Supplementary Information

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

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Synthesis of CmOhpNCn

1. The molecular structure of CmOhpNCn is shown as follows,

![Molecular Structure]

\[ \text{C}_m\text{H}_{2m+1}\text{OCH}_2\text{CHCH}_2\text{N}^+\text{C}_n\text{H}_{2n+1} \cdot \text{Br}^- \]

\[ m, n = 10, 8; 10, 14; 12, 8; 12, 10; 12, 12; 12, 14; 14, 8 \text{ and } 14, 10 \]

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-dimethyldecylamine, N, N-dimethyldodecylamine, N, N-dimethyltetradecylamine were purchased from Tokyo Chemical Industry Co., Ltd (Japan). All the reagents used were of analytical grade.

2. Synthetic routes

![Synthetic Route]

3. A detailed description about the synthesis
This compound was synthesized with the method reported by Tianhua Zhou, 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 under reduced pressure. The product was recrystallized from ethyl acetate three times, followed by vacuum drying to give C\(\text{m}_{\text{m}}\)OhpNC\(\text{n}\) (m, n = 10, 8; 10, 14; 12, 8; 12, 10; 12, 12; 14, 14 and 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\textit{10}OhpNC\(\text{8} \ (400\text{MHz, CDCl}_{3},\text{ TMS})\): d 0.87-0.88 (t, 6H, 2CH\(3\)-CH\(2\)), 1.26-1.34 (m, 24H, CH\(2\)-(CH\(2\))\(\text{m}\)-CH\(2\)-CH\(2\)-O- and CH\(3\)-(CH\(2\))\(\text{n}\)-CH\(2\)-CH\(2\)-N'(CH\(3\))-), 1.52-1.53 (m, 2H, CH\(2\)-(CH\(2\))\(\text{m}\)-CH\(2\)-CH\(2\)-O-CH\(2\)), 1.74 (m, 2H, -CH\(2\)-CH\(2\)-N'(CH\(3\))-CH\(2\)), 3.39-3.49 (m, 10H, -CH\(2\)-N'(CH\(3\))-CH\(2\), -CH\(2\)-N'(CH\(3\))-CH\(2\)-CH(OH)- and -CH\(2\)-CH\(2\)-O-CH\(2\)-CH(OH)-), 3.51-3.60 (m, 4H, -CH\(2\)-O-CH\(2\)-CH(OH)- and -N'(CH\(3\))-CH\(2\)-CH(OH)-), and 4.48 ppm (m, 1H, -O-CH\(2\)-CH(OH)-CH\(2\)-N'(CH\(3\))-); Anal Calcd for C\(\text{m}_{\text{m}}\)H\(\text{m}\)BrNO\(\text{m}\): C, 64.90; H, 11.64; N, 2.61. Found: C, 60.66; H, 11.49; N, 2.72.

C\textit{16}OhpNC\(\text{14} \ (400\text{MHz, CDCl}_{3},\text{ TMS})\): d 0.81-0.83 (t, 6H, 2CH\(3\)-CH\(2\)), 1.18 (m, 36H, CH\(2\)-(CH\(2\))\(\text{m}\)-CH\(2\)-CH\(2\)-O- and CH\(3\)-(CH\(2\))\(\text{n}\)-CH\(2\)-CH\(2\)-N'(CH\(3\))-), 1.44-1.47 (m, 2H, CH\(2\)-(CH\(2\))\(\text{m}\)-CH\(2\)-CH\(2\)-O-CH\(2\)), 1.67 (m, 2H, -CH\(2\)-CH\(2\)-N'(CH\(3\))-CH\(2\)), 3.31-3.36 (m, 10H, -CH\(2\)-N'(CH\(3\))-CH\(2\), -CH\(2\)-N'(CH\(3\))-CH\(2\)-CH(OH)- and -CH\(2\)-CH\(2\)-O-CH\(2\)-CH(OH)-), 3.48-3.52 (m, 4H, -CH\(2\)-O-CH\(2\)-CH(OH)- and -N'(CH\(3\))-CH\(2\)-CH(OH)-), and 4.50 ppm (m, 1H, -O-CH\(2\)-CH(OH)-CH\(2\)-N'(CH\(3\))-); Caled for C\(\text{m}_{\text{m}}\)H\(\text{m}\)BrNO\(\text{m}\): C, 64.90; H, 11.64; N, 2.61. Found: C, 63.93; H, 12.08; N, 2.09.

C\textit{12}OhpNC\(\text{8} \ (400\text{MHz, CDCl}_{3},\text{ TMS})\): d 0.88 (t, 6H, 2CH\(3\)-CH\(2\)-), 1.26 (m, 28H, CH\(3\)-(CH\(2\))\(\text{m}\)-CH\(2\)-CH\(2\)-O- and CH\(3\)-(CH\(2\))-CH\(2\)-CH\(2\)-N'(CH\(3\))-), 1.52 (m, 2H, CH\(2\)-(CH\(2\))-CH\(2\)-CH\(2\)-O-CH\(2\)), 1.74 (m, 2H, -CH\(2\)-CH\(2\)-N'(CH\(3\))-CH\(2\)), 3.39-3.42 (m, 10H, -CH\(2\)-N'(CH\(3\))-CH\(2\), -CH\(2\)-N'(CH\(3\))-CH\(2\)-CH(OH)- and -CH\(2\)-CH\(2\)-O-CH\(2\)-CH(OH)-), 3.57 (m, 4H, -CH\(2\)-O-CH\(2\)-CH(OH-) and -N'(CH\(3\))-CH\(2\)-CH(OH)-), and 4.49 ppm (m, 1H, -O-CH\(2\)-CH(OH)-CH\(2\)-N'(CH\(3\))-); Caled for C\(\text{m}_{\text{m}}\)H\(\text{m}\)BrNO\(\text{m}\): C, 62.48; H, 11.33; N, 2.91. Found: C, 62.17; H, 11.52; N, 2.54.

C\textit{12}OhpNC\(\text{10} \ (400\text{MHz, CDCl}_{3},\text{ TMS})\): d 0.88 (t, 6H, 2CH\(3\)-CH\(2\)-), 1.26 (m, 32H, CH\(3\)-(CH\(2\))-CH\(2\)-CH\(2\)-O- and CH\(3\)-(CH\(2\))-CH\(2\)-CH\(2\)-N'(CH\(3\))-), 1.52 (m, 2H, CH\(2\)-(CH\(2\))-CH\(2\)-CH\(2\)-O-CH\(2\)), 1.74 (m, 2H, -CH\(2\)-CH\(2\)-N'(CH\(3\))-CH\(2\)-), 3.39-3.43 (m, 10H, -CH\(2\)-N'(CH\(3\))-CH\(2\), -CH\(2\)-N'(CH\(3\))-CH\(2\)-CH(OH)- and -CH\(2\)-CH\(2\)-O-CH\(2\)-CH(OH)-), 3.56 (m, 4H, -CH\(2\)-O-CH\(2\)-CH(OH-) and -N'(CH\(3\))-CH\(2\)-CH(OH)-), and 4.49 ppm (m, 1H, -O-CH\(2\)-CH(OH)-CH\(2\)-N'(CH\(3\))-); Caled for C\(\text{m}_{\text{m}}\)H\(\text{m}\)BrNO\(\text{m}\): C, 63.75; H, 11.49; N, 2.75. Found: C, 63.01; H, 11.38; N, 2.47.

C\textit{12}OhpNC\(\text{12} \ (400\text{MHz, CDCl}_{3},\text{ TMS})\): d 0.81 (t, 6H, 2CH\(3\)-CH\(2\)-), 1.24 (m, 36H, CH\(3\)-(CH\(2\))-CH\(2\)-CH\(2\)-O- and CH\(3\)-(CH\(2\))-CH\(2\)-CH\(2\)-N'(CH\(3\))-), 1.45 (m, 2H, CH\(3\)-(CH\(2\))-CH\(2\)-CH\(2\)-O-CH\(2\)), 1.67 (m, 2H, -CH\(2\)-CH\(2\)-N'(CH\(3\))-CH\(2\)), 3.32-3.37 (m, 10H, -CH\(2\)-N'(CH\(3\))-CH\(2\), -CH\(2\)-N'(CH\(3\))-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\(3\))-CH\(2\)-CH(OH)-), and 4.41 ppm (m, 1H, -O-CH\(2\)-CH(OH)-CH\(2\)-N'(CH\(3\))-); Caled for C\(\text{m}_{\text{m}}\)H\(\text{m}\)BrNO\(\text{m}\): C, 64.90; H, 11.64; N, 2.61. Found: C, 63.86; H, 12.12; N, 2.29.
C_{12}OhpNC_{14} (400MHz, CDCl₃, TMS): d 0.82 (t, 6H, 2CH₃-CH₂-), 1.24 (m, 40H, CH₃-(CH₂)₉-CH₂-CH₂-O- and CH₃-(CH₂)₁₁-CH₂-CH₂-N⁺(CH₃)₂-), 1.46 (m, 2H, CH₃-(CH₂)₁₁-CH₂-CH₂-O-CH₂-), 1.67 (m, 2H, -CH₂-CH₂-N⁺(CH₃)₂-CH₂-), 3.32-3.37 (m, 10H, -CH₂-N⁺(CH₃)₂-CH₂-,-CH₂-N⁺(CH₃)₂-CH₂-CH₂(CH(OH))- and -CH₂-CH₂-O-CH₂-CH₂(CH(OH))-), 3.51 (m, 4H, -CH₂-O-CH₂-CH₂(CH(OH))- and -N⁺(CH₃)₂-CH₂-CH₂(CH(OH))-), and 4.42 ppm (m, 1H, -O-CH₂-CH₂(CH(OH))-CH₂-N⁺(CH₃)₂-); Caled for C₃₁H₆₆BrNO₂: C, 65.93; H, 11.78; N, 2.48. Found: C, 63.30; H, 12.11; N, 2.32.

C_{14}OhpNC_{8} (400MHz, CDCl₃, TMS): d 0.82 (t, 6H, 2CH₃-CH₂-), 1.19-1.28 (m, 32H, CH₃-(CH₂)₁₁-CH₂-CH₂-O- and CH₃-(CH₂)₁₁-CH₂-CH₂-N⁺(CH₃)₂-), 1.44-1.47 (m, 2H, CH₃-(CH₂)₁₁-CH₂-CH₂-O-CH₂-), 1.68 (m, 2H, -CH₂-CH₂-N⁺(CH₃)₂-CH₂-), 3.31-3.37 (m, 10H, -CH₂-N⁺(CH₃)₂-CH₂-,-CH₂-N⁺(CH₃)₂-CH₂-CH₂(CH(OH))- and -CH₂-CH₂-O-CH₂-CH₂(CH(OH))-), 3.50-3.54 (m, 4H, -CH₂-O-CH₂-CH₂(CH(OH))- and -N⁺(CH₃)₂-CH₂-CH₂(CH(OH))-), and 4.43 ppm (m, 1H, -O-CH₂-CH₂(CH(OH))-CH₂-N⁺(CH₃)₂-); Caled for C₃₂H₇₈BrNO₂: C, 63.75; H, 11.49; N, 2.75. Found: C, 63.07; H, 12.15; N, 2.59.

C_{14}OhpNC_{10} (400MHz, CDCl₃, TMS): d 0.81 (t, 6H, 2CH₃-CH₂-), 1.19-1.28 (m, 36H, CH₃-(CH₂)₁₁-CH₂-CH₂-O- and CH₃-(CH₂)₁₁-CH₂-CH₂-N⁺(CH₃)₂-), 1.44-1.47 (m, 2H, CH₃-(CH₂)₁₁-CH₂-CH₂-O-CH₂-), 1.67 (m, 2H, -CH₂-CH₂-N⁺(CH₃)₂-CH₂-), 3.32-3.37 (m, 10H, -CH₂-N⁺(CH₃)₂-CH₂-,-CH₂-N⁺(CH₃)₂-CH₂-CH₂(CH(OH))- and -CH₂-CH₂-O-CH₂-CH₂(CH(OH))-), 3.50-3.53 (m, 4H, -CH₂-O-CH₂-CH₂(CH(OH))- and -N⁺(CH₃)₂-CH₂-CH₂(CH(OH))-), and 4.42 ppm (s, 1H, -O-CH₂-CH₂(CH(OH))-CH₂-N⁺(CH₃)₂-); Caled for C₃₄H₈₂BrNO₂: C, 64.90; H, 11.64; N, 2.61. Found: C, 63.56; H, 12.03; N, 2.28.

Measurements of CₘOhpNCₙ

1 Krafft temperature

The electric conductivities of CₘOhpNCₙ were measured by Model Delta 326 conductometer with the temperature ranging from 15 to 70 °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_{m}OhpNC_{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$_{16}$, (e) C$_{12}$OhpNC$_{12}$, (f) C$_{12}$OhpNC$_{14}$, (g) C$_{14}$OhpNC$_8$, (h) C$_{14}$OhpNC$_{10}$. 
References
