



Synthesis and properties of gemini-type hydrocarbon–fluorocarbon hybrid surfactants

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ABSTRACT

Gemini-type hybrid surfactants with two fluorocarbon chains connected through a hydrocarbon spacer, $F(CF_2)_m(CH_2)_2CH(OSO_3Na)(CH_2)_nCH(OSO_3Na)(CH_2)_2(CF_2)_mF$ [$Fm(Hn)FmOS$, $m = 4, 6$; $n = 5, 6, 7, 8$], were synthesized and their surface chemical properties were examined with the aim to have highly functional and highly water-soluble fluorinated surfactants when compared with the conventional fluorinated surfactants. Comparisons of the surface chemical properties of the synthesized gemini-type hybrid surfactants with those of monounit-type hybrid surfactants, $F(CF_2)_m(CH_2)_2CH(OSO_3Na)(CH_2)_nH$ [$FmEHnOS$, $m = 4, 6$; $n = 3, 5$], revealed that gemination causes a remarkable lowering (about 1/100) in cmc value while it produces little changes in Krafft point (below 0 °C) and surface tension at cmc (γ_{cmc}).

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1. Introduction

Fluorinated surfactants with a fluorocarbon chain as hydrophobic group reduce the surface tension of water and form micelles at concentrations lower than those for the corresponding hydrocarbon surfactants [1]. Yet, they still have shortcomings to be improved, such as their limited use due to low solubility in water, high price and their accumulation in the environment. The present authors have synthesized various double-chain “hybrid surfactants” that have a molecular structure in which expensive fluorinated surfactant is “diluted” with inexpensive hydrocarbon chain. While the hydrocarbon content rises in these hybrid surfactants, they still keep the high surface tension lowering ability, characteristic of fluorinated surfactants. The hybrid surfactants thus synthesized still have a shortcoming, namely, low solubility in water, common for many fluorinated surfactants. Double chain-double hydrophilic group-type surfactants with two surfactant units connected through a spacer, namely, gemini-type surfactants, meanwhile, have an excellent surface activity and micelle forming ability without losing solubility in water when

compared with monounit-type surfactants with the same chain length [2].

Guo et al. synthesized sulfate ester-type hybrid surfactants with a hydrocarbon chain and a fluorocarbon chain in their molecule, $F(CF_2)_mCH(OSO_3Na)(CH_2)_nH$, $FmHn$, in 1992. These surfactants were found to have a surface tension lowering ability as high as that for fluorinated surfactants and a good affinity with water and hydrocarbon. Nevertheless, they were easily hydrolyzed because a strongly electron attractive fluorocarbon group and hydrophilic sulfate ester group are bound to the same carbon atom. They then needed to be stored in a desiccator at -25 °C and the physical properties of their solutions had to be measured within 20 h after preparation, thus making them poorly practical [3]. The present authors succeeded in 1995 in synthesizing sulfonate-type hybrid surfactants with a fluorocarbon chain and a hydrocarbon chain as hydrophobic groups and having a $-C_6H_4CO-$ group ($C_6H_4 = p$ -phenylene) between the hydrophobic and hydrophilic groups as spacer, $F(CF_2)_mC_6H_4COCH(SO_3Na)(CH_2)_nH$, $FmHnS$. These novel surfactants permitted us to co-emulsify mutually immiscible hydrocarbon oil and fluorocarbon oil in water, form long life micelles, and prepare highly viscoelastic gel-like liquid, all of which were impossible with the conventional surfactants [4–13,15]. Because of their very high Krafft points (48 °C for F6H6S, 98 °C for F8H6S), however, an improvement in their solubility in water had to be made. An attempt was then made to improve their solubility in water by synthesizing hybrid surfactants having an ethylene chain instead of benzene ring as spacer and a sulfate

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group replacing sulfonate group as hydrophilic group in their molecule, $F(CF_2)_m(CH_2)_2CH(OSO_3Na)(CH_2)_nH$ [$FmEHnOS$, $m = 4, 6$; $n = 3, 5$] [14,15], since those surfactants which have benzene ring in their molecule are in general poorly water soluble.

This article reports the synthesis of gemini-type hybrid fluorinated surfactants, $Fm(Hn)FmOS$ ($m = 4, 6$; $n = 5, 6, 7, 8$), in which two fluorinated surfactant molecules are connected through a hydrocarbon spacer, with the aim to obtain such fluorinated surfactants that are more functional and water-soluble than the conventional fluorinated surfactants. Comparisons are also made in the article of the surface chemical properties of the newly synthesized surfactants with those of monounit-type fluorinated hybrid surfactants, $F(CF_2)_m(CH_2)_2CH(OSO_3Na)(CH_2)_nH$ [$FmEHnOS$ ($m = 4, 6$; $n = 3, 5$)] [14]. Moreover, the effect of the chain length of spacer, n , was examined.

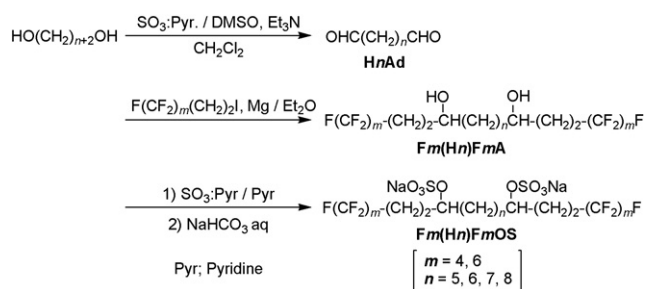
2. Results and discussion

2.1. Synthesis of gemini-type hybrid surfactants

Scheme 1 shows the synthetic process of gemini-type hybrid surfactants. The starting materials, α,ω -alkanediols were oxidized with sulfur trioxide:pyridine complex in dichloromethane to give aldehydes, $HnAd$ ($n = 5, 6, 7, 8$). Hybrid alcohols with fluorocarbon chain introduced, $Fm(Hn)FmA$ ($m = 4, 6$; $n = 5, 6, 7, 8$), were then obtained by the Grignard reaction of $HnAd$ with 2-(perfluoroalkyl)ethyl iodide. The hybrid alcohols obtained were oxidized with sulfur trioxide:pyridine complex in pyridine to yield the final products, $Fm(Hn)FmOS$ ($m = 4, 6$; $n = 5, 6, 7, 8$). The overall yields from the starting materials to the final products were 17–20%.

2.2. Krafft points, cmc values, and surface tension values for $Fm(Hn)FmOS$

Table 1 lists the measured Krafft points, cmc values, and surface tension values of $Fm(Hn)FmOS$, together with those of $FmEHnOS$ taken from the previous work [14]. Comparisons of the properties of gemini-type $F4(H6)F4OS$ with the corresponding monounit-type $F4EH3OS$ showed that the Krafft points are below $0^\circ C$ and the values of γ_{cmc} are almost equal for both types of fluorinated surfactants while the cmc value of the former is about 1/100 of the latter's, indicating that gemination produces an increase in the micelle forming ability of surfactant. A similar trend was also found between the other gemini-type surfactants and the corresponding monounit-type surfactants. When the properties of $Fm(H6)FmOS$ were compared with those of $Fm(H8)FmOS$, the former was found to have a cmc value higher and a micelle forming ability lower than those of the latter, respectively, while the value of γ_{cmc} for the former was lower than that of the latter, indicating its higher surface activity. This would be caused by a denser packing of shorter Fm chains at the air/water interface. Comparisons of the



Scheme 1.

Table 1
The Krafft points (K_p), cmc and surface tension (γ_{cmc}) of surfactants

Surfactant	K_p ($^\circ C$)	cmc ^a (mM)	γ_{cmc} ^a (mN m ⁻¹)
F4(H5)F4OS	<0	1.56	22
F6(H5)F6OS	<0	0.06	19
F4(H6)F4OS	<0	0.32	20
F6(H6)F6OS	<0	0.04	20
F4(H7)F4OS	<0	0.45	19
F6(H7)F6OS	<0	0.03	20
F4(H8)F4OS	<0	0.13	23
F6(H8)F6OS	<0	0.02	21
F4EH3OS	<0	25	23
F6EH3OS	<0	4	19
F4EH5OS	<0	14	20
F6EH5OS	<0	1.3	20

^a By Wilhelmy plate method at $25^\circ C$.

properties of $Fm(H5)FmOS$ with those of $Fm(H7)FmOS$ showed a similar trend between them.

The cmc values of $F4(H5)F4OS$ and $F4(H7)F4OS$ with odd numbers of carbon atoms in their spacer hydrocarbon chains were larger than those of $F4(H6)F4OS$ and $F4(H8)F4OS$ with even numbers of carbon atoms while no such trend was found for $F6(Hn)F6OS$. The lengths of spacer hydrocarbon chain and fluorocarbon chain hardly affected the value of γ_{cmc} (Figs. 1–4).

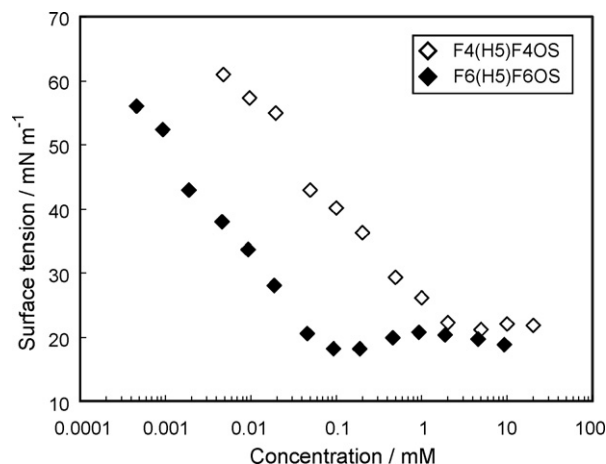


Fig. 1. Surface tension plots of $F4(H5)F4OS$ and $F6(H5)F6OS$ against concentration at $25^\circ C$.

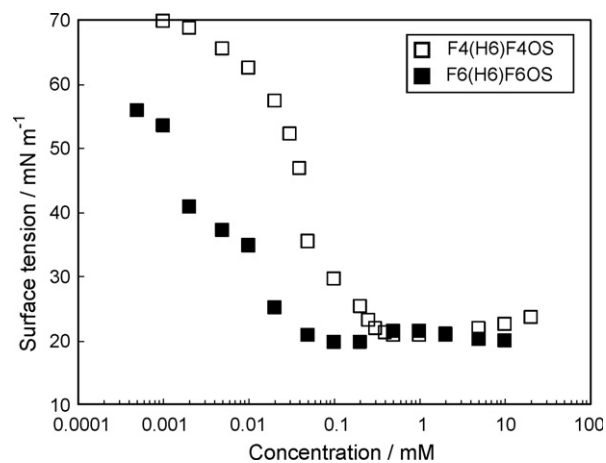


Fig. 2. Surface tension plots of $F4(H6)F4OS$ and $F6(H6)F6OS$ against concentration at $25^\circ C$.

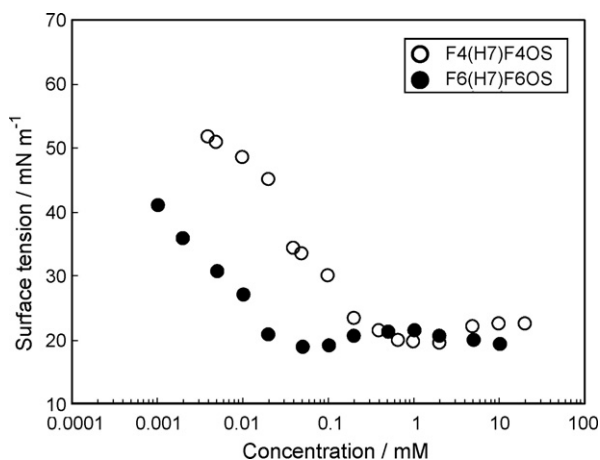


Fig. 3. Surface tension plots of F4(H7)F4OS and F6(H7)F6OS against concentration at 25 °C.

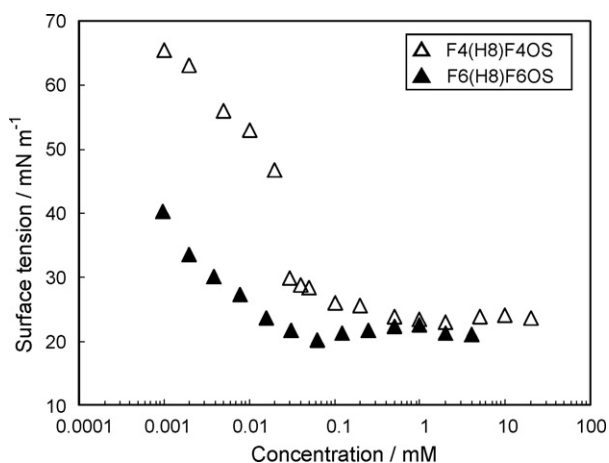


Fig. 4. Surface tension plots of F4(H8)F4OS and F6(H8)F6OS against concentration at 25 °C.

3. Conclusions

Gemini-type hybrid surfactants, $Fm(Hn)FmOS$ ($m = 4, 6$; $n = 5, 6, 7, 8$) were obtained as a white solid in the whole yields of 17–20% from the starting materials. Comparisons of the properties of the gemini-type surfactants with those of monounit-type hybrid surfactants, $FmEHnOS$ [$F(CF_2)_m(CH_2)_2CH(OSO_3Na)(CH_2)_nH$ ($m = 4, 6$; $n = 3, 5$)] showed that the Krafft points are all below 0 °C and the values of surface tension at cmc (γ_{cmc}) are almost the same for both types of surfactants while the values of cmc for the gemini-type surfactants are about 1/100 of those for the monounit-type surfactants.

4. Experimental

4.1. Materials

Heptane-1,7-diol, octane-1,8-diol, nonane-1,9-diol, decane-1,10-diol (Tokyo Chemical Industries), 2-(perfluorobutyl)ethyl iodide, 2-(perfluorohexyl)ethyl iodide (Daikin Finechemical Laboratory), sulfur trioxide:pyridine complex (Aldrich), triethylamine, hydrochloric acid, sodium hydrogencarbonate (Kanto Chemical), sodium borohydride, magnesium sulfate (nacalai tesque), magnesium (Acros Organics), and silica gel (Wakogel C-300) were used as supplied. Dichloromethane, dimethyl sulfoxide, and tetrahydrofuran were used after being predehydrated with calcium chloride, dehydrated further with calcium hydride added,

and distilled under nitrogen atmosphere. Diethyl ether was used in a nitrogen atmosphere. Methanol was used being after dehydrated with calcium hydride. The other solvents (chloroform, pyridine, hexane) were used as purchased.

4.2. Measurements and instruments

1H -NMR (400 MHz, $CDCl_3$, TMS standard) and ^{19}F NMR (377 MHz, CD_3OD , no standard) spectra were measured at 30 °C using a Bruker DPX-400 spectrometer. FT-IR (cm^{-1}), EI-MS (70 eV, (rel. int.)), and FAB-MS (70 eV, m/z (rel. int.)) and high resonance mass spectra were measured respectively with a Nicolet Avatar 360 FT-IR spectrometer, Hewlett Packard HP 6890 series GC System and Hewlett Packard 5973 Mass Selective Detector, and a JEOL JMX SX102A. A TG-DTA TG8120 (Thermo Plus) was used to measure TG-DTA. Melting point measurements were performed using a digital melting point measuring apparatus (IA9200, MRK-Electrothermal). Surface tension measurements were made at 25 °C on solutions of the synthesized eight kinds of surfactants, $Fm(Hn)FmOS$, using a Krüss Model K12 surface tensiometer (Wilhelmy plate method) in the following way. Aqueous surfactant stock solutions at given high concentrations were prepared using accurately weighed samples. Each of the stock solutions thus prepared was diluted successively with water to give sample solutions for measurement. Krafft point measurements were performed electroconductometrically using a DKK-TOA conductivity meter CM-60G on solutions at given high concentrations placed in a thermostat while gently heating. All graphs obtained were almost linear and the Krafft points of the surfactants were determined to be below 0 °C.

4.3. Synthesis of heptanedial (H5Ad)

All reactions were carried out under nitrogen atmosphere. Heptane-1,7-diol (5.0 g, 37.8 mmol) was taken into a 500 mL two-neck round flask equipped with a dropping funnel, to which were added dropwise dichloromethane (100 mL), dimethyl sulfoxide (100 mL), and triethylamine (38.3 g, 378.2 mmol) in this order while the flask was ice-cooled, and the iced mixture was stirred for 5 min. Then, sulfur trioxide:pyridine complex (36.1 g, 226.9 mmol) was added to the iced mixture and the reaction mixture was stirred for 30 min. The dichloromethane-soluble part was extracted from the reaction mixture after the stirring was completed and the extracted solution was distilled after dehydration with magnesium sulfate to give aldehyde H5Ad [16,17].

4.3.1. H5Ad

Colorless liquid, yield (%) 2.5 g (52%), bp 44 °C/18 Pa, 1H NMR: δ 1.39 (m (multiplet), 2H, a), 1.62–1.70 (tb (triplet (broad)), 4H, $J = 7.5$ (broad) Hz, b), 2.43–2.47 (dt (doublet (triplet)), 4H, $J = 5.5$ (1.5) Hz, c), 9.765–9.774 (t, 2H, $J = 1.7$ Hz, d) for $CH_2^a[CH_2^bCH_2^cCH^dO]_2$; EI-MS: 128 $[M]^+$ (0.5), 110 $[M-H_2O]^+$ (9), 81 $[M-H_2O-CHO]^+$ (19), 67 $[C_5H_8]^+$ (55), 57 $[(CH_2)_2CHO]^+$ (100), 55 $[C_4H_7]^+$ (64); IR: 2593–3028 (ν_{C-H}), 1599–1851 ($\nu_{C=O}$).

4.4. Synthesis of octanedial (H6Ad), nonanedial (H7Ad), and decanedial (H8Ad)

H6Ad, H7Ad, and H8Ad were synthesized as in Section 4.3 using octane-1,8-diol, nonane-1,9-diol, and decane-1,10-diol as the starting materials.

4.4.1. H6Ad

Colorless liquid, yield (%) 7.6 g (78%), bp 58 °C/10 Pa, 1H NMR: δ 1.33–1.37 (tb, 4H, $J = 3.7$ (broad) Hz, a), 1.61–1.65 (tb, 4H, $J = 7.7$

(broad) Hz, *b*), 2.41–2.45 (dt, 4H, *J* = 5.5 (1.5) Hz, *c*), 9.758–9.766 (t, 2H, *J* = 1.7 Hz, *d*) for $[\text{CH}_2^a\text{CH}_2^b\text{CH}_2^c\text{CH}^d\text{O}]_2$; EI-MS: 142 $[\text{M}]^+$ (0.5), 124 $[\text{M}-\text{H}_2\text{O}]^+$ (14), 95 $[\text{M}-\text{H}_2\text{O}-\text{CHO}]^+$ (26), 81 $[\text{C}_6\text{H}_9]^+$ (100), 67 $[\text{C}_5\text{H}_8]^+$ (36), 57 $[(\text{CH}_2)_2\text{CHO}]^+$ (100), 55 $[\text{C}_4\text{H}_7]^+$ (69); IR: 2627–3017 ($\nu_{\text{C-H}}$), 1656–1837 ($\nu_{\text{C=O}}$).

4.4.2. H7Ad

Colorless liquid, yield (%) 3.6 g (40%), bp 52 °C/16 Pa, ^1H NMR: δ 1.27–1.37 (s, 6H, *a, b*), 1.61–1.64 (tb, 4H, *J* = 7.1 (broad) Hz, *c*), 2.40–2.44 (dt, 4H, *J* = 5.6 (1.5) Hz, *d*), 9.756–9.765 (t, 2H, *J* = 1.7 Hz, *e*) for $[\text{CH}_2^a\text{CH}_2^b\text{CH}_2^c\text{CH}^d\text{O}]_2$; EI-MS: 156 $[\text{M}]^+$ (0.6), 138 $[\text{M}-\text{H}_2\text{O}]^+$ (6), 110 $[\text{M}-\text{H}_2\text{O}-\text{CHO}]^+$ (11), 95 $[\text{C}_7\text{H}_{11}]^+$ (100), 67 $[\text{C}_5\text{H}_8]^+$ (48), 57 $[(\text{CH}_2)_2\text{CHO}]^+$ (64), 55 $[\text{C}_4\text{H}_7]^+$ (48); IR: 2649–2997 ($\nu_{\text{C-H}}$), 1675–1787 ($\nu_{\text{C=O}}$).

4.4.3. H8Ad

Colorless liquid, yield (%) 7.0 g (70%), bp 80 °C/10 Pa, ^1H NMR: δ 1.28–1.37 (s, 8H, *a, b*), 1.61–1.64 (tb, 4H, *J* = 7.5 (broad) Hz, *c*), 2.40–2.44 (dt, 4H, *J* = 5.5 (1.5) Hz, *d*), 9.756–9.765 (t, 2H, *J* = 1.7 Hz, *e*) for $[\text{CH}_2^a\text{CH}_2^b\text{CH}_2^c\text{CH}^d\text{O}]_2$; EI-MS: 170 $[\text{M}]^+$ (0.3), 152 $[\text{M}-\text{H}_2\text{O}]^+$ (2), 123 $[\text{M}-\text{H}_2\text{O}-\text{CHO}]^+$ (6.4), 95 $[\text{C}_7\text{H}_{11}]^+$ (27), 81 $[\text{C}_6\text{H}_9]^+$ (48), 67 $[\text{C}_5\text{H}_8]^+$ (100), 57 $[(\text{CH}_2)_2\text{CHO}]^+$ (79), 55 $[\text{C}_4\text{H}_7]^+$ (87); IR: 2658–3003 ($\nu_{\text{C-H}}$), 1669–1790 ($\nu_{\text{C=O}}$).

4.5. Synthesis of 1,11-bis(perfluorobutyl)-3,9-undecanediol (F4(H5)F4A)

All reactions were performed under nitrogen atmosphere. Magnesium (0.84 g, 34.6 mmol) was taken into a two-neck round bottom flask in an ice bath and a dilute 2-(perfluorobutyl)ethyl iodide (16.4 g, 34.6 mmol) solution in diethyl ether was added dropwise to the flask. After the iced solution was stirred for 2 h, H5Ad (1.5 g, 34.6 mmol) (20 times diluted (in volume) diethyl ether solution) was added dropwise to it. The Grignard reaction was stopped by adding water and 1 M hydrochloric acid to the reaction mixture after it was stirred for 24 h at room temperature. The diethyl ether-soluble part was extracted and separated from the reaction mixture and sodium borohydride (0.18 g, 4.89 mmol), tetrahydrofuran (15 mL), and methanol (3.13 g, 97.8 mmol) were added in this order to the ether solution and the resultant solution was stirred for 6 h at room temperature. The reaction product was then recrystallized from chloroform to give F4(H5)F4A [14,15].

4.5.1. F4(H5)F4A

White solid, yield (%) 4.62 g (64%), mp 88–93 °C, ^1H NMR: δ 1.30–1.52 (m, 10H, *a, b, c*), 1.68 (m, 4H, *e*), 2.28 (m, 4H, *f*), 3.56 (m, 2H, *d*) for $[\text{CH}_2^a\text{CH}_2^b\text{CH}_2^c\text{CH}^d(\text{OH})\text{CH}_2^e\text{CH}_2^f(\text{CF}_2)_4\text{F}]_2$; ^{19}F NMR: δ –82.7 (t, 3F, *J* = 9.6 Hz, *d*), –115.65 (m, 2F, *a*), –125.5 (m, 2F, *b*), –127.25 (m, 2F, *c*) for $[\text{CF}_3^f\text{CF}_2^e\text{CF}_2^d\text{CF}_2^c\text{CF}_2^b\text{CF}_2^a(\text{CH}_2)_2\text{CH}(\text{OH})(\text{CH}_2)_2]_2\text{CH}_2$; EI-MS: 588 $[\text{M}-2\text{OH}]^+$ (2), 360 $[\text{M}-\text{OH}-(\text{CH}_2)_2(\text{CF}_2)_4\text{F}]^+$ (27), 341 $[\text{C}_9\text{H}_{18}(\text{CH}_2)_2(\text{CF}_2)_4\text{F}]^+$ (100), 277 $[\text{CH}(\text{OH})(\text{CH}_2)_2(\text{CF}_2)_4\text{F}]^+$ (39), 55 $[\text{C}_4\text{H}_7]^+$ (19); IR: 3216–3517 ($\nu_{\text{O-H}}$), 2857–2938 ($\nu_{\text{C-H}}$), 1253 ($\nu_{\text{C-F}}$).

4.6. Syntheses of 1,11-bis(perfluorohexyl)undecane-3,9-diol (F6(H5)F6A) and other diols

These diols were obtained from heptanediol (H5Ad), octanediol (H6Ad), nonanediol (H7Ad), and decanediol (H8Ad) according to the method in Section 4.5.

4.6.1. F6(H5)F6A

White solid, yield (%) 6.42 g (50%), mp 104–109 °C, ^1H NMR: δ 1.31–1.52 (m, 10H, *a, b, c*), 1.69 (m, 4H, *e*), 2.28 (m, 4H, *f*), 3.56 (m, 2H, *d*) for $[\text{CH}_2^a\text{CH}_2^b\text{CH}_2^c\text{CH}^d(\text{OH})\text{CH}_2^e\text{CH}_2^f(\text{CF}_2)_6\text{F}]_2$; ^{19}F NMR: δ –82.4

(t, 3F, *J* = 10.9 Hz, *f*), –115.3 (m, 2F, *a*), –122.95 (m, 2F, *b*), –123.85 (m, 2F, *c*), –124.5 (m, 2F, *d*), –127.3 (m, 2F, *e*) for $[\text{CF}_3^f\text{CF}_2^e\text{CF}_2^d\text{CF}_2^c\text{CF}_2^b\text{CF}_2^a(\text{CH}_2)_2\text{CH}(\text{OH})(\text{CH}_2)_2]_2\text{CH}_2$; EI-MS: 788 $[\text{M}-2\text{OH}]^+$ (13), 474 $[\text{M}-\text{OH}-(\text{CH}_2)_2(\text{CF}_2)_6\text{F}]^+$ (31), 441 $[\text{C}_7\text{H}_{14}(\text{CH}_2)_2(\text{CF}_2)_6\text{F}]^+$ (100), 377 $[\text{CH}(\text{OH})(\text{CH}_2)_2(\text{CF}_2)_6\text{F}]^+$ (38), 55 $[\text{C}_4\text{H}_7]^+$ (15); IR: 3219–3523 ($\nu_{\text{O-H}}$), 2857–2939 ($\nu_{\text{C-H}}$), 1256 ($\nu_{\text{C-F}}$).

4.6.2. F4(H6)F4A

White solid, yield (%) 5.21 g (58%), mp 84–96 °C, ^1H NMR: δ 1.30–1.51 (m, 12H, *a, b, c*), 1.68 (m, 4H, *e*), 2.27 (m, 4H, *f*), 3.56 (m, 2H, *d*) for $[\text{CH}_2^a\text{CH}_2^b\text{CH}_2^c\text{CH}^d(\text{OH})\text{CH}_2^e\text{CH}_2^f(\text{CF}_2)_4\text{F}]_2$; ^{19}F NMR: δ –82.7 (t, 3F, *J* = 9.6 Hz, *d*), –115.5 (m, 2F, *a*), –125.45 (m, 2F, *b*), –127.2 (m, 2F, *c*) for $[\text{CF}_3^d\text{CF}_2^c\text{CF}_2^b\text{CF}_2^a(\text{CH}_2)_2\text{CH}(\text{OH})(\text{CH}_2)_3]_2$; EI-MS: 602 $[\text{M}-2\text{OH}]^+$ (3), 374 $[\text{M}-\text{OH}-(\text{CH}_2)_2(\text{CF}_2)_4\text{F}]^+$ (35), 355 $[\text{C}_8\text{H}_{16}(\text{CH}_2)_2(\text{CF}_2)_4\text{F}]^+$ (100), 277 $[\text{CH}(\text{OH})(\text{CH}_2)_2(\text{CF}_2)_4\text{F}]^+$ (56), 55 $[\text{C}_4\text{H}_7]^+$ (16); IR: 3277–3458 ($\nu_{\text{O-H}}$), 2854–2937 ($\nu_{\text{C-H}}$), 1239 ($\nu_{\text{C-F}}$).

4.6.3. F6(H6)F6A

White solid, yield (%) 7.08 g (60%), mp 95–103 °C, ^1H NMR: δ 1.29–1.50 (m, 12H, *a, b, c*), 1.67 (m, 4H, *e*), 2.28 (m, 4H, *f*), 3.55 (m, 2H, *d*) for $[\text{CH}_2^a\text{CH}_2^b\text{CH}_2^c\text{CH}^d(\text{OH})\text{CH}_2^e\text{CH}_2^f(\text{CF}_2)_6\text{F}]_2$; ^{19}F NMR: δ –82.4 (t, 3F, *J* = 10.9 Hz, *f*), –115.3 (m, 2F, *a*), –112.9 (m, 2F, *b*), –123.8 (m, 2F, *c*), –124.5 (m, 2F, *d*), –127.3 (m, 2F, *e*) for $[\text{CF}_3^f\text{CF}_2^e\text{CF}_2^d\text{CF}_2^c\text{CF}_2^b\text{CF}_2^a(\text{CH}_2)_2\text{CH}(\text{OH})(\text{CH}_2)_3]_2$; EI-MS: 802 $[\text{M}-2\text{OH}]^+$ (3), 474 $[\text{M}-\text{OH}-(\text{CH}_2)_2(\text{CF}_2)_6\text{F}]^+$ (39), 455 $[\text{C}_8\text{H}_{16}(\text{CH}_2)_2(\text{CF}_2)_6\text{F}]^+$ (100), 377 $[\text{CH}(\text{OH})(\text{CH}_2)_2(\text{CF}_2)_6\text{F}]^+$ (47), 55 $[\text{C}_4\text{H}_7]^+$ (10); IR: 3250–3489 ($\nu_{\text{O-H}}$), 2857–2933 ($\nu_{\text{C-H}}$), 1253 ($\nu_{\text{C-F}}$).

4.6.4. F4(H7)F4A

White solid, yield (%) 3.25 g (40%), mp 86–96 °C, ^1H NMR: δ 1.32–1.50 (m, 14H, *a, b, c, d*), 1.66 (m, 4H, *f*), 2.25 (m, 4H, *g*), 3.55 (m, 2H, *e*) for $[\text{CH}_2^a\text{CH}_2^b\text{CH}_2^c\text{CH}^d(\text{OH})\text{CH}_2^e\text{CH}_2^f(\text{CF}_2)_4\text{F}]_2$; ^{19}F NMR: δ –82.7 (t, 3F, *J* = 9.6 Hz, *d*), –115.5 (m, 2F, *a*), –125.45 (m, 2F, *b*), –127.25 (m, 2F, *c*) for $[\text{CF}_3^d\text{CF}_2^c\text{CF}_2^b\text{CF}_2^a(\text{CH}_2)_2\text{CH}(\text{OH})(\text{CH}_2)_3]_2\text{CH}_2$; EI-MS: 616 $[\text{M}-2\text{OH}]^+$ (3), 387 $[\text{M}-\text{OH}-(\text{CH}_2)_2(\text{CF}_2)_4\text{F}]^+$ (41), 369 $[\text{C}_9\text{H}_{18}(\text{CH}_2)_2(\text{CF}_2)_4\text{F}]^+$ (100), 277 $[\text{CH}(\text{OH})(\text{CH}_2)_2(\text{CF}_2)_4\text{F}]^+$ (86), 55 $[\text{C}_4\text{H}_7]^+$ (19); IR: 3200–3497 ($\nu_{\text{O-H}}$), 2854–2930 ($\nu_{\text{C-H}}$), 1250 ($\nu_{\text{C-F}}$).

4.6.5. F6(H7)F6A

White solid, yield (%) 6.66 g (41%), mp 105–110 °C, ^1H NMR: δ 1.30–1.51 (m, 14H, *a, b, c, d*), 1.67 (m, 4H, *f*), 2.28 (m, 4H, *g*), 3.56 (m, 2H, *e*) for $[\text{CH}_2^a\text{CH}_2^b\text{CH}_2^c\text{CH}^d(\text{OH})\text{CH}_2^e\text{CH}_2^f(\text{CF}_2)_6\text{F}]_2$; ^{19}F NMR: δ –82.4 (t, 3F, *J* = 10.9 Hz, *f*), –115.35 (m, 2F, *a*), –112.9 (m, 2F, *b*), –123.8 (m, 2F, *c*), –124.5 (m, 2F, *d*), –127.3 (m, 2F, *e*) for $[\text{CF}_3^f\text{CF}_2^e\text{CF}_2^d\text{CF}_2^c\text{CF}_2^b\text{CF}_2^a(\text{CH}_2)_2\text{CH}(\text{OH})(\text{CH}_2)_3]_2\text{CH}_2$; EI-MS: 816 $[\text{M}-2\text{OH}]^+$ (3), 487 $[\text{M}-\text{OH}-(\text{CH}_2)_2(\text{CF}_2)_6\text{F}]^+$ (42), 469 $[\text{C}_9\text{H}_{18}(\text{CH}_2)_2(\text{CF}_2)_6\text{F}]^+$ (100), 377 $[\text{CH}(\text{OH})(\text{CH}_2)_2(\text{CF}_2)_6\text{F}]^+$ (66), 55 $[\text{C}_4\text{H}_7]^+$ (21); IR: 3246–3636 ($\nu_{\text{O-H}}$), 2855–2930 ($\nu_{\text{C-H}}$), 1249 ($\nu_{\text{C-F}}$).

4.6.6. F4(H8)F4A

White solid, yield (%) 2.71 g (69%), mp 88–99 °C, ^1H NMR: δ 1.29–1.49 (m, 16H, *a, b, c, d*), 1.66 (m, 4H, *f*), 2.27 (m, 4H, *g*), 3.55 (m, 2H, *e*) for $[\text{CH}_2^a\text{CH}_2^b\text{CH}_2^c\text{CH}^d(\text{OH})\text{CH}_2^e\text{CH}_2^f(\text{CF}_2)_4\text{F}]_2$; ^{19}F NMR: δ –82.7 (t, 3F, *J* = 9.6 Hz, *d*), –115.55 (m, 2F, *a*), –125.4 (m, 2F, *b*), –127.25 (m, 2F, *c*) for $[\text{CF}_3^d\text{CF}_2^c\text{CF}_2^b\text{CF}_2^a(\text{CH}_2)_2\text{CH}(\text{OH})(\text{CH}_2)_4]_2$; EI-MS: 630 $[\text{M}-2\text{OH}]^+$ (7), 401 $[\text{M}-\text{OH}-(\text{CH}_2)_2(\text{CF}_2)_4\text{F}]^+$ (57), 383 $[\text{C}_{10}\text{H}_{20}(\text{CH}_2)_2(\text{CF}_2)_4\text{F}]^+$ (97), 277 $[\text{CH}(\text{OH})(\text{CH}_2)_2(\text{CF}_2)_4\text{F}]^+$ (100), 55 $[\text{C}_4\text{H}_7]^+$ (24); IR: 3247–3635 ($\nu_{\text{O-H}}$), 2854–2930 ($\nu_{\text{C-H}}$), 1250 ($\nu_{\text{C-F}}$).

4.6.7. F6(H8)F6A

White solid, yield (%) 5.08 g (50%), mp 99–101 °C, ^1H NMR: δ 1.29–1.50 (m, 16H, *a, b, c, d*), 1.67 (m, 4H, *f*), 2.26 (m, 4H, *g*), 3.56 (m, 2H, *e*) for $[\text{CH}_2^a\text{CH}_2^b\text{CH}_2^c\text{CH}^d(\text{OH})\text{CH}_2^e\text{CH}_2^f(\text{CF}_2)_6\text{F}]_2$; ^{19}F NMR: δ –82.4 (t, 3F, *J* = 10.9 Hz, *f*), –115.35 (m, 2F, *a*), –123.8 (m, 2F, *b*), –123.85 (m,

2F, c), –124.5 (m, 2F, d), –127.3 (m, 2F, e) for $[\text{CF}_3^f\text{CF}_2^e\text{CF}_2^d\text{CF}_2^c\text{CF}_2^b\text{C}-\text{F}_2^a(\text{CH}_2)_2\text{CH}(\text{OH})(\text{CH}_2)_4]_2$; EI-MS: 830 $[\text{M}-2\text{OH}]^+$ (10), 501 $[\text{M}-\text{OH}-(\text{CH}_2)_2(\text{CF}_2)_6\text{F}]^+$ (58), 483 $[\text{C}_{10}\text{H}_{20}(\text{CH}_2)_2(\text{CF}_2)_6\text{F}]^+$ (100), 377 $[\text{CH}(\text{OH})(\text{CH}_2)_2(\text{CF}_2)_6\text{F}]^+$ (98), 55 $[\text{C}_4\text{H}_7]^+$ (33); IR: 3281–3548 ($\nu_{\text{O-H}}$), 2854–2938 ($\nu_{\text{C-H}}$), 1248 ($\nu_{\text{C-F}}$).

4.7. Synthesis of 1,11-bis(perfluorobutyl)undecane 3,9-disulfate (F4(H5)F4OS)

All reactions were carried out in a nitrogen atmosphere. F4(H5)F4A (1.56 g, 2.56 mmol) and sulfur trioxide pyridine complex (1.19 g, 7.50 mmol) were taken into a 100 mL two-neck round bottom flask. Pyridine was added into the flask to dissolve the content completely and the solution was stirred for 24 h at 50 °C. Aqueous saturated sodium hydrogencarbonate solution was added until gas release ceased to neutralize the reaction mixture, and then pyridine and water were removed from the solution by distillation at a reduced pressure. The methanol-soluble part was passed through a silica gel column (hexane medium) to adsorb the reaction product, which was then desorbed and dissolved in methanol to give a gemini-type surfactant, F4(H5)F4OS.

4.7.1. F4(H5)F4OS

White solid, yield (%) 1.53 g (74%), decompose point (decomp.) 125 °C, ^1H NMR: δ 1.32–1.51 (m, 6H, a, b), 1.57–2.05 (m, 8H, c, e), 2.30 (m, 4H, f), 4.39 (m, 2H, d) for $\text{CH}_2^a[\text{CH}_2^b\text{CH}_2^c\text{CH}^d(\text{OSO}_3\text{Na})-\text{CH}_2^e\text{CH}_2^f(\text{CF}_2)_4\text{F}]_2$; ^{19}F NMR: δ –82.7 (tt, 3F, $J = 9.5$ (2.7) Hz, d), –115.7 (tb, 2F, $J = 14.6$ (broad) Hz, a), –125.40 (m, 2F, b), –127.21 (m, 2F, c) for $[\text{CF}_3^f\text{CF}_2^e\text{CF}_2^d\text{CF}_2^c\text{CF}_2^b\text{CF}_2^a(\text{CH}_2)_2\text{CH}(\text{OSO}_3\text{Na})(\text{CH}_2)_2]_2\text{CH}_2$; FAB-MS: 805 $[\text{M}-\text{Na}]^+$ (100), 685 $[\text{M}-\text{Na}-\text{OSO}_3\text{Na}]^+$ (19); HRMS: obsd. 805.0211 [100.0, (calcd. 805.0210 for C19 H20 O8 F18 S2 Na1)]; IR: 2864–2950 ($\nu_{\text{C-H}}$), 1222 ($\nu_{\text{C-F}}$).

4.8. Syntheses of 1,11-bis(perfluorohexyl)undecane 3,9-disulfate (F6(H5)F6OS) and other gemini-type hybrid surfactants

Similarly, these gemini-type hybrid surfactants were obtained from the corresponding Fm(Hn)FmA according to the method in Section 4.7.

4.8.1. F6(H5)F6OS

White solid, yield (%) 1.31 g (86%), decomp. 147 °C, ^1H NMR: δ 1.30–1.50 (m, 6H, a, b), 1.60–2.04 (m, 8H, c, e), 2.36 (m, 4H, f), 4.39 (m, 2H, d) for $\text{CH}_2^a[\text{CH}_2^b\text{CH}_2^c\text{CH}^d(\text{OSO}_3\text{Na})\text{CH}_2^e\text{CH}_2^f(\text{CF}_2)_6\text{F}]_2$; ^{19}F NMR: δ –82.4 (tb, 3F, $J = 9.7$ (broad) Hz, f), –115.4 (tb, 2F, $J = 18.2$ Hz, a), –122.90 (m, 2F, b), –123.88 (m, 2F, c), –124.39 (m, 2F, d), –127.30 (m, 2F, e) for $[\text{CF}_3^f\text{CF}_2^e\text{CF}_2^d\text{CF}_2^c\text{CF}_2^b\text{CF}_2^a(\text{CH}_2)_2\text{CH}(\text{OSO}_3\text{Na})(\text{CH}_2)_2]_2\text{CH}_2$; FAB-MS: 1005 $[\text{M}-\text{Na}]^+$ (100), 885 $[\text{M}-\text{Na}-\text{OSO}_3\text{Na}]^+$ (21); HRMS: obsd. 1005.0082 [100.0, (calcd. 1005.0082 for C23 H20 O8 F26 S2 Na1)]; IR: 2865–2951 ($\nu_{\text{C-H}}$), 1223 ($\nu_{\text{C-F}}$).

4.8.2. F4(H6)F4OS

White solid, yield (%) 2.76 g (81%), decomp. 127 °C, ^1H NMR: δ 1.30–1.49 (m, 8H, a, b), 1.55–2.03 (m, 8H, c, e), 2.34 (m, 4H, f), 4.38 (m, 2H, d) for $[\text{CH}_2^a\text{CH}_2^b\text{CH}_2^c\text{CH}^d(\text{OSO}_3\text{Na})\text{CH}_2^e\text{CH}_2^f(\text{CF}_2)_4\text{F}]_2$; ^{19}F NMR: δ –82.7 (tt, 3F, $J = 9.7$ (3.0) Hz, d), –115.81 (m, 2F, a), –125.48 (m, 2F, b), –127.29 (m, 2F, c) for $[\text{FCF}_3^d\text{CF}_2^c\text{CF}_2^b\text{CF}_2^a(\text{CH}_2)_2\text{CH}(\text{OSO}_3\text{Na})(\text{CH}_2)_3]_2$; FAB-MS: 1655 $[\text{M}-\text{Na}]^+$ (2), 819 $[\text{M}-\text{Na}]^+$ (100), 699 $[\text{M}-\text{Na}-\text{OSO}_3\text{Na}]^+$ (19); HRMS: obsd. 819.0363 [100.0 (calcd. 819.0366 for C20 H22 O8 F18 S2 Na1)]; IR: 2864–2950 ($\nu_{\text{C-H}}$), 1219 ($\nu_{\text{C-F}}$).

4.8.3. F6(H6)F6OS

White solid, yield (%) 1.53 g (74%), decomp. 142 °C, ^1H NMR: δ 1.30–1.49 (m, 8H, a, b), 1.56–2.04 (m, 8H, c, e), 2.36 (m, 4H, f), 4.37

(m, 2H, d) for $[\text{CH}_2^a\text{CH}_2^b\text{CH}_2^c\text{CH}^d(\text{OSO}_3\text{Na})\text{CH}_2^e\text{CH}_2^f(\text{CF}_2)_6\text{F}]_2$; ^{19}F NMR: δ –82.2 (tb, 3F, $J = 9.7$ (broad) Hz, f), –115.4 (tb, 2F, $J = 18.2$ (broad) Hz, a), –122.90 (m, 2F, b), –123.88 (m, 2F, c), –124.39 (m, 2F, d), –127.29 (m, 2F, e) for $[\text{CF}_3^f\text{CF}_2^e\text{CF}_2^d\text{CF}_2^c\text{CF}_2^b\text{CF}_2^a(\text{CH}_2)_2-\text{CH}(\text{OSO}_3\text{Na})(\text{CH}_2)_3]_2$; FAB-MS: 1953 $[\text{M}-\text{Na}]^+$ (1), 1019 $[\text{M}-\text{Na}]^+$ (100), 899 $[\text{M}-\text{Na}-\text{OSO}_3\text{Na}]^+$ (18); HRMS: obsd. 1019.0241 [100.0 (calcd. 1019.0239 for C24 H22 O8 F26 S2 Na1)]; IR: 2865–2950 ($\nu_{\text{C-H}}$), 1220 ($\nu_{\text{C-F}}$).

4.8.4. F4(H7)F4OS

White solid, yield (%) 2.61 g (80%), decomp. 131 °C, ^1H NMR: δ 1.28–1.49 (m, 10H, a, b, c), 1.56–2.04 (m, 8H, d, f), 2.35 (m, 4H, g), 4.36 (m, 2H, e) for $\text{CH}_2^a[\text{CH}_2^b\text{CH}_2^c\text{CH}_2^d\text{CH}^e(\text{OSO}_3\text{Na})\text{CH}_2^f\text{CH}_2^g(\text{CF}_2)_4\text{F}]_2$; ^{19}F NMR: δ –82.7 (tb, 3F, $J = 9.7$ (broad) Hz, d), –115.81 (m, 2F, a), –125.47 (m, 2F, b), –127.30 (m, 2F, c) for $[\text{CF}_3^f\text{CF}_2^e\text{CF}_2^d\text{CF}_2^c\text{CF}_2^b\text{CF}_2^a(\text{CH}_2)_2-\text{CH}(\text{OSO}_3\text{Na})(\text{CH}_2)_3]_2\text{CH}_2$; FAB-MS: 1683 $[\text{M}-\text{Na}]^+$ (1), 833 $[\text{M}-\text{Na}]^+$ (100), 713 $[\text{M}-\text{Na}-\text{OSO}_3\text{Na}]^+$ (17); HRMS: obsd. 833.0524 [100.0 (calcd. 833.0523 for C21 H24 O8 F18 S2 Na1)]; IR: 2864–2935 ($\nu_{\text{C-H}}$), 1227 ($\nu_{\text{C-F}}$).

4.8.5. F6(H7)F6OS

White solid, yield (%) 1.46 g (86%), decomp. 153 °C, ^1H NMR: δ 1.30–1.49 (m, 10H, a, b, c), 1.56–2.04 (m, 8H, d, f), 2.36 (m, 4H, g), 4.38 (m, 2H, e) for $\text{CH}_2^a[\text{CH}_2^b\text{CH}_2^c\text{CH}_2^d\text{CH}^e(\text{OSO}_3\text{Na})\text{CH}_2^f\text{CH}_2^g(\text{CF}_2)_6\text{F}]_2$; ^{19}F NMR: δ –82.4 (tb, 3F, $J = 9.7$ (broad) Hz, f), –115.4 (tb, 2F, $J = 18.2$ (broad) Hz, a), –122.90 (m, 2F, b), –123.88 (m, 2F, c), –124.40 (m, 2F, d), –127.29 (m, 2F, e) for $[\text{CF}_3^f\text{CF}_2^e\text{CF}_2^d\text{CF}_2^c\text{CF}_2^b\text{CF}_2^a(\text{CH}_2)_2\text{CH}(\text{OSO}_3\text{Na})(\text{CH}_2)_3]_2\text{CH}_2$; FAB-MS: 2225 $[\text{M}-\text{Na}]^+$ (1), 1033 $[\text{M}-\text{Na}]^+$ (100), 913 $[\text{M}-\text{Na}-\text{OSO}_3\text{Na}]^+$ (24); HRMS: obsd. 1033.0394 [100.0 (calcd. 1033.0395 for C25 H24 O8 F26 S2 Na1)]; IR: 2864–2938 ($\nu_{\text{C-H}}$), 1239 ($\nu_{\text{C-F}}$).

4.8.6. F4(H8)F4OS

White solid, yield (%) 2.07 g (88%), decomp. 132 °C, ^1H NMR: δ 1.31–1.50 (m, 12H, a, b, c), 1.54–2.02 (m, 8H, d, f), 2.34 (m, 4H, g), 4.36 (m, 2H, e) for $[\text{CH}_2^a\text{CH}_2^b\text{CH}_2^c\text{CH}_2^d\text{CH}^e(\text{OSO}_3\text{Na})\text{CH}_2^f\text{CH}_2^g(\text{CF}_2)_4\text{F}]_2$; ^{19}F NMR: δ –82.6 (tb, 3F, $J = 9.7$ (broad) Hz, d), –115.69 (m, 2F, a), –125.50 (m, 2F, b), –127.20 (m, 2F, c) for $[\text{CF}_3^f\text{CF}_2^e\text{CF}_2^d\text{CF}_2^c\text{CF}_2^b\text{CF}_2^a(\text{CH}_2)_2-\text{CH}(\text{OSO}_3\text{Na})(\text{CH}_2)_4]_2$; FAB-MS: 1717 $[\text{M}-\text{Na}]^+$ (3), 847 $[\text{M}-\text{Na}]^+$ (100), 727 $[\text{M}-\text{Na}-\text{OSO}_3\text{Na}]^+$ (8); HRMS: obsd. 847.0681 [100.0 (calcd. 847.0679 for C22 H26 O8 F18 S2 Na1)]; IR: 2856–2935 ($\nu_{\text{C-H}}$), 1231 ($\nu_{\text{C-F}}$).

4.8.7. F6(H8)F6OS

White solid, yield (%) 2.23 g (76%), decomp. 153 °C, ^1H NMR: δ 1.31–1.49 (m, 12H, a, b, c), 1.55–2.03 (m, 8H, d, f), 2.36 (m, 4H, g), 4.38 (m, 2H, e) for $[\text{CH}_2^a\text{CH}_2^b\text{CH}_2^c\text{CH}_2^d\text{CH}^e(\text{OSO}_3\text{Na})\text{CH}_2^f\text{CH}_2^g(\text{CF}_2)_6\text{F}]_2$; ^{19}F NMR: δ –82.3 (tb, 3F, $J = 9.7$ (broad) Hz, f), –115.4 (tb, 2F, $J = 18.2$ (broad) Hz, a), –122.90 (m, 2F, b), –123.88 (m, 2F, c), –124.39 (m, 2F, d), –127.29 (m, 2F, e) for $[\text{CF}_3^f\text{CF}_2^e\text{CF}_2^d\text{CF}_2^c\text{CF}_2^b\text{CF}_2^a(\text{CH}_2)_2\text{CH}(\text{OSO}_3\text{Na})(\text{CH}_2)_4]_2$; FAB-MS: 2117 $[\text{M}-\text{Na}]^+$ (1), 1047 $[\text{M}-\text{Na}]^+$ (100), 927 $[\text{M}-\text{Na}-\text{OSO}_3\text{Na}]^+$ (15); HRMS: obsd. 1047.0552 [100.0 (calcd. 1047.0552 for C26 H26 O8 F26 S2 Na1)]; IR: 2854–2930 ($\nu_{\text{C-H}}$), 1239 ($\nu_{\text{C-F}}$).

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