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含有酰胺基或酯基的可降解阳离子 Gemini 表面活性剂在水溶液中的聚集行为

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Aggregation of Biodegradable Cationic Gemini Surfactants with Amide or Ester Groups

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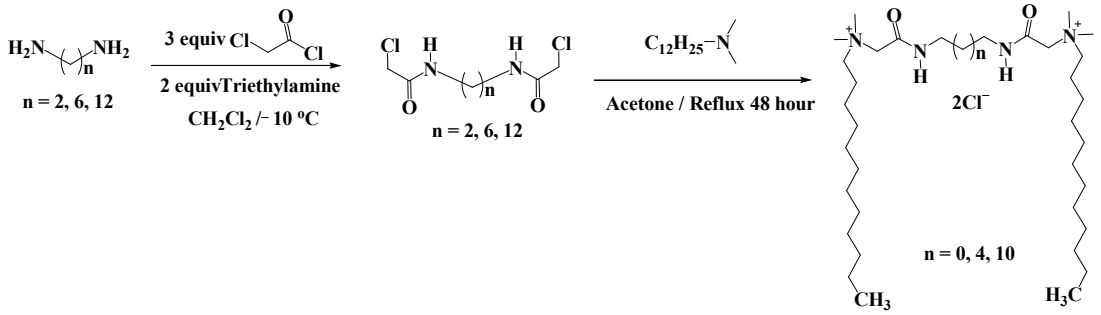
实验试剂和原料

n-十二胺(98%)，*N*,*N*-二甲基十二胺(分析纯)和1,12-二溴代十二烷(98%)购自Acros Organics。*N*,*N*,*N*',*N*'-四甲基-1,6-己二胺(化学纯)，*N*,*N*,*N*',*N*-四甲基-1,2-乙二胺购(96%)自Fluka公司。1,2-乙二胺(化学纯)，1,6-己二胺(化学纯)，1,12-十二二胺(分析纯)，三乙胺(分析纯)由Aldrich Chemical Co提供。二甲胺(化学纯)，三甲胺(化学纯)，1,6-己二醇(分析纯)，*n*-十二醇(分析纯)，*n*-溴代十二烷(96%)和氯乙酰氯(化学纯)购自北京化学试剂公司。重水(D_2O，99.9%氘含量)由CIL Cambridge Isotope Laboratories提供。上述各种试剂均未做任何处理直接使用。实验过程中使用的各种溶剂均为分析纯，必要时经蒸馏或除水处理后使用。样品性质测试过程中溶液配制均使用三次蒸馏水。

表面活性剂合成及谱图表征

C_{12}-AC$_n$A-C_{12}的合成方法(方案1)：

在温度为263 K下，向搅拌着的烷基二胺(30 mmol)和三乙胺(60 mmol)的二氯甲烷溶液中缓慢滴加氯乙酰氯(90 mmol)。滴加完成后除去冰浴，常温搅拌室温继续搅拌5 h。停止反应后向体系中加入25 mL 浓度为0.5 mol·L^{-1} Na_2CO_3水溶液，搅拌10 min后静置分层分出有机相，并用CH_2Cl_2 (3 × 25 mL)萃取水相。合并有机相并旋蒸除去溶剂可得做为联接基团的淡黄色固体。向溶解于30 mL丙酮中的*N*,*N*-二甲基十二胺中缓慢加入溶解于丙酮中的上述联接基团化合物，滴加过程中需快速搅拌。待联接基团全部加入后，继续回流搅拌48 h，反应过程中不断有白色固体析出，待反应结束后减压过滤除去溶剂，并用丙酮洗涤样品若干次。之后，在乙醇-丙酮混合溶剂(1 : 1)中将样品重结晶三次，可得到白色粉末或晶状C_{12}-AC$_n$A-C_{12}。



方案1　C_{12}-AC$_n$A-C_{12}的合成路线图

Scheme 1　Reaction routes for the synthesis of gemini surfactants with amide groups in spacer group, C_{12}-AC$_n$A-C_{12}.

C_{12}-AC_2A-C_{12}的联接基团:

ESI-MS (APEXII FT-ICR)：[M + H^+] ($C_6H_{10}Cl_2N_2O_2H^+$): Calcd: 213.0，Found: 213.1；[M + Na^+] ($C_6H_{10}Cl_2N_2O_2Na^+$)：Calcd: 235.0，Found: 235.0。

C_{12}-AC_2A-C_{12} ($C_{34}C_{72}Cl_2N_4O_2$): white crystals, yield: 88%

IR (KBr) (cm^{-1}): 3177 (***H*-*N***-C(＝O)), 2921 (-***C*H_2**-), 2853 (***C*H_3**-CH_2-), 1679 (H-N-***C*(＝*O*)**), 1564 (***H*-*N***-C(＝O)). ^{1}H NMR (400 MHz, D_2O, δ in ppm): δ = 0.78 (t, 3H, ***C*H_3**), 1.19–1.26 (m, 18H, CH_3-**(*C*H_2)$_9$**-CH_2-CH_2), 1.69 (m, 2H, CH_3-$(CH_2)_9$-***C*H_2**-CH_2-N^+), 3.18 (s, 6H, CH_3-$(CH_2)_9$-CH_2-CH_2-N^+**(*C*H_3)$_2$**), 3.27 (t, 2H, CH_3-$(CH_2)_9$-CH_2-***C*H_2**-N^+), 3.51 (t, 2H, N^+-CH_2-C(＝O)(H)N-***(C*H_2)$_2$**-N(H)C(＝O)-CH_2-N^+), 4.04 (s, 2H, N^+-***C*H_2**-C(=O)(H)N-$(CH_2)_2$-N(H)C(＝O)-***C*H_2**-N^+). ^{13}C NMR (100 MHz, D_2O, δ in ppm): δ = 13.9 (***C*H_3**), 22.5 − 31.9 (CH_3-***(C*H_2)$_{10}$**-CH_2), 38.9 (N^+-CH_2-C(＝O)(H)N-***(C*H_2)$_2$**-N(H)C(＝O)-CH_2-N^+) 52.8 (N^+***(C*H_3)$_2$**), 62.0 (CH_3-$(CH_2)_9$-CH_2-***C*H_2**-N^+), 63.8 (N^+-***C*H_2**-C(＝O)(H)N-$(CH_2)_2$-N(H)C(＝O)-***C*H_2**-N^+), 163.4 (N^+-CH_2-***C*(＝*O*)**(H)N-$(CH_2)_2$-N(H)***C*(＝*O*)**-CH_2-N^+). ESI-MS (APEXII FT-ICR): [M-2Cl^-]$^{2+}$/2 ($C_{34}H_{72}N_4O_2^{2+}$)/2: Calcd: 284.3, Found: 284.6. Elemental analysis (%) Calcd: C, 63.82; H, 11.34; N, 8.76. Found: C, 63.76; H, 11.39; N, 8.84.

C_{12}-AC_6A-C_{12}的联接基团：

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 1.37 − 1.39 (m, 2H, N-CH_2-CH_2-***(C*H_2)$_2$**-CH_2-CH_2-N), 1.59 (m, 2H, N-CH_2-***C*H_2**-$(CH_2)_2$-***C*H_2**-CH_2-N), 3.30 (q, 2H, N-***C*H_2**-$(CH_2)_4$-***C*H_2**-N), 4.05 (s, 2H, Cl-***C*H_2**-C(＝O)(H)N-

$(CH_2)_6$-N(H)C(= O)-***CH_2***-Cl), 6.60 (brs, 1H, Cl-CH_2-C(= O)***(H)***N-$(CH_2)_6$-N***(H)***C(= O)-CH_2-Cl). ESI-MS (APEXII FT-ICR): $[M + H^+]$ ($C_{10}H_{18}Cl_2N_2O_2H^+$): Calcd: 268.1, Found: 268.2; $[M + Na^+]$ ($C_{16}H_{30}Cl_2N_2O_2Na^+$): Calcd: 291.1, Found: 291.1.

C_{12}-AC_6A-C_{12}, ($C_{38}H_{80}Cl_2N_4O_2$): white crystals yield: 87%

IR (KBr) (cm^{-1}): 3194 (***H-N***-C(=O)), 2922 (-***CH_2***-), 2853 (***CH_3***-CH_2-), 1681 (H-N-***C(=O)***), 1551 (***H-N***-C(=O)). ^{1}H NMR (400 MHz, D_2O, δ in ppm): δ = 0.80 (t, 3H, ***CH_3***), 1.22 − 1.27 (m, 20H, CH_3-***$(CH_2)_9$***-CH_2-CH_2; N^+-CH_2-C(=O) N(H)-$(CH_2)_2$-***$(CH_2)_2$***-$(CH_2)_2$-N(H)C(=O)-CH_2-N^+), 1.48 (m, 2H, N(H)-CH_2-***CH_2***-$(CH_2)_2$-***CH_2***-CH_2-N(H)), 1.72 (m, 2H, CH_3-$(CH_2)_9$-***CH_2***-CH_2-N^+), 3.16 (m, 2H, N^+-CH_2-C(= O)N(H)-***CH_2*** $(CH_2)_4$-***CH_2***-N(H)C(=O)-CH_2-N^+), 3.23 (s, 6H, CH_3-$(CH_2)_9$-CH_2-CH_2-N^+***$(CH_3)_2$***), 3.48 (t, 2H, CH_3-$(CH_2)_9$-CH_2-***CH_2***-N^+), 4.04 (s, 2H, N^+-***CH_2***-C(=O)(H)N-$(CH_2)_6$-N(H)C(=O)-***CH_2***-N^+). ^{13}C NMR (100 MHz, D_2O, δ in ppm): δ = 13.9 (***CH_3***), 22.4 − 32.0 (CH_3-***$(CH_2)_{10}$***-CH_2; N(H)-CH_2-***$(CH_2)_4$***-CH_2-N(H)), 39.0 (N(H)-***CH_2***-$(CH_2)_4$-***CH_2***-N(H)) 53.2 (N^+***$(CH_3)_2$***), 61.8 (CH_3-$(CH_2)_9$-CH_2-***CH_2***-N^+), 63.3 (N^+-***CH_2***-C(=O)(H)N-$(CH_2)_6$-N(H)C(=O)-***CH_2***-N^+), 163.4 (N^+-CH_2-***C(=O)***(H)N-$(CH_2)_6$-N(H)***C(=O)***-CH_2-N^+). ESI-MS (APEXII FT-ICR): $[M\text{-}Cl^-]^+$ ($C_{38}H_{80}ClN_4O_2^+$): Calcd: 659.6, Found: 659.7; $[M\text{-}2Cl^-]^{2+}/2$ ($C_{38}H_{80}N_4O_2^{2+}$)/2: Calcd: 312.3, Found: 312.6. Elemental analysis (%) Calcd: C, 65.58; H, 11.59; N, 8.05. Found: C, 65.39; H, 11.42; N, 7.95.

C_{12}-AC_{12}A-C_{12}的联接基团

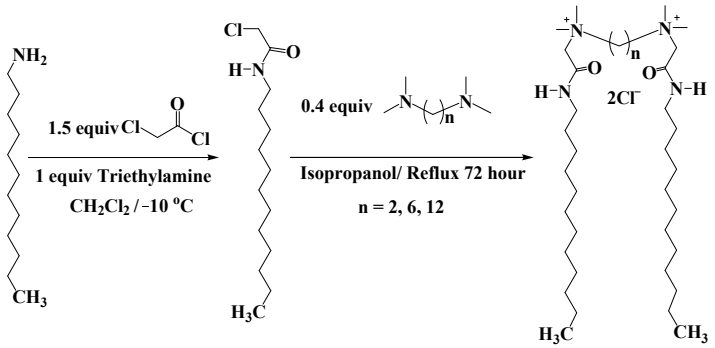
^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 1.26 − 1.32 (m, 16H, N-CH_2-CH_2-***$(CH_2)_8$***-CH_2-CH_2-N), 1.55 (m, 4H, N-CH_2-***CH_2***-$(CH_2)_8$-***CH_2***-CH_2-N), 3.30 (q, 4H, N-***CH_2***-CH_2-$(CH_2)_8$-CH_2-***CH_2***-N(H)), 4.05 (s, 4H, Cl-***CH_2***-C(=O)(H)N-$(CH_2)_{12}$-N(H)C(=O)-***CH_2***-Cl), 6.57 (brs, 2H, Cl-CH_2-C(=O)***(H)***N-$(CH_2)_{12}$-N***(H)***C(=O)-CH_2-Cl). ESI-MS (APEXII FT-ICR): $[M + H^+]$ ($C_{16}H_{30}Cl_2N_2O_2H^+$): Calcd: 353.2, Found: 353.3; $[M + Na^+]$ ($C_{16}H_{30}Cl_2N_2O_2Na^+$): Calcd: 375.2, Found: 375.2.

C_{12}-AC_{12}A-C_{12}, ($C_{44}H_{92}Cl_2N_4O_2$): white power, and yield: 70%

IR (KBr) (cm^{-1}): 3193 (***H-N***-C(=O)), 2922 (-***CH_2***-), 2853 (***CH_3***-CH_2-), 1681 (H-N-***C(=O)***), 1551 (***H-N***-C(=O)). ^{1}H NMR (400 MHz, D_2O, δ in ppm): δ = 0.78 (t, 3H, ***CH_3***), 1.22 − 1.27 (m, 26H, CH_3-***$(CH_2)_9$***-CH_2-CH_2; N^+-CH_2-C(=O) N(H)-$(CH_2)_2$-***$(CH_2)_8$***-$(CH_2)_2$-N(H)C(=O)-CH_2-N^+), 1.48 (m, 2H, N(H) -CH_2-***CH_2***-$(CH_2)_8$-***CH_2***-CH_2-N(H)), 1.68 (m, 2H, CH_3-$(CH_2)_9$-***CH_2***-CH_2-N^+), 3.14 (t, 2H, N^+-CH_2-C(=O)N(H)-***CH_2*** $(CH_2)_{10}$-***CH_2***-N(H)C(=O)-CH_2-N^+), 3.23 (s, 6H, CH_3-$(CH_2)_9$-CH_2-CH_2-N^+***$(CH_3)_2$***), 3.41 (t, 2H, CH_3-$(CH_2)_9$-CH_2-***CH_2***-N^+), 4.01 (s, 2H, N^+-***CH_2***-C(=O)(H)N-$(CH_2)_{12}$-N(H)C(=O)-***CH_2***-N^+). ^{13}C NMR (100 MHz, D_2O, δ in ppm): δ = 13.9 (***CH_3***), 22.4-39.8 (CH_3-***$(CH_2)_{10}$***-CH_2; N(H)-CH_2-***$(CH_2)_{10}$***-CH_2-N(H)), 39.1 (N(H)-***CH_2***-$(CH_2)_{10}$-***CH_2***-N(H)) 53.5 (N^+***$(CH_3)_2$***), 61.9 (CH_3-$(CH_2)_9$-CH_2-***CH_2***-N^+), 63.2 (N^+-***CH_2***-C(= O)(H)N-$(CH_2)_{12}$-N(H)C(= O)-***CH_2***-N^+), 163.5 (N^+-CH_2-***C(=O)***(H)N-$(CH_2)_{12}$-N(H)***C(=O)***-CH_2-N^+). ESI-MS (APEXII FT-ICR): $[M\text{-}2Cl^-]^{2+}/2$ ($C_{44}H_{92}N_4O_2^{2+}$)/2: Calcd: 354.4, Found: 354.7. Elemental analysis (%) Calcd: C, 67.74; H, 11.89; N, 7.18. Found: C, 67.70; H, 11.77; N, 7.11.

C_{12}A-C*n*-AC_{12}的合成方法(方案2)：

在温度为263 K条件下，向溶解于二氯甲烷溶液中*n*-十二胺(30 mmol)和三乙胺(30 mmol)中缓慢滴加氯乙酰氯(45 mmol)。当滴加完成后除去冰浴，室温下继续搅拌5 h。停止反应，向体系中加入25 mL浓度为0.5 $mol\cdot L^{-1}$ Na_2CO_3水溶液，搅拌10 min后静置分层取出有机相，并用CH_2Cl_2 (3 × 25 mL)萃取水相。合并有机相并旋蒸除去溶剂，可得作为疏水链的淡黄色固体。向溶解于30 mL异丙醇中的*N*,*N*,*N*',*N*'-四甲基-烷基二胺中缓慢加入上述疏水链化合物，滴加过程中需快速搅拌。待疏水链化合物全部加入后，继续回流搅拌72 h。反应结束后，减压过滤除去溶剂，并用丙酮洗涤样品三次。在乙醇-丙酮混合溶剂(1：1)中将样品重结晶三次，可得晶状C_{12}A-C*n*-AC_{12}。



方案2　$C_{12}A\text{-}C_n\text{-}AC_{12}$的合成路线图

Scheme 2　Reaction routes for the synthesis of gemini surfactants with amide groups in hydrophobic chains, $C_{12}A\text{-}C_n\text{-}AC_{12}$.

$C_{12}A\text{-}C_2\text{-}AC_{12}$的疏水链

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 0.82 (t, 3H, ***CH₃***), 1.25-1.32 (m, 18H, CH_3-***(CH₂)₉***-CH_2-CH_2), 1.55 (m, 2H, CH_3-$(CH_2)_9$-***CH₂***-CH_2), 3.30 (q, 2H, CH_3-$(CH_2)_{10}$-***CH₂***-N(H)C(=O)-CH_2-Cl), 4.05 (s, 2H, CH_3-$(CH_2)_{11}$-N(H)C(＝O)-***CH₂***-Cl), 6.57 (brs, 1H, CH_3-$(CH_2)_{11}$-N***(H)***C(＝O)-CH_2-Cl). ESI-MS (APEXII FT-ICR): [M+H$^+$] ($C_{14}H_{28}ClNOH^+$): Calcd: 262.2, Found: 262.3.

$C_{12}A\text{-}C_2\text{-}AC_{12}$, ($C_{34}C_{72}Cl_2N_4O_2$), shiny white crystals, yield: 90%

IR (KBr) (cm^{-1}): 3177 (***H-N***-C(=O)), 2922 (-***CH₂***-), 2852 (***CH₃***-CH_2-), 1676 (H-N-***C(＝O)***), 1554 (***H-N***-C(＝O)). ^{1}H NMR (400 MHz, D_2O, δ in ppm): δ = 0.77 (t, 3H, ***CH₃***), 1.20 (m, 18H, CH_3-***(CH₂)₉***-CH_2-CH_2), 1.46 (m, 2H, CH_3-$(CH_2)_9$-***CH₂***-CH_2), 3.10 (t, 2H, CH_3-$(CH_2)_{10}$-***CH₂***-N(H)C(＝O)-CH_2-N$^+$), 3.32 (s, 6H, CH_3-$(CH_2)_{10}$-CH_2-N(H)C(＝O)-CH_2-N$^+$***(CH₃)₂***), 4.20 (s, 2H, CH_3-$(CH_2)_{11}$-N(H)C(＝O)-CH_2-N$^+$$(CH_3)_2$-***CH₂***) 4.28 (s, 2H, CH_3-$(CH_2)_{11}$-N(H)C(＝O)-***CH₂***-N$^+$). ^{13}C NMR (100 MHz, D_2O, δ in ppm): δ = 13.7 (***CH₃***), 21.7-31.8 (CH_3-***(CH₂)₁₀***-CH_2;), 39.7 (CH_3-$(CH_2)_{10}$-***CH₂***), 52.2 (N$^+$***(CH₃)₂***), 60.2 (N$^+$-***CH₂***-***CH₂***-N$^+$)　67.0 (CH_3-$(CH_2)_{11}$-N(H)C(＝O)-***CH₂***-N$^+$), 163.5 (CH_3-$(CH_2)_{11}$-N(H)***C(＝O)***-CH_2-N$^+$). ESI-MS (APEXII FT-ICR): [M-2Cl$^-$]$^{2+}$/2 ($C_{34}H_{72}N_4O_2^{2+}$)/2: Calcd: 284.3, Found: 284.6. Elemental analysis (%) Calcd: C, 63.82; H, 11.34; N, 8.76. Found: C, 64.10; H, 11.44; N, 9.04.

$C_{12}A\text{-}C_6\text{-}AC_{12}$, ($C_{38}H_{80}Cl_2N_4O_2$), shiny white crystals, yield: 90%

IR (KBr) (cm^{-1}): 3202 (***H-N***-C(＝O)), 2922 (-***CH₂***-), 2852 (***CH₃***-CH_2-), 1680 (H-N-***C(＝O)***), 1550 (***H-N***-C(＝O)). ^{1}H NMR (400 MHz, D_2O, δ in ppm): δ = 0.78 (t, 3H, ***CH₃***), 1.20 (m, 18H, CH_3-***(CH₂)₉***-CH_2-CH_2), 1.34 (m, 2H, N$^+$-$(CH_2)_2$-***(CH₂)₂***-$(CH_2)_2$-N$^+$), 1.55 (m, 2H, CH_3-$(CH_2)_9$-***CH₂***-CH_2), 1.77 (m, 2H, N$^+$-CH_2-***CH₂***-$(CH_2)_2$-***CH₂***-CH_2-N$^+$), 3.10 (t, 2H, CH_3-$(CH_2)_{10}$-***CH₂***-N(H)C(＝O)-CH_2-N$^+$), 3.21 (s, 6H, CH_3-$(CH_2)_{10}$-CH_2-N(H)C(＝O)-CH_2-N$^+$***(CH₃)₂***), 3.50 (t, 2H, CH_3-$(CH_2)_{11}$-N(H)C(＝O)-CH_2-N$^+$$(CH_3)_2$-***CH₂***) 4.16 (s, 2H, CH_3-$(CH_2)_{11}$-N(H)C(＝O)-***CH₂***-N$^+$). ^{13}C NMR (100 MHz, D_2O, δ in ppm): δ = 13.8 (***CH₃***), 21.9 − 31.9 (CH_3-***(CH₂)₁₀***-CH_2; N$^+$-CH_2-***(CH₂)₄***-CH_2-N$^+$), 39.6 (CH_3-$(CH_2)_{10}$-***CH₂***), 52.8 (N$^+$***(CH₃)₂***), 62.2 (N$^+$-***CH₂***-$(CH_2)_4$-***CH₂***-N$^+$)　64.1 (CH_3-$(CH_2)_{11}$-N(H)C(＝O)-***CH₂***-N$^+$), 163.4 (CH_3-$(CH_2)_{11}$-N(H)***C(＝O)***-CH_2-N$^+$). ESI-MS (APEXII FT-ICR): [M-Cl$^-$]$^+$ ($C_{38}H_{80}ClN_4O_2^+$): Calcd: 659.6, Found: 659.8; [M-2Cl$^-$]$^{2+}$/2 ($C_{38}H_{80}N_4O_2^{2+}$)/2: Calcd: 312.3, Found: 312.8. Elemental analysis (%) Calcd: C, 65.58; H, 11.59; N, 8.05. Found: C, 65.40; H, 11.78; N, 8.08.

$C_{12}A\text{-}C_{12}\text{-}AC_{12}$的联接基团

ESI-MS (APEXII FT-ICR): [M+H$^+$] ($C_{16}H_{36}N_2H^+$): Calcd: 257.3, Found: 257.4; [M + 2H$^+$]/2 ($C_{16}H_{36}N_22H^+$)/2: Calcd: 129.2, Found: 129.3.

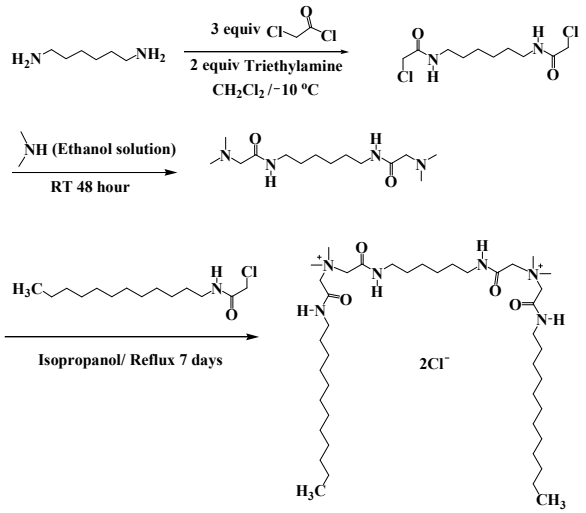
$C_{12}A\text{-}C_{12}\text{-}AC_{12}$, ($C_{44}H_{92}Cl_2N_4O_2$), white power, yield: 68%

IR (KBr) (cm^{-1}): 3185 (***H-N***-C(＝O)), 2916 (-***CH₂***-), 2852 (***CH₃***-CH_2-), 1675 (H-N-***C(＝O)***), 1570 (***H-N***-C(＝O)). ^{1}H NMR (400 MHz, D_2O, δ in ppm): δ = 0.77 (t, 3H, ***CH₃***), 1.18 − 1.23 (m, 26H, CH_3-***(CH₂)₉***-CH_2-CH_2; N$^+$-$(CH_2)_2$-***(CH₂)₈***-$(CH_2)_2$-N$^+$), 1.43 (m, 2H, CH_3-$(CH_2)_9$-***CH₂***-CH_2), 1.73 (m, 2H, N$^+$-CH_2-***CH₂***-$(CH_2)_8$-***CH₂***-CH_2-N$^+$), 3.10 (t, 2H, CH_3-$(CH_2)_{10}$-***CH₂***-N(H)C(＝O)-CH_2-N$^+$), 3.22 (s, 6H, CH_3-$(CH_2)_{10}$-CH_2-N(H)C(＝O)-CH_2-N$^+$***(CH₃)₂***),

3.45 (t, 2H, CH_3-$(CH_2)_{11}$-N(H)C(=O)-CH_2-$N^+(CH_3)_2$-***CH_2***) 4.04 (s, 2H, CH_3-$(CH_2)_{11}$-N(H)C(=O)-***CH_2***-N^+). ^{13}C NMR (100 MHz, D_2O, δ in ppm): δ = 13.8 (***CH_3***), 21.9-31.9 (CH_3-***$(CH_2)_{10}$***-CH_2; N^+-CH_2-(***$CH_2)_{10}$***-CH_2-N^+), 39.2 (CH_3-$(CH_2)_{10}$-***CH_2***), 53.5 (N^+***$(CH_3)_2$***), 61.9 (N^+-***CH_2***-$(CH_2)_{10}$-***CH_2***-N^+) 63.4 (CH_3-$(CH_2)_{11}$-N(H)C(=O)-***CH_2***-N^+), 163.7 (CH_3-$(CH_2)_{11}$-N(H)***C(=O)***-CH_2-N^+). ESI-MS (APEXII FT-ICR): $[M\text{-}2Cl^-]^{2+}/2$ ($C_{44}H_{92}N_4O_2^{2+}$)/2: Calcd: 354.4, Found: 354.7. Elemental analysis (%) Calcd: C, 67.74; H, 11.89; N, 7.18. Found: C, 67.51; H, 11.97; N, 7.20.

$C_{12}A\text{-}AC_6A\text{-}AC_{12}$的合成方法(方案3)：

制备联接基团化合物和烷基链化合物的方法分别参看前面方案1和方案2。向溶解于30 mL异丙醇中的烷基链化合物中缓慢加入联接基团化合物，滴加过程中需快速搅拌。待联接基团化合物全部加入后，继续回流搅拌7天。反应结束后减压过滤除去溶剂，并用丙酮洗涤样品若干次。在乙醇-丙酮混合溶剂(1 : 1)中将样品重结晶三次，可得到晶状Gemini表面活性剂$C_{12}A\text{-}AC_nA\text{-}AC_{12}$。



方案3　$C_{12}A\text{-}AC_6A\text{-}AC_{12}$的合成路线图

Scheme 3　Reaction routes for the synthesis of gemini surfactant with amide groups in both spacer group and hydrophobic chains, $C_{12}A\text{-}AC_6A\text{-}AC_{12}$.

$C_{12}A\text{-}AC_6A\text{-}AC_{12}$的联接基团：

ESI-MS (APEXII FT-ICR): $[M + H^+]$ ($C_{14}H_{30}N_4O_2H^+$): Calcd: 287.2, Found: 287.2; $[M + 2H^+]/2$ ($C_{14}H_{30}N_4O_22H^+$)/2: Calcd: 144.1, Found: 144.3.

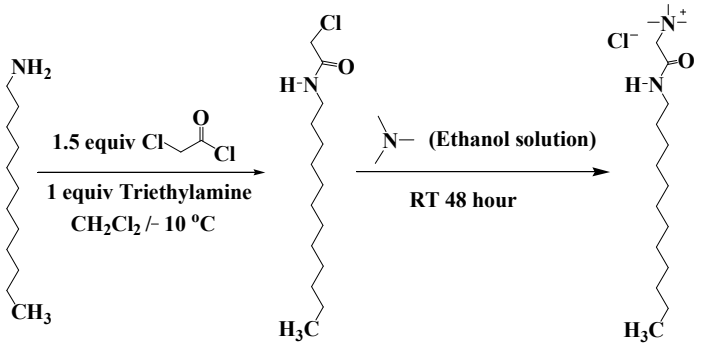
$C_{12}A\text{-}AC_6A\text{-}AC_{12}$, ($C_{42}H_{86}Cl_2N_6O_2$), shiny white crystals, yield: 65%

IR (KBr) (cm^{-1}): 3203 (***H-N***-C(=O)), 2924 (-***CH_2***-), 2854 (***CH_3***-CH_2-), 1678 (H-N-***C(=O)***), 1557 (***H-N***-C(=O)). ^{1}H NMR (400 MHz, D_2O, δ in ppm): δ = 0.74 (t, 3H, ***CH_3***), 1.15 − 1.23 (m, 20H, CH_3-***$(CH_2)_9$***-CH_2-CH_2; N(H)-$(CH_2)_2$-(***$CH_2)_2$***-$(CH_2)_2$-N(H)), 1.40 (m, 4H, CH_3-$(CH_2)_9$-***CH_2***-CH_2; N(H)-CH_2-***CH_2***-$(CH_2)_2$-***CH_2***-CH_2-N(H)), 3.10 (t, 4H, CH_3-$(CH_2)_{10}$-***CH_2***-N(H); N(H)-***CH_2***-$(CH_2)_4$-***CH_2***-N(H)), 3.34 (s, 6H, CH_3-$(CH_2)_{10}$-CH_2-N(H)C(=O)-CH_2-N^+***$(CH_3)_2$***), 4.33 and 4.37 (t, 2H, CH_3-$(CH_2)_{11}$-N(H)C(=O)-***CH_2***-$N^+(CH_3)_2$-***CH_2***-N(H)C(=O)). ^{13}C NMR (100 MHz, D_2O, δ in ppm): δ = 13.8 (***CH_3***), 22.6-31.9 (CH_3-***$(CH_2)_{10}$***-CH_2; N(H)-CH_2-(***$CH_2)_4$***-CH_2-N(H)), 39.2 (CH_3-$(CH_2)_{10}$-***CH_2***; N(H)-***CH_2***-$(CH_2)_4$-***CH_2***-N(H)), 54.6 (N^+***$(CH_3)_2$***), 63.4 (CH_3-$(CH_2)_{11}$-N(H)C(=O)-***CH_2***-$N^+(CH_3)_2$-***CH_2***-N(H)C(=O)), 163.8 and 163.9 (CH_3-$(CH_2)_{11}$-N(H)***C(=O)***-CH_2-$N^+(CH_3)_2$-CH_2-N(H)***C(=O)***). ESI-MS (APEXII FT-ICR): $[M\text{-}2Cl^-]^{2+}/2$ ($C_{42}H_{86}N_6O_2^{2+}$)/2: Calcd: 369.4, Found: 369.6. Elemental analysis (%) Calcd: C, 62.27; H, 10.70; N, 10.37. Found: C, 61.99; H, 10.71; N, 10.46.

单链表面活性剂$C_{12}A$的合成方法(方案4)：

制备疏水烷基链化合物的方法参看前面方案2。将溶解于30 mL丙酮中的5 mmol烷基链化合物缓慢加入

到含有12 mmol三甲胺乙醇溶液中。待联接基团全部加入后，继续室温搅拌48 h。反应结束后减压过滤除去溶剂，并用乙酸乙酯洗涤样品一次。在乙醇-丙酮混合溶剂(1：1)中将样品重结晶三次可得到晶状单链表面活性剂$C_{12}A$。



方案4　$C_{12}A$的合成路线图

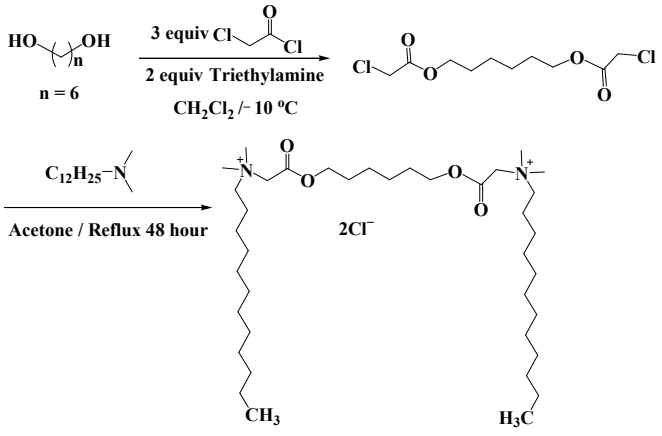
Scheme 4　Reaction routes for the synthesis of corresponding monomeric surfactant with amide group, $C_{12}A$.

$C_{12}A$, ($C_{17}C_{37}ClN_2O$), shiny white crystals, yield: 90%

IR (KBr) (cm^{-1}): 3161 (***H-N***-C(＝O)), 2922 (-***CH_2***-), 2852 (***CH_3***-CH_2-), 1679 (H-N-***C(＝O)***), 1546 (***H-N***-C(＝O)). ^{1}H NMR (400 MHz, D_2O, δ in ppm): δ = 0.89 (t, 3H, ***CH_3***), 1.31 (m, 18H, CH_3-***$(CH_2)_9$***-CH_2-CH_2), 1.56 (m, 2H, CH_3-$(CH_2)_9$-***CH_2***-CH_2), 3.23 (t, 2H, CH_3-$(CH_2)_{10}$-***CH_2***-N(H)C(＝O)-CH_2-$N^+(CH_3)_3$), 3.36 (s, 9H, CH_3-$(CH_2)_{10}$-CH_2-N(H)C(＝O)-CH_2-N^+***$(CH_3)_3$***), 4.17 (s, 2H, CH_3-$(CH_2)_{11}$-N(H)C(＝O)-***CH_2***-$N^+(CH_3)_3$). ^{13}C NMR (100 MHz, D_2O, δ in ppm): δ = 13.8 (***CH_3***), 22.7-31.9 (CH_3-***$(CH_2)_{10}$***-CH_2), 39.6 (CH_3-$(CH_2)_{10}$-***CH_2***-N(H)C(＝O)), 54.2 (N^+***$(CH_3)_3$***), 65.2 (CH_3-$(CH_2)_{11}$-N(H)C(＝O)-***CH_2***-$N^+(CH_3)_3$), 163.5 (CH_3-$(CH_2)_{11}$-N(H)***C(＝O)***-CH_2-$N^+(CH_3)_3$). ESI-MS (APEXII FT-ICR): $[M\text{-}Cl^-]^+$ ($C_{17}H_{37}N_2O^+$): Calcd: 285.5, Found: 285.4. Elemental analysis (%) Calcd: C, 63.62; H, 11.62; N, 8.73. Found: C, 63.46; H, 11.64; N, 8.57.

C_{12}-EC_6E-C_{12}的合成方法(方案5)：

除用1,6-己二醇代替1,6-己二胺外，Gemini表面活性剂C_{12}-EC_6E-C_{12}的合成方法与C_{12}-AC_6A-C_{12}的相同。



方案5　C_{12}-EC_6E-C_{12}的合成路线图

Scheme 5　Reaction routes for the synthesis of Gemini surfactant with ester groups in spacer group, C_{12}-EC_6E-C_{12}.

C_{12}-EC_6E-C_{12}的联接基团

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 1.37 − 1.44 (m, 4H, O-CH_2-CH_2-***$(CH_2)_2$***-CH_2-CH_2-O), 1.69 (m, 4H, O-CH_2-***CH_2***-$(CH_2)_2$-***CH_2***-CH_2-O), 4.06 (s, 4H, Cl-***CH_2***-C(＝O)O-$(CH_2)_6$-OC(＝O)-***CH_2***-Cl), 4.20 (t, 4H, O-

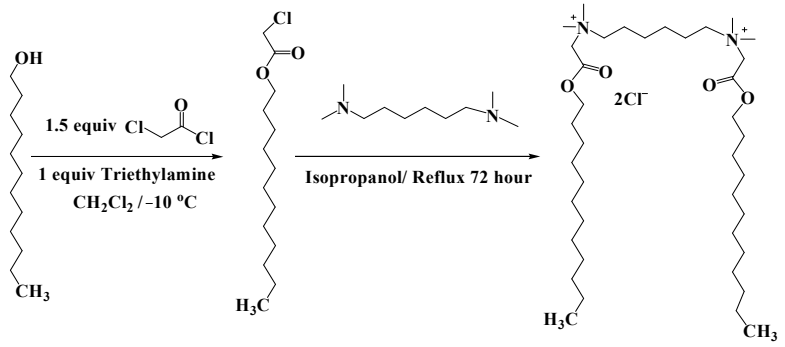
CH₂--CH_2 $(CH_2)_4$-***CH₂***-O). ESI-MS (APEXII FT-ICR): $[M + Na^+]$ ($C_{10}H_{16}Cl_2O_4Na^+$): Calcd: 293.0, Found: 293.0.

C_{12}-EC_6E-C_{12}, ($C_{38}H_{78}Cl_2N_2O_4$), floppy white solid, yield: 72%

IR (KBr) (cm^{-1}): 2923 (-***CH₂***-), 2853 (***CH₃***-CH_2-), 1744 (O-***C(=O)***). ^{1}H NMR (400 MHz, D_2O, δ in ppm): δ = 0.79 (t, 3H, ***CH₃***), 1.19 – 1.25 (m, 18H, CH_3-***(CH₂)₉***-CH_2-CH_2), 1.33 (m, 2H, N^+-CH_2-C(=O) O-$(CH_2)_2$-***(CH₂)₂***-$(CH_2)_2$-OC(=O)-CH_2-N^+), 1.64 (m, 4H, CH_3-$(CH_2)_9$-***CH₂***-CH_2; N^+-CH_2-C(=O)O-CH_2-***CH₂***-$(CH_2)_2$-***CH₂***-CH_2-OC(=O)-CH_2-N^+), 3.22 (s, 6H, CH_3-$(CH_2)_{10}$-CH_2-N^+***(CH₃)₂***), 3.52 (t, 2H, CH_3-$(CH_2)_9$-CH_2-***CH₂***), 4.17 (t, 2H, N^+-CH_2-C(=O)O-***CH₂***-$(CH_2)_4$-***CH₂***-OC(=O)-CH_2-N^+), 4.29 (s, 2H, N^+-***CH₂***-C(=O)O-$(CH_2)_6$-OC(=O)-***CH₂***-N^+). ^{13}C NMR (100 MHz, D_2O, δ in ppm): δ = 13.9 (***CH₃***), 22.3–32.0 (CH_3-***(CH₂)₁₀***-CH_2; O-CH_2-***(CH₂)₄***-CH_2-O), 52.6 (N^+***(CH₃)₂***), 60.2 (N^+-***CH₂***-C(=O)O-$(CH_2)_6$-OC(=O)-***CH₂***-N^+), 63.2 (CH_3-$(CH_2)_{11}$-***CH₂***-N^+), 66.3 (N^+-CH_2-C(=O)O-***CH₂***-$(CH_2)_4$-***CH₂***-OC(= O)-CH_2-N^+), 165.2 (N^+-CH_2-***C(= O)***O-$(CH_2)_6$-O***C(= O)***-CH_2-N^+). ESI-MS (APEXII FT-ICR): $[M\text{-}Cl^-]^+$ ($C_{38}H_{78}ClN_2O_4$)$^+$: Calcd: 661.6, Found: 661.6; $[M\text{-}2Cl^-]^{2+}$/2 ($C_{38}H_{78}N_2O_4$)$^{2+}$/2: Calcd: 313.3, Found: 312.7. Elemental analysis (%) Calcd: C, 65.39; H, 11.26; N, 4.01. Found: C, 65.13; H, 11.27; N, 4.16.

C_{12}E-C_6-EC_{12}的合成方法(方案6)：

除用*n*-十二醇代替*n*-十二胺外，Gemini表面活性剂C_{12}E-C_6-EC_{12}的合成方法与C_{12}A-C_6-AC_{12}的相同。



方案6　C_{12}E-C_6-EC_{12}的合成路线图

Scheme 6　Reaction routes for the synthesis of gemini surfactant with ester groups in hydrophobic chains, C_{12}E-C_6-EC_{12}.

C_{12}E-C_6-EC_{12}的疏水链

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 0.87 (t, 3H, ***CH₃***), 1.25–1.30 (m, 18H, CH_3-***(CH₂)₉***-CH_2-CH_2), 1.60 (m, 2H, CH_3-$(CH_2)_9$-***CH₂***-CH_2), 2.40 (s, 6H, CH_3-$(CH_2)_{10}$-CH_2-OC(=O)-CH_2-N***(CH₃)₂***), 3.20 (s, 2H, CH_3-$(CH_2)_{11}$-OC(=O)-***CH₂***-N), 4.13 (t, 2H, CH_3-$(CH_2)_{10}$-***CH₂***-OC(=O)-CH_2-N). ESI-MS (APEXII FT-ICR): $[M + H^+]$ ($C_{16}H_{33}NO_2H^+$): Calcd: 272.3, Found: 272.3.

C_{12}E-C_6-EC_{12}, ($C_{38}H_{78}Cl_2N_2O_4$), white power, yield: 85%

IR (KBr) (cm^{-1}): 2923 (-***CH₂***-), 2852 (***CH₃***-CH_2-), 1749 (O-***C(=O)***). ^{1}H NMR (400 MHz, D_2O, δ in ppm): δ = 0.77 (t, 3H, ***CH₃***), 1.18–1.21 (m, 18H, CH_3-***(CH₂)₉***-CH_2-CH_2), 1.31 (m, 2H, N^+-$(CH_2)_2$-***(CH₂)₂***-$(CH_2)_2$-N^+), 1.58 (m, 2H, N^+-CH_2-***CH₂***-$(CH_2)_2$-***CH₂***-CH_2-N^+), 1.69 (m, 2H, CH_3-$(CH_2)_9$-***CH₂***-CH_2), 3.22 (s, 6H, CH_3-$(CH_2)_{10}$-CH_2-OC(=O)-CH_2-N^+***(CH₃)₂***), 3.52 (t, 2H, CH_3-$(CH_2)_{11}$-OC(=O)-CH_2-$N^+(CH_3)_2$-***CH₂***), 4.10 (t, 2H, CH_3-$(CH_2)_9$-CH_2-***CH₂***), 4.34 (s, 2H, CH_3-$(CH_2)_{11}$-OC(=O)-***CH₂***-$N^+(CH_3)_2$-CH_2). ^{13}C NMR (100 MHz, D_2O, δ in ppm): δ = 13.8 (***CH₃***), 22.7–32.0 (CH_3-***(CH₂)₁₀***-CH_2; N^+-CH_2-***(CH₂)₄***-CH_2-N^+), 52.6 (N^+***(CH₃)₂***), 60.3 (CH_3-$(CH_2)_{11}$-OC(=O)-***CH₂***-N^+), 64.2 (CH_3-$(CH_2)_{11}$-OC(=O)-CH_2-$N^+(CH_3)_2$-***CH₂***), 65.0 (CH_3-$(CH_2)_9$-CH_2-***CH₂***), 165.2 (CH_3-$(CH_2)_{11}$-O***C(=O)***-CH_2-N^+). ESI-MS (APEXII FT-ICR): $[M\text{-}2Cl^-]^{2+}$/2 ($C_{38}H_{78}N_2O_4$)$^{2+}$/2: Calcd: 313.3, Found: 312.5. Elemental analysis (%) Calcd: C, 65.39; H, 11.26; N, 4.01. Found: C, 65.25; H, 11.30; N, 4.15.