

Synthesis of gemini with various counterions.

The high viscosity of water solutions of gemini bromide makes the ion exchange difficult, therefore methanol (Rectapur, VWR PROLABO except for 16-2-16 DIPH and n-2-n PH obtained in methanol Baker Analysed, J.T. Baker), has been used instead of water for all geminis obtained. Depending on the pKa of the acid (referred as HX) corresponding to the counterion wanted (referred as X), two ways of ion exchange have been used (**Scheme 1**).

a) For the acids HX with pKa higher than 3, the starting product is a gemini bromide n-2-n BR, and the silver salt of the counterion (referred as AgX) is used to perform the exchange. The surfactant molecule, n-2-n BR, consists of two amphiphilic moieties ($C_nH_{2n+1}(CH_3)_2N^+Br^-$) with an ethylene spacer $(CH_2)_2$ connecting the two polar head groups, i.e., the ammonium ions. Gemini n-2-n BR are obtained by reaction of ethanediyl- α,ω -bis(dimethyl-amine) (99%, Aldrich) with 1-Bromoalkane (ACROS Organics) performed in dry acetonitrile (Chromanorm, VWR PROLABO) under reflux ($T \approx 80^\circ C$) for 48 h in the presence of a 50% excess of bromoalkane to ensure as much as possible a complete biquaternization. The n-2-n BR surfactants were recrystallized at least two times, by solvation in a mixture (chloroform/methanol 9/1) (Laboratory reagent grade, Fischer Scientific) and precipitation induced by adding acetone (Normapur, VWR PROLABO), until the complete removing of bromoalkane in excess. The purity was verified by 1H NMR.

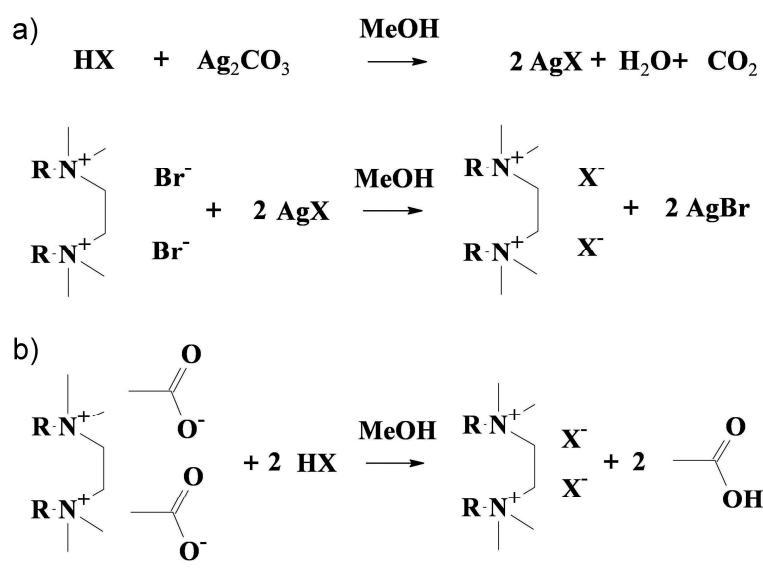
The silver salt AgX is produced by adding silver carbonate Ag_2CO_3 (99%, ACROS Organics) to the corresponding acid HX solution in methanol. In the case of dianionic counterions, tartrate and diphenate, one equivalent of silver salt is added by gemini bromide. After 15 minutes of stirring under vacuum to remove the carbon dioxide and enhance the silver salt formation, the gemini bromide solution is added. The black color of the silver bromide appears after a few minutes indicating that the exchange has been done. The silver bromide and is filtrated with Celite, ensuring the complete removing of silver salts, methanol

is evaporated and the gemini in powder is obtained by precipitating with acetone, ethyl acetate (VWR PROLABO) or anhydrous diethyl ether (“Baker”, J.T. Baker) depending on counterion and chain length of the gemini. Ethyl acetate and ether are preferred for shorter chain length and more hydrophilic counterions. As the bromide counterion is not seen in proton NMR spectra, the complete ion exchange is verified by adding silver acetate to a sample of the product. If the melt becomes black, it indicates that gemini bromide is still in the sample and reacts with silver acetate to produce black silver bromide, and that further silver salt AgX must be added to the sample.

The n-2-n X surfactants were recrystallized in various solvent mixtures (methanol/acetone or (chloroform/methanol 9/1)/acetone for gemini with longer chain length and methanol/ether (ethyl acetate) or (chloroform/methanol 9/1)/ether (ethyl acetate) for gemini with shorter chain length.

Purity of amphiphile molecules and especially the ratio between cations and anions is important to obtain reproducible results. Although the purity was verified by ^1H -NMR, to remove counterion excess which can occur, the gemini were centrifuged in water, acetone or cyclohexane (Analytical reagent, J.T. Baker) depending on the solubility of the gemini and of the corresponding acid. All sample were dried under vacuum or lyophilized prior to the measurements.

The yields of ion exchange are between 60 and 90 %, depending on the gemini synthesized.



Scheme S1: Procedures of exchange of ions used for the preparation of the gemini n-2-n X of this study. a) Method used when acid HX has a pKa higher than 3, b) Method used when acid HX has a pKa lower than 3.

b) For the acids with a pKa lower than the acetic acid pKa, and which don't have any proton in evidence with NMR experiment, the ion exchange starts up with a gemini acetate n-2-n C1 previously prepared by the method a) with silver acetate (99%, ACROS Organics). The gemini in powder is obtained by methanol and acetic acid evaporation, dissolution in methanol or chloroform/methanol 9/1 and precipitation with acetone, ethyl acetate or diethyl ether depending on the counterion. The disappearing of the acetate peak in the ^1H NMR spectrum indicates that the exchange is complete. Although the purity was verified by ^1H -NMR, to remove acid excess which can occur, the gemini were centrifuged in water or acetone depending on the solubility of the gemini and of the corresponding acid. ^1H NMR spectra are all available in the supporting informations paragraph.

^1H NMR: the following NMR peak indexing of the gemini are classified by counterion. For each counterion, only one typical example will be presented, whatever the chain length of the gemini. Attributions related to the counterions are written in fat.

Small counterions : All the counterions of this family are invisible with the ^1H NMR, so that only the peaks of the gemini are visible. The spectra of these products all are carried out in a deuterated chloroform/methanol mixture (9:1) (Euroisotop) except for the gemini PH which are carried out in D_2O (Euroisotop) and for the gemini C0 which are reported in the following paragraph, so that the chemical shifts of the peaks of the gemini are very similar for all these products. To avoid the redundancies, we will give only attributions of peaks obtained on 18BR, by knowing that they are valid for all the gemini n-2-n with small counterion except for gemini pH.

Typical example of 18BR, RMN ^1H (400 MHz, $\text{CDCl}_3/\text{MeOD}$ (9:1), 25°C , δ in ppm). The peak of CHCl_3 is set at 7,26 ppm, the small peak of the methanol is at 3,3 ppm approximately, the large peak is mobile depending to the proportion of methanol in chloroform. $\delta = 0,8$ (t, 6H, $\underline{\text{CH}_3}-(\text{CH}_2)_n\text{-N}^+$ -), 1,1-1,4 (m, 44H, $\text{CH}_3-(\underline{\text{CH}_2})_n\text{-CH}_2\text{-CH}_2\text{-N}^+$ -), 1,7 (m, 4H, $\text{CH}_3-(\text{CH}_2)_n\text{-}\underline{\text{CH}_2}\text{-CH}_2\text{-N}^+$ -), 3,2 (s, 12H, $(\underline{\text{CH}_3})_2\text{-N}^+-(\text{CH}_2)_2\text{-N}^+-(\underline{\text{CH}_3})_2$), 3,4-3,5 (m, 4H, $\text{CH}_3-(\text{CH}_2)_n\text{-CH}_2\text{-}\underline{\text{CH}_2}\text{-N}^+$ -), 4,2 (s, 4H, $(\text{CH}_3)_2\text{-N}^+-(\underline{\text{CH}_2})_2\text{-N}^+-(\text{CH}_3)_2$).

Typical example of 18PH, RMN ^1H (400 MHz, D_2O , 25°C , δ in ppm). The peak of H_2O is at 3,23 ppm. $\delta = 0,8$ (t, 6H, $\underline{\text{CH}_3}-(\text{CH}_2)_n\text{-N}^+$ -), 1,1-1,4 (m, 44H, $\text{CH}_3-(\underline{\text{CH}_2})_n\text{-CH}_2\text{-CH}_2\text{-N}^+$ -), 1,7 (m, 4H, $\text{CH}_3-(\text{CH}_2)_n\text{-}\underline{\text{CH}_2}\text{-CH}_2\text{-N}^+$ -), 3,1 (s, 12H, $(\underline{\text{CH}_3})_2\text{-N}^+-(\text{CH}_2)_2\text{-N}^+-(\underline{\text{CH}_3})_2$), 3,3 (m, 4H, $\text{CH}_3-(\text{CH}_2)_n\text{-CH}_2\text{-}\underline{\text{CH}_2}\text{-N}^+$ -), 3,8 (s, 4H, $(\text{CH}_3)_2\text{-N}^+-(\underline{\text{CH}_2})_2\text{-N}^+-(\text{CH}_3)_2$).

The gemini F synthesized showed problems of instability occurring a few hours after the synthesis (22-2-22 F on the other hand seems to remain stable). The white product obtained at the end of the synthesis rather quickly takes a yellowish color and a nauseous odor. ^1H NMR analysis indicates the presence of an impurity which is growing with time in the product. The

appearance of additional peaks around 5 and 6 ppm indicates that a new species containing an unsaturated chain was created. Moreover, the peaks of the protons α and β of the chains, and of the methyls of the polar head are doubled of a second peak generally better definite, characteristic of a molecule containing a long hydrophobic chain. It is noticed on the other hand that the peak of the spacer is not accompanied by an additional peak. These observations indicates that there was an elimination: the ion fluoride collects a proton of the spacer what causes elimination, and the rupture of the spacer.

Aliphatic carboxylate counterions Cm ($C_mH_{2n+1}COO^-$)

The spectra of these products all are carried out in a deuterated chloroform/methanol mixture (9:1) or in pure $CDCl_3$. The peak of $CHCl_3$ is set at 7,26 ppm, the small peak of the methanol is at 3,3 ppm approximately, the large peak is mobile depending to the proportion of methanol in chloroform.

*Typical example of 18C0, RMN 1H (400 MHz, $CDCl_3/MeOD$ (9:1), 25°C, δ in ppm). $\delta = 0,8$ (t, 6H, $\underline{CH_3}-(CH_2)_n-N^+$), 1,2-1,4 (m, 44H, $CH_3-(\underline{CH_2})_n-CH_2-CH_2-N^+$), 1,7 (m, 4H, $CH_3-(CH_2)_n-\underline{CH_2}-CH_2-N^+$), 3,3 (s, 12H, $(\underline{CH_3})_2-N^+-(CH_2)_2-N^+-(\underline{CH_3})_2$), 3,5-3,6 (m, 4H, $CH_3-(CH_2)_n-CH_2-\underline{CH_2}-N^+$), 4,7 (s, 4H, $(CH_3)_2-N^+-(\underline{CH_2})_2-N^+-(CH_3)_2$), **8,3 (s, 2H, $\underline{H}-COO^-$)**.*

*Typical example of 14C1, RMN 1H (400 MHz, $CDCl_3/MeOD$ (9:1), 25°C, δ in ppm). $\delta = 0,8$ (t, 6H, $\underline{CH_3}-(CH_2)_n-N^+$), 1,2-1,4 (m, 44H, $CH_3-(\underline{CH_2})_n-CH_2-CH_2-N^+$), 1,7 (m, 4H, $CH_3-(CH_2)_n-\underline{CH_2}-CH_2-N^+$), **1,9 (s, 6H, $\underline{CH_3}-COO^-$)**, 3,3 (s, 12H, $(\underline{CH_3})_2-N^+-(CH_2)_2-N^+-(\underline{CH_3})_2$), 3,5-3,6 (m, 4H, $CH_3-(CH_2)_n-CH_2-\underline{CH_2}-N^+$), 4,7 (s, 4H, $(CH_3)_2-N^+-(\underline{CH_2})_2-N^+-(CH_3)_2$).*

*Typical example of 14C2, RMN 1H (400 MHz, $CDCl_3/MeOD$ (9:1), 25°C, δ in ppm). $\delta = 0,8$ (t, 6H, $\underline{CH_3}-(CH_2)_n-N^+$), **1,2 (t, 6H, $\underline{CH_3}-CH_2-COO^-$)**, 1,2-1,4 (m, 44H, $CH_3-(\underline{CH_2})_n-CH_2-CH_2-N^+$), 1,75 (m, 4H, $CH_3-(CH_2)_n-\underline{CH_2}-CH_2-N^+$), **2,2 (q, 4H, $CH_3-\underline{CH_2}-COO^-$)**, 3,4 (s, 12H, $(\underline{CH_3})_2-N^+-(CH_2)_2-N^+-(\underline{CH_3})_2$), 3,6 (m, 4H, $CH_3-(CH_2)_n-CH_2-\underline{CH_2}-N^+$), 4,7 (s, 4H, $(CH_3)_2-N^+-(\underline{CH_2})_2-N^+-(CH_3)_2$).*

Typical example of 14C3, RMN 1H (400 MHz, $CDCl_3/MeOD$ (9:1), 25°C, δ in ppm). $\delta =$ **0,9** (m, 6H, $\underline{CH_3}-(CH_2)_n-N^+$ - et 6H, $\underline{CH_3-CH_2-CH_2-COO^-}$), 1,2-1,4 (m, 44H, $CH_3-(\underline{CH_2})_n-CH_2-CH_2-N^+$ -), **1,6** (h, **4H**, $CH_3-\underline{CH_2-CH_2-COO^-}$), 1,7 (m, 4H, $CH_3-(CH_2)_n-\underline{CH_2-CH_2-N^+}$ -), 2,1 (t, 4H, $CH_3-CH_2-\underline{CH_2-COO^-}$), 3,3 (s, 12H, $(\underline{CH_3})_2-N^+-(CH_2)_2-N^+-(\underline{CH_3})_2$), 3,5-3,6 (m, 4H, $CH_3-(CH_2)_n-CH_2-\underline{CH_2-N^+}$ -), 4,7 (s, 4H, $(CH_3)_2-N^+-(\underline{CH_2})_2-N^+-(CH_3)_2$).

Typical example of 14C5, RMN 1H (400 MHz, $CDCl_3$, 25°C, δ in ppm). $\delta =$ 0,6 (t, 6H, $\underline{CH_3}-(CH_2)_n-N^+$ -), **0,94** (t, **6H**, $\underline{CH_3-CH_2-CH_2-CH_2-CH_2-COO^-}$) **0,98-1,1** (m, 44H, $CH_3-(\underline{CH_2})_n-CH_2-CH_2-N^+$ - et **8H**, $CH_3-\underline{CH_2-CH_2-CH_2-CH_2-COO^-}$), 1,35 (qt, **4H**, $CH_3-CH_2-CH_2-\underline{CH_2-CH_2-COO^-}$), 1,45 (m, 4H, $CH_3-(CH_2)_n-\underline{CH_2-CH_2-N^+}$ -), **1,9** (t, **4H**, $CH_3-CH_2-CH_2-CH_2-\underline{CH_2-COO^-}$), 3,1 (s, 12H, $(\underline{CH_3})_2-N^+-(CH_2)_2-N^+-(\underline{CH_3})_2$), 3,4 (m, 4H, $CH_3-(CH_2)_n-CH_2-\underline{CH_2-N^+}$ -), 4,5 (s, 4H, $(CH_3)_2-N^+-(\underline{CH_2})_2-N^+-(CH_3)_2$).

Typical example of 14C7, RMN 1H (400 MHz, $CDCl_3$, 25°C, δ in ppm). $\delta =$ 0,6 (m, 6H, $\underline{CH_3}-(CH_2)_n-N^+$ - et **6H**, $\underline{CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-COO^-}$), **0,9-1,2** (m, 44H, $CH_3-(\underline{CH_2})_n-CH_2-CH_2-N^+$ - et **16H**, $CH_3-\underline{CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-COO^-}$), 1,3 (M, **4H**, $CH_3-CH_2-CH_2-CH_2-CH_2-\underline{CH_2-CH_2-COO^-}$), 1,45 (m, 4H, $CH_3-(CH_2)_n-\underline{CH_2-CH_2-N^+}$ -), **1,9** (t, **4H**, $CH_3-CH_2-CH_2-CH_2-CH_2-\underline{CH_2-COO^-}$), 3,1 (s, 12H, $(\underline{CH_3})_2-N^+-(CH_2)_2-N^+-(\underline{CH_3})_2$), 3,4 (m, 4H, $CH_3-(CH_2)_n-CH_2-\underline{CH_2-N^+}$ -), 4,55 (s, 4H, $(CH_3)_2-N^+-(\underline{CH_2})_2-N^+-(CH_3)_2$).

Typical example of 14C9, RMN 1H (400 MHz, $CDCl_3$, 25°C, δ in ppm). $\delta =$ 0,6 (m, 6H, $\underline{CH_3}-(CH_2)_n-N^+$ - et **6H**, $\underline{CH_3-(CH_2)_6-CH_2-CH_2-COO^-}$), **0,9-1,2** (m, 44H, $CH_3-(\underline{CH_2})_n-CH_2-CH_2-N^+$ - et **24H**, $CH_3-(\underline{CH_2})_6-CH_2-CH_2-COO^-$), 1,3 (M, **4H**, $CH_3-(CH_2)_6-\underline{CH_2-CH_2-COO^-}$), 1,45 (m, 4H, $CH_3-(CH_2)_n-\underline{CH_2-CH_2-N^+}$ -), **1,9** (t, **4H**, $CH_3-(CH_2)_6-CH_2-\underline{CH_2-COO^-}$), 3,1 (s, 12H, $(\underline{CH_3})_2-N^+-(CH_2)_2-N^+-(\underline{CH_3})_2$), 3,4 (m, 4H, $CH_3-(CH_2)_n-CH_2-\underline{CH_2-N^+}$ -), 4,55 (s, 4H, $(CH_3)_2-N^+-(\underline{CH_2})_2-N^+-(CH_3)_2$).

Typical example of 14C11, RMN 1H (400 MHz, $CDCl_3$, 25°C, δ in ppm). $\delta =$ 0,7 (m, 6H, $\underline{CH_3}-(CH_2)_n-N^+$ - et **6H**, $\underline{CH_3-(CH_2)_{10}-COO^-}$), **1,0-1,2** (m, 44H, $CH_3-(\underline{CH_2})_n-CH_2-CH_2-N^+$ - et

32H, CH₃-(CH₂)₈-CH₂-CH₂-COO⁻), 1,3 (M, 4H, CH₃-(CH₂)₈-CH₂-CH₂-COO⁻), 1,45 (m, 4H, CH₃-(CH₂)_n-CH₂-CH₂-N⁺-), 1,9 (t, 4H, CH₃-(CH₂)₈-CH₂-CH₂-COO⁻), 3,1 (s, 12H, (CH₃)₂-N⁺-(CH₂)₂-N⁺-(CH₃)₂), 3,4 (m, 4H, CH₃-(CH₂)_n-CH₂-CH₂-N⁺-), 4,7 (s, 4H, (CH₃)₂-N⁺-(CH₂)₂-N⁺-(CH₃)₂).

Typical example of 14C15, RMN ¹H (400 MHz, CDCl₃), 25°C, δ in ppm). δ= 0,8 (m, 6H, CH₃-(CH₂)_n-N⁺ et 6H, CH₃-(CH₂)₁₄-COO⁻), 1,0-1,2 (m, 44H, CH₃-(CH₂)_n-CH₂-CH₂-N⁺ et 48H, CH₃-(CH₂)₁₂-CH₂-CH₂-COO⁻), 1,3 (M, 4H, CH₃-(CH₂)₁₂-CH₂-CH₂-COO⁻), 1,45 (m, 4H, CH₃-(CH₂)_n-CH₂-CH₂-N⁺-), 1,9 (t, 4H, CH₃-(CH₂)₁₂-CH₂-CH₂-COO⁻), 3,2 (s, 12H, (CH₃)₂-N⁺-(CH₂)₂-N⁺-(CH₃)₂), 3,5 (m, 4H, CH₃-(CH₂)_n-CH₂-CH₂-N⁺-), 4,7 (s, 4H, (CH₃)₂-N⁺-(CH₂)₂-N⁺-(CH₃)₂).

Aromatic carboxylate counterions

The solvent used for the gemini of this family was preferentially deuterated methanol, because the chemical shift of the peak of CHCl₃ is too close to that of the protons of the aromatic cycle. The small peak of methanol is fixed at 3,3 ppm, the large peak is at 4,9 ppm.

Typical example of 22BENZ, RMN ¹H (400 Mhz, MeOD), 25°C, δ in ppm). δ= 0,9 (t, 6H, CH₃-(CH₂)_n-N⁺-), 1,2-1,5 (m, 76H, CH₃-(CH₂)_n-CH₂-CH₂-N⁺-), 1,8 (m, 4H, CH₃-(CH₂)_n-CH₂-CH₂-N⁺-), 3,2 (s, 12H, (CH₃)₂-N⁺-(CH₂)₂-N⁺-(CH₃)₂), 3,4 (m, 4H, CH₃-(CH₂)_n-CH₂-CH₂-N⁺-), 4 (s, 4H, (CH₃)₂-N⁺-(CH₂)₂-N⁺-(CH₃)₂), 7,3-7,5 (m, 6H, m-C₆H₅COO⁻ et p-C₆H₅COO⁻), 8,0 (d, 4H, o-C₆H₅COO⁻).

Typical example of 14SAL, RMN ¹H (400 Mhz, MeOD), 25°C, δ in ppm). δ= 0,9 (t, 6H, CH₃-(CH₂)_n-N⁺-), 1,2-1,5 (m, 76H, CH₃-(CH₂)_n-CH₂-CH₂-N⁺-), 1,8 (m, 4H, CH₃-(CH₂)_n-CH₂-CH₂-N⁺-), 3,2 (s, 12H, (CH₃)₂-N⁺-(CH₂)₂-N⁺-(CH₃)₂), 3,4 (m, 4H, CH₃-(CH₂)_n-CH₂-CH₂-N⁺-), 4 (s, 4H, (CH₃)₂-N⁺-(CH₂)₂-N⁺-(CH₃)₂), 6,8 (m, 4H, m-C₆H₅COO⁻ et p-C₆H₅COO⁻), 7,3 (t, 2H, m-C₆H₅COO⁻ et p-C₆H₅COO⁻), 8,0 (d, 2H, o-C₆H₅COO⁻).

Typical example of 14MHB, RMN 1H (400 Mhz, MeOD), 25°C, δ in ppm). δ = 0,9 (t, 6H, $\underline{CH_3}-(CH_2)_n-N^+$), 1,2-1,5 (m, 76H, $CH_3-(\underline{CH_2})_n-CH_2-CH_2-N^+$), 1,8 (m, 4H, $CH_3-(CH_2)_n-\underline{CH_2}-CH_2-N^+$), 3,2 (s, 12H, $(\underline{CH_3})_2-N^+-(CH_2)_2-N^+-(\underline{CH_3})_2$), 3,4 (m, 4H, $CH_3-(CH_2)_n-CH_2-\underline{CH_2}-N^+$), 4 (s, 4H, $(CH_3)_2-N^+-(\underline{CH_2})_2-N^+-(CH_3)_2$), **6,85 (d, 2H, m-C₆H₅COO⁻)**, **7,18 (t, 2H, p-C₆H₅COO⁻)**, **7,39 (s, 2H, o-C₆H₅COO⁻)**, **7,42 (d, 2H, o-C₆H₅COO⁻)**.

Typical example of 18PHB, RMN 1H (400 Mhz, MeOD), 25°C, δ in ppm). δ = 0,9 (t, 6H, $\underline{CH_3}-(CH_2)_n-N^+$), 1,2-1,5 (m, 76H, $CH_3-(\underline{CH_2})_n-CH_2-CH_2-N^+$), 1,8 (m, 4H, $CH_3-(CH_2)_n-\underline{CH_2}-CH_2-N^+$), 3,2 (s, 12H, $(\underline{CH_3})_2-N^+-(CH_2)_2-N^+-(\underline{CH_3})_2$), 3,4 (m, 4H, $CH_3-(CH_2)_n-CH_2-\underline{CH_2}-N^+$), 4,0 (s, 4H, $(CH_3)_2-N^+-(\underline{CH_2})_2-N^+-(CH_3)_2$), **6,70 (d, 4H, m-C₆H₅COO⁻)**, **7,80 (d, 4H, o-C₆H₅COO⁻)**.

Typical example of 14DHB, RMN 1H (400 Mhz, MeOD), 25°C, δ in ppm). δ = 0,9 (t, 6H, $\underline{CH_3}-(CH_2)_n-N^+$), 1,2-1,5 (m, 76H, $CH_3-(\underline{CH_2})_n-CH_2-CH_2-N^+$), 1,8 (m, 4H, $CH_3-(CH_2)_n-\underline{CH_2}-CH_2-N^+$), 3,2 (s, 12H, $(\underline{CH_3})_2-N^+-(CH_2)_2-N^+-(\underline{CH_3})_2$), 3,4 (m, 4H, $CH_3-(CH_2)_n-CH_2-\underline{CH_2}-N^+$), 4,0 (s, 4H, $(CH_3)_2-N^+-(\underline{CH_2})_2-N^+-(CH_3)_2$), **6,35 (t, 2H, p-C₆H₅COO⁻)**, **6,90 (d, 4H, o-C₆H₅COO⁻)**.

Typical example of 14PA, RMN 1H (400 Mhz, MeOD), 25°C, δ in ppm). δ = 0,85 (t, 6H, $\underline{CH_3}-(CH_2)_n-N^+$), 1,2-1,5 (m, 76H, $CH_3-(\underline{CH_2})_n-CH_2-CH_2-N^+$), 1,75 (m, 4H, $CH_3-(CH_2)_n-\underline{CH_2}-CH_2-N^+$), 3,15 (s, 12H, $(\underline{CH_3})_2-N^+-(CH_2)_2-N^+-(\underline{CH_3})_2$), 3,35 (m, 4H, $CH_3-(CH_2)_n-CH_2-\underline{CH_2}-N^+$), **3,45 (s, 4H, C₆H₅-CH₂-COO⁻)**, 3,95 (s, 4H, $(CH_3)_2-N^+-(\underline{CH_2})_2-N^+-(CH_3)_2$), **7,15 (t, 2H, p-C₆H₅-CH₂-COO⁻)**, **7,25 (t, 2H, m-C₆H₅-CH₂-COO⁻)**, **7,3 (d, 4H, o-C₆H₅-CH₂-COO⁻)**.

Typical example of 14MAND, RMN 1H (400 Mhz, MeOD), 25°C, δ in ppm). δ = 0,85 (t, 6H, $\underline{CH_3}-(CH_2)_n-N^+$), 1,2-1,5 (m, 76H, $CH_3-(\underline{CH_2})_n-CH_2-CH_2-N^+$), 1,75 (m, 4H, $CH_3-(CH_2)_n-\underline{CH_2}-CH_2-N^+$), 3,15 (s, 12H, $(\underline{CH_3})_2-N^+-(CH_2)_2-N^+-(\underline{CH_3})_2$), 3,35 (m, 4H, $CH_3-(CH_2)_n-CH_2-\underline{CH_2}-N^+$), 3,95 (s, 4H, $(CH_3)_2-N^+-(\underline{CH_2})_2-N^+-(CH_3)_2$), **4,85 (s, 2H, C₆H₅-CH(OH)-COO⁻)**,

7,25 (t, 2H, p-C₆H₅-CH(OH)-COO⁻), 7,3 (t, 2H, m-C₆H₅-CH(OH)-COO⁻), 7,45 (d, 4H, o-C₆H₅-CH(OH)-COO⁻).

Orphan counterions

Like the gemini with small counterions, gemini TFA present only the peaks of the gemini in NMR ¹H. The spectra of these two products are carried out in the CDCl₃/MeOD mixture, and are similar to that of 18BR presented above. The spectra of other products are carried out in a deuterated chloroforme/méthanol mixture (9:1), in pure deuterated chloroform or in pure deuterated methanol. The peak of CHCl₃ is set at 7,26 ppm, the small peak of the methanol is at 3,3 ppm approximately, the large peak is mobile depending to the proportion of methanol in chloroform. In pure methanol, the small peak of methanol is fixed at 3,3 ppm, the large peak is at 4,9 ppm.

Typical example of 16DIPH, RMN ¹H (400 Mhz, MeOD), 25°C, δ in ppm). δ= 0,85 (t, 6H, CH₃-(CH₂)_n-N⁺-), 1,2-1,5 (m, 76H, CH₃-(CH₂)_n-CH₂-CH₂-N⁺-), 1,75 (m, 4H, CH₃-(CH₂)_n-CH₂-CH₂-N⁺-), 3,15 (s, 12H, (CH₃)₂-N⁺-(CH₂)₂-N⁺-(CH₃)₂), 3,35 (m, 4H, CH₃-(CH₂)_n-CH₂-CH₂-N⁺-), 3,95 (s, 4H, (CH₃)₂-N⁺-(CH₂)₂-N⁺-(CH₃)₂), **7,25 (m, 4H, (p-C₆H₅-COO⁻)₂ et (m-C₆H₅-COO⁻)₂), 7,45 (m, 2H, (o-C₆H₅-COO⁻)₂), 7,5 (d, 2H, (o-C₆H₅-COO⁻)₂).**

Typical example of 14MeOAc, RMN ¹H (400 MHz, CDCl₃), 25°C, δ in ppm). δ= 0,8 (t, 6H, CH₃-(CH₂)_n-N⁺-), 1,2-1,4 (m, 44H, CH₃-(CH₂)_n-CH₂-CH₂-N⁺-), 1,7 (m, 4H, CH₃-(CH₂)_n-CH₂-CH₂-N⁺-), **3,4 (m, 18H, (CH₃)₂-N⁺-(CH₂)₂-N⁺-(CH₃)₂ et CH₃-O-CH₂-COO⁻), 3,6 (m, 4H, CH₃-(CH₂)_n-CH₂-CH₂-N⁺-), 3,8 (s, 4H, CH₃-O-CH₂-COO⁻), 4,8 (s, 4H, (CH₃)₂-N⁺-(CH₂)₂-N⁺-(CH₃)₂).**

Typical example of 14LACT, RMN ¹H (400 MHz, CDCl₃/MeOD (9:1), 25°C, δ in ppm). δ= 0,8 (t, 6H, CH₃-(CH₂)_n-N⁺-), **1,1-1,4 (m, 50H, CH₃-(CH₂)_n-CH₂-CH₂-N⁺- et CH₃-CH(-OH)-COO⁻), 1,65 (m, 4H, CH₃-(CH₂)_n-CH₂-CH₂-N⁺-), 3,1 (s, 12H, (CH₃)₂-N⁺-(CH₂)₂-N⁺-**

(CH₃)₂), 3,3 (m, 4H, CH₃-(CH₂)_n-CH₂-CH₂-N⁺-), 3,9 (q, 2H, **CH₃-CH(-OH)-COO⁻**), , 4,1 (s, 4H, (CH₃)₂-N⁺-(CH₂)₂-N⁺-(CH₃)₂).

Typical example of 14TART, RMN ¹H (400 MHz, CDCl₃/MeOD (9:1), 25°C, δ in ppm).
 δ= 0,8 (t, 6H, CH₃-(CH₂)_n-N⁺-), 1,1-1,4 (m, 44H, CH₃-(CH₂)_n-CH₂-CH₂-N⁺-), 1,65 (m, 4H, CH₃-(CH₂)_n-CH₂-CH₂-N⁺-), 3,1 (s, 12H, (CH₃)₂-N⁺-(CH₂)₂-N⁺-(CH₃)₂), 3,3 (m, 4H, CH₃-(CH₂)_n-CH₂-CH₂-N⁺-), 3,9 (s, 4H, (CH₃)₂-N⁺-(CH₂)₂-N⁺-(CH₃)₂), **4,2 (s, 2H, (CH(-OH)-COO⁻)₂).**

Spectrofluorometric measurements

Fluorescence emission was recorded on a FL3-22 SPEX spectrofluorometer equipped with a thermostatted cell holder. To a solution of gemini (2.5 mL) in a quartz cell (10 mm), 1 μL of pyrene (2.5·10⁻⁴ M stock solution in 100% ethanol) was added (pyrene: 98%, ACROS Organics recrystallized from absolute ethanol). Final pyrene concentration is 5·10⁻⁷ M. Aliquots of a fluorescence quencher Coumarin 153 (C153, laser grade, ACROS Organics, 1·10⁻³ M stock solution in 100% ethanol) were added to the cell. At each step, the fluorescence emission spectrum was recorded. The maximal final concentration of ethanol did not exceed 1.5%. Pyrene emission was collected from 350 to 500 nm (λ_{ex} = 337 nm). All fluorescence experiments were performed at 20⁰C after equilibration for at least 30 min.

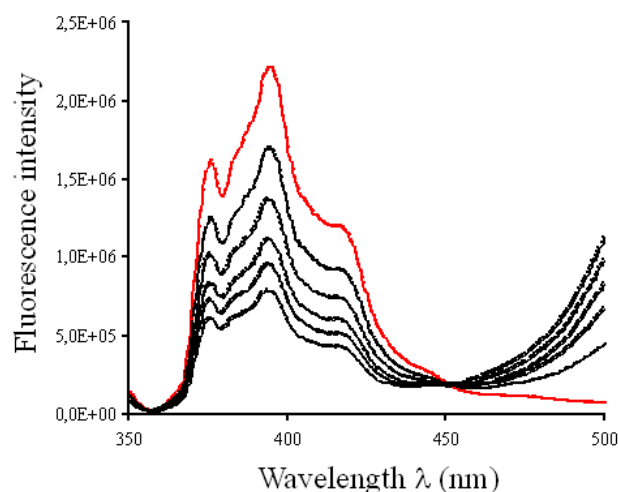


Figure S1: Quenching of pyrene fluorescence by coumarine 153 (C153) in presence of 14BR (D_0 0,25 mM). Fluorescence spectra recorded for pyrene alone (upper curve) and coumarine 153 added in following concentrations: 0.997 μM , 1.99 μM , 2.99 μM , 3.98 μM , 4.97 μM .

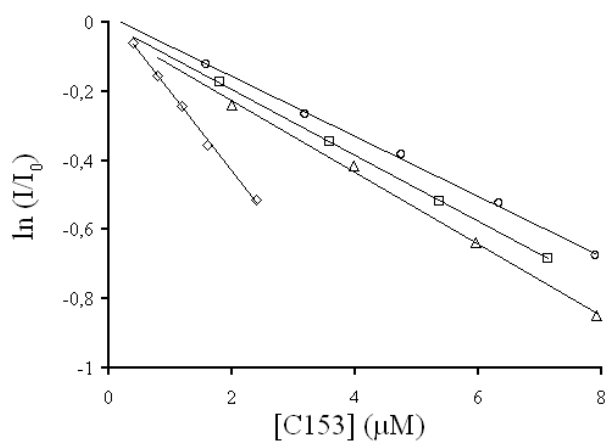


Figure S2 Quenching of pyrene fluorescence by coumarine 153 (C153) in presence of four different concentration of 14CL. Straight lines correspond to following surfactant concentration: 0.511 mM - open circles; 0.45 mM – squares; 0.41 mM – triangles; 0.304 mM- diamonds

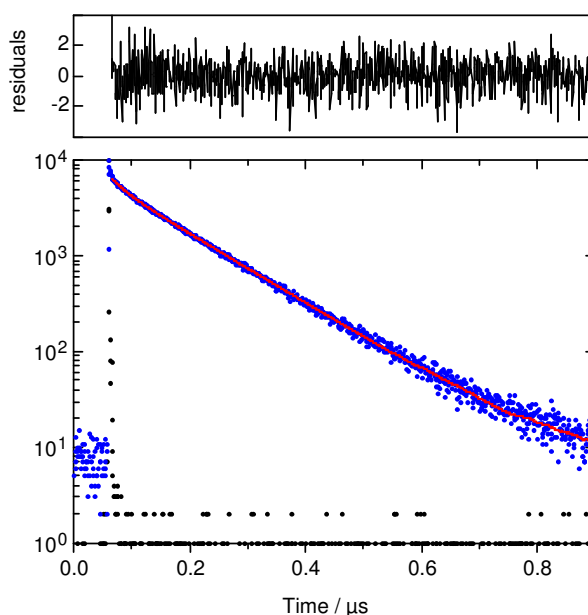


Figure S3. Time-resolved fluorescence emission of 1-methylpyrene ($4.8 \cdot 10^{-7}$ M) in water in the presence C2 (0.607 mM, $2 \cdot \text{CMC}$) and 2,3-dimethylbenzophenone ($3.34 \mu\text{M}$). Red line represents best fit to the Infelta-Tachiya model with $\tau_0 = 120$ ns, $k_q = 2.6 \times 10^7 \text{ s}^{-1}$, and $\langle n \rangle = 0.24$ ($\chi^2 = 1.14$).

Time Resolved Fluorescence Quenching

The probe and quencher were added as ethanolic solutions (probe: $5 \mu\text{L}$ of a $2.88 \cdot 10^{-4}$ M solution, $[\text{probe}] = 4.8 \cdot 10^{-7}$ M, quencher: $2 \mu\text{L}$ of a 5mM solution, $[\text{quencher}] = 3.34 \cdot 10^{-6}$ M). Excited state lifetimes were determined using a Fluorolog 3 instrument equipped with a pulsed 310-nm wavelength diode and a Hamamatsu 2658 cooled photomultiplier. Fluorescence decays were collected at 390 nm and analyzed (see S. I. Fig. S3) according to the Infelta-Tachiyama model: $F(t) = F(0) \exp[-k_0 t - \langle n \rangle \{1 - \exp(-k_q t)\}]$,ⁱ which assumes that the micelles are of equal size, that the probe is stationary over the course of its excited state lifetime, that the probe and quencher are distributed according to a Poissonian distribution and that quencher molecules do not interact. Under these conditions, the occupation number $\langle n \rangle$ gives the aggregation number according to $\langle n \rangle = [\text{quencher}] / [\text{micelles}]$.

Although, aggregation numbers obtained using steady-state fluorescence quenching are accurate only in cases where the quenching process is static within the micelle, Unfortunately, TRFQ technique proved difficult to apply to other counterions, due to the low CMC's ($\sim 10^{-4}$ mol/L) of 14-2-14 X, and very limited concentration range in which spherical micelles are observed (between the CMC and twice the CMC). In the case of TRFQ measurements, it meant that exceedingly low concentrations of probe and quencher must be used. However, since the chain length of the gemini surfactant is fixed to C14, we can reasonably assume that the hydrophobic core of the micelles are similar, and that the microviscosity within the micelles will be the same regardless of the counterion for micelles of similar size. Therefore, any systematic errors in the determination of N using steady-state fluorescence quenching will be similar over the entire series.

Dynamic Light Scattering

The hydrodynamic diameter (R_h) of the spherical micelles at concentration twice the CMC were determined by dynamic light scattering CGS-3 (ALV-GmbH, Malvern). The calculated volume assuming a spherical shape of the micelles using the gyration radius ($0.77 \cdot R_h$) was divided by the molecular volume to obtain the aggregation number. The molecular volume was obtained by the molecular weight (629g/mol for 14-2-14 Ac) of the gemini and the estimated density = 1.1 g / mL previously reported by us for a similar molecule gemini tartrate.ⁱⁱ

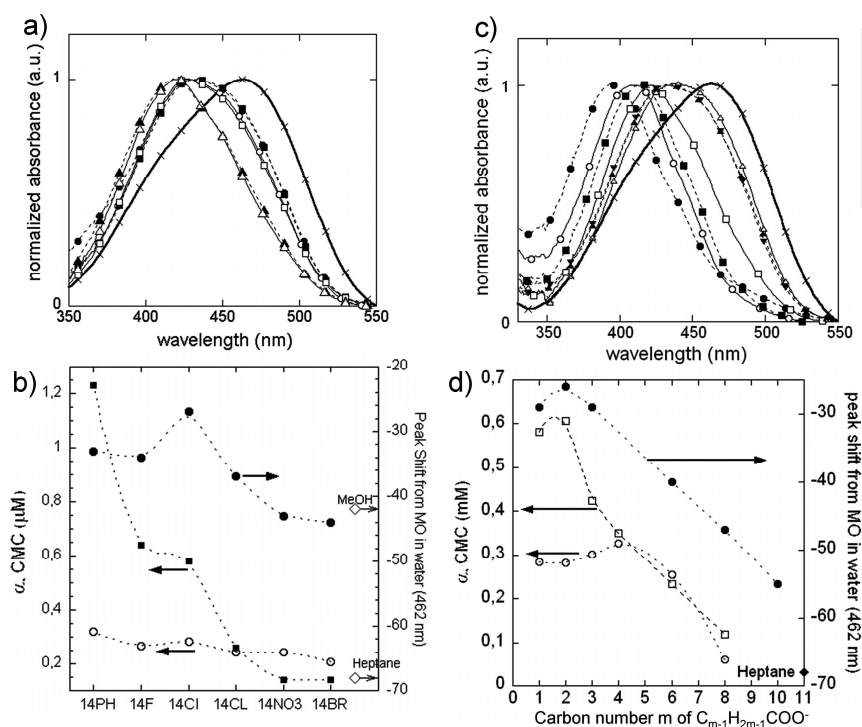


Figure S4; (a) UV π - π^* transition peak of Methyl Orange co-micellized with gemini (●) 14PH (○) 14F (■) 14C1 (□) 14CL (▲) 14NO₃ (△) 14BR (×) H₂O at gemini concentration corresponding to 2.0*CMC. (b) UV peak shift (●) for the gemini-small anions compared with CMC(■) and $\alpha_{b,25}$ (○). (c) UV π - π^* transition peak of Methyl Orange co-micellized with gemini (●) 14C12 (○) 14C10 (■) 14C8 (□) 14C6 (▲) 14C3 (△) 14C2 (▼) 14C1 (×) H₂O gemini concentration corresponding to 2.0*CMC. (d) UV peak shift (●) for the gemini-small anions compared with CMC(□) and $\alpha_{\beta,25}$ (○). Lines are guide to the eyes.

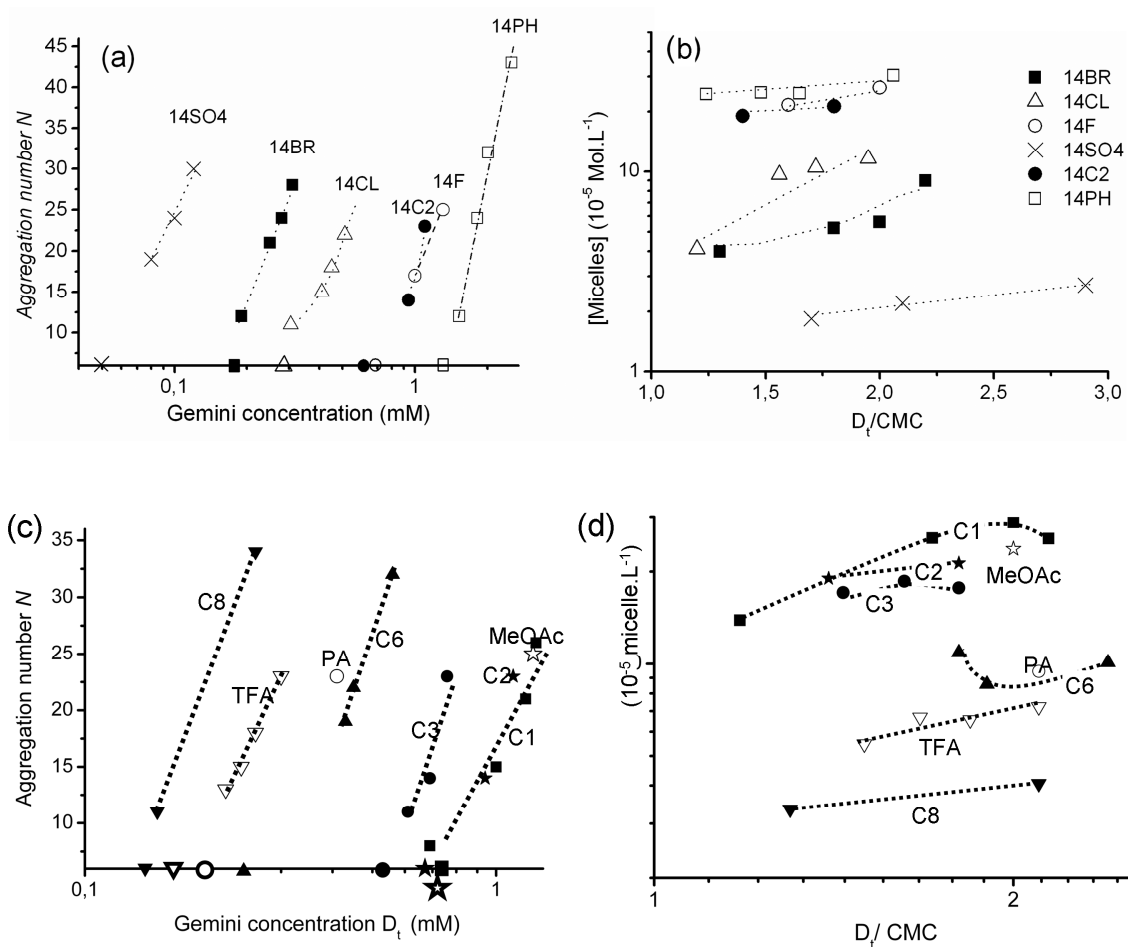


Figure S5: The N values and concentration of micelles $[Mic]$ of 14-2-14 with small counterions (a and b) and other counterions (c and d) obtained from fluorescence quenching measurements are represented *versus* the surfactant concentration D_t and normalized concentration with CMC, D_t/CMC respectively. In this concentration range, the aggregation numbers of gemini micelles increased linearly with surfactant concentration (a and c). Higher micelle concentration are observed for the counterions with higher CMC at a given D_t/CMC , vice versa (b and d).

ⁱ (a) Infelta, P. P.; Grätzel, M. *J. Chem. Phys.* 1979, 70, 179; (b) Kalayanasundaram, K. *Photochemistry in Microheterogeneous Systems*, Academic Press, Orlando, 1987.

ⁱⁱ Oda, R.; Laguerre, M.; Huc, I.; Artzner, F.; *J. Am. Chem. Soc.* 2008 130 (44), 14705–14712