Supporting information

Ionic liquid crystals with novel thermal properties formed by the Gemini surfactants containing four hydroxyl groups

Lan Lei,[a] Lin Feng,[a] Binglei Song,*[a] Zhaolan Zhai,[b] Shibin Shang,[b] and Zhanqian Song*[b]

a. Key Laboratory of Food Colloids and Biotechnology, Ministry of Education, School of Chemical & Materials Engineering, Jiangnan University, Wuxi, Jiangsu 214122, China.

b. Key Laboratory of Biomass Energy and Materials, Jiangsu Province, Institute of Chemical Industry of Forestry Products, CAF, Nanjing, Jiangsu 210042, China.

1 Synthesis

The synthetic scheme of Alkanediyl-α,ω-bis[di(2-hydroxylethyl) dodecylammonium bromide] (12(2OH)-s-12(2OH)) is shown in Fig. S1.

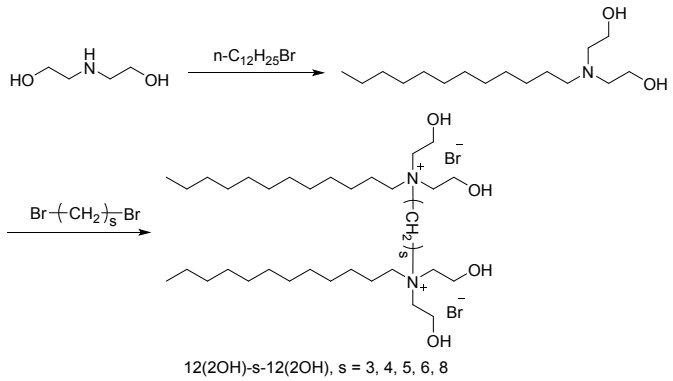


Fig. S1 The synthetic scheme of 12(2OH)-s-12(2OH).

(1) Synthesis of N-dodecyldiethanolamine.

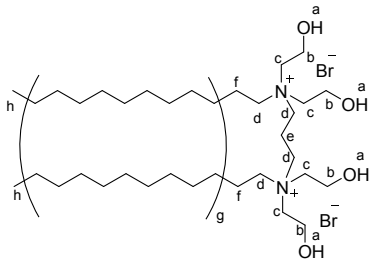
In 200 mL ethanol, 1-bromododecane (100 g, 0.4 mol), diethanolamine (170 g, 1.62 mol) were added and stirred at 60 °C for 48 h. After cooling, sodium hydroxide (20 g, 0.5 mol) was added and stirred for another 1 h. After removing the ethanol, 150 mL distilled water was added into the residue and the mixture was extracted with ether three times. The extracts were combined and washed with water. The ether solution was dried with anhydrous magnesium sulfate and the ether was then removed. The residue was distilled under vacuum to get the product as viscous liquid (210 °C/5 mmHg). Yield: 73.1%.

(2) Synthesis of alkanediyl-*α*, *ω*-bis(dihydroxyethylalkylammonium bromide) surfactants.

*[a] E-mail: ccfsbl@jiangnan.edu.cn
*[b] E-mail: lhssxly@hotmail.com

Synthesis of 12(2OH)-3-12(2OH)

In a sealed system, N-dodecyldiethanolamine (20 g, 0.073 mol), 1,3-dibromopropane (6.6 g, 0.033 mol) and 20 mL ethanol were mixed and stirred. The reaction was performed at 115 °C for 72 h. After cooling and removal of ethanol, the residue was recrystallized with ethanol and ethyl acetate three times. The product was dried under vacuum and obtained as white sheet-like solid. Yield: 37.6%.



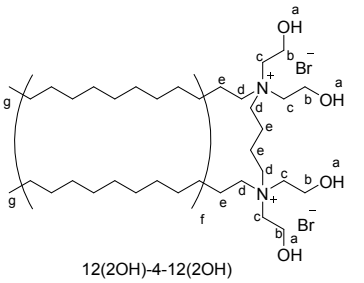
12(2OH)-3-12(2OH)

^{1}H NMR (400 MHz, DMSO) δ 5.29 (a-H, t, *J* = 5.0 Hz, 4H), 3.82 (b-H, d, *J* = 4.0 Hz, 8H), 3.50 (c-H, s, 8H), 3.42-3.32 (d-H, m, 8H), 2.12 (e-H, s, 2H), 1.65 (f-H, s, 4H), 1.36-1.17 (g-H, m, 36H), 0.86 (h-H, t, *J* = 6.8 Hz, 6H).

Elemental analysis for $C_{35}H_{76}Br_2N_2O_4$: C, 56.14; H, 10.23; N, 3.74. Found: C, 56.11; H, 10.11; N, 3.39.

Synthesis of 12(2OH)-4-12(2OH)

In a sealed system, N-dodecyldiethanolamine (14.7 g, 0.054 mol), 1,4-dibromobutane (5.2 g, 0.024 mol) and 15 mL ethanol were mixed and stirred. The reaction was performed at 115 °C for 72 h. After cooling and removal of ethanol, the residue was recrystallized with ethanol and ethyl acetate three times. The product was dried under vacuum and obtained as white sheet-like solid. Yield: 49.2%.



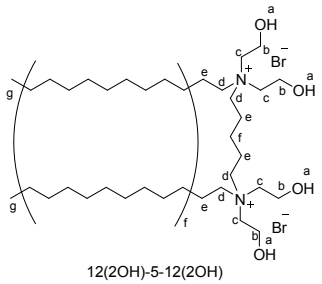
12(2OH)-4-12(2OH)

^{1}H NMR (400 MHz, DMSO) δ 5.27 (a-H, t, *J* = 4.9 Hz, 4H), 3.81 (b-H, d, *J* = 4.0 Hz, 8H), 3.43 (c-H, s, 8H), 3.40-3.30 (d-H, m, 8H), 1.67 (e-H, s, 8H), 1.35-1.19 (f-H, m, 36H), 0.86 (g-H, t, *J* = 6.8 Hz, 6H).

Elemental analysis for $C_{36}H_{78}Br_2N_2O_4$: C, 56.68; H, 10.31; N, 3.67. Found: C, 56.61; H, 10.34; N, 3.28.

Synthesis of 12(2OH)-5-12(2OH)

In a sealed system, N-dodecyldiethanolamine (30 g, 0.11 mol), 1,5-dibromopentane (11 g, 0.048 mol) and 30 mL ethanol were mixed and stirred. The reaction was performed at 115 °C for 72 h. After cooling and removal of ethanol, the residue was recrystallized with ethanol and ethyl acetate three times. The product was dried under vacuum and obtained as white solid. Yield: 58.1%.

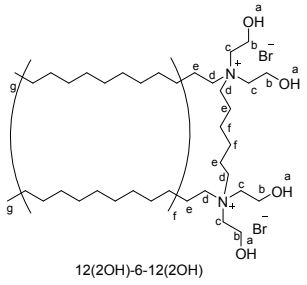


^{1}H NMR (400 MHz, DMSO), δ 5.25 (a-H, t, J = 5.1 Hz, 4H), 3.80 (b-H, d, J = 4.4 Hz, 8H), 3.43 (c-H, s, 8H), 3.38-3.27 (d-H, m, 8H), 1.67 (e-H, s, 8H), 1.36-1.19 (f-H, m, 38H), 0.86 (g-H, t, J = 6.8 Hz, 6H).

Elemental analysis for $C_{37}H_{80}Br_2N_2O_4$: C, 57.20; H, 10.38; N, 3.61. Found: C, 57.19; H, 10.16; N, 3.34.

Synthesis of 12(2OH)-6-12(2OH)

In a sealed system, N-dodecyldiethanolamine (25 g, 0.091 mol), 1,6-dibromohexane (10 g, 0.041 mol) and 20 mL ethanol were mixed and stirred. The reaction was performed at 120 °C for 96 h. After cooling and removal of ethanol, the residue was first washed with acetone and then recrystallized with ethanol and ethyl acetate three times. The product was dried under vacuum and obtained as white powder. Yield: 21.3%.

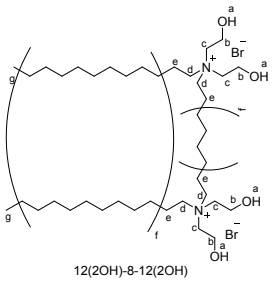


^{1}H NMR (400 MHz, DMSO) δ 5.24 (a-H, t, *J* = 5.2 Hz, 4H), 3.80 (b-H, d, *J* = 4.6 Hz, 8H), 3.43 (c-H, s, 8H), 3.39-3.27 (d-H, m, 8H), 1.65 (e-H, s, 8H), 1.38-1.17 (f-H, m, 40H), 0.86 (g-H, t, *J* = 6.8 Hz, 6H).

Elemental analysis for $C_{38}H_{82}Br_2N_2O_4$: C, 57.71; H, 10.45; N, 3.54. Found: C, 57.37; H, 10.36; N, 3.25.

Synthesis of 12(2OH)-8-12(2OH)

In a sealed system, N-dodecyldiethanolamine (20 g, 0.073 mol), 1,8-dibromooctane (8.5 g, 0.031 mol) and 25 mL ethanol were mixed and stirred. The reaction was performed at 120 ^{o}C for 120 h. After cooling and removal of ethanol, the residue was recrystallized with ethanol and ethyl acetate three times (Long time is needed for the crystallization). The product was dried under vacuum and obtained as white powder. Yield: 18.2%.



^{1}H NMR (400 MHz, DMSO) δ 5.24 (a-H, t, *J* = 5.1 Hz, 4H), 3.79 (b-H, d, *J* = 4.6 Hz, 8H), 3.41 (c-H, s, 8H), 3.37-3.25 (d-H, m, 8H), 1.63 (e-H, s, 8H), 1.36-1.20 (f-H, m, 44H), 0.85 (g-H, t, *J* = 6.8 Hz, 6H).

Elemental analysis for $C_{40}H_{86}Br_2N_2O_4$: C, 58.67; H, 10.58; N, 3.42. Found: C, 58.94; H, 10.23; N, 3.16.

2 The thermogravimetric analysis (TGA)

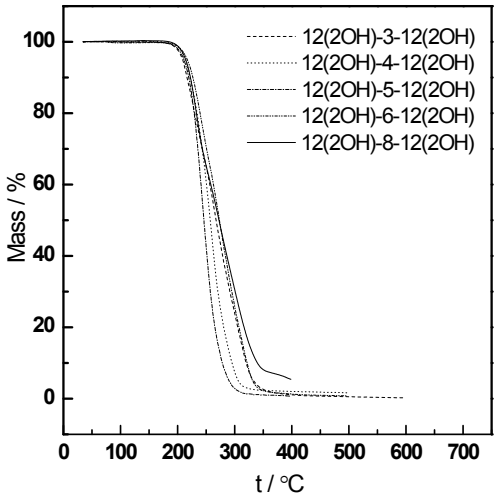


Fig. S2 The TGA curves of 12(2OH)-s-12(2OH) (s=3, 4, 5, 6, 8).

3 The differential scanning calorimetry (DSC) measurements

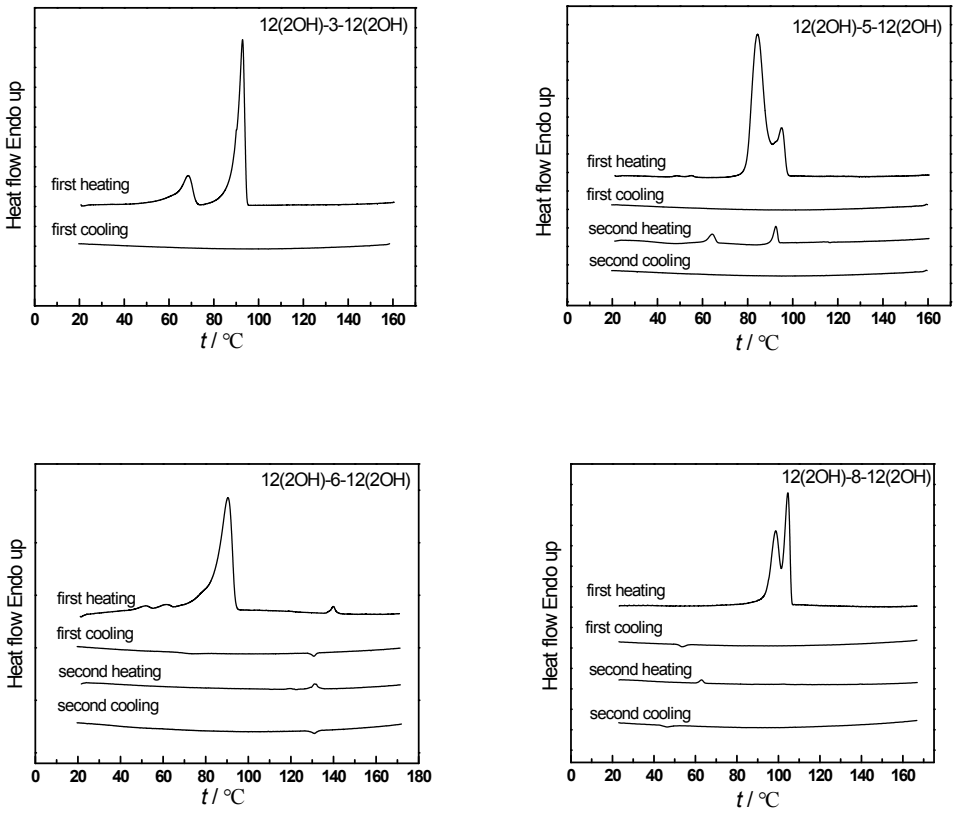


Fig. S3 The DSC curves of 12(2OH)-s-12(2OH) (s=3, 5, 6, 8).