Supplementary Information

Aggregation morphologies of a series of heterogemini surfactants with a hydroxyl headgroup in aqueous solution

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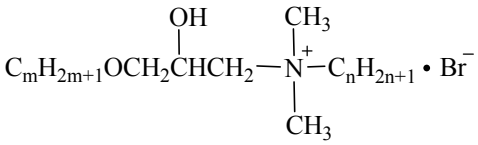
Synthesis of C_mOhpNC_n

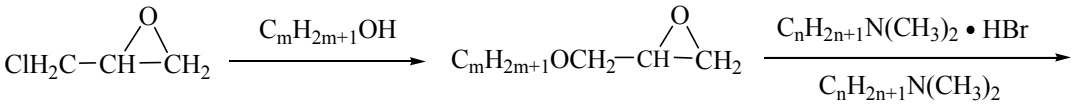
1. The molecular structure of $C_mOhpNC_n$is shown as follows,

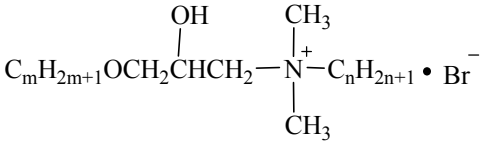


m, *n* = 10, 8; 10, 14; 12, 8; 12, 10; 12, 12; 12, 14; 14, 8 and 14, 10

Starting materials: Epichlorohydrin, *N*, *N*-dimethyldecylamine, *n*-decanol, *n*-dodecanol, *n*-tetradecanol, *n*-hexadecanol, hydrobromide were purchased from Sinopharm Chemical Reagent Co., Ltd (China)., *N*, *N*-dimethyloctylamine *N*, *N*-dimethyldodecylamine, *N*, *N*-dimethyltetra-decylamine were purchased from Tokyo Chemical Industry Co., Ltd (Japan) ,All the reagents used were of analytical grade.

2. Synthetic routes





3. A detailed description about the synthesis

This compound was synthesized with the method reported by Tianhua Zhou[1], which is briefly described as follows: *N*, *N*-dimethylalkyl amine (0.01mol, 1.0 equiv) and *N*, *N*-dimethylalkyl amine hydrobromide (0.01mol, 1.0 equiv) were added into a mixed ethanol-water solution (80:20, 60ml). The mixture was heated to 50°C under stirring,and then alkyl glycidyl ether (0.01mmol, 1.0 equiv) prepared from epichlorohydrin[1, 2] were added under vigorous agitation. After reacting for 4 hours, the mixture was cooled and the solvent was removed underreduced pressure. The product was recrystallized from ethyl acetate three times, followed by vacuum drying to give C_mOhpNC_n (*m*, *n* = 10, 8; 10, 14; 12, 8; 12, 10; 12, 12; 12, 14; 14, 8 and 14, 10) as white solids. The overall yield is from 29 to 79%.

4. ^{1}HNMR and elemental analysis of final products

C_{10}OhpNC_8 (400MHz, $CDCl_3$, TMS): d 0.87-0.88 (*t*, 6H, 2*C*H_3-CH_2-), 1.26-1.34 (*m*, 24H, CH_3-(*C*H_2)$_7$-CH_2-CH_2-O- and CH_3-(*C*H_2)$_5$-CH_2-CH_2-$N^+(CH_3)_2$-), 1.52-1.53 (*m*, 2H, CH_3-$(CH_2)_7$-*C*H_2-CH_2-O-CH_2-), 1.74 (*m*, 2H, -*C*H_2-CH_2-$N^+(CH_3)_2$-CH_2-), 3.39-3.49 (*m*, 10H, -CH_2-N^+(*C*H_3)$_2$-CH_2-, -*C*H_2-$N^+(CH_3)_2$-CH_2-CH(OH)- and -CH_2-*C*H_2-O-CH_2-CH(OH)-), 3.51-3.60 (*m*, 4H, -CH_2-O-*C*H_2-CH(OH)- and -$N^+(CH_3)_2$-*C*H_2-CH(OH)-), and 4.48 ppm (*m*, 1H, -O-CH_2-*C*H(OH)-CH_2-$N^+(CH_3)_2$-); Anal Calcd for $C_{23}H_{50}BrNO_2$: C, 61.04; H, 11.14; N, 3.10. Found: C, 60.66; H, 11.49; N, 2.72.

C_{10}OhpNC_{14}(400MHz, $CDCl_3$, TMS):d 0.81-0.83 (*t*, 6H, 2*C*H_3-CH_2-), 1.18 (*m*, 36H, CH_3-(*C*H_2)$_7$-CH_2-CH_2-O- and CH_3-(*C*H_2)$_{11}$-CH_2-CH_2-$N^+(CH_3)_2$-), 1.44-1.47 (*m*, 2H, CH_3-$(CH_2)_7$-*C*H_2-CH_2-O-CH_2-), 1.67 (*m*, 2H, -*C*H_2-CH_2-$N^+(CH_3)_2$-CH_2-), 3.31-3.36 (*m*, 10H, -CH_2-N^+(*C*H_3)$_2$-CH_2-, -*C*H_2-$N^+(CH_3)_2$-CH_2-CH(OH)- and -CH_2-*C*H_2-O-CH_2-CH(OH)-), 3.48-3.52 (*m*, 4H, -CH_2-O-*C*H_2-CH(OH)- and -$N^+(CH_3)_2$-*C*H_2-CH(OH)-), and 4.50 ppm (*m*, 1H, -O-CH_2-*C*H(OH)-CH_2-$N^+(CH_3)_2$-); Calcd for $C_{29}H_{62}BrNO_2$: C, 64.90; H, 11.64; N, 2.61. Found: C, 63.93; H, 12.08; N, 2.09.

C_{12}OhpNC_8 (400MHz, $CDCl_3$, TMS):d 0.88 (*t*, 6H, 2*C*H_3-CH_2-), 1.26 (*m*, 28H, CH_3-(*C*H_2)$_9$-CH_2-CH_2-O- and CH_3-(*C*H_2)$_5$-CH_2-CH_2-$N^+(CH_3)_2$-), 1.52 (*m*, 2H, CH_3-$(CH_2)_7$-*C*H_2-CH_2-O-CH_2-), 1.74 (*m*, 2H, -*C*H_2-CH_2-$N^+(CH_3)_2$-CH_2-), 3.39-3.42 (*m*, 10H, -CH_2-N^+(*C*H_3)$_2$-CH_2-, -*C*H_2-$N^+(CH_3)_2$-CH_2-CH(OH)- and-CH_2-*C*H_2-O-CH_2-CH(OH)-), 3.57 (*m*, 4H, -CH_2-O-*C*H_2-CH(OH)- and -$N^+(CH_3)_2$-*C*H_2-CH(OH)-), and 4.49 ppm (*m*, 1H, -O-CH_2-*C*H(OH)-CH_2-$N^+(CH_3)_2$-); Calcd for $C_{25}H_{54}BrNO_2$: C, 62.48; H, 11.33; N, 2.91. Found: C, 62.17; H, 11.52; N, 2.54.

C_{12}OhpNC_{10} (400MHz, $CDCl_3$, TMS): d 0.88 (*t*, 6H, 2*C*H_3-CH_2-), 1.26 (*m*, 32H, CH_3-(*C*H_2)$_9$-CH_2-CH_2-O- and CH_3-(*C*H_2)$_7$-CH_2-CH_2-$N^+(CH_3)_2$-), 1.52 (*m*, 2H, CH_3-$(CH_2)_7$-*C*H_2-CH_2-O-CH_2-), 1.74 (*m*, 2H, -*C*H_2-CH_2-$N^+(CH_3)_2$-CH_2-), 3.39-3.43 (*m*, 10H, -CH_2-N^+(*C*H_3)$_2$-CH_2-, -*C*H_2-$N^+(CH_3)_2$-CH_2-CH(OH)- and-CH_2-*C*H_2-O-CH_2-CH(OH)-), 3.56 (*m*, 4H, -CH_2-O-*C*H_2-CH(OH)- and -$N^+(CH_3)_2$-*C*H_2-CH(OH)-), and 4.49 ppm (*m*, 1H, -O-CH_2-*C*H(OH)-CH_2-$N^+(CH_3)_2$-); Calcd for $C_{27}H_{58}BrNO_2$: C, 63.75; H, 11.49; N, 2.75. Found: C, 63.01; H, 11.38; N, 2.47.

C_{12}OhpNC_{12}(400MHz, $CDCl_3$, TMS): d 0.81 (*t*, 6H, 2*C*H_3-CH_2-), 1.24 (*m*, 36H, CH_3-(*C*H_2)$_9$-CH_2-CH_2-O- and CH_3-(*C*H_2)$_9$-CH_2-CH_2-$N^+(CH_3)_2$-), 1.45 (*m*, 2H, CH_3-$(CH_2)_7$-*C*H_2-CH_2-O-CH_2-), 1.67 (*m*, 2H, -*C*H_2-CH_2-$N^+(CH_3)_2$-CH_2-), 3.32-3.37 (*m*, 10H, -CH_2-N^+(*C*H_3)$_2$-CH_2-, -*C*H_2-$N^+(CH_3)_2$-CH_2-CH(OH)- and -CH_2-*C*H_2-O-CH_2-CH(OH)-), 3.51(*m*, 4H, -CH_2-O-*C*H_2-CH(OH)- and -$N^+(CH_3)_2$-*C*H_2-CH(OH)-), and 4.41 ppm (*m*, 1H, -O-CH_2-*C*H(OH)-CH_2-$N^+(CH_3)_2$-); Calcd for $C_{29}H_{62}BrNO_2$: C, 64.90; H, 11.64; N, 2.61. Found: C, 63.86; H, 12.12; N, 2.29.

C_{12}OhpNC$_{14}$ (400MHz, $CDCl_3$, TMS): d 0.82 (*t*, 6H, 2*CH*$_3$-CH$_2$-), 1.24 (*m*, 40H, CH$_3$-(*CH*$_2$)$_9$-CH$_2$-CH$_2$-O- and CH$_3$-(*CH*$_2$)$_{11}$-CH$_2$-CH$_2$-N$^+$(CH$_3$)$_2$-), 1.46 (*m*, 2H, CH$_3$-(CH$_2$)$_7$-*CH*$_2$-CH$_2$-O-CH$_2$-), 1.67 (*m*, 2H, -*CH*$_2$-CH$_2$-N$^+$(CH$_3$)$_2$-CH$_2$-), 3.32-3.37 (*m*, 10H, -CH$_2$-N$^+$(*CH*$_3$)$_2$-CH$_2$-, -*CH*$_2$-N$^+$(CH$_3$)$_2$-CH$_2$-CH(OH)- and -CH$_2$-*CH*$_2$-O-CH$_2$-CH(OH)-), 3.51(*m*, 4H, -CH$_2$-O-*CH*$_2$-CH(OH)- and -N$^+$(CH$_3$)$_2$-*CH*$_2$-CH(OH)-), and 4.42 ppm (*m*, 1H, -O-CH$_2$-*CH*(OH)-CH$_2$-N$^+$(CH$_3$)$_2$-); Calcd for $C_{31}H_{66}BrNO_2$: C, 65.93; H, 11.78; N, 2.48. Found: C, 63.30; H, 12.11; N, 2.32.

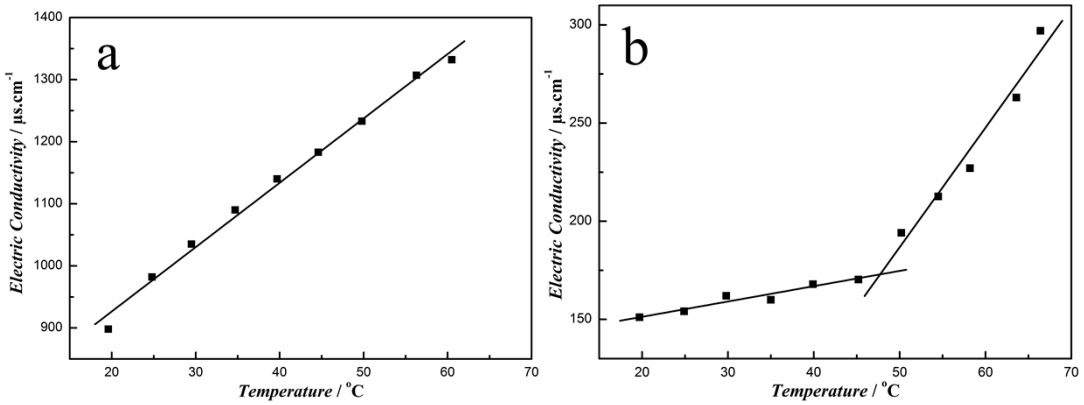
C_{14}OhpNC$_8$ (400MHz, $CDCl_3$, TMS):d 0.82 (*t*, 6H, 2*CH*$_3$-CH$_2$-), 1.19-1.28 (*m*, 32H, CH$_3$-(*CH*$_2$)$_{11}$-CH$_2$-CH$_2$-O- and CH$_3$-(*CH*$_2$)$_5$-CH$_2$-CH$_2$-N$^+$(CH$_3$)$_2$-), 1.44-1.47 (*m*, 2H, CH$_3$-(CH$_2$)$_7$-*CH*$_2$-CH$_2$-O-CH$_2$-), 1.68 (*m*, 2H, -*CH*$_2$-CH$_2$-N$^+$(CH$_3$)$_2$-CH$_2$-), 3.31-3.37 (*m*, 10H, -CH$_2$-N$^+$(*CH*$_3$)$_2$-CH$_2$-, -*CH*$_2$-N$^+$(CH$_3$)$_2$-CH$_2$-CH(OH)- and -CH$_2$-*CH*$_2$-O-CH$_2$-CH(OH)-), 3.50-3.54 (*m*, 4H, -CH$_2$-O-*CH*$_2$-CH(OH)- and -N$^+$(CH$_3$)$_2$-*CH*$_2$-CH(OH)-), and 4.43 ppm (*m*, 1H, -O-CH$_2$-*CH*(OH)-CH$_2$-N$^+$(CH$_3$)$_2$-); Calcd for $C_{27}H_{58}BrNO_2$: C, 63.75; H, 11.49; N, 2.75. Found: C, 63.07; H, 12.15; N, 2.59.

C_{14}OhpNC$_{10}$ (400MHz, $CDCl_3$, TMS): d 0.81 (*t*, 6H, 2*CH*$_3$-CH$_2$-), 1.19-1.28 (*m*, 36H, CH$_3$-(*CH*$_2$)$_{11}$-CH$_2$-CH$_2$-O- and CH$_3$-(*CH*$_2$)$_7$-CH$_2$-CH$_2$-N$^+$(CH$_3$)$_2$-), 1.44-1.47 (*m*, 2H, CH$_3$-(CH$_2$)$_7$-*CH*$_2$-CH$_2$-O-CH$_2$-), 1.67 (*m*, 2H, -*CH*$_2$-CH$_2$-N$^+$(CH$_3$)$_2$-CH$_2$-), 3.32-3.37 (*m*, 10H, -CH$_2$-N$^+$(*CH*$_3$)$_2$-CH$_2$-, -*CH*$_2$-N$^+$(CH$_3$)$_2$-CH$_2$-CH(OH)- and -CH$_2$-*CH*$_2$-O-CH$_2$-CH(OH)-), 3.50-3.53 (*m*, 4H, -CH$_2$-O-*CH*$_2$-CH(OH)- and -N$^+$(CH$_3$)$_2$-*CH*$_2$-CH(OH)-), and 4.42 ppm (*s*, 1H, -O-CH$_2$-*CH*(OH)-CH$_2$-N$^+$(CH$_3$)$_2$-); Calcd for $C_{29}H_{62}BrNO_2$: C, 64.90; H, 11.64; N, 2.61. Found: C, 63.56; H, 12.03; N, 2.28.

Measurements of C_mOhpNC$_n$

1 Krafft temperature

The electric conductivities of C_mOhpNC$_n$ were measured by Model Delta 326 conductometer with the temperature ranging from 15 to 70 ^{o}C. The Krafft temperatures were determined by the break of conductivity vs. temperature plots.[2]



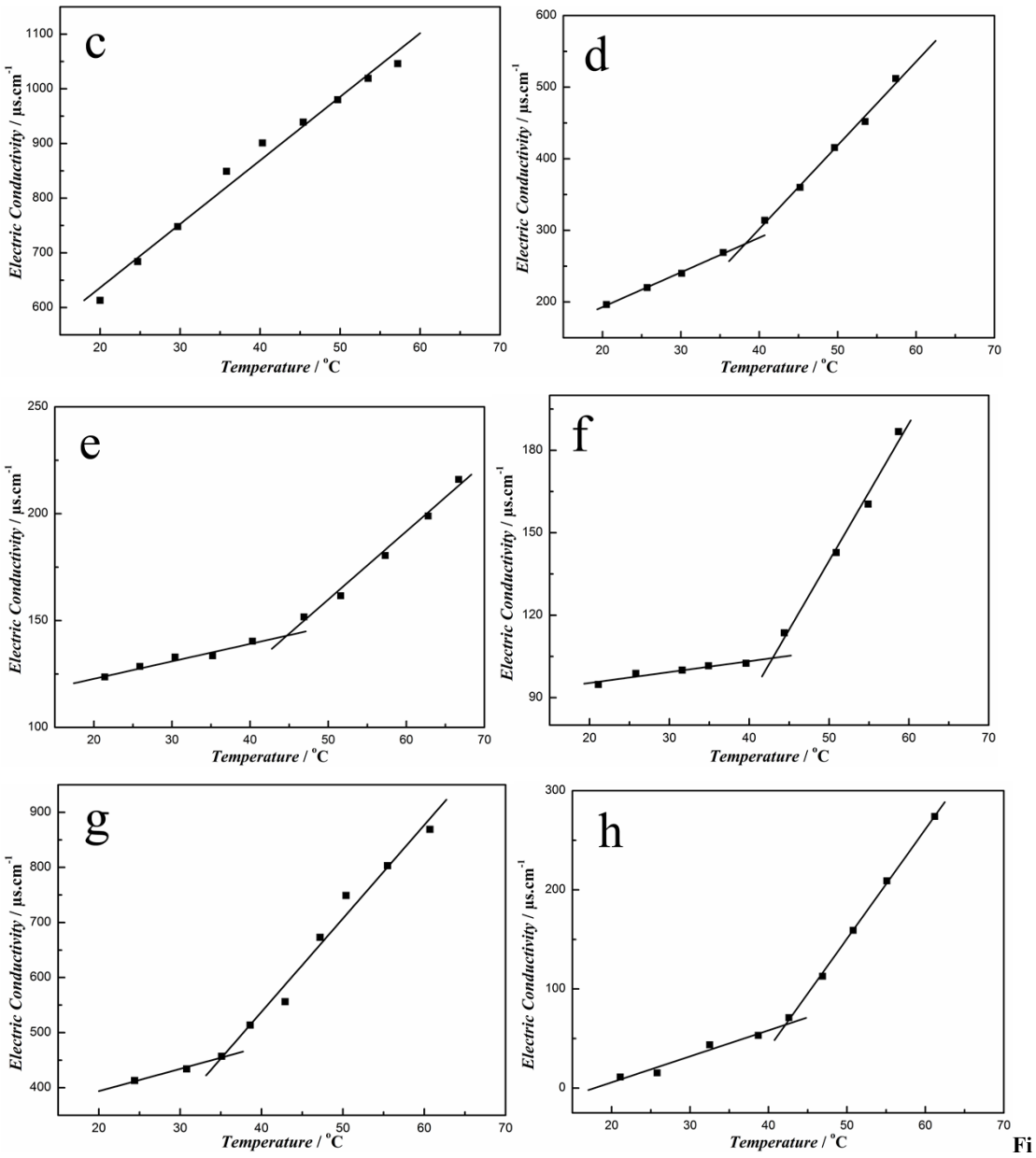


Fig. S1 The electric conductivities of different gemini surfactants as a function of temperature: (a) $C_{10}OhpNC_8$, (b) $C_{10}OhpNC_{14}$, (c) $C_{12}OhpNC_8$, (d) $C_{12}OhpNC_{10}$, (e) $C_{12}OhpNC_{12}$, (f) $C_{12}OhpNC_{14}$, (g) $C_{14}OhpNC_8$, (h) $C_{14}OhpNC_{10}$.

2 CMC

The electric conductivities of C_mOhpNC_n were measured by Model Delta 326 conductometer at 50°C. The CMC values were determined by the break of conductivity vs. concentration plots.

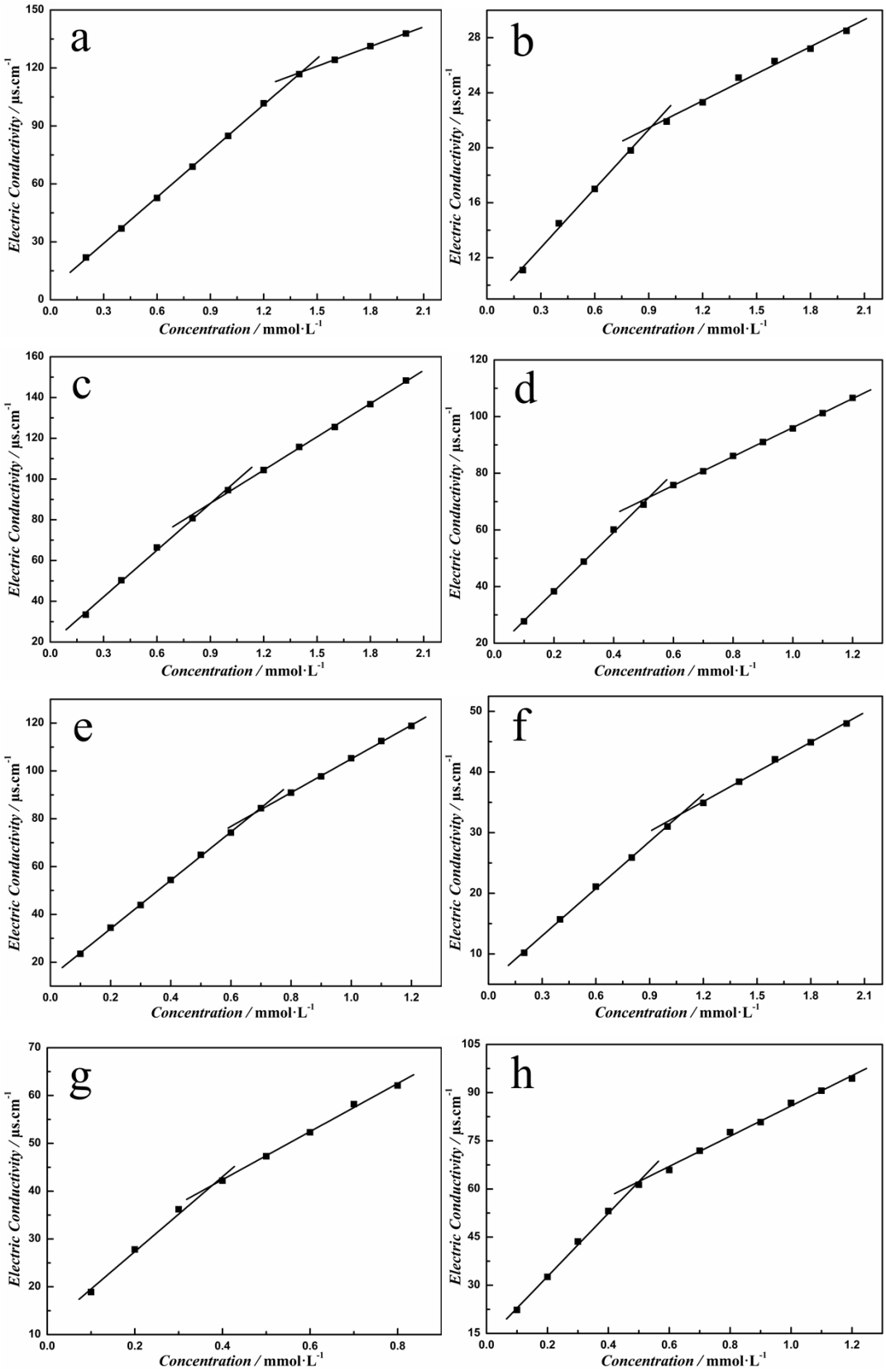


Fig. S2 The electric conductivities of different gemini surfactants as a function of concentration: (a) $C_{10}OhpNC_8$, (b) $C_{10}OhpNC_{14}$, (c) $C_{12}OhpNC_8$, (d) $C_{12}OhpNC_{10}$, (e) $C_{12}OhpNC_{12}$, (f) $C_{12}OhpNC_{14}$, (g) $C_{14}OhpNC_8$, (h) $C_{14}OhpNC_{10}$.

References

1T. H. Zhou, J. X. Zhao, *J. Colloid Interface Sci.*, 2009, **331**, 476-483.

2 R. Zana, H. Lévy, D. Danino, Y. Talmon and K. Kwetkat,*Langmuir*, 1997, **13**, 402-408.