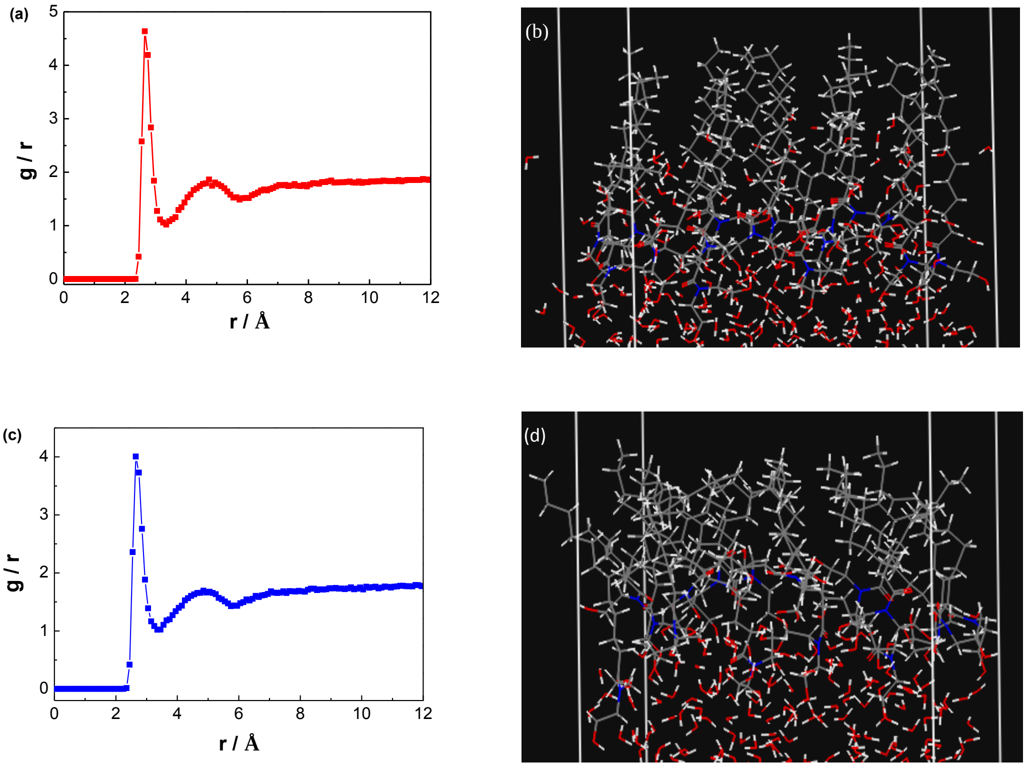


Figure S4: (a) The RDF of water molecules (the oxygen atom was assigned to be label atom) to DDA head group (the nitrogen atom was chosen to be label atom) and (b) the corresponding equilibrated configuration snapshot at the end of MD simulation for DDA/water binary system with 68.00 wt% water at 313 K. (c) The RDF of water molecules to DDA head group and (d) the corresponding equilibrated configuration snapshot at the end of MD simulation for DDA/water binary system with 68.00 wt% water at 348 K.

The coordination number of water molecules to DDA head group got by the RDF calculation was almost the same for DDA/water binary system with 68.00 wt% water at 313 and 348 K (Figure S4(a) and S4(c)). But less free water molecules were found inside the DDA-water interface layer at 348 K comparing with that at 313 K, and the stretching degree of the surfactant hydrophobic tail decreased clearly at 348 K comparing with that at 313 K. The above results hinted that the surfactant head group could arrange more closely at higher temperature, which would be benefit for the transportation efficiency of the charge carrier.

References

1 S. Zhang, P. Zhu, Y. Sun, Y. Yang, X. Cao, X. Song, Y. Li, *RSC Adv.* 2014, **4**, 41831.

2 E. Khurana, S. O. Nielsen, M. L. Klein, *J. Phys. Chem. B* 2006, **110**, 22136.

3 M. D. Segall, P. Lindan, M. J. Probet, C. J. Pickard, P. J. Hasnip, S. J. Clark, M. C. Payne, *J. Phys. Condens. Matter*. 2002, **14**, 2717:1–2717:3.

4 J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett*. 1996, **77**, 3865.

5 D. Vanderbilt, *Phys. Rev. B*. 1990, **41**, 7892.

6 Q. Yao, H. Xing, and L. Meng, *Chin. J. Nonferr. Metals* 2007, **17**, 1297.

7 C.Y. Wu, A.A. Skelton, M.J. Chen, L. Vlček, P.T. Cummings, *Langmuir* 2012, **28**, 2799.

8 R. Yuan, Y. Li, C. Li, H. Fang, W. Wang, *Colloids and Surfaces A: Physicochem. Eng. Aspects* 2013, **434**, 16.

9 Y. Li, X. He, X. Cao, Y. Shao, Z. Li, F. Dong, *Mol. Simul.* 2005, **31**, 1027.

10 M.Y. Kuo, H.C. Yang, C.Y. Hua, C.L. Chen, S.Z. Mao, F. Deng, H.U. Wang, Y.R. Du, *Chem. Phys. Chem.* 2004, **5**, 575.

11 R.D. Groot, P.B. Warren, *J. Chem. Phys.*1997, **107**, 4423.

12 E. Ryjkina, H. Kuhn, H. Rehage, *Angew. Chem. Int. Ed.* 2002, **41**, 983.

13 (a) R. D. Groot, *Langmuir* **2000**, *16*, 7493; (b) R. D. Groot, *J. chem. Phys.* 2003, **118**, 11265.