Synthesis and surface-active properties of new gemini surfactants with symmetrical perfluoroalkyl groups

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New perfluoroalkylated gemini amphiphiles were prepared from F-alkylated ureas and carbamates with high yields. Their surface activity was studied as a function of their molecular structure.

In recent years, bolaform-type and gemini-type surfactants have received increasing attention because of their unusual properties. As shown in Fig. 1 their structure differs from conventional surfactants. Bolaform-type compounds contain two polar head groups connected by one or more hydrocarbon chains,[1–3] while gemini-type surfactants are made of two hydrophilic head groups bearing an identical hydrophobic chain and linked by a rigid or flexible spacer.[4–12]

The literature mentions nonionic bolaphiles and gemini surfactants synthesized from carbohydrate derivatives.[13,14] Lattes *et al.* described bisgluconamides and bislactobionamides as bolaform surfactants with two sugar head groups[15] and showed that these surfactants were capable of forming vesicles.[16] Villa *et al.* also prepared novel bis(glycosyl)ethers as bolaphiles[17] and Plusquellec *et al.* novel sugar bolaphiles with a pseudo-macrocyclic structure.[18]Recently Cirelli *et al.* synthesized 1,5-bis[6-*O*-(*n*-butyl-α-D-glucopyranoside)] glutarate as the first example of a nonionic gemini surfactant where alkyl glucosides are linked through a spacer at C-6.[19]

The properties of micellar and vesicular aggregates of bolaphiles have been studied by several authors.[20–30] When dissolved in aqueous media, upon sonication the bolaphiles self-organize into monolayered vesicles (MLM, monolayered lipid membranes) that are highly stable over time with variations of temperature and ionic strength. The literature reports membrane-disrupting systems based on bis(oligoethylene oxide) bolaphiles,[31] related polymeric derivatives[32,33] and bis(crown ether) bolaphiles.[34] A number of bolaphiles capable of forming pores in vesicle and bilayer membranes are also described.[35–41] Gemini or dimeric surfactants have better micellar properties than conventional (monomeric) surfactants. They adsorb more efficiently at the aqueous–air interface, reducing the surface tension and forming micelles;[9] they have very low Krafft temperatures[42] and show better lime-soap dispersing properties.[43] Zana *et al.* have studied the effect of the spacer chain length on the CMC of gemini surfactants[5] and on the micellar structure.[44] It was also found that the novel cationic gemini surfactants butane-2-3-dioldiyl-1,4-bis(alkyldimethyl ammonium bromide) had very strong interactions with anionic surfactants.[45] Recently alkane diyl-α,ω-bis(alkyldimethyl ammonium bromide) systems have been shown to form vesicles, elongated or thread-like micelles and spherical micelles depending on the spacer carbon number.[46] The aggregation behaviour of sodium di(octadecanoyloxy)butane-1,4-diyl biphosphate[47,48] and other amphitropic diammonium surfactants were also reported.[49]

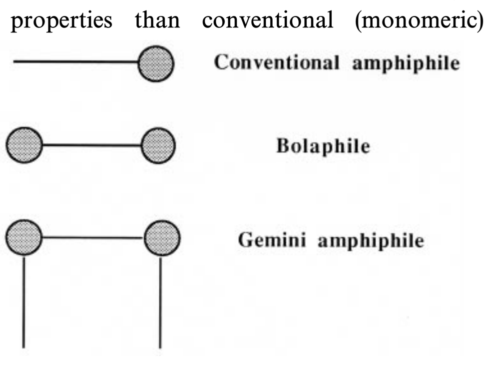
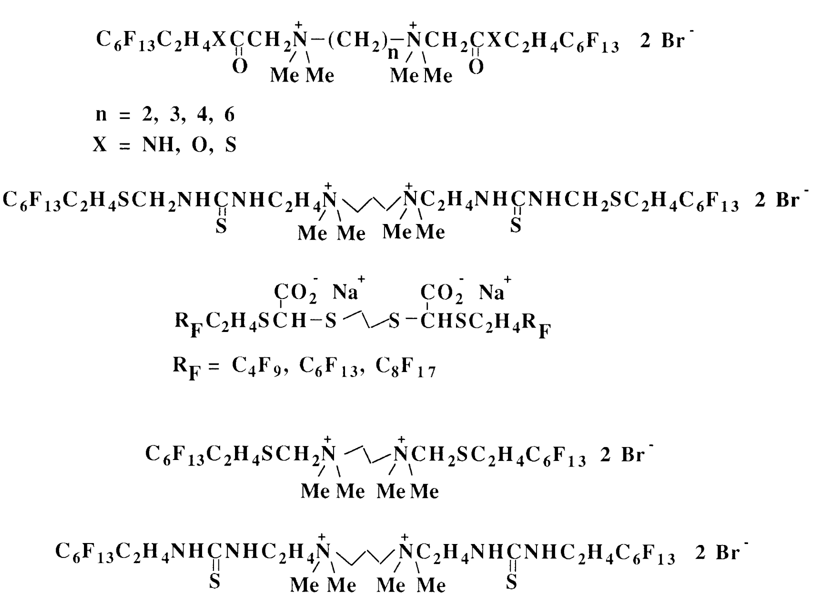


Fig. 1 Schematic molecular structure of dimeric amphiphiles.

Gemini surfactants have been used in other fields as bactericides.[50,51] Notably Infante and co-workers have shown the high antimicrobial activity of gemini surfactants such as *N*,*N*-bis(*N*-dodecyl-*N*,*N*-dimethyl glycine)cystamine dihydrochloride or *N*,*N*′-bis(*N*-dodecyl-*N*,*N*′-dimethyl glycine)-1,4-diaminobutane dihydrochloride.[10] The function of bis(quaternary ammonium) gemini surfactants as phase-transfer catalysts was also recently described.[52]

Several authors have prepared gemini surfactants with different structures. Candau *et al.* described the effect of the dissymmetry of gemini surfactants bearing hydrophobic chains of different lengths on their self-assembled structures in aqueous solutions.[53] Lebeau *et al.* reported the first synthesis of asymmetrical gemini surfactants having two identical hydrophobic chains and two different hydrophilic head groups: one is a poly(oxyethylene) moiety and the second is a sulfonic acid sodium salt.[54] Tri(quaternary ammonium) surfactants made up of three amphiphilic moieties connected at the level of the head groups by two propanediyl spacers were also prepared by Zana *et al.*[55] Several papers have been published on gemini surfactants with spacers having various chemical structures, such as $-CH_2N(CH_3)CH_2-$, $-CH_2SCH_2-$ or oxyethylene.[56–60] Recently, Zana *et al.* studied the adsorption on silica of four alkanediyl-α-ω-bis(dodecyl dimethylammonium bromide dimeric surfactants.[61]

In this paper we present the synthesis and surface-active properties of new gemini surfactants that contain symmetrical perfluoroalkyl chains. We have recently reported some examples of gemini surfactants containing perfluoroalkyl



$$C_6F_{13}C_2H_4X\underset{O}{\overset{\|}{C}}CH_2\overset{+}{N}(Me)_2-(CH_2)_n-\overset{+}{N}(Me)_2CH_2\underset{O}{\overset{\|}{C}}XC_2H_4C_6F_{13}\ 2\,Br^-$$

n = 2, 3, 4, 6
X = NH, O, S

$$C_6F_{13}C_2H_4SCH_2NH\underset{S}{\overset{\|}{C}}NHC_2H_4\overset{+}{N}(Me)_2(CH_2)_n\overset{+}{N}(Me)_2C_2H_4NH\underset{S}{\overset{\|}{C}}NHCH_2SC_2H_4C_6F_{13}\ 2\,Br^-$$

$$R_FC_2H_4S\overset{CO_2^-\,Na^+}{CH}-S(CH_2)_nS-\overset{CO_2^-\,Na^+}{CH}SC_2H_4R_F$$

R_F = C_4F_9, C_6F_{13}, C_8F_{17}

$$C_6F_{13}C_2H_4SCH_2\overset{+}{N}(Me)_2(CH_2)_n\overset{+}{N}(Me)_2CH_2SC_2H_4C_6F_{13}\ 2\,Br^-$$

$$C_6F_{13}C_2H_4NH\underset{S}{\overset{\|}{C}}NHC_2H_4\overset{+}{N}(Me)_2(CH_2)_n\overset{+}{N}(Me)_2C_2H_4NH\underset{S}{\overset{\|}{C}}NHC_2H_4C_6F_{13}\ 2\,Br^-$$

Scheme 1 Molecular structures of fluorinated gemini amphiphiles[62–65]

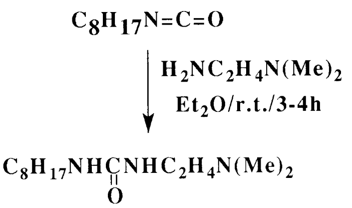
groups.[62–65] Notably we showed that they could form stable vesicular aggregates upon sonication in aqueous solution.[62] Scheme 1 presents the different molecular structures of gemini surfactants prepared in our laboratory. To our knowledge, the preparation and properties of such perfluoroalkylated dimeric surfactants have not been reported until now.

Results and discussion

All the gemini surfactants described in this paper were prepared from alkylated urea, perfluoroalkylated urea and carbamate. We used octyl isocyanate, 2-F-alkyl ethyl isocyanates[66] and 3′-[2-(*F*-octyl)ethylthio] propyl isocyanates[67] as raw materials for producing the urea and carbamate intermediates.

We first prepared the *N*-octyl-*N*-(2-dimethylaminoethyl) urea **1** by reaction of octyl isocyanates with 2-dimethylaminoethylamine as shown in Scheme 2. To generate the perfluoroalkylated ureas **2**–**4**, we used the same method described previously.[68] As shown in Scheme 3, *N*-[2-(F-alkyl)ethyl]-*N*′-(2-dimethylaminoethyl)ureas **2**, **3** and *N*-{3′-[2-(F-octyl)ethylthio]propyl}-*N*′-(2-dimethylaminoethyl)urea **4** are obtained by reaction of 2-(F-alkyl)ethyl isocyanates and 3′-[2-(F-octyl)ethylthio] propyl isocyanates with 2-dimethylaminoethylamine. We have also synthesized the *N*-[2-(F-octyl)ethyl]-*O*-(2-dimethylaminoethyl)carbamate **5** by condensation of 2-(dimethylamino)ethanol with 2-(F-octyl)ethyl isocyanate as shown in Scheme 4. Yields and melting points of ureas **1**–**4** and carbamate **5** are collected in Table 1.

Perfluoroalkylated bolaphiles **6**–**18** were prepared by quaternization of these starting materials. A typical procedure involved mixing two moles of compounds **1**–**5** with one mole of α,ω-dibromoalkanes in $CHCl_3$ at reflux as shown in Scheme 5. Yields, melting points, surface and interfacial tensions of gemini surfactants **6**–**18** are given in Table 2. In comparison with amphiphiles **6**–**8**, aqueous 0.1% (w/w) solutions of amphiphiles **9**–**18** exhibit a strong reduction of surface tension at the air–water interface because of the presence of both perfluoroalkylated chains. The interfacial tensions between cyclohexane and water are also lowered compared with perfluoroalkylated single-chain surfactants, which generally show interfacial tension values around 4–6 mN m^{-1}. Otherwise the presence of both positively charged ammonium-type polar heads favours their solubility in water.

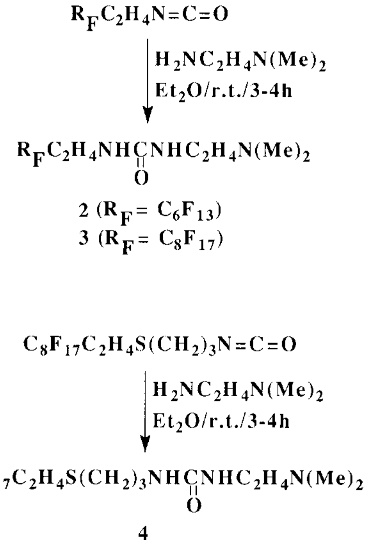


$$C_8H_{17}N{=}C{=}O\ \xrightarrow[Et_2O/r.t./3\text{-}4h]{H_2NC_2H_4N(Me)_2}\ C_8H_{17}NH\underset{O}{\overset{\|}{C}}NHC_2H_4N(Me)_2$$

1

Scheme 2 Preparation of *N*-octyl-*N*′-(2-dimethylaminoethyl)urea **1**.

Curves showing the variation of surface tension as a function of amphiphilic concentration are displayed in Figs 2–4. Each curve shows a break corresponding to a CMC around 0.1 mole l^{-1}, whatever the type and length of chain. Under normal conditions the three types of surfactants **6**–**8** (C_8H_{17}



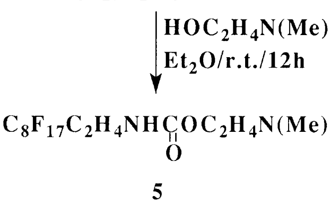
$$R_FC_2H_4N{=}C{=}O\ \xrightarrow[Et_2O/r.t./3\text{-}4h]{H_2NC_2H_4N(Me)_2}\ R_FC_2H_4NH\underset{O}{\overset{\|}{C}}NHC_2H_4N(Me)_2$$

2 (R_F = C_6F_{13})
3 (R_F = C_8F_{17})

$$C_8F_{17}C_2H_4S(CH_2)_3N{=}C{=}O\ \xrightarrow[Et_2O/r.t./3\text{-}4h]{H_2NC_2H_4N(Me)_2}\ C_8F_{17}C_2H_4S(CH_2)_3NH\underset{O}{\overset{\|}{C}}NHC_2H_4N(Me)_2$$

4

Scheme 3 Preparation of *N*-[2-(F-alkyl)ethyl]-*N*′-(2-dimethylaminoethyl)ureas **2**, **3** and *N*-{3′-[2-(F-octyl)ethylthio]propyl]}-*N*-(2-dimethylaminoethyl)urea **4**.



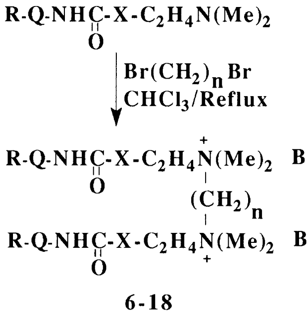
$$C_8F_{17}C_2H_4N{=}C{=}O\ \xrightarrow[Et_2O/r.t./12h]{HOC_2H_4N(Me)_2}\ C_8F_{17}C_2H_4NH\underset{O}{\overset{\|}{C}}OC_2H_4N(Me)_2$$

5

Scheme 4 Preparation of *N*-[2-(F-octyl)ethyl]-*O*-(2-dimethylaminoethyl)carbamate **5**.

Table 1 Yields and melting points of compounds **1**–**5**.

	R	Q	X	Yield/%	*F*/°C
1	C_8H_{17}	—	NH	81	76
2	$C_6F_{13}C_2H_4$	—	NH	85	54
3	$C_8F_{17}C_2H_4$	—	NH	87	62
4	$C_8F_{17}C_2H_4$	$-S(CH_2)_3-$	NH	68	58
5	$C_8F_{17}C_2H_4$	—	O	75	52



6-18

6-8: R = C_8H_{17}; X = NH; n = 3, 6, 12.
9-11: R = $C_6F_{13}C_2H_4$; X = NH; n = 3, 6, 12.
12-14: R = $C_8F_{17}C_2H_4$; X = NH; n = 3, 6, 12.
15,16: $C_8F_{17}C_2H_4$; Q = $-S(CH_2)_3-$; X = NH; n = 3, 6.
17,18: $C_8F_{17}C_2H_4$; X = O; n = 3, 6.

Scheme 5 Preparation of bisammonium gemini amphiphiles **6**–**18**.

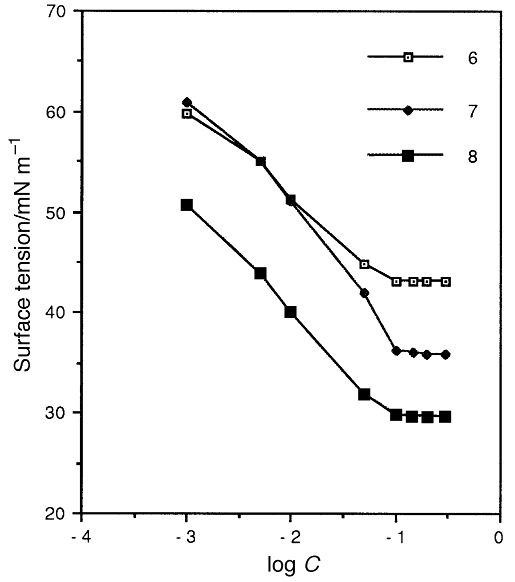


Fig. 2 Plot of surface tension as a function of the logarithm of the concentration (in mol L^{-1}) of gemini surfactants **6**–**8** in water at 20 °C.

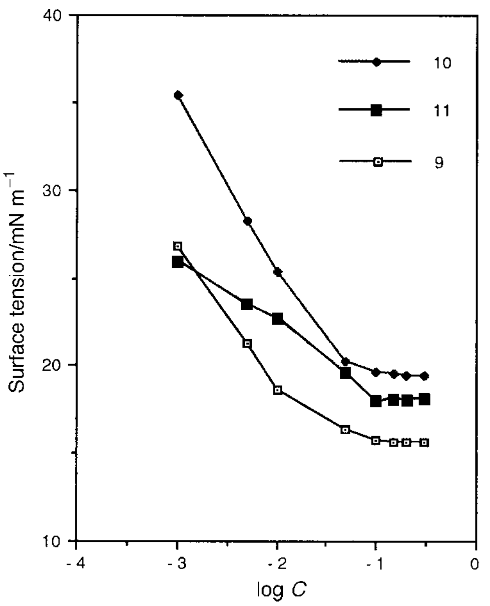


Fig. 3 Plot of surface tension as a function of the logarithm of the concentration (in mol L^{-1}) of gemini surfactants **9**–**11** in water at 20 °C.

chain), **9**–**11** (C_6F_{13} chain) and **12**–**14** (C_8F_{17} chain) should have shown widely differing CMCs in the order $C_8H_{17} < C_6F_{13} < C_8F_{17}$. This anomalous behaviour is probably due to the gemini surfactant's unique structure, but also to possible premicellization effects notably described by Menger and Littau.[7] The bisammonium gemini amphiphiles we prepared are characterized by a hydrocarbon spacer group composed of $n = 3$, 6 and 12 methylene groups. For all values of *n*, the surface tension values of gemini amphiphiles **6**–**8** with hydrocarbon chains are always higher than those of their perfluoroalkylated analogues **9**–**14**, as shown in Figs 2–4. The dependence of the surface activity on the structure of gemini amphiphiles **6**–**14** has been studied taking into consideration the length of the hydrocarbon spacer $(CH_2)_n$ and the length of the perfluoroalkylated chain. The conclusions drawn are that for the gemini amphiphiles **9**–**14** it is only the length of the spacer that seems to have some influence on the surface tension values while the length of the perfluoroalkyl chain has no effect. Table 2 shows that the lowest surface tension corresponds to bringing the polar heads closer together ($n = 3$: compounds **9** and **12**). Increasing the distance between the polar heads first leads to increasing surface tension values ($n = 6$: compounds **10** and **13**) but we then observe decreasing surface tension values ($n = 12$: compounds **11** and **14**). This

Table 2 Yields, melting points, surface and interfacial tensions of compounds **6**–**18**

	R	Q	X	*n*	Yield/%	*F*/°C	$\gamma_s{}^a$/mN m^{-1}	$\gamma_i{}^a$ mN m^{-1}
6	C_8H_{17}	—	NH	3	88	164	43.1	1.2
7	C_8H_{17}	—	NH	6	90	169	36.2	1.7
8	C_8H_{17}	—	NH	12	91	[b]	29.8	2.4
9	$C_6F_{13}C_2H_4$	—	NH	3	89	158	15.7	0.5
10	$C_6F_{13}C_2H_4$	—	NH	6	91	[c]	19.6	1.2
11	$C_6F_{13}C_2H_4$	—	NH	12	93	[b]	18.0	1.2
12	$C_8F_{17}C_2H_4$	—	NH	3	91	143	16.2	1.2
13	$C_8F_{17}C_2H_4$	—	NH	6	95	152	24.0	2.7
14	$C_8F_{17}C_2H_4$	—	NH	12	94	[c]	20.9	0.6
15	$C_8F_{17}C_2H_4$	$-S(CH_2)_3-$	NH	3	83	179	18.0	1.3
16	$C_8F_{17}C_2H_4$	$-S(CH_2)_3-$	NH	6	85	[c]	22.7	1.1
17	$C_8F_{17}C_2H_4$	—	O	3	81	146	26.1	4.0
18	$C_8F_{17}C_2H_4$	—	O	6	86	154	20.3	1.2

[a] Aqueous 0.1% (w/w) solution at 20 °C. [b] Product is a viscous liquid. [c] Product is a paste.

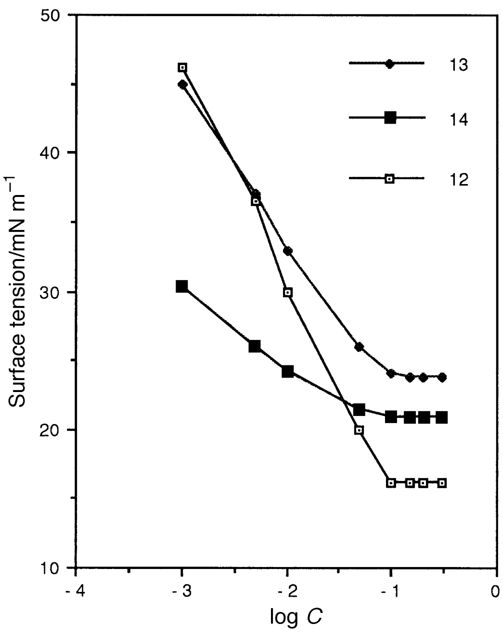


Fig. 4 Plot of surface tension as a function of the logarithm of the concentration (in mol L^{-1}) of gemini surfactants **12**–**14** in water at 20 °C.

phenomenon is probably due to the progressive penetration of the spacer into the micelle hydrophilic core as the spacer length increases. There are conformation changes of the amphiphiles in a way that the hydrocarbon spacer adds to the hydrophobicity of the perfluoroalkylated chains, leading to lower surface tension values. These results are in accordance with those found by Devinsky *et al.*[4] who noticed that in the structure of hydrocarbon gemini surfactants, increasing the length of the hydrocarbon chain spacer accompanies an increase in the hydrophobicity. When the spacer is short ($n < 10$) the linking chain remains in contact with water; when the spacer is longer ($n > 10$) the more flexible linking chain has a tendency to enter inside the micelle in order to minimize its contact with water, thus adopting a "wicket-like" or a loop-like conformation at the air–water interface

Experimental

General

Melting points determined on a Büchi apparatus are uncorrected. IR: Brucker IFS 45. NMR: Brucker WH200 (200 and 84.67 MHz for ^{1}H and ^{19}F, respectively). For ^{1}H NMR, $CDCl_3$ or CD_3OD as solvent, TMS as internal standard; for ^{19}F NMR, $CDCl_3$ or CD_3OD as solvent, $CFCl_3$ as internal standard. MS: Nermag-Ribermag R 10-10C (70 eV). Elemental analyses were performed by the CNRS central facilities in Vernaison (France).

Surface tension measurements (γ_s) were performed by an automatic digital tensiometer Krüss K10T employing the Wilhelmy vertical plate technique. The solution contained 0.1% (w/w) of amphiphile in deionized water and was measured at 20.0 ± 0.1 °C. Interfacial tensions (γ_i) of the amphiphilic solutions were determined towards cyclohexane solutions by the same technique at 20.0 ± 0.1 °C

Octyl isocyanate, 2-dimethylaminoethylamine, 2-dimethylaminoethanol, diethylether, chloroform, 1,3-dibromopropane, 1,6-dibromohexane and 1,12-dibromododecane were purchased from Aldrich Chemical Co. and used as received.

Syntheses

N-Octyl-N'-(2-dimethylaminoethyl)urea (1). To a solution of 0.88 g (10^{-2} mol) of 2-dimethylaminoethylamine in 15 ml of anhydrous diethylether, 1.55 g (10^{-2} mol) of octyl isocyanate is added dropwise at room temperature (the addition must be performed very slowly because the reaction is rapid and exothermic). The mixture is stirred at room temperature for 3–4 h. The end of the reaction is monitored by GC or TLC. The solvent is evaporated and the residue obtained is abundantly washed with petroleum ether, filtrated and dried. Yield: 1.97 g (81%), mp 76 °C. IR (KBr): $\nu = 3317$–3326 cm^{-1} (N—H), 2925–2852 (C—H), 1621–1583 (C=O). ^{1}H NMR ($CDCl_3$)/TMS): $\delta = 5.50$ [s, 1H, —CONH—], 5.40 [s, 1H, —NHCO—], 3.20 [q, 2H, —NHCH_2—], 3.10 [q, 2H, —CH_2NH—], 2.40 [t, 2H, —CH_2N(CH_3)$_2$], 2.20 [s, 6H, —N(CH_3)$_2$], 1.30 (s, 10H, CH_3(CH_2)$_5$$CH_2CH_2$NHCO—], 0.85 (t, 3H, C$H_3$($CH_2$)$_5$$CH_2CH_2$NHCO—]. Anal. $C_{13}H_{29}N_{30}$ (243.39): calcd C 64.15, H 12.01, N 17.26; found C 34.08, H 12.13, N 17.29

N-[2-(F-Hexyl)ethyl]-N'-(2-dimethylaminoethyl)urea(2). The same procedure described above is applied to a mixture of 3.89 g (10^{-2} mol) of 2-(F-hexyl)ethyl isocyanate and 0.88 g (10^{-2} mol) of dimethylaminoethylamine. Yield: 4 g (85%), mp 54 °C. IR (KBr): $\nu = 3360$ cm^{-1} (N—H), 2951–2866 (C—H), 1638–1563 (C=O), 1300–1100 (C—F). ^{1}H NMR ($CDCl_3$/TMS): $\delta = 6.4$ [t, 1H, —NHCO—], 5.80 [t, 1H, —CONH—], 3.65 [q, 2H, —CH_2NH—], 3.30 [q, 2H, —NHCH_2—], 2.55 [t, 2H, —CH_2N(CH_3)$_2$], 2.45 [m, 8H, —CH_2N(CH_3)$_2$ and C_6F_{13}CH_2]. ^{19}F NMR ($CDCl_3$/$CFCl_3$): $\delta = -81.3$ [m, 3F, CF_3], −114.1 [m, 2F, CF_2], −122.4 [m, 2F, CF_2], −123.3 [m, 2F, CF_2], −124.2 [m, 2F, CF_2], −126.7 [m, 2F, CF_2]. Anal. $C_{13}H_{16}F_{13}N_3O$ (477.27): calcd C 32.72, H 3.38, F 51.75, N 8.80; found C 32.81, H 3.49, F 51.83, N 8.84.

N-[2-(F-Octyl)ethyl]N'-(2-dimethylaminoethyl)urea (3). The same procedure used for compound **1** is applied to a mixture of 4.89 g (10^{-2} mol) of 2-(F-octyl)ethyl isocyanate and 0.88 g (10^{-2} mol) of 2-dimethylaminoethylamine. Yield: 5 g (87%), mp 62 °C. IR (KBr): $\nu = 3338$ cm^{-1} (N—H), 2980–2947 (C—H), 1636–1560 (C=O), 1300–1100 (C—F). ^{1}H NMR ($CDCl_3$/TMS): $\delta = 6.30$ [t, (H, —NHCO—], 5.75 [t, 1H, —CONH—], 3.70 [q, 2H, —CH_2NH—], 3.27 [q, 2H, —NHCH_2—], 2.60 [t, 2H, —CH_2N(CH_3)$_2$], 2.51 [m, 8H, —CH_2N(CH_3)$_2$ and C_8F_{17}CH_2—]. ^{19}F NMR ($CDCl_3$/$CFCl_3$): $\delta = -81.4$ (m, 3F, CF_3), −114.2 (m, 2F, CF_2), −122.5 (m, 8F, 4CF_2), −123.5 (m, 2F, CF_2), −126.8 (m, 2F, CF_2). Anal. $C_{15}H_{16}F_{17}N_3O$ (577.28): calcd C 31.21, H 2.79, F 55.95, N 7.28, found C 31.28, H 2.90, F 56.40, N 7.33.

N-{3′-[2-(F-Octyl)ethylthio]propyl}-N'-(2-dimethylaminoethyl)urea (4). The same procedure described above is used with 0.88 g (10^{-2} mol) of 2-dimethylaminoethylamine and 5.63 g (10^{-2} mol) of 3′-[2-(F-octyl)ethylthio]propyl isocyanate. Yield: 4.36 g (68%), mp 58 °C. IR (KBr): $\nu = 3340$ cm^{-1} (N—H), 2978–2948 (C—H), 1638–1568 (C=O), 1300–1100 (C—F). ^{1}H NMR ($CDCl_3$/TMS): $\delta = 5.80$–5.20 [d, 2H, —NHCO—], 3.30 [m, 4H, —CH_2NH— and —NHCH_2—], 2.75 [t, 2H, —CH_2S—], 2.65 [t, 2H, —SCH_2], 2.45 [m, 4H, C_8F_{17}CH_2— and —CH_2N(CH_3)$_2$], 2.25 [s, 6H, —N(CH_3)$_2$], 1.80 [m, 2H, —SCH_2C$H_2$$CH_2$—]. ^{19}F NMR ($CDCl_3$/$CFCl_3$): $\delta = -81.3$ (m, 3F, CF_3), −114.9 (m, 2F, CF_2), −122.4 (m, 8F, 4CF_2), −123.8 (m, 2F, CF_2), −126.7 (m, 2F, CF_2). MS (70 eV) m/z (%): 652 (6) $[M + 1]^+$, 651 (1) $[M]^+$ 607 (3), 581 (3), 521

(3), 507 (2), 493 (5), 204 (16), 115 (16), 131 (4), 72 (7), 58 (100).

***N*-[2-(F-Octyl)ethyl]-*O*-(2-dimethylaminoethyl)carbamate (5).** The synthesis is performed as described above with 0.89 g (10^{-2} mol) of 2-(dimethylamino)ethanol and 4.89 g (10^{-2} mol) of 2-(F-octyl)ethyl isocyanate. Yield: 3.67 g (75%), mp 52 °C. IR (KBr): $\nu = 3366\ \mathrm{cm}^{-1}$ (N—H), 2975–2951 (C—H), 1702–1540 (C═O), 1300–1100 (C—F). ^{1}H NMR ($\mathrm{CDCl_3}$/TMS): $\delta = 5.25$ [s, 1H, $-\mathrm{N}H\mathrm{CO}-$], 4.20 [t, 2H, $-\mathrm{OC}H_2-$], 3.50 q, 2H, $-\mathrm{C}H_2\mathrm{NH}-$], 2.50 [t, 2H, $-\mathrm{C}H_2\mathrm{N(CH_3)_2}$], 2.25 (m, 8H, $\mathrm{C_8F_{17}C}H_2-$ and $-\mathrm{N(C}H_3)_2$]. ^{19}F NMR ($\mathrm{CDCl_3/CFCl_3}$): $\delta = -81.4$ (m, 3F, $\mathrm{CF_3}$), -114.7 (m, 2F, $\mathrm{CF_2}$), -122.5 (m, 8F, $4\mathrm{CF_2}$), -123.8 (m, 2F, $\mathrm{CF_2}$), -126.7 (m, 2F, $\mathrm{CF_2}$). Anal. $\mathrm{C_{15}H_{15}F_{17}N_2O_2}$ (578.27): calcd C 31.16, H 2.61, F 55.85, N 4.84; found C 31.22, H 2.72, F 55.93, N 4.87.

Bisammonium gemini amphiphile 7. To a solution of 4.86 g (2×10^{-2} mol) of urea **1** in $\mathrm{CHCl_3}$, is added 2.44 g (10^{-2} mol) of 1,6-dibromohexane. The mixture is heated at reflux for between 36 and 48 h. When the temperature has cooled to room temperature, an excess of diethylether is poured into the solution in order to precipitate the bisammonium compound. After 1 h of stirring at room temperature the solvent is removed by filtration; the residue obtained is washed with diethylether and dried. Yield: 6.57 g (90%), mp 169 °C. IR (KBr): $\nu = 3364\ \mathrm{cm}^{-1}$ (N—H), 2931–2851 (C—H), 1642–1563 (C═O). ^{1}H NMR ($\mathrm{CDCl_3}$/TMS): $\delta = 6.75$ [s, 2H, $2(-\mathrm{CON}H-)$], 5.95 [s, 2H, $2(-\mathrm{N}H\mathrm{CO}-)$], 3.55 [m, 8H, $2(-\mathrm{C}H_2\mathrm{NHCONH\text{-}C}H_2-)$], 3.35 [m, 4H, $2(-\mathrm{CONHCH_2\text{-}C}H_2\mathrm{N}-)$], 3.25 {s, 12H, $2[-\mathrm{N(C}H_3)_2]$}, 2.95 [m, 4H, $-\mathrm{NC}H_2\mathrm{(CH_2)_4C}H_2\mathrm{N}-$], 1.80 [m, 4H, $\mathrm{NCH_2C}H_2\mathrm{(CH_2)_2\text{-}C}H_2\mathrm{CH_2N}-$], 1.35 [m, 4H, $-\mathrm{N(CH_2)_2C}H_2\mathrm{C}H_2\mathrm{(CH_2)_2N}-$], 1.15 {m, 20H, $2[\mathrm{CH_3(C}H_2)_5\mathrm{CH_2CH_2NHCO}]$}, 0.80 {t, 6H, $2[\mathrm{C}H_3\mathrm{(CH_2)_5CH_2CH_2NHCO}]$}. MS (70 eV) *m*/*z* (%): 649 (40) $[\mathrm{M-Br}]^{+}$.

Bisammonium gemini amphiphile 11. The same procedure used for compound **7** is applied to a mixture of 9.54 g (2×10^{-2} mol) of urea **2** and 3.28 g (10^{-2} mol) of 1,12-dibromododecane. Yield: 11.92 g of a viscous liquid (93%). IR (KBr): $\nu = 3322\ \mathrm{cm}^{-1}$ (N—H), 2953–2858 (C—H), 1664–1564 (C═O), 1300–1100 (C—F). ^{1}H NMR ($\mathrm{CDCl_3}$/TMS): $\delta = 7.00$ (t, 2H, $2(-\mathrm{N}H\mathrm{CO}-)$], 6.35 [t, 2H, $2(-\mathrm{CON}H-)$], 3.40 [m, 8H, 2 $(-\mathrm{CONHC}H_2\mathrm{C}H_2\mathrm{N}-)$], 3.20 {m, 16H, $2[-\mathrm{N(C}H_3)_2]$ and $-\mathrm{NC}H_2\mathrm{(CH_2)_{10}C}H_2\mathrm{N}-$}, 2.30 [m, 4H, $2(\mathrm{C_6F_{13}\text{-}C}H_2-)$], 1.70 [m, 4H, $-\mathrm{NCH_2C}H_2\mathrm{(CH_2)_8C}H_2\mathrm{CH_2N}-$], 1.40–1.10 [m, 16H, $-\mathrm{NCH_2CH_2(C}H_2)_8\mathrm{CH_2CH_2N}-$]. ^{19}F NMR ($\mathrm{CDCl_3/CFCl_3}$): $\delta = -81.3$ (m, 6F, $2\mathrm{CF_3}$), -114.8 (m, 4F, $2\mathrm{CF_2}$), -122.6 (m, 4F, $2\mathrm{CF_2}$), -123.6 (m, 4F $2\mathrm{CF_2}$), -124.2 (m, 4F, $2\mathrm{CF_2}$), -126.7 (m, 4F, $2\mathrm{CF_2}$).

Bisammonium gemini amphiphile 13. The same procedure described previously is applied to a mixture of 11.54 g (2×10^{-2} mol) of urea **3** and 2.44 g (10^{-2} mol) of 1,6-dibromohexane. Yield: 13.28 g (95%), mp 152 °C. IR (KBr): $\nu = 3398\text{–}3288\ \mathrm{cm}^{-1}$ (N—H), 2953–2851 (C—H), 1638–1578 (C═O), 1300–1100 (C—F). ^{1}H NMR ($\mathrm{CD_3OD}$/TMS): $\delta = 4.90$ [s, 4H, $2(-\mathrm{N}H\mathrm{CON}H-)$], 3.65 [t, 4H, $2(-\mathrm{C}H_2\mathrm{NHCONH}-)$], 3.55–3.40 {m, 12H, $2[-\mathrm{CONHC}H_2\text{-}\mathrm{C}H_2\mathrm{N}-]$ and $[-\mathrm{NC}H_2\mathrm{(CH_2)_4C}H_2\mathrm{N}-]$}, 3.20 {s, 12H, $2[(-\mathrm{N(C}H_3)_2]$}, 2.40 [m, 4H, $2(\mathrm{C_8F_{17}C}H_2-)$], 1.90 {m, 4H, $[-\mathrm{NCH_2C}H_2\mathrm{(CH_2)_2CH_2C}H_2\mathrm{N}-]$}, 1.50 {m, 4H, $[-\mathrm{N(CH_2)_2C}H_2\mathrm{C}H_2\mathrm{(CH_2)_2N}-]$}. ^{19}F NMR ($\mathrm{CD_3OD/CFCl_3}$): $\delta = -81.0$ (m, 6F, $2\mathrm{CF_3}$), -113.9 (m, 4F, $2\mathrm{CF_2}$), -121.6 (m, 12F, $6\mathrm{CF_2}$), -122.4 (m, 4F, $2\mathrm{CF_2}$), -123.3 (m, 4F, $2\mathrm{CF_2}$), -125.9 (m, 4F, $2\mathrm{CF_2}$), MS (70 eV) *m*/*z* (%): 1203 (18) $[\mathrm{M-Br}]^{+}$.

Bisammonium gemini amphiphile 15. The same procedure described previously is applied to a mixture of 12.82 g (2×10^{-2} mol) of urea **4** and 2 g (10^{-2} mol) of 1,3-dibromopropane. Yield: 12.32 g (83%), mp 179 °C. IR (KBr): $\nu = 3380\ \mathrm{cm}^{-1}$ (N—H), 2931–2851 (C—H), 1654–1560 (C═O), 1300–1100 (C—F). ^{1}H NMR ($\mathrm{CD_3OD}$/TMS): $\delta = 3.65$ [s, 4H, $2(-\mathrm{N}H\mathrm{CON}H-)$], 3.60–3.40 [q, 8H, $2(-\mathrm{C}H_2\mathrm{NHCONH\text{-}C}H_2-)$], 3.30 [m, 4H, $-\mathrm{C}H_2\mathrm{N(CH_2)_3NC}H_2-$], 3.25 {s, 12H, $2[-\mathrm{N(C}H_3)_2]$}, 3.20 (t, 4H, $\mathrm{NC}H_2\mathrm{CH_2C}H_2\mathrm{N}-$), 2.75 [t, 4H, $2(-\mathrm{C}H_2\mathrm{S}-)$], 2.60 [t, 4H, $2(-\mathrm{SC}H_2-)$], 2.45 [m, 6H, $2(\mathrm{C_8F_{17}C}H_2-)$ and $(-\mathrm{NCH_2C}H_2\mathrm{CH_2N}-)$], 1.75 [q, 4H, $2(-\mathrm{SCH_2C}H_2\mathrm{CH_2NHCO}-)$]. ^{19}F NMR ($\mathrm{CD_3OD/CFCl_3}$): $\delta = -81.0$ (m, 6F, $2\mathrm{CF_3}$), -114.1 (m, 4F, $2\mathrm{CF_2}$), -121.5 (m, 12F, $6\mathrm{CF_2}$), -122.4 (m, 4F, $2\mathrm{CF_2}$), -123.0 (m, 4F, $2\mathrm{CF_2}$, -126.0 (m, 4F, $2\mathrm{CF_2}$). MS (70 eV) *m*/*z* (%): 1319 (18) $[\mathrm{M-Br}]^{+}$.

Bisammonium gemini amphiphile 17. The same procedure described previously is applied to a mixture of 11.56 g (2×10^{-2} mol) of urea **5** and 2 g (10^{-2} mol) of 1,3-dibromopropane. Yield 11 g (81%), mp 146 °C. IR (KBr): $\nu = 3399\ \mathrm{cm}^{-1}$ (N—H), 2960–2851 (C—H), 1715–1578 (C═O), 1300–1100 (C—F). ^{1}H NMR ($\mathrm{CD_3OD}$/TMS): $\delta = 4.90$ [t, 2H, $2(-\mathrm{N}H\mathrm{COO}-)$], 4.45 [m, 4H, $2(-\mathrm{C}H_2\mathrm{NHCOO}-)$], 3.45 [t, 4H, $2(-\mathrm{COOCH_2C}H_2\mathrm{N}-)$], 3.40 [t, 4H, $-\mathrm{NHC}H_2\text{-}\mathrm{CH_2C}H_2\mathrm{N}-$], 3.15 {s, 12H, $2[-\mathrm{N(C}H_3)_2]$}, 2.40 [m, 6H, $2(\mathrm{C_8F_{17}C}H_2-)$ and $(-\mathrm{NCH_2C}H_2\mathrm{CH_2N}-]$}. ^{19}F NMR ($\mathrm{CD_3OD/CFCl_3}$): $\delta = -82.0$ (m, 6F, $2\mathrm{CF_3}$), -115.1 (m, 4F, $2\mathrm{CF_2}$), -123.1 (m, 12F, $6\mathrm{CF_2}$), -124.0 (m, 4F, $2\mathrm{CF_2}$), -123.3 (m, 4F, $2\mathrm{CF_2}$), -124.9 (m, 4F, $2\mathrm{CF_2}$), -127.5 (m, 4F, $2\mathrm{CF_2}$). MS (70 eV) *m*/*z* (%): 1279 (40) $[\mathrm{M-Br}]^{+}$.

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