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Perfluoroalkyl Epoxides: Synthesis and Conversion into Ionic Surfactants

Abdelhamid Ayari, Henda Mekni, Najeh Grayaa Jaoued and Ahmed Hedhli*

Université de Tunis, Laboratoire de Chimie Moléculaire Organique, Ecole Supérieure des Sciences et Techniques de Tunis, 5, avenue Taha Hussein, Montfleury, 1089 Tunis, Tunisia

Abstract: Perfluoroalkylated surfactants having a quaternary ammonium surrounded by three hydroxyl groups as hydrophilic moiety and a perfluoroalkyl chain as tail were obtained by coupling diethanolamine with perfluoroalkylated epoxide followed by quaternisation. The amphiphilic properties of these surfactants were investigated by measuring their surface and interfacial tensions.

Keywords: Surfactant, Fluorine, Diethanolamine, Epoxide, Surface tension.

Introduction

It is quite known that single tail fluorinated surfactants having one polar head perform higher stability and lower surface tension, better than their hydrocarbon homologues[1] and have extensive potential applications.

In connection with our interest in surfactants design and properties improvement, we have reported about the structure-properties relationship of some fluorinated surfactants.[2-4] We noted then the necessity to make these molecules more hydrophilic[5] to obtain better performance in aqueous solution. Thus, we describe herein the synthesis of new ionic perfluoroalkyl surfactants via perfluoroalkyl epoxide as a key intermediate.

Results and Discussion

As shown in scheme 1, preparation of surfactant **4** involves three steps, (i) epoxide preparation, (ii) coupling of epoxide with diethanolamine and (iii) quaternisation of the tertiary amine.

Epoxide preparation:

Epoxides **2** were prepared from the corresponding fluorinated alcohol or thiol using phase transfer catalysis (PTC) technique[6] (scheme 1). The reaction was solvent-free and the excess of epichlorohydrin was recovered under vacuum.

Surfactant preparation:

Aminolysis of epoxides to β-aminoalcohols under mild and neutral conditions is very important in modern synthesis. However, standard methods for nucleophilic opening of epoxides are not always satisfactory and suffer from disadvantages such as unsatisfactory, regioselectivity,[7-13] non catalytic nature of the reagent[14] and long reaction time.[13]

**Corresponding author:*
E-mail address: ahmed.hedhli@esstt.rnu.tn
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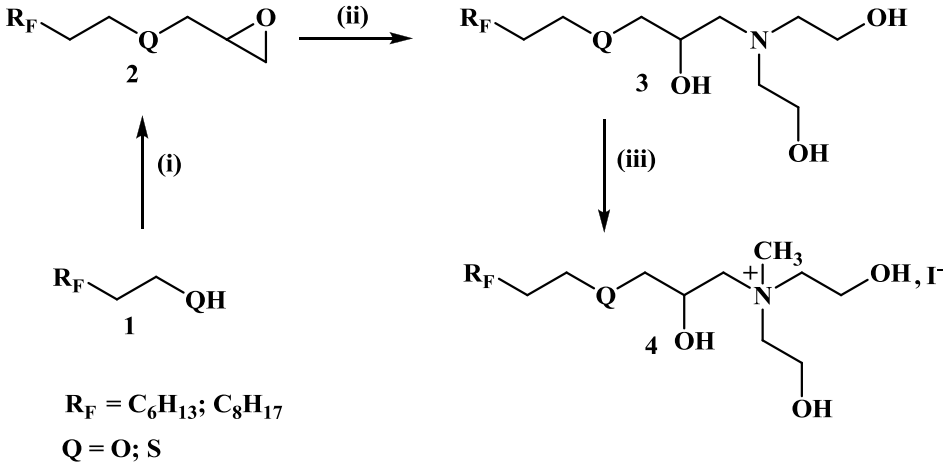
Oxiranic bridge opening of perfluoroalkylated epoxides with alkylamines[14-19] or ammonia[20, 21] is described in literature as regioselective reaction. The presence of perfluoroalkyl group is assumed to enhance regioselectivity in such reaction.

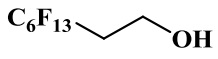
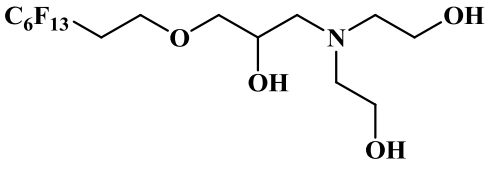
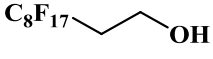
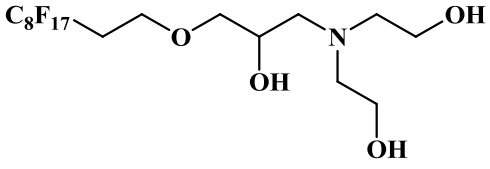
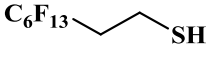
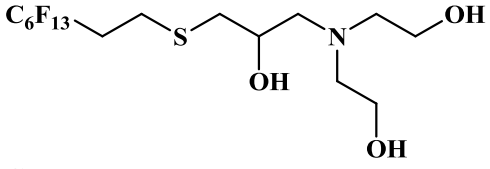
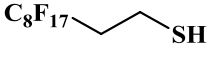
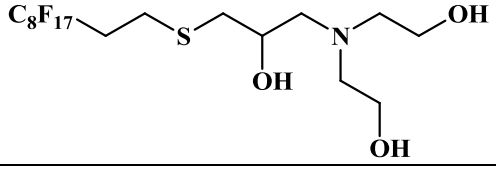


(i) Epichlorohydrin, NaOH/PTC; (ii) diethanolamine, 80°C, 48 h; (iii) CH_3I, 40°C, 24 h.

Scheme 1

When the perfluoroalkylated epoxides **2** are submitted to diethanolamine action, aminoalcohols **3** are obtained regioselectively as shown in scheme 1. The quaternisation[5,22] of compounds **3** with methyl iodide leads to surfactants **4** in good yields (scheme 1).
The obtained aminoalcohols **3** are outlined in table I.

Table I: Aminoalcohols **3** prepared

Alcohol/thiol **1**		Aminoalcohol* **3**		Overall yield (%)
	**1a**		**3a**	66
	**1b**		**3b**	72
	**1c**		**3c**	62
	**1d**		**3d**	70

*Viscous oil

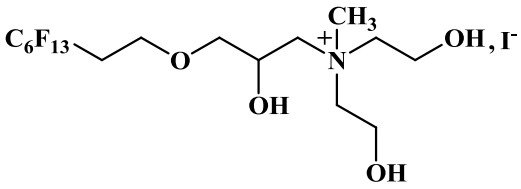
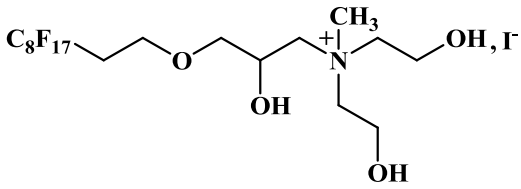
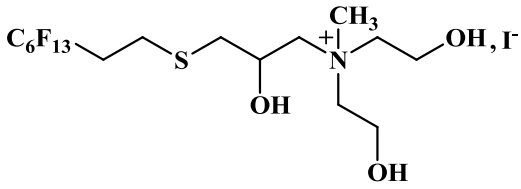
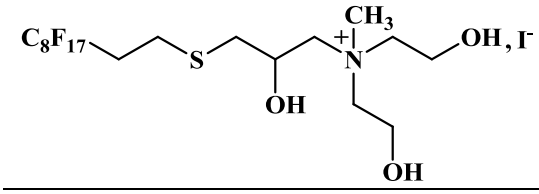
Surface and interfacial tensions of surfactants **4** have been measured by the Wilhelmey plate method and collected in Table II.

Surfactants **4** properties:

Surfactants **4** possess three hydroxyl and a quaternary ammonium groups which provide an improved hydrophilicity to the polar head. On the other hand, the hydrophobic tail and polar head are attached by Q, which constitutes an ether or thioether bridge when Q is respectively an oxygen or sulphur atom.

According to literature,[23] surface and interfacial tensions γ_s tension γ_i decrease as the perfluoroalkyl chain length increases and this, independently of Q. However, thio-surfactants (Q = S) exhibit lower surface tension when compared to those having an ether unit. Actually, a sulphur atom inserted within the hydrophobic chain of a surfactant is usually considered as a hydrophobic unit. Sulfide group might be considered as a methylene regarding its behaviour in aqueous media. Evidence for this assertion comes from the unfavourable affinity toward water of sulfur atom owing to its poor hydrogen bond accepter properties[24] and the Hansch partition constant between octanol and water for $–SCH_3$ which favours octanol (π = 0.45), whereas the constant for $–OCH_3$ favours water (π = -0.47).[25] So, in thio-surfactants **4b** and **c**, it is as if the hydrophobic chain was longer by a methylene and this asserts the lowering of the surface tension. Such observations were already reported by Menger et *al*.[26] and Pucci et *al*.[27]

Table II: surfactants **4** prepared

Surfactant[a] **4**		Yield (%)	γ_s (mN.m^{-1})	γ_i[b] (mN.m^{1})
	**4a**	90	18.7	9.5
	**4b**	90	18.4	7.2
	**4c**	91	18.3	9.6
	**4d**	95	18.0	6.9

[a] Viscous oil

[b] Cyclohexane/Water

Conclusion

In this work, a series of highly fluorinated ionic surfactants was prepared from the corresponding epoxides and then characterized. The surface activity of these new amphiphiles in aqueous solutions has been investigated from surface and interface tensions measurements. Articulation of the hydrophilic/hydrophobic system around the heteroatom link was considered with O and S atoms.

Experimental Section

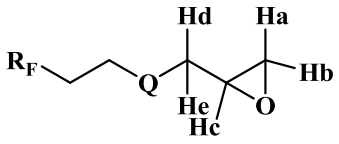
Materials

IR spectra were recorded on a Bruker IFS 66v/s. ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded on a Bruker AC 300 spectrometer (300 MHz proton, 282 MHz fluorine, 75 MHz carbon). All spectra were obtained using $CDCl_3$ or CD_3OD as solvent and referenced to TMS for ^{1}H, ^{13}C NMR and $CFCl_3$ for ^{19}F NMR. The following abbreviations are used to denote multiplicity of the signals in the NMR spectra; s, singlet; d, doublet; t, triplet; dd, doublet of doublets; m, multiplet. Analytical TLC was conducted using percolated aluminium TLC plates: silica gel/UV 254. Column chromatography was carried out with silica gel (ACROS 0.035-0.07 mm) γ_s and γ_i were measured by the Wolhemey plate method using 0.1% (m/v) aqueous solution.

Epoxide **2** preparation: General procedure

In a 100 mL three necked round-bottomed flask equipped with a mechanical stirrer was introduced sodium hydroxide (7.5 g) dissolved in water (7.5 mL), tetrabutylammonium hydrogensulfate 0.51 g (1.5 mmol) and epichlorohydrin (7.5 mL). Fluorinated alcohol (or thiol) (15 mmol) was added dropwise at 0°C for 15 mn, the mixture was then stirred at room temperature for 7h (TLC, eluent: petroleum ether/chloroform, 70/30). The mixture was poured into ice water (30 mL) and extracted with diethyl ether (3x30 mL). The combined organic layer was washed with water and dried over anhydrous Na_2SO_4. Solvent was removed and the excess of epichlorohydrin was recovered under vacuum. The residue was distilled at reduced pressure to give the corresponding epoxide **2**.

Epoxide **2a**: bp: 68/0.50 (°C/mmHg), yield: 74%
Epoxide **2b**: bp: 72/0.30 (°C/mmHg), yield: 77%
Epoxide **2c**: bp: 58/0.15 (°C/mmHg), yield: 75%
Epoxide **2d**: bp: 88/0.35 (°C/mmHg), yield: 76%



R_F = C_6H_{13}; C_8H_{17}

Q = O; S

Structure of compound 2:

Epoxide (**2a)**: IR (cm^{-1}) $\nu_{C\text{-}O\text{-}C}$ = 712, $\nu_{C\text{-}F}$ = 1140-1197. ^{1}H NMR (CD_3OD/TMS) δ (ppm): 2.43 (m, 2H, $OCH_2C\underline{H}_2C_6F_{13}$), 2.61 (dd, 1H, Ha, $^{3}J_{HaHc}$ = 2.94 Hz, $^{2}J_{HaHb}$ = 4.95 Hz), 2.80 (m,

1H, Hb), 3.16 (m, 1H, Hc), 3,35 (dd, 1H, He, $^3J_{HeHc}$ = 5.88 Hz, $^2J_{HeHd}$ = 11.77 Hz), 3.82 (m, 3H, He and $OC\underline{H}_2CH_2C_6F_{13}$). ^{13}C-{^{1}H} NMR δ (ppm): 31.6 (t, 1C, $OCH_2\underline{C}H_2C_6F_{13}$, $^2J_{CF}$= 21.58 Hz), 44.02 (s, 1C, $OCH_2CHO\underline{C}H_2$), 50.51 (s, 1C, $OCH_2\underline{C}HOCH_2$), 63.23 (s, 1C, $O\underline{C}H_2CH_2C_6F_{13}$, $^3J_{CF}$= 4.58 Hz), 71.34 (s, 1C, $O\underline{C}H_2CHOCH_2$), 110.93-129 (m, 6C, C_6F_{13}). ^{19}F NMR ($CD_3OD/CFCl_3$) δ (ppm): -82.15 (m, 3F, CF_3, $^3J_{FF}$= 9.73 Hz), -114.62 (m, 2F, $CF_{2\alpha}$), -123.08 (m, 2F, $CF_{2\beta}$), -124.08 (m, 2F, $CF_{2\gamma}$), -124.85 (m, 2F, $CF_{2\delta}$), -127.4 (m, 2F, $CF_{2\omega}$).

Epoxide (**2b)**: IR (cm^{-1}) $\nu_{C\text{-}O\text{-}C}$ = 714, $\nu_{C\text{-}F}$ = 1145-1204. ^{1}H NMR (CD_3OD/TMS) δ (ppm): 2.43 (m, 2H, $OCH_2C\underline{H}_2C_8F_{17}$), 2.61 (dd, 1H, Ha, $^3J_{HaHc}$ = 21.28 Hz, $^2J_{HaHb}$ = 4.78 Hz), 2.8 (m, 1H, Hb), 3,38 (dd, 1H, He, $^3J_{HeHc}$ = 5.88 Hz, $^2J_{HeHd}$ = 11.76 Hz), 3.78 (m, 3H, He and $OCH_2C\underline{H}_2C_8F_{17}$). ^{13}C-{^{1}H} NMR δ (ppm): 31.35 (t, 1C, $OCH_2\underline{C}H_2C_8F_{17}$, $^2J_{CF}$= 21.28 Hz), 43.73 (s, 1C, $OCH_2CHO\underline{C}H_2$), 50.26 (s, 1C, $OCH_2\underline{C}HOCH_2$), 62.99 (s, 1C, $O\underline{C}H_2CH_2C_8F_{17}$, $^2J_{CF}$= 4.60 Hz), 70.91 (s, 1C, $O\underline{C}H_2CHOCH_2$), 107.96-129.40 (m, 8C, C_8F_{17}). ^{19}F NMR ($CD_3OD/CFCl_3$) δ (ppm): -82.05 (m, 3F, CF_3), -114.55 (m, 2F, $CF_{2\alpha}$), -114.06 (m, 6F, $CF_{2\beta}$, $CF_{2\gamma}$, $CF_{2\delta}$), -123.9 (m, 2F, $CF_{2\varepsilon}$), -124.8 (m, 2F, $CF_{2\xi}$), -127.35 (.m, 2F, $CF_{2\omega}$).

Epoxide (**2c)**: IR (cm^{-1}) $\nu_{C\text{-}O\text{-}C}$ = 708, $\nu_{C\text{-}F}$ = 1143-1197. ^{1}H NMR (CD_3OD/TMS) δ (ppm): 2.43 (m, 2H, $SCH_2C\underline{H}_2C_6F_{13}$), 2.62 (m, 2H, Ha and Hb), 2.70 (m, 1H, Hd,), 2.84 (m, 3H, $SCH_2C\underline{H}_2C_6F_{13}$ and He), 3.16 (m, 1H, Hc). ^{13}C-{^{1}H} NMR δ (ppm): 23.18 (t, 1C, $S\underline{C}H_2CH_2C_6F_{13}$, $^3J_{CF}$= 4.63 Hz), 32.35 (t, 1C, $SCH_2\underline{C}H_2C_6F_{13}$, $^2J_{CF}$= 21.88 Hz), 34.67 (s, 1C, $S\underline{C}H_2CHOCH_2$), 46.56 (s, 1C, $SCH_2CHO\underline{C}H_2$), 51.88 (s, 1C, $SCH_2\underline{C}HOCH_2$), 121.07 (m, 6C, C_6F_{13}). ^{19}F NMR ($CD_3OD/CFCl_3$) δ (ppm): -82.19 (m, 3F, CF_3, $^3J_{FF}$= 9.89 Hz), -115.56 (m, 2F, $CF_{2\alpha}$), -123.10 (m, 2F, $CF_{2\beta}$), -124.09 (m, 2F, $CF_{2\gamma}$), -124.59 (m, 2F, $CF_{2\delta}$), -127.42 (m, 2F, $CF_{2\omega}$).

Epoxide (**2c)**: IR (cm^{-1}) $\nu_{C\text{-}O\text{-}C}$ = 716, $\nu_{C\text{-}F}$ = 1147-1204. ^{1}H NMR (CD_3OD/TMS) δ (ppm): 2.43 (m, 2H, $SCH_2C\underline{H}_2C_8F_{17}$), 2.68 (m, 2H, Ha and Hb), 2.78 (m, 1H, Hd,), 3.14 (m, 3H, $SCH_2C\underline{H}_2C_8F_{17}$ and He), 3.78 (m, 1H, Hc). ^{13}C-{^{1}H} NMR δ (ppm): 22.98 (t, 1C, $S\underline{C}H_2CH_2C_8F_{17}$, $^3J_{CF}$= 5.14 Hz), 32.15 (t, 1C, $SCH_2\underline{C}H_2C_8F_{17}$, $^2J_{CF}$= 22.64 Hz), 34.47 (s, 1C, $S\underline{C}H_2CHOCH_2$), 46.34 (s, 1C, $SCH_2CHO\underline{C}H_2$), 51.67 (s, 1C, $SCH_2\underline{C}HOCH_2$), 106.61-129.56 (m, 8C, C_8F_{17}). ^{19}F NMR ($CD_3OD/CFCl_3$) δ (ppm): -82.29 (m, 3F, CF_3, $^3J_{FF}$= 9.93 Hz), -115.64 (m, 2F, $CF_{2\alpha}$), -123.01 (m, 6F, $CF_{2\beta}$, $CF_{2\gamma}$, $CF_{2\delta}$), -124.06 (m, 2F, $CF_{2\varepsilon}$), -124.63 (m, 2F, $CF_{2\xi}$), -127.52 (m, 2F, $CF_{2\omega}$).

Aminoalcohol 3 preparation: General procedure

In a 100 mL round-bottomed flask equipped with a reflux condenser and a drying tube, a mixture of perfluoroalkylated epoxide **2** (1 equiv) and diethanolamine (5 equiv) was stirred, heated progressively to 80°C and kept at this temperature until completion of the reaction (48 h) as indicated by TLC (eluent: MeOH/$CHCl_3$ 40/60).The mixture was poured into ice water (30 mL) and extracted with CH_2Cl_2 (3x30 ml). The combined organic layer was washed with water, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to provide a viscous oil which was purified on column chromatography (silicagel; methanol/chloroform : 40/60).

1-[bis(2-hydroxyethyl)amino]-3-[2-(perfluorohexyl)ethoxy]propan-2-ol (**3a**): IR (cm^{-1}) $\nu_{C\text{-}F}$ = 1039-1235, ν_{OH} = 3365, $\nu_{C\text{-}O}$ = 1145. ^{1}H NMR (CD_3OD/TMS) δ (ppm): 2.49 (m, 2H, $CH_2C\underline{H}_2C_6F_{13}$), 2.75 (m, 6H, 3×$NC\underline{H}_2$), 2.95 (m, 2H, $OC\underline{H}_2CHOH$), 3.76 (m, 6H, $OC\underline{H}_2CH_2C_6F_{13}$, 2×$NCH_2C\underline{H}_2OH$), 4.40 (m, 1H, $OCH_2C\underline{H}OH$). ^{13}C-{^{1}H} NMR δ (ppm): 32.41 (t, 1C, $OCH_2\underline{C}H_2C_6F_{13}$, $^2J_{CF}$= 21.28 Hz), 59.62 (s, 2C, 2×$N\underline{C}H_2CH_2OH$), 61.33 (s, 2C, 2×$NCH_2\underline{C}H_2OH$), 63.81(s, 1C, $HOCH\underline{C}H_2N$), 64.91 (s, 1C, $O\underline{C}H_2CH_2C_6F_{13}$), 67.15 (s, 1C,

$OCH_2\underline{C}HOH$), 72.66 (s, 1C, $O\underline{C}H_2CHOH$), 113.52-121.01(m, 6C, C_6F_{13}). ^{19}F NMR ($CD_3OD/CFCl_3$) δ (ppm): -83.11 (m, 3F, CF_3), -114.35 (m, 2F, $CF_{2\alpha}$), -122.89 (m, 2F, $CF_{2\beta}$), -123.88 (m, 2F, $CF_{2\gamma}$), -124.61 (m, 2F, $CF_{2\delta}$), -127.16 (m, 2F, $CF_{2\omega}$). Anal. Calcd. for $C_{15}H_{20}F_{13}NO_4$, C, 34.30, H, 3.84, N, 2.67. Found: C, 34.2, H, 3.64, N, 2.46.

1-[bis(2-hydroxyethyl)amino]-3-[2-(perfluorooctyl)ethoxy]propan-2-ol (**3b**): IR (cm^{-1}) ν_{C-F} = 1045-1204, ν_{OH} = 3365, ν_{C-O} = 1151. ^1H NMR (CD_3OD/TMS) δ (ppm): 2.49 (m, 2H, $CH_2C\underline{H}_2C_8F_{17}$), 2.70 (m, 6H, 3×$NC\underline{H}_2$), 2.90 (m, 2H, $OC\underline{H}_2CHOH$), 3.58 (m, 6H, $OC\underline{H}_2CH_2C_8F_{17}$, 2×$NCH_2C\underline{H}_2OH$), 4.42 (m, 1H, $OCH_2C\underline{H}OH$). ^{13}C-{^1H} NMR (CD_3OD/TMS) δ (ppm): 32.18 (t, 1C, $OCH_2\underline{C}H_2C_8F_{17}$, $^2J_{CF}$= 21.36 Hz), 45.03 (s, 2C, $HOCH\underline{C}H_2N$), 59.14 (s, 2C, 2×$N\underline{C}H_2CH_2OH$), 61.17 (s, 2C, 2×$NCH_2\underline{C}H_2OH$), 63.60 (s, 1C, $O\underline{C}H_2CH_2C_8F_{17}$), 66.88 (s, 1C, $OCH_2\underline{C}HOH$), 72.13 (s, 1C, $O\underline{C}H_2CHOH$), 115.12-122.31(m, 8C, $\underline{C}_8F_{17}$). ^{19}F NMR ($CD_3OD/CFCl_3$) δ (ppm): -79.23 (m, 3F, CF_3), -111.26 (m, 2F, $CF_{2\alpha}$), -119.61 (m, 6F, $CF_{2\beta}$, $CF_{2\gamma}$, $CF_{2\delta}$), -120.66 (m, 2F, $CF_{2\varepsilon}$), -121.54 (m, 2F, $CF_{2\xi}$), -124.20 (m, 2F, $CF_{2\omega}$). Anal. Calcd. for $C_{17}H_{20}F_{17}NO_4$, C, 32.65, H, 3.22, N, 2.24. Found, C, 32.45, H, 3.02, N, 2.04.

1-[bis(2-hydroxyethyl)amino]-3-[2-(perfluorohexyl)ethylsulfanyl]propan-2-ol (**3c**): IR (cm^{-1}) ν_{C-F} = 1046-1204, ν_{OH} = 3356, ν_{C-S} =643. ^1H NMR (CD_3OD/TMS) δ (ppm): 2.60 (m, 2H, $CH_2C\underline{H}_2C_6F_{13}$), 2.69 (m, 8H, $SC\underline{H}_2CHOH$, 3×$NC\underline{H}_2CH_2OH$), 2.85 (m, 2H, $SC\underline{H}_2CH_2C_6F_{13}$), 3.62 (m, 4H, 2×$NCH_2C\underline{H}_2OH$), 3.85 (m, 1H, $SCH_2C\underline{H}OH$). ^{13}C-{^1H} NMR (CD_3OD/TMS) δ (ppm): 24.16 (s, 1C, $S\underline{C}H_2CH_2C_6F_{13}$), 33.16 (t, 1C, $SCH_2\underline{C}H_2C_6F_{13}$, $^2J_{CF}$ = 21.58 Hz), 38.17 (s, 1C, $S\underline{C}H_2CHOH$), 58.62 (s, 2C, 2×$N\underline{C}H_2CH_2OH$), 60.69 (s, 2C, 2×$NCH_2\underline{C}H_2OH$), 61.09 (s, 1C, $HOCH\underline{C}H_2N$), 70.30 (s, 1C, $SCH_2\underline{C}HOH$), 112.39-120.37 (m, 6C, $\underline{C}_6F_{13}$). ^{19}F NMR ($CD_3OD/CFCl_3$) δ (ppm): -79.32 (m, 3F, CF_3), -114.23 (m, 2F, $CF_{2\alpha}$),-117.85 (m, 2F, $CF_{2\beta}$), -118.83 (m, 2F, $CF_{2\gamma}$), -119.32 (m, 2F, $CF_{2\delta}$), -122.25 (m, 2F, $CF_{2\omega}$). Anal. Calcd. for $C_{15}H_{20}F_{13}NO_3S$, C, 33.28, H, 3.72, N, 2.59, S, 5.92. Found, C, 33.08, H, 3.52, N, 2.39, S, 5.72.

1-[bis(2-hydroxyethyl)amino]-3-[2-(perfluorooctyl)ethylsulfanyl]propan-2-ol (**3d**): IR (cm^{-1}) ν_{C-F} = 1048-1204, ν_{OH} = 3365, ν_{C-S} =641. ^1H NMR (CD_3OD/TMS) δ (ppm): 2.60 (m, 2H, $CH_2C\underline{H}_2C_8F_{17}$), 2.65 (m, 8H, $SC\underline{H}_2CHOH$, 3×$NC\underline{H}_2$), 2.81 (m, 2H, $SC\underline{H}_2CH_2C_8F_{17}$), 3.32 (m, 4H, 2×$NCH_2C\underline{H}_2OH$), 3.60 (m, 1H, $SCH_2C\underline{H}OH$). ^{13}C-{^1H} NMR (CD_3OD/TMS) δ (ppm): 24.32 (s, 1C, $S\underline{C}H_2CH_2C_8F_{17}$), 33.12 (t, 1C, $SCH_2\underline{C}H_2C_8F_{17}$, $^2J_{CF}$ = 22.14 Hz), 37.71 (s, 1C, $S\underline{C}H_2CHOH$), 58.65 (s, 2C, 2×$N\underline{C}H_2CH_2OH$), 60.65 (s, 2C, 2×$NCH_2\underline{C}H_2OH$), 61.74 (s, 1C, $HOCHC\underline{H}_2N$), 70.26 (s, 1C, $SCH_2\underline{C}HOH$), 116.13-123.43(m, 8C, $\underline{C}_8F_{17}$). ^{19}F NMR ($CD_3OD/CFCl_3$) δ (ppm): -79.21 (m, 3F, CF_3), -121.15 (m, 2F, $CF_{2\alpha}$), -119.80 (m, 6F, $CF_{2\beta}$, $CF_{2\gamma}$, $CF_{2\delta}$), -120.64 (m, 2F, $CF_{2\varepsilon}$), -121.05 (m, 2F, $CF_{2\xi}$), -124.17 (m, 2F, $CF_{2\omega}$). Anal. Calcd. for $C_{17}H_{20}F_{17}NO_3S$, C, 31.83, H, 3.14, N, 2.18, S, 5. Found, C, 31.63, H, 2.96, S, 4.8.

Surfactant 4 preparation: General procedure

Methyl iodide (5 equiv) was added to diethanolaminoalcohol **3** (1 equiv) dissolved in diethyl ether (3 mL). The mixture was stirred and heated at 40°C under nitrogen atmosphere for 24 h (TLC: methanol/chloroform 40/60). Solvent and methyl iodide excess were removed at reduced pressure. The obtained crude residue was dried under vacuum to supply compound **4** as a yellowish paste.

Ammonium iodide (**4a**): IR (cm^{-1}) ν_{C-F} = 1043-1297, ν_{OH} = 3365, ν_{C-O} = 1134. ^1H NMR (CD_3OD/TMS) δ (ppm): 2.51 (m, 2H, $CH_2C\underline{H}_2C_6F_{13}$), 2.83 (s, 3H, $NC\underline{H}_3$), 3.18 (m, 2H, $OC\underline{H}_2CHOH$), 3.35 (m, 2H, $OC\underline{H}_2CH_2C_6F_{13}$), 3.72 (m, 6H, 3×$NC\underline{H}_2$), 4.03 (m, 4H, 2×$NCH_2C\underline{H}_2OH$), 4.15 (m, 1H, $OCH_2C\underline{H}OH$). ^{13}C-{^1H} NMR (CD_3OD/TMS) δ (ppm) : 32.39 (t, 1C, $OCH_2\underline{C}H_2C_6F_{13}$, $^2J_{CF}$ = 11.49 Hz), 55.81 (s, 2C, 2×$NCH_2\underline{C}H_2OH$), 59.24 (s, 1C,

N$\underline{C}H_3$), 61.92 (s, 1C, HOCH$\underline{C}H_2$N), 62.78 (s, 1C, O$\underline{C}H_2CH_2C_6F_{13}$), 63.88 (s, 1C, 2×N$\underline{C}H_2CH_2$OH), 65.75 (s, 1C, OCH$_2\underline{C}$HOH), 69.98 (s, 1C, O$\underline{C}H_2$CHOH), 111.30-128.98 (m, 6C, $\underline{C}_6F_{13}$). ^{19}F NMR ($CD_3OD/CFCl_3$) δ (ppm): -79.27 (t, 3F, CF_3, $^3J_{FF}$ = 9.01 Hz), -111.24 (m, 2F, $CF_{2\alpha}$), -119.79 (m, 2F, $CF_{2\beta}$), -120.78 (m, 2F, $CF_{2\gamma}$), -121.30 (m, 2F, $CF_{2\delta}$), -124.20 (m, 2F, $CF_{2\omega}$). Anal. Calcd. for $C_{16}H_{23}F_{13}NO_4I$, C, 28.80, H, 3.47, N, 2.01. Found: C, 28.6, H, 3.27, N, 1.81.

Ammonium iodide (**4b**): IR (cm^{-1}) ν_{C-F} = 1045-1204, ν_{OH} = 3365, ν_{C-O} = 1148. ^{1}H NMR (CD_3OD/TMS) δ (ppm): 2.52 (m, 2H, $CH_2C\underline{H}_2C_8F_{17}$), 2.80 (s, 3H, NC$\underline{H}_3$), 3.12 (m, 2H, OC$\underline{H}_2$CHOH), 3.34 (m, 2H, OC$\underline{H}_2CH_2C_8F_{17}$), 3.66 (m, 6H, 3×NC$\underline{H}_2$), 4.01 (m, 4H, 2×NCH$_2C\underline{H}_2$OH), 4.12 (m, 1H, OCH$_2C\underline{H}$OH). ^{13}C-{^{1}H} NMR (CD_3OD/TMS) δ (ppm): 32.13 (t, 1C, OCH$_2\underline{C}H_2C_8F_{17}$, $^2J_{CF}$ = 11.53 Hz), 43.67 (s, 1C, HOCH$\underline{C}H_2$N), 55.76 (s, 2C, 2×NCH$_2\underline{C}$H$_2$OH), 59.21 (s, 1C, N$\underline{C}H_3$), 62.27 (s, 1C, O$\underline{C}H_2CH_2C_8F_{17}$), 63.71 (s, 2C, 2×N$\underline{C}H_2CH_2$OH), 64.01 (s, 1C, OCH$_2\underline{C}$HOH), 70.52 (s, 1C, O$\underline{C}H_2$CHOH), 110.95-127.71 (m, 8C, $\underline{C}_8F_{17}$). ^{19}F NMR ($CD_3OD/CFCl_3$) δ (ppm):-79.21 (t, 3F, CF_3, $^3J_{FF}$ = 9.04 Hz), -111.2 (m, 2F, $CF_{2\alpha}$), -119.57 (m, 6F, $CF_{2\beta}$, $CF_{2\gamma}$, $CF_{2\delta}$), -120.64 (m, 2F, $CF_{2\varepsilon}$), -121.44 (m, 2F, $CF_{2\xi}$,),-124.19 (m, 2F, $CF_{2\omega}$). Anal. Calcd. for $C_{18}H_{23}F_{13}NO_4I$, C, 28.18, H, 1.83, N, 3.02. Found: C, 29.98, H, 1.63, N, 2.88.

Ammonium iodide (**4c**): IR (cm^{-1}) ν_{C-F} = 1048-1204, ν_{OH} = 3365, ν_{C-S} = 640. ^{1}H NMR (CD_3OD/TMS) δ (ppm): 2.52 (m, 2H, $CH_2C\underline{H}_2C_6F_{13}$), 2.81 (dd, 2H, SC$\underline{H}_2$CHOH, $^3J_{HH}$= 6.18 Hz, $^2J_{HH}$= 16.59 Hz), 2.91 (m, 2H, SC$\underline{H}_2CH_2C_6F_{13}$), 3.34 (s, 3H, NC$\underline{H}_3$), 3.75 (m, 6H, 3×NC$\underline{H}_2$), 4.06 (m, 4H, 2×NCH$_2C\underline{H}_2$OH), 4.47 (m, 1H, SCH$_2C\underline{H}$OH). ^{13}C-{^{1}H} NMR (CD_3OD/TMS) δ (ppm): 32.99 (t, 1C, SCH$_2\underline{C}H_2C_6F_{13}$, $^2J_{CF}$ = 11.77 Hz), 38.59 (s, 1C, S$\underline{C}$H$_2$CHOH), 51.70 (s, 2C, 2×NCH$_2\underline{C}$H$_2$OH), 56.83 (s, 1C, N$\underline{C}H_3$), 58.12 (s, 2C, 2×N$\underline{C}$H$_2$CH$_2$OH), 66.48 (s, 1C, HOCH$\underline{C}$H$_2$N), 68.02 (s, 1C, SCH$_2\underline{C}$HOH), 111.39-129.78 (m, 6C, $\underline{C}_6F_{13}$). ^{19}F NMR ($CD_3OD/CFCl_3$) δ (ppm): -79.28 (t, 3F, CF_3, $^3J_{FF}$ = 9.06 Hz), -112.07 (m, 2F, $CF_{2\alpha}$), -119.80 (m, 2F, $CF_{2\beta}$), -120.80 (m, 2F, $CF_{2\gamma}$), -121.23 (m, 2F, $CF_{2\delta}$), -124.23 (m, 2F, $CF_{2\omega}$). Anal. Calcd. for $C_{16}H_{23}F_{13}NO_3SI$, C, 28.12, H, 3.39, N, 2.05, S, 4.6. Found, C, 29.94, H, 3.19, N, 1.85, S, 4.4.

Ammonium iodide (**4d**): IR (cm^{-1}) ν_{C-F} = 1048-1204, ν_{OH} = 3365, ν_{C-S} = 644. ^{1}H NMR (CD_3OD/TMS) δ (ppm): 2.52 (m, 2H, $CH_2C\underline{H}_2C_8F_{17}$), 2.74 (m, 2H, SC$\underline{H}_2$CHOH), 2.90 (m, 2H, SC$\underline{H}_2CH_2C_8F_{17}$), 3.33 (s, 3H, NC$\underline{H}_3$), 3.74 (m, 6H, 3×NC$\underline{H}_2$), 4.04 (m, 4H, 2×NCH$_2C\underline{H}_2$OH), 4.43 (m, 1H, SCH$_2C\underline{H}$OH). ^{13}C-{^{1}H} NMR (CD_3OD/TMS) δ (ppm) : 22.41 (s, 1C, S$\underline{C}H_2CH_2C_8F_{17}$), 33.14 (t, 1C, SCH$_2\underline{C}H_2C_8F_{17}$, $^2J_{CF}$ = 12.44 Hz), 36.93 (s, 1C, S$\underline{C}$H$_2$CHOH), 55.34 (s, 2C, 2×NCH$_2\underline{C}$H$_2$OH), 58.06 (s, 1C, N$\underline{C}H_3$), 63.12 (s, 2C, 2×N$\underline{C}$H$_2$CH$_2$OH), 66.12 (s, 1C, HOCH$\underline{C}$H$_2$N), 68.79 (s, 1C, SCH$_2\underline{C}$HOH), 111.68-128.43 (m, 8C, $\underline{C}_8F_{17}$). ^{19}F NMR ($CD_3OD/CFCl_3$) δ (ppm): -79.18 (t, 3F, CF_3, $^3J_{FF}$ = 9.11 Hz), -112.11 (m, 2F, $CF_{2\alpha}$), -119.77 (m, 6F, $CF_{2\beta}$, $CF_{2\gamma}$, $CF_{2\delta}$), -120.61 (m, 2F, $CF_{2\varepsilon}$), -121.97 (m, 2F, $CF_{2\xi}$,),-124.16 (m, 2F, $CF_{2\omega}$). Anal. Calcd. for $C_{18}H_{23}F_{17}NO_3SI$, C, 27.6, H, 2.96, N, 1.79, S, 4. Found, C, 27.4, H, 2.94, S, 3.8.

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