

Toroidal micelles formed in viscoelastic aqueous solutions of a double-tailed surfactant with two quaternary ammonium head groups

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1. Synthesis of Di-C12-N2

The detailed synthetic process, which is shown in **Figure 1**, is described as follows.

(1) Synthesis of Compound 1. Sodium hydride (31.3 g, 0.78 mol) was added into a three-necked flask, and then a small amount of petroleum ether was added. After precipitation, the supernatant was removed. 500 mL of tetrahydrofuran was added. Diethyl malonate (125.3 g, 0.78 mol) was added slowly at room temperature, resulting in the release of H₂. 1-Bromododecane (150 g, 0.60 mol) was added and the mixture was stirred for 6 h at 70°C. After cooling, the mixture was washed once with citric acid solution and then twice with deionized water until the pH = 7. The organic layer was dried with anhydrous magnesium sulfate and then filtered under reduced pressure. The filtrate was evaporated under reduced pressure to remove THF. Finally, the residue was distilled under reduced pressure to give compound 1, which was a light yellow liquid. Yield: 75%.

(2) Synthesis of Compound 2. Sodium hydride (17 g, 0.43 mol) was added to a 1000 mL three-necked flask and washed several times with petroleum ether. After addition of 500 mL of THF, compound 1 (105.8 g, 0.32 mol) was slowly dropped in at 60°C. 1-Bromododecane (84.3 g, 0.34 mol) was added. The reaction was continued for 6 h at 72°C. After cooling, the mixture was

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washed once with citric acid solution and then twice with deionized water until pH = 7. The organic layer was dried with anhydrous magnesium sulfate and then filtered under reduced pressure. The filtrate was evaporated under reduced pressure to remove THF. Finally, the residue was distilled under reduced pressure to give compound 2, which was a light yellow liquid. Yield: 57%.

(3) Synthesis of Compound 3. Sodium hydroxide (23.3 g, 0.58 mol), 300 mL ethanol and a small amount of water were added to a 1000 mL three-neck flask and heated to 70°C. Compound 2 (72.3 g, 0.15 mol) was added, and the mixture was stirred for 24 h at 80°C. After the reaction, the mixture was placed in the refrigerator. The resulted precipitates were collected by filtration. Then 150 mL of deionized water was added, and the mixture was adjusted to pH = 2 with concentrated hydrochloric acid. After heating to 50°C and stirring for 2 h, the solid was obtained by filtration and then washed with deionized water. The washed solid was placed in a bottle and heated to 180°C for 4 h. The crude product was recrystallized three times with methanol and dried under vacuum at 55°C to give compound 3, which was a white solid. Yield: 67%.

(4) Synthesis of Compound 4. Compound 3 (33.7 g, 0.08 mol) was added into a 500 mL three-necked flask. A few drops of DMF were added, and thionyl chloride (12.1 g, 0.10 mol) was slowly added at 60°C. The generated acid gas was absorbed with the alkali solution. After the reaction was completed, excess thionyl chloride was removed by evaporation under reduced pressure. The raw compound 4 was obtained as a light yellow liquid.

(5) Synthesis of Compound 5. An appropriate amount of dichloromethane, triethylamine (25.8 g, 0.26 mol), and 3-(dimethylamino)-1-propylamine (9.6 g, 0.09 mol) were placed in a 500 ml three-necked flask with an ice bath. Compound 4 (35.3 g, 0.09 mol) was drop added. After the addition

was completed, the mixture was allowed to react for 6 h at room temperature. After the reaction, an appropriate amount of dichloromethane and deionized water were added for extraction. The crude product was recrystallized three times with ethanol and dried under vacuum at 55°C to give compound 3, which was a white solid. Yield: 65%.

(6) Synthesis of the compound **Di-C12-N2**. Compound 5 (25.5 g, 0.053 mol), 3-bromopropyl-N,N,N-trimethyl ammonium bromide (12.6 g, 0.048 mol) and 200 mL ethanol were placed in a single-necked flask and reacted for 48 h at 92°C. After the reaction, the mixture was cooled to room temperature and the solvent was removed by evaporation under reduced pressure. The crude product was recrystallized three times with ethanol/ethyl acetate and dried under vacuum at 55°C to give Di-C12-N2, which was a white powder. Yield: 79%.

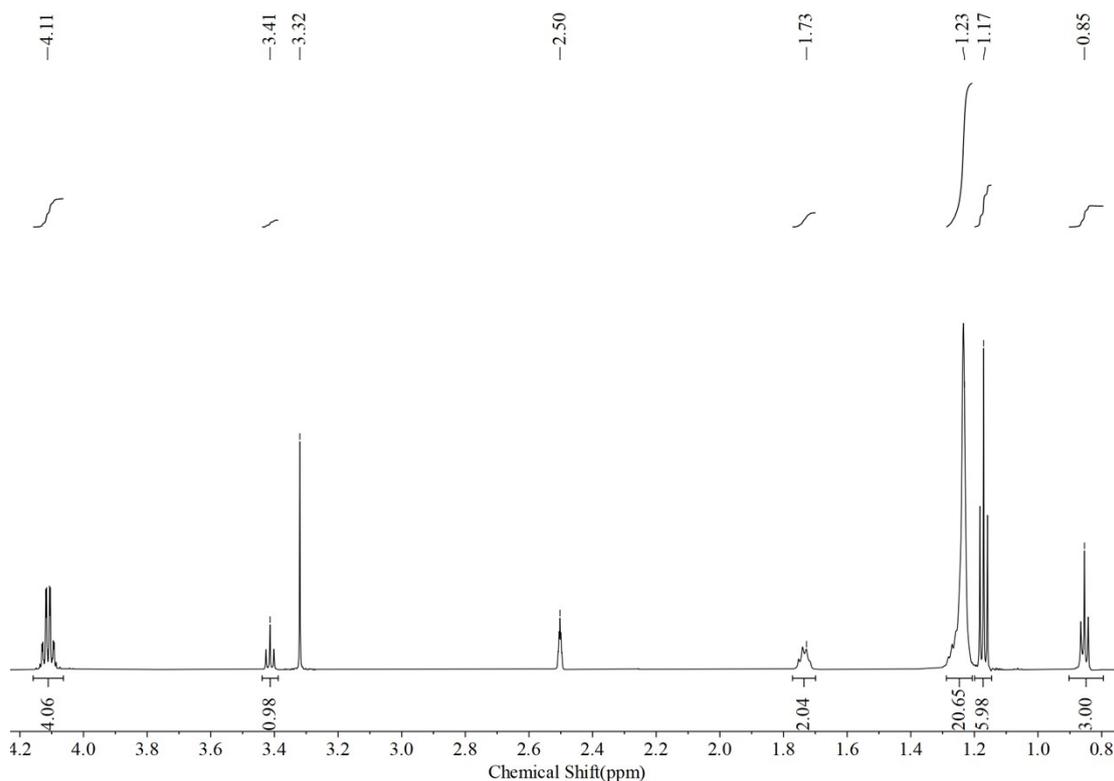
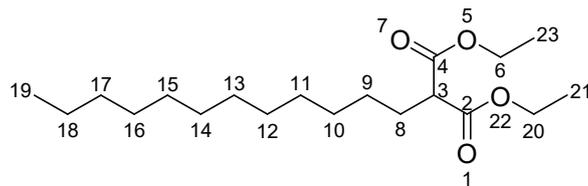


Fig. S1 ¹H NMR spectrum of compound 1 (DMSO)



$^1\text{H NMR}$ (600 MHz, DMSO) δ 4.11 (q, 4H, C6-2H, C20-2H), 3.41 (t, 1H, C3-1H), 1.73 (q, 2H, C8-2H), 1.23 (s, 21H, C18-2H, C17-2H, C16-2H, C15-2H, C14-2H, C13-2H, C12-2H, C11-2H, C10-2H, C9-2H), 1.17 (t, 6H, C21-3H, C23-3H), 0.85 (t, 3H, C19-3H).

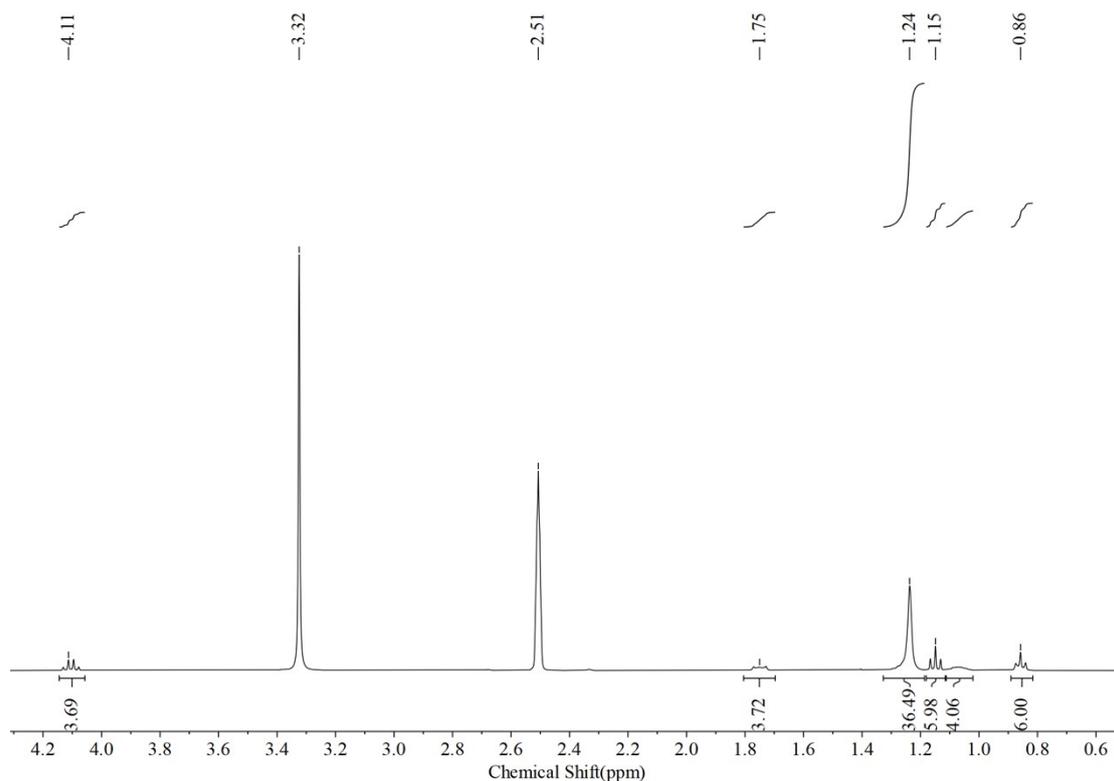
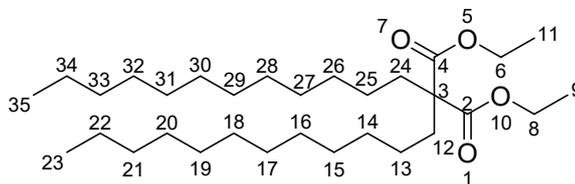


Fig. S2 $^1\text{H NMR}$ spectrum of compound 2 (DMSO)



$^1\text{H NMR}$ (400 MHz, DMSO) δ 4.11 (q, 4H, C6-2H, C8-2H), 1.75 (m, 4H, C12-2H, C24-2H), 1.24 (s, 36H, C22-2H, C21-2H, C20-2H, C19-2H, C18-2H, C17-2H, C16-2H, C15-2H, C14-2H, C34-2H, C33-2H, C32-2H, C31-2H, C30-2H, C29-2H, C28-2H, C27-2H, C26-2H), 1.15 (t, 6H, C9-2H, C11-2H), 1.07 (m, 4H, C13-2H, C25-2H), 0.86 (t, 6H, C23-3H, C35-3H).

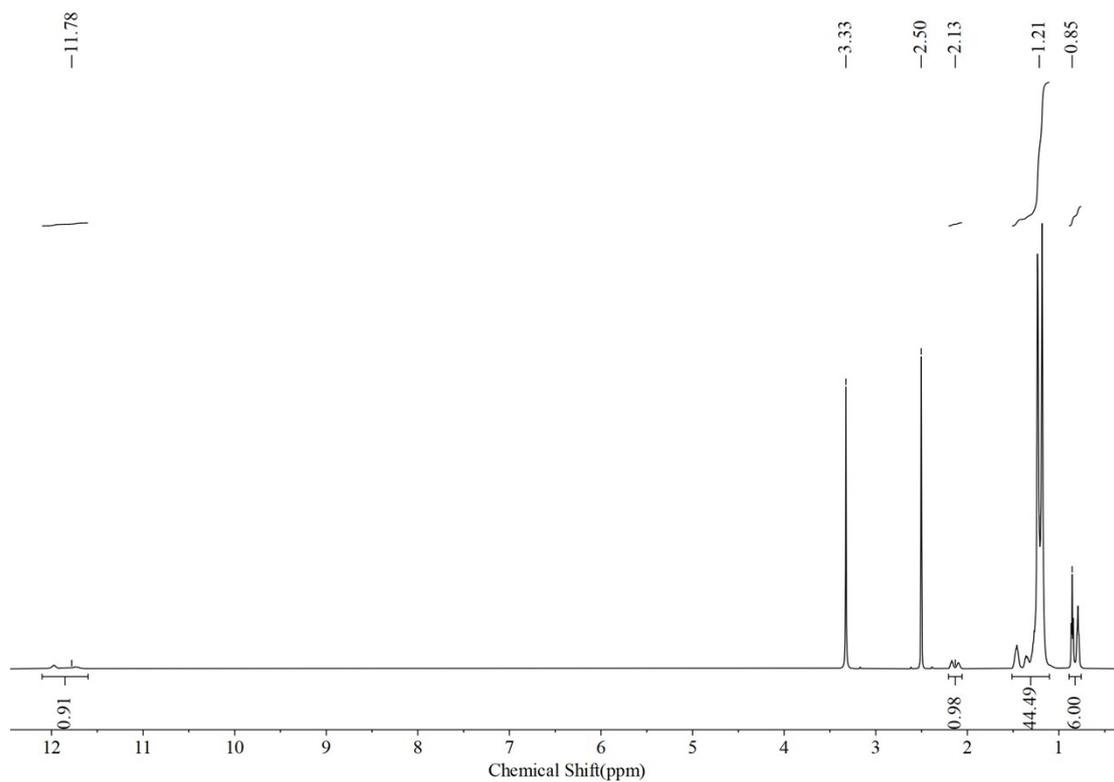
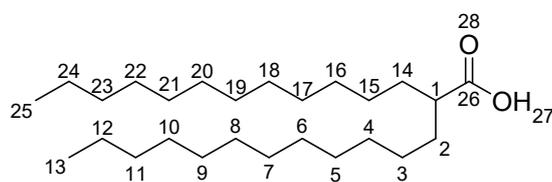


Fig. S3 ^1H NMR spectrum of compound 3 (DMSO)



^1H NMR (600 MHz, DMSO) δ 11.78 (d, 1H, COOH), 2.13 (m, 1H, C1-1H), 1.21 (m, 44H, C12-2H, C11-2H, C10-2H, C9-2H, C8-2H, C7-2H, C6-2H, C5-2H, C4-2H, C3-2H, C2-2H, C24-2H, C23-2H, C22-2H, C21-2H, C20-2H, C19-2H, C18-2H, C17-2H, C16-2H, C15-2H, C14-2H), 0.85 (t, 6H, C13-3H, C25-3H).

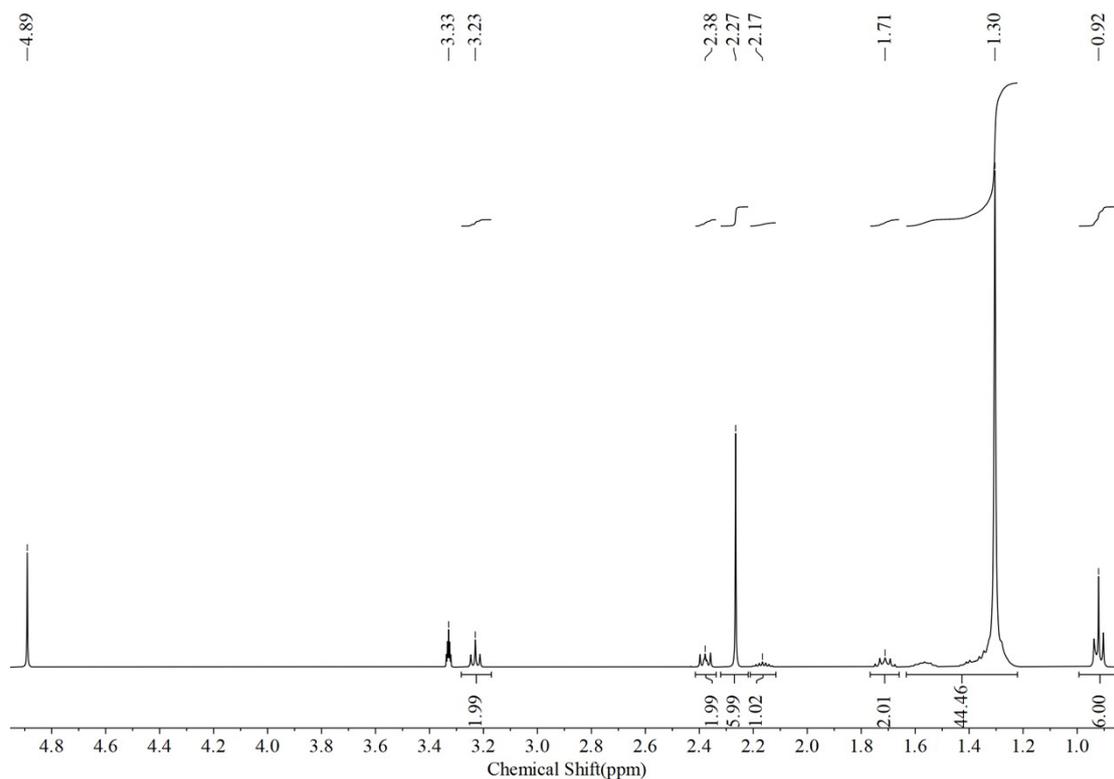
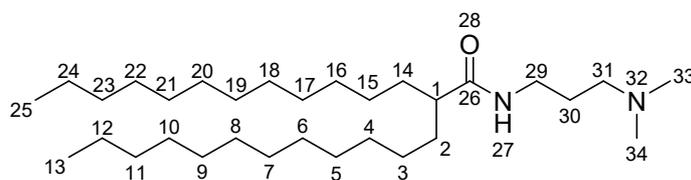


Fig. S4 ^1H NMR spectrum of compound 5 (MeOD)



^1H NMR (400 MHz, MeOD) δ 3.23 (t, 2H, C29-2H), 2.38 (m, 2H, C31-2H), 2.27 (s, 6H, C33-3H, C34-3H), 2.17 (m, 1H, C1-1H), 1.71 (m, 2H, C30-2H), 1.30 (m, 44H, C12-2H, C11-2H, C10-2H, C9-2H, C8-2H, C7-2H, C6-2H, C5-2H, C4-2H, C3-2H, C2-2H, C24-2H, C23-2H, C22-2H, C21-2H, C20-2H, C19-2H, C18-2H, C17-2H, C16-2H, C15-2H, C14-2H), 0.92 (t, 6H, C13-3H, C25-3H).

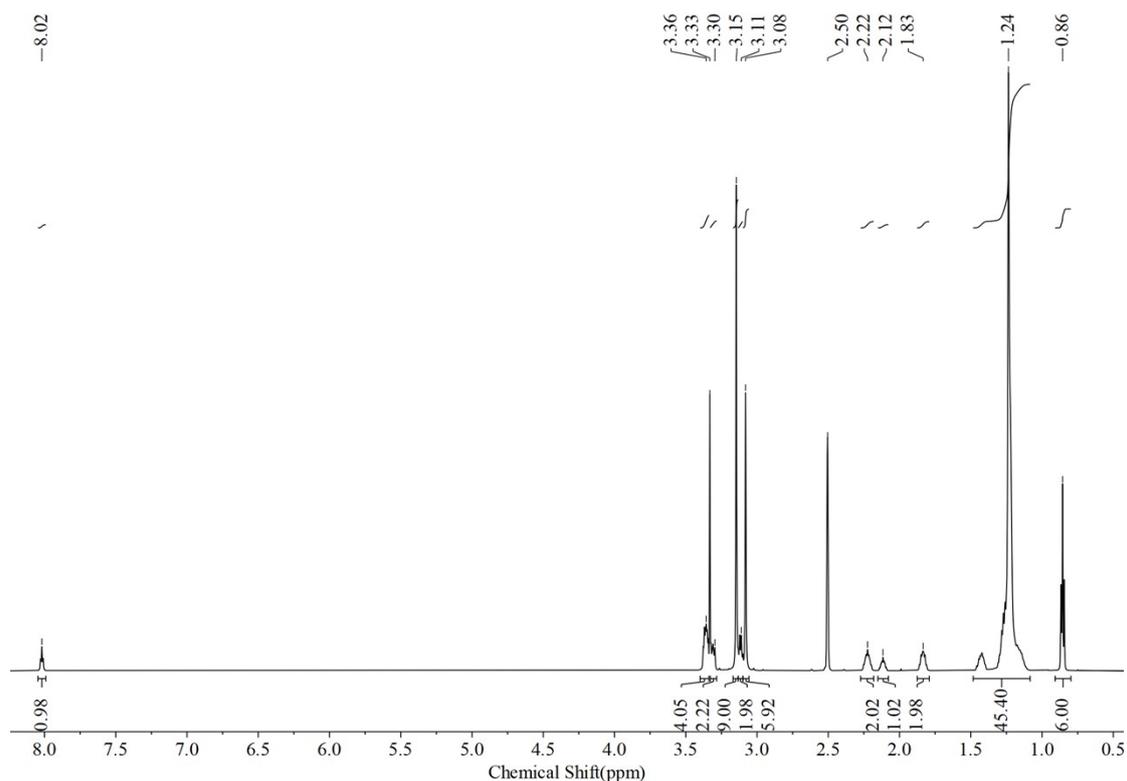
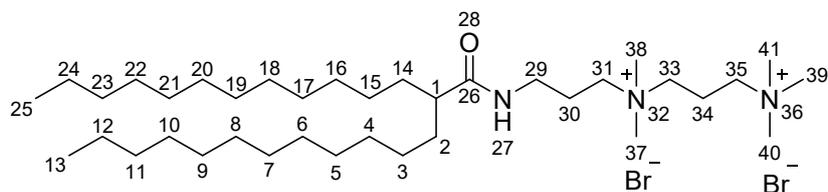


Fig. S5 ^1H NMR spectrum of compound Di-C12-N2 (DMSO)



^1H NMR (600 MHz, DMSO) δ 8.02 (t, 1H, NH), 3.36, 3.30 (m, 6H, C37-3H, C38-3H), 3.15 (s, 9H, C39-3H, C40-3H, C41-3H), 3.11 (q, 2H, C29-2H), 3.08 (s, 6H, C31-2H, C33-2H, C35-2H), 2.22 (t, 2H, C34-2H), 2.12 (t, 1H, C1-1H), 1.83 (t, 2H, C30-2H), 1.24 (m, 45H, C12-2H, C11-2H, C10-2H, C9-2H, C8-2H, C7-2H, C6-2H, C5-2H, C4-2H, C3-2H, C2-2H, C24-2H, C23-2H, C22-2H, C21-2H, C20-2H, C19-2H, C18-2H, C17-2H, C16-2H, C15-2H, C14-2H), 0.86 (t, 6H, C13-3H, C25-3H).

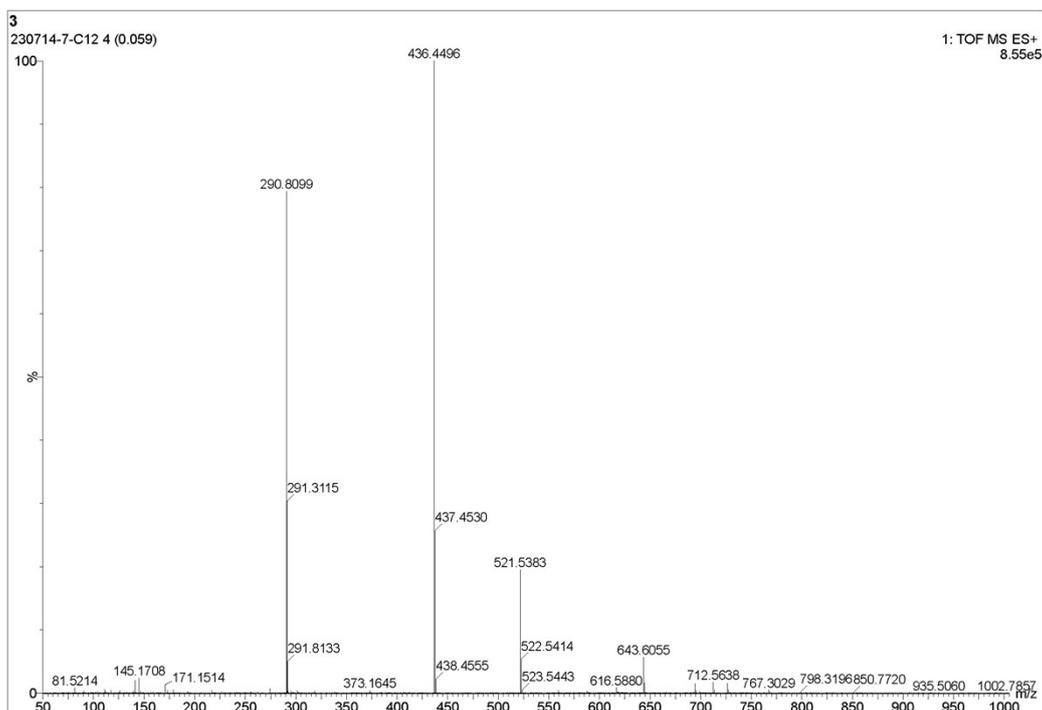


Fig. S6 HRMS of Di-C12-N2

HRMS m/z calcd for $C_{37}H_{79}N_3O^{2+}$ (M-2Br): 290.8106, found 290.8099; $C_{29}H_{58}NO^+$: 436.4513, found 436.4496.

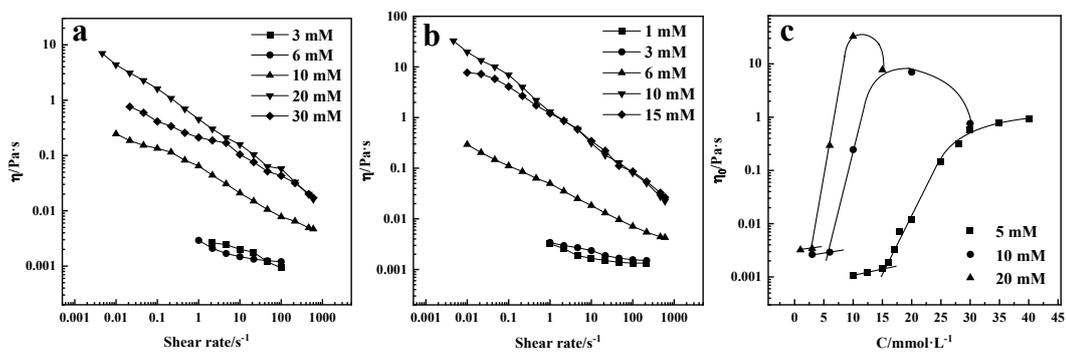


Fig. S7 Steady-shear rheological behavior of (a) 10 mM and (b) 20 mM Di-C12-N2 aqueous solutions in the presence of NaCl with different concentrations. (c) The variation of zero shear viscosity of Di-C12-N2 solutions with NaCl concentrations.