Supporting Information

Synthesis of three new anionic Gemini Surfactants and Comparative studies of assemble behavior in the presence of Bovine Serum Albumin

Procedure for the synthesis of surfactant Ⅲ

[1] Synthesis of N-phenyl lauramide

Lauroyl chloride was prepared in order to synthesize N-phenyl lauramide. Lauric acid (0.18mol) was added to thionyl chloride (100mL). The solution was stirred at 50℃ for about 40 minutes, and then 90℃ for another 3 hours. After excess thionyl chloride was removed by distillation, lauroyl chloride (0.17mol) was obtained by collecting the fraction between 135~138℃ (10mmHg).

Aniline (0.10mol) and triethylamine (24mL) were dissolved in dried dichloromethane (120mL), the stirred solution was cooled to 0℃ with an ice bath. Lauroyl chloride (0.16mol) was added in a dropwise manner to the stirred solution under nitrogen atmosphere. Then the reaction was continued for 48 hours at room temperature. The reaction mixture was transferred to a separating funnel and washed with water (200mL). The water layer was extracted twice with dichloromethane. The organic layer was combined, washed with brine and then dried with anhydrous sodium sulfate. The crude product was recrystallized from petroleum ether to give N-phenyl lauramide (0.08mol) as white solid.

[2] Synthesis of N-Dodecylaniline

To a stirred suspension of $LiAlH_4$ (0.16mol) in anhydrous THF (150mL), N-phenyl lauramide (0.08mol) dissolved in anhydrous THF (150mL) was added dropwise under nitrogen atmosphere. The reaction mixture was heated at reflux for 8 h and then cooled to 0℃,water was added to quench the reaction. The mixture was stirred for another 1 hour. The white precipitation was removed by filtration and the filtrate was dried with anhydrous sodium sulfate, filtered and concentrated. The crude product was purified by column chromatography with petroleum ether: ethyl acetate (10:1) as an eluent. N-dodecylaniline (0.07mol) was obtained as a pale yellow solid.

[3] Synthesis of 1,1'-(hexane-1,6-diyl)bis(3-dodecyl-3-phenylurea) (precursor) of the surfactant Ⅲ

1, 6-hexamethylene diisocyanate (0.04mol) was added to a stirred solution of N-dodecylaniline (0.07mol) in dichloromethane (100 mL). The reaction mixture was stirred over night at room temperature. After evaporation of the solvent, the crude product was subject to column chromatography with petroleum ether: ethyl acetate (4:1) as an eluent. The product was further purified by recrystallized from ether to give precursor (0.03mol) as white powder.

[4] Synthesis of the surfactant Ⅲ

Precursor (0.003mol) was cooled to 0℃ under nitrogen atmosphere, then chlorosulfonic acid (0.05mol) was added and the reaction mixture was continued at 0℃ for 3 hours. The mixture was poured to crushed ice (100mL), and the pH of the solution was adjusted to 7.0 by NaOH solution (1mol/L). After the solvent was removed by evaporation, the pale yellow residue was desalted in methanol. The crude product was purified by column chromatography with dichloromethane: methanol (4:1) as an eluent. Surfactant Ⅲ (0.0016mol) was obtained as a white solid.

Synthesis of the surfactant Ⅰ and surfactant Ⅱ

The synthesis method of the surfactant Ⅰ and surfactant Ⅱ was the same with that of surfactant Ⅲ. Only that firstly octanoic acid and capric acid were used to control the length of the hyphobic tail.

Characterization of three surfactants

Surfactant Ⅰ

^{1}H NMR (300 MHz, D_2O): δ= 0.65 (t, 3H, CH_3), 1.01 (m, 12H, CH_3-$(CH_2)_6$-CH_2-N), 1.18 (m, 8H, N-CH_2-$(CH_2)_4$-CH_2-N), 2.84 (s, 2H, N-CH_2-$(CH_2)_4$-CH_2-N), 3.36 (s, 2H, CH_3-$(CH_2)_6$-CH_2-N), 7.04-7.61 (m, 4H, N-C_6H_4-SO_3^-).

ESI–MS (HP1100LC–MSD): [M-Na^+] $(C_{40}H_{64}N_4O_8S_2Na)^-$: Calcd: 759, Found: 759.4, [M-2Na^++H] (C_{40} $H_{65}N_4O_8S_2$) : Calcd: 737, Found: 737.4, [M-2Na^+]/2 $(C_{40}H_{64}N_4O_8S_2)^{2-}$/2 : Calcd: 368, Found: 368.9.

IR (KBr) (cm^{-1}): 2927 (ν_{as} C-H), 2855 (ν_s C-H), 1644 (ν_s C=O), 1520 (ν_s C=C), 1192 (ν_s S-O).

Surfactant Ⅱ

^{1}H NMR (300 MHz, D_2O): δ= 0.62 (t, 3H, CH_3), 1.00 (m, 12H, CH_3-$(CH_2)_6$-CH_2-N), 1.14 (m, 8H, N-CH_2-$(CH_2)_4$-CH_2-N), 2.85 (s, 2H, N-CH_2-$(CH_2)_4$-CH_2-N), 3.31 (s, 2H, CH_3-$(CH_2)_6$-CH_2-N), 6.97-7.56 (m, 4H, N-C_6H_4-SO_3^-).

ESI–MS (HP1100LC–MSD): [M-Na^+] $(C_{42}H_{68}N_4O_8S_2Na)^-$: Calcd: 815, Found: 815.5, [M-2Na^++H] (C_{42} $H_{69}N_4O_8S_2$) : Calcd: 849, Found: 848.6, [M-2Na^+]/2 $(C_{42}H_{68}N_4O_8S_2)^{2-}$/2 : Calcd: 424, Found: 424.5.

IR (KBr) (cm^{-1}): 2925 (ν_{as} C-H), 2854 (ν_s C-H), 1665 (ν_s C=O), 1519 (ν_s C=C), 1192 (ν_s S-O).

Surfactant Ⅲ

^{1}H NMR (300 MHz, D_2O): δ= 0.65 (t, 3H, CH_3), 1.05 (m, 12H, CH_3-$(CH_2)_6$-CH_2-N), 1.15 (m, 8H, N-CH_2-$(CH_2)_4$-CH_2-N), 2.84 (s, 2H, N-CH_2-$(CH_2)_4$-CH_2-N), 3.32 (s, 2H, CH_3-$(CH_2)_6$-CH_2-N), 6.97-7.55 (m, 4H, N-C_6H_4-SO_3^-). ^{13}C NMR (75 MHz, D_2O): δ = 16.59 (CH_3), 25.36-28.42 (N-CH_2-$(CH_2)_4$-CH_2-N), 31.17-34.69 (CH_3-$(CH_2)_{10}$-CH_2-N), 42.85 (N-CH_2-$(CH_2)_4$-CH_2-N), 52.13 (CH_3-$(CH_2)_{10}$-CH_2-N), 129.78, 130.61, 143.98 and 147.36 (N-C_6H_4-SO_3^-), 160.71 (N-C=O).

ESI–MS (HP1100LC–MSD): [M-Na^+] $(C_{44}H_{72}N_4O_8S_2Na)^-$: Calcd: 871, Found: 871.6, [M-2Na^++H] (C_{44} $H_{73}N_4O_8S_2$) : Calcd: 849, Found: 848.6, [M-2Na^+]/2 $(C_{44}H_{72}N_4O_8S_2)^{2-}$/2 : Calcd: 424, Found: 424.5.

IR (KBr) (cm^{-1}): 2624 (ν_{as} C-H), 2853 (ν_s C-H), 1666 (ν_s C=O), 1518 (ν_s C=C), 1193 (ν_s S-O).

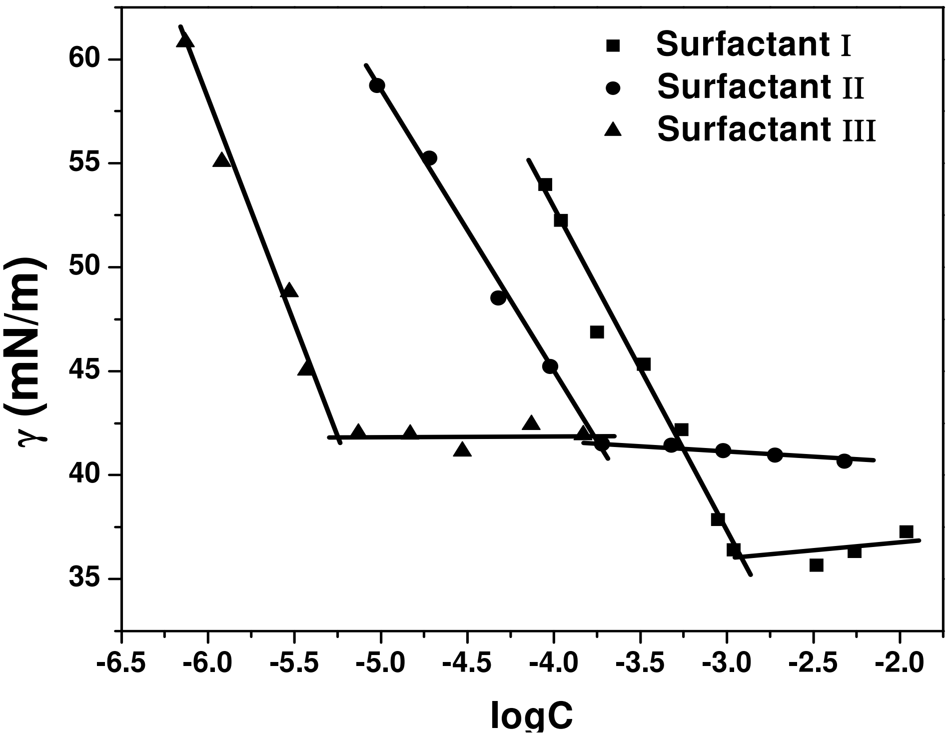

Fig. S1 γ-logC curves of the three anionic sulfonic gemini surfactants.

Tab. S1 CMC of the three anionic sulfonic gemini surfactants (T=298K).

Surfactant	I	II	III
CMC/mol L^{-1}	1.16×10^{-3}	1.89×10^{-4}	5.78×10^{-6}