

Novel Fluorinated Gemini Surfactants with γ-Butyrolactone Segments

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Abstract: In this work, novel γ -butyrolactone-type monomeric and dimeric (gemini) surfactants with a semifluoroalkyl group [Rf– (CH₂)₃–; Rf = C₄F₉, C₆F₁₃, C₈F₁₇] as the hydrophobic group were successfully synthesized. Dimethyl malonate was dimerized or connected using Br(CH₂)₃Br (s = 0, 1, 2, 3) to give tetraesters, and they were bis-allylated. Radical addition of fluoroalkyl using Rf–I and an initiator, i.e., 2,2'-azobisisobutyronitrile for C₄F₉ or di-*t*-butyl peroxide for C₆F₁₃ and C₈F₁₇, was perform at high temperature, with prolonged heating, to obtain bis(semifluoroalkyl)-dilactone diesters. These dilactone diesters were hydrolyzed using KOH/EtOH followed by decarboxylation in AcOH to afford γ -butyrolactone-type gemini surfactants. Common 1 + 1 semifluoroalkyl lactone surfactants were synthesized using the same method.

Their surfactant properties [critical micelle concentration (CMC), γ_{CMC} , pC_{20} , Γ_{CMC} , and A_G] were investigated by measuring the surface tension of the γ -hydroxybutyrate form prepared in aqueous tetrabutylammonium hydroxide solution. As expected, the CMC values of the gemini surfactants were more than one order of magnitude smaller than those of the corresponding 1 + 1 surfactants. Other properties also showed the excellent ability of the gemini structure to reduce the surface tension. These surfactants were easily and quantitatively recovered by acidification. The monomeric surfactant was recovered in the γ -hydroxybutyric acid form, and the gemini surfactant as a mixture of γ -butyrolactone and γ -hydroxybutyric acid forms.

Key words: Gemini surfactant, semifluoroalkyl, y-butyrolactone, surface tension, recovery

1 INTRODUCTION

Fluorosurfactants (fluorinated surfactants) are synthetic organofluorine chemicals with a fluorinated tail and a hydrophilic head^{1, 2)}. Fluorosurfactants can lower the surface tension of water to a value half of that achieved using hydrocarbon surfactants³⁾. Also, organofluorine chemicals are known to be more lipophobic than hydrocarbon surfactants.

Fluorosurfactants are more stable and suitable for harsh conditions than hydrocarbon surfactants because of the stability of the carbon–fluorine bond. However, perfluorinated surfactants persist in the environment⁴⁾, and some fluorosurfactants, such as perfluorooctanesulfonic acid and perfluorooctanoic acid cause environmental problems because of their persistence, toxicity, and widespread occurrence in the blood of humans and wildlife⁵⁾. Studies have shown that longer fluorosurfactants are more bioaccumulative and toxic but not shorter fluorosurfactants with

a fluoroalkyl chain length of C5 or below^{6,7)}. There is therefore an urgent need to develop fluorosurfactants with shorter fluoroalkyl chains for the situation where low surface tensions are needed.

Interest in dimeric (gemini) surfactants has recently grown, because of their unusual surfactant properties in solution⁸⁻¹²⁾. They consist of two conventional single-chain surfactant units connected at the neighbor of head groups by an alkyl chain (spacer), i.e., gemini surfactants have two polar head groups and two hydrophobic groups. Compared to the corresponding monomeric (1 + 1 type) surfactants, gemini surfactants usually have greater abilities to lower the critical micelle concentration (CMC) and surface tension, i.e., the gemini structure is highly effective in reducing the amount of surfactant consumed.

Previously, we developed SO₃H-type gemini surfactants with semifluoroalkyl groups (RfCH₂-; Rf = C₄F₉, C₆F₁₃, C₈F₁₇) from 1,4-pentadiene¹³⁾ and CO₂H-type malonic ester-

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Fig. 1 γ-Butyrolactone type surfactants with semifluoroalkyl group.

based gemini surfactants $(Rf-(CH_2)_n-; Rf=C_4F_9, C_6F_{13}, C_8F_{17} \text{ and } n=2,3)^{14})$, and their surface properties were studied. Surface tension measurements confirmed the superiority of the surfactant properties of the gemini structure, and it was concluded that the gemini structure would be excellent at achieving low surface tension, even with a fluoroalkyl chain length of C5 or below.

In this work, we investigated the synthesis and surfactant properties of novel lactone-type gemini surfactants with semifluoroalkyl groups as the hydrophobic segment, shown in Fig. 1, and their recoverabilities from aqueous solution.

2 EXPERIMENTAL PROCEDURES

2.1 Materials

All reagents and solvents were purchased from Wako Pure Chemical Industries, Ltd. Tetrahydrofuran (THF) and dimethylformamide (DMF) were dried over Na/benzophenone and CaH₂, respectively, and distilled just before use. Other reagents were used as received. Water was prepared by ultra-filtration of distilled water using an Advantec pure water system RFU354BA. Infrared (IR) spectra were recorded using a Nicolet Avator 370 DTGS FTIR spectrometer, and ¹H-nuclear magnetic resonance (NMR) spectra were recorded using a Brucker AC-300 spectrometer, with CDCl₃ as the solvent. Mass spectra were obtained using a JEOL Mstation JMS-700 mass spectrometer.

2.2 Synthesis

For detailed spectroscopic data for the synthesized gemini surfactants, see the Supporting Information. 2.2.1 Linkage of Dimethyl Malonate

2.2.1.1 Tetramethyl 1,1,2,2-Ethanetetracarboxylate $(\mathbf{1}_{s=0})$

Based on the procedure reported by Li *et al.*¹⁵⁾, dimethyl malonate (52.8 g, 0.4 mol) was added dropwise to a fresh sodium methoxide solution (1 mol/L, 400 mL) under stirring, and the mixture was kept for 1 h at room temperature. Br₂(32 g, 0.2 mol) in MeOH (100 mL) was slowly added to this mixture, and stirring was continued for 1 h. The

mixture was neutralized using 1 M HCl, and MeOH was removed under vacuum. The residue was subjected to Soxhlet extraction with CH_2Cl_2 . After removal of CH_2Cl_2 , the residue was recrystallized from MeOH–acetone to give $\mathbf{1}_{s=0}(33.1 \text{ g}, \text{yield: } 63\%)$.

2.2.1.2 Tetramethyl 1,1,3,3-Propanetetracarboxylate $(\mathbf{1}_{s=1})$ and Tetramethyl 1,1,5,5-Pentanetetracarboxylate $(\mathbf{1}_{s=3})$

Based on the procedure reported by Newkome *et al.*¹⁶⁾, a mixture of 1,1-dibromomethane (8.7 g, 50 mmol), dimethyl malonate (13.2 g, 100 mmol), and finely ground anhydrous $K_2CO_3(13.8 g, 24 mmol)$ in DMF (100 mL) was vigorously stirred at 25°C for 24 h, and heated to 100°C for 2 h. The mixture was filtered, and the solid was washed with DMF (50 mL). The combined filtrate was concentrated. The residue was dissolved in toluene (200 mL), washed sequentially with water (2×100 mL), 15% NaOH (2×100 mL), and water (2×100 mL), dried over anhydrous MgSO₄, and concentrated. The residue was distilled using a glass tube oven to give the tetraester $\mathbf{1}_{s=1}(11.0 \text{ g}, \text{yield } 67\%)$.

Similarly, using 1,3-dibromopropane, tetraester $\mathbf{1}_{s=3}$ was obtained in 46% yield after distillation.

2.2.1.3 Tetramethyl 1,1,4,4-Butanetetracarboxylate $(1_{s=2})$

Dimethyl malonate (52.8 g, 400 mmol) was added dropwise to a fresh sodium methoxide solution (1 mol/L, 400 mL) under stirring and kept for 1 h at room temperature. 1,2-Dibromoethane (7.52 g, 40 mmol) in MeOH (20 mL) was slowly added to this mixture at room temperature. After complete addition, the mixture was heated under reflux for 72 h. The mixture was neutralized using 1 M HCl, and concentrated. The residue was treated in a similar manner to that described above. The residue was recrystallized from diethyl ether to give $\mathbf{1}_{s=2}(2.36 \text{ g}, \text{ yield } 20\%)$. Dimethyl 1,1-cyclopropanedicarboxylate was obtained from the filtrate in 60% yield.

2.2.2 Tetramethyl 1,2-Diallyl-1,1,2,2-ethanetetra
carboxylate $(\mathbf{2}_{s=0})$

Compound $\mathbf{1}_{s=0}(23.5 \text{ g}, 90 \text{ mmol})$ was added dropwise to a fresh sodium methoxide solution (0.5 mol/L, 180 mL) under stirring and kept for 1 h at room temperature. Allyl bromide (12.0 g, 100 mmol) in MeOH (20 mL) was slowly added to this mixture at room temperature and then the mixture was heated under reflux for 24 h, with stirring. The mixture was neutralized using 1 M HCl and concentrated. The residue was dissolved in ether (200 mL), washed with water (2×150 mL), dried over anhydrous Na₂SO₄, and concentrated. The residue was distilled to give the monoallyl tetraester $\mathbf{5}_{s=0}(22.8 \text{ g}, \text{yield } 84\%)$.

Compound $5_{s=0}(3.0 \text{ g}, 10 \text{ mmol})$ in THF–DMF (3:1, 40 mL) was added dropwise to a suspension of NaH (60% oil dispersion, 0.48 g, 12 mmol) in THF–DMF (3:1, 160 mL) under ice-bath cooling and kept for 1 h at room temperature. After addition of a small amount of tetrabutylammonium iodide (TBAI), allyl bromide (2.0 g, 15 mmol) in THF–

DMF (3:1, 40 mL) was slowly added to the mixture at room temperature and the mixture was heated under reflux overnight. After neutralizing with 1 M HCl, the solvent was removed. The residue was dissolved in diethyl ether (100 mL), washed with water (3×50 mL), dried over Na₂SO₄, and concentrated. The residue was subjected to column chromatography on silica, eluted with hexane–AcOEt(5:1), to obtain diallyl tetraester $2_{s=0}$ (2.9 g, yield 88%).

2.2.3 Tetramethyl 1,3-Diallyl-1,1,3,3-ethanetetra
carboxylate($\mathbf{2}_{s=1})$

Compound $\mathbf{1}_{s=1}(9.7 \text{ g}, 35 \text{ mmol})$ in THF (20 mL) was added dropwise to a suspension of NaH(84 mmol) in THF (100 mL) under ice-bath cooling and kept for 1 h at room temperature. Allyl bromide (12.7 g, 105 mmol) in THF (20 mL) was slowly added at room temperature. After stirring for 6 h at room temperature, the mixture was neutralized and the solvent and excess allyl bromide were removed. The residue was dissolved in diethyl ether (100 mL), washed with water (3×50 mL), dried over Na₂SO₄, and concentrated. The residue was subjected to column chromatography on silica, eluted with hexane–AcOEt(5:1), to obtain diallyl tetraester $\mathbf{2}_{s=1}(9.2 \text{ g}, yield 74\%)$.

Similarly, using $\mathbf{1}_{s=2}$ and $\mathbf{1}_{s=3}$, diallyl tetraesters $\mathbf{2}_{s=2}$ and $\mathbf{2}_{s=3}$ were obtained in 89% and 92% yields, respectively. 2.2.4 Bis (perfluoroalkyl) Dilactone Diester **7** 2.2.4.1 Monolactone Triester $\mathbf{8}_{s=0}$

A typical monolactone triester with a perfluoroalkyl group, i.e., $8a_{s=0}$, was synthesized as follows. A mixture of $C_4F_9I(17.3 \text{ g}, 50 \text{ mmol})$, monoallyl tetraester $5_{s=0}(3.02 \text{ g}, 10 \text{ mmol})$, and 2,2'-azobisisobutyronitrile (AIBN; 0.16 g, 1 mmol) was introduced into a 100 mL flask and subjected to vacuum-flushing with argon after freezing with liquid nitrogen. This mixture was heated under reflux with stirring for 8 h. After recovery of unreacted C_4F_9I , the resulting oil was purified by column chromatography on silica, eluted with hexane–AcOEt(5:1), to yield monolactone triester $8a_{s=0}$

Similarly, using $C_6F_{13}I$ and $C_8F_{17}I$, monolactone triesters $\mathbf{8b}_{s=0}$ and $\mathbf{8c}_{s=0}$ were obtained in 89% and 87% yields, respectively. In these reactions, di-*t*-butyl peroxide (DTBPO) was used instead of AIBN, and reaction temperature was raised to 120°C.

2.2.4.2 Allyl Monolactone Triester s $9a_{s=0}$ and $9a_{s=0}$

(4.38 g, yield 87%).

Compound $8a_{s=0}(10.1 \text{ g}, 20 \text{ mmol})$ in THF–DMF (20 mL) was added dropwise to a suspension of NaH(40 mmol) in THF–DMF (200 mL) with ice-bath cooling, and kept for 1 h at room temperature. A small amount of TBAI was added, and allyl bromide (7.26 g, 60 mmol) in THF–DMF (20 mL) was slowly added at room temperature; the mixture was heated under reflux for 24 h. After neutralization, the solvent was removed *in vacuo*. The residue was dissolved in diethyl ether (100 mL), washed with water (3 × 50 mL), dried over Na₂SO₄, and concentrated *in vacuo*. The residue was subjected to column chromatography on silica,

eluted with hexane–AcOEt (5:1), to obtain two stereoisomers of the monoallyl triester: $9a_{s=0}(5.29 \text{ g}, \text{ yield } 49\%)$ and $9'a_{s=0}(2.38 \text{ g}, \text{ yield } 22\%)$.

Similarly, pairs of allyl monolactone triesters, i.e., $9\mathbf{b}_{s=0}$ and $9'\mathbf{b}_{s=0}$, and $9\mathbf{c}_{s=0}$ and $9'\mathbf{c}_{s=0}$, were obtained and separated using column chromatography.

2.2.4.3 Dilactone Diester $7_{s=0}$

A typical dilactone diester $7a_{s=0}$ was synthesized as follows. A mixture of C_4F_9I , (6.9 g, 20 mmol), $9a_{s=0} + 9'a_{s=0}$ (1.09 g, 10 mmol), and AIBN(0.032 g, 0.2 mmol) was introduced into a 30 mL flask, and subjected to vacuum-flushing with argon. This mixture was heated under reflux with stirring for 8 h. After removal of unreacted C_4F_9I , the resulting oil was purified by column chromatography, with hexane– AcOEt(5:1) as the eluent, to yield dilactone diester $7a_{s=0}$ (0.2 g, yield 13%).

Similarly, using $C_6F_{13}I$ and $C_8F_{17}I$, dilactone diesters $7b_{s=0}$ and $7c_{s=0}$ were obtained in 21% and 31% yields, respectively. In these reactions, DTBPO was used instead of AIBN and the reaction temperature was raised to 120°C.

2.2.4.4 Dilactone Diester $7_{s=1,2,3}$

The general procedure for the synthesis of dilactone diesters **7** with spacer lengths s = 1, 2, and 3 was as follows. A mixture of perfluoroalkyl iodide (50 mmol), $2_{s=1,2,3}$ (5 mmol), and DTBPO (0.5 mmol) was introduced into a 100 mL flask, and subjected to vacuum-flushing with argon. This mixture was heated at 90°C for 72 h(C₄F₉I) or 120°C for 8 h(C₆F₁₃I and C₈F₁₇I) under stirring. After removal of unreacted iodide, the resulting oil was purified by column chromatography on silica, eluted with hexane–AcOEt(5:1), to yield dilactone diesters $7_{s=1,2,3}$.

2.2.4.5 Dilactone Diacid $10_{s=0, 1, 2, 3}$

A mixture of 7(1 mmol) and KOH(20 mmol) in EtOH– H₂O(1:5, 30 mL) was heated under reflux for 12 h with stirring. The clear solution was added dropwise to 1 M HCl(80 mL), and this acidified mixture was left for 1 h. The resulting precipitate 10 was filtered and dried *in vacuo* for at least 12 h without further purification.

2.2.4.6 Gemini Dilactones $11_{s=0, 1, 2, 3}$

The resulting white solid **10** was dissolved in AcOH(50 mL) and heated under reflux for 24 to 48 h with stirring. Complete decarboxylation of **10** was confirmed using thinlayer chromatography, and then the AcOH was removed *in* vacuo. The residue was extracted with CH_2Cl_2 , washed twice with water, dried over Na_2SO_4 , and concentrated. The residue was dissolved in a small amount of THF and reprecipitated by adding hexane, to afford the gemini dilactone **11**. Total yields of **11** from **7** were determined. All yields and spectroscopic data for **11** are summarized in **Table 1**.

2.2.5 1+1-Type Perfluoroalkyl lactone 15

The general procedure for the synthesis of 1 + 1 perfluoroalkyl lactones 15 was as follows. Dimethyl allylmalonate 12 was prepared by the reaction of dimethyl malonate and

Abbreviation	Rf	-(CH ₂) _s -	yield (%)	¹ H-NMR (300MHz, CDCl ₃) δ	IR (cm ⁻¹)	HR-FABMS m/z: [M+H] ⁺
$11a_{s}=0$		s=0	38 ^a	1.91-3.12 (10H, m), 4.82-5.03 (2H, m)	1764	635.0527 (636.0605) [°]
$11a_{s=1}$		s=1	27 ^a	1.73-1.94 (4H, m), 2.30-3.13 (8H, m), 4.72-4.98 (2H, m)	1785	649.0684 (649.0683) [°]
$11a_{s=2}$	C4F9	s=2	21^{a}	1.66-2.16 (2H, m), 2.26-2.40 (4H, m), 2.62-2.74 (6H, m), 4.69-4.95(2H, m) 1.49-1.89 (6H, m), 2.23-2.40 (4H, m), 2.59-2.66 (6H, m), 4.68-4.94 (2H, m)	1780	663.0834 (663.0839) [°]
$11a_{s=3}$		s=3	68 ^a		1780	677.0970 (677.0996) [°]
$11b_{\mathcal{S}}=0$		s=0	54 ^a	insoluble in CDCl ₃	1765	835.0397 (835.0399) ^c
$11b_{s=1}$	$C_{6}F_{13}$	s=1	44 ^a	1.72-1.90 (4H, m), 2.29-3.11 (8H, m), 4.72-5.01 (2H, m)	1777	849.0557 (849.0555) [°]
$11b_{s=2}$		s=2	22 ^a	1.61-2.04 (4H, m), 2.25-2.38 (4H, m), 2.40-2.67 (6H, m), 4.72-4.96 (2H, m)	1771	863.0725 (863.0712) ^c
$11b_{s=3}$		s=3	64 ^a	1.61-1.91 (6H, m), 2.23-2.39 (4H, m), 2.59-2.74 (6H, m), 4.68-4.92 (2H, m)	1776	877.0858 (877.0868) [°]
$11c_{s=0}$		s=0	42 ^a	insoluble in CDCl ₃	1764	1035.0264 (1035.0271) ^c
$11c_{s=1}$	C_8F_{17}	s=1	50^{a}	insoluble in CDCl ₃	1777	1049.0399 (1049.0427) ^c
11 $c_{s=2}$		s=2	53 ^a	insoluble in CDCl ₃	1777	1063.0573 (1063.0584) ^c
11c _{s=3}		s=3	36 ^a	1.61-1.91 (6H, m), 2.23-2.39 (4H, m), 2.59-2.74 (6H, m), 4.68-4.92 (2H, m)	1773	1077.0699 (1077.0740) ^c
15a	C ₄ F ₉	-	86 ^b	1.99-2.50(2H, m), 2.54-2.77 (4H, m), 4.85 (1H, m)	1783	319.0376 (319.0381) ^c
15b	$C_{6}F_{13}$	-	82 ^b	2.04-2.41 (2H, m), 2.50-2.85 (4H, m), 4.85 (1H, m)	1772	419.0307 (419.0317) ^c
15c	C_8F_{17}	-	82 ^b	2.00-2.6 (2H, m), 2.50-2.75 (4H, m), 4.86 (1H, m)	1770	519.0303 (519.0253) ^c

 Table 1
 List of yields and spectral data of gemini dilactone 11 and 1 + 1 lactone 15.

a: Yield was calculated from dilactone diester 7. b: Yield was calculated from allyl malonate.

c: All values in parenthesis are calculated ones.

allyl bromide, using NaH as the base, in THF. A mixture of perfluoroalkyl iodide (60 mmol), **12** (20 mmol), and AIBN for C_4F_9I , or DTBPO for $C_6F_{13}I$ and $C_8F_{17}I(2 \text{ mmol})$, was introduced into a 100 mL flask, and subjected to vacuum-flushing with argon. This mixture was heated at 90°C for 12 h(AIBN) or 120°C for 8 h(DTBPO) under stirring. After removal of unreacted iodide, the resulting oil was confirmed to be the monoiodo ester **13** by ¹H NMR spectroscopy, and was directly used in the next lactonization step.

The residue **13** was introduced into a 10 mL flask, subjected to vacuum-flushing with argon, and heated at 140° C under stirring for 24 h. The resulting oil was purified by column chromatography on silica with hexane-AcOEt(5:1) as the eluent, to afford lactone ester **14**.

Similar to the gemini compound synthesis, hydrolysis of 14 using KOH in EtOH– H_2O followed by decarboxylation of the resulting lactone acid in AcOH was performed. After removal of AcOH, the residue was subjected to column chromatography on silica, eluted with hexane–AcOEt(5:1),

to afford 1 + 1 perfluoroalkyl lactone **15**. Total yields of **15** from **12** were determined. Yields and spectroscopic data for **15** are summarized in **Table 1**.

2.3 Surface Tension Measurements

Surface tension measurements were performed using a Shimadzu surface tensiometer (ST-1) at 25°C. Samples were prepared as follows. A precise weight of **11**, for example **11b**_{s=3}(87.74 mg, 1 mmol), was added to aqueous tetrabutylammonium hydroxide (TBAH) solution (40%, 3 mL), and heated at 90°C for 2 h under stirring. The resulting clear solution was completely transferred to a 100 mL measuring flask, diluted with distilled water, and subjected to ultrasonication. This mother solution was used to obtain solutions of desired concentrations. The sample solutions were stored at 25°C for 12 h before measurements.

3 RESULTS AND DISCUSSION

There are three components involved in the synthesis of gemini surfactants: hydrophobic tails, hydrophilic heads, and connecting groups (spacers). In fluoroalkylated gemini surfactants, fluoroalkyl groups are introduced into the tail segment; this is generally achieved by radical addition of a perfluoroalkyl iodide to a $H_2C = CH_2$ group, as described by Brace¹⁷⁾. In our previous study¹⁴⁾, CO₂H-type malonic acidbased gemini surfactants containing semifluoroalkyl groups $(Rf-(CH_2)_n-; Rf=C_4F_9, C_6F_{13}, C_8F_{17} \text{ and } n=2, 3) \text{ and } (CH_2)_s$ - spacers (s = 3, 4) were successfully synthesized via the connection of $Rf-(CH_2)_3$ -malonic esters, which were synthesized by radical addition of Rf–I to the $H_2C = CH$ – CH₂- moiety of allvlmalonic ester, followed by reduction with Zn/AcOH, linking with $Br(CH_2)_sBr(s=3, 4)$ to tetraesters, and then hydrolysis and decarboxylation. In this synthetic route, the introduction of the fluoroalkyl group into the tail segment is the initial step.

In this work, as shown in **Scheme 1**, we devised a new strategy for the synthesis of CO_2H -type malonic acid-based gemini surfactants **4**. This is a sequential process involving connection of dimethyl malonate to tetraester **1**, diallylation **2** at the connecting points, radical addition of Rf–I, reduction, hydrolysis, and decarboxylation.

3.1 Synthesis of Diallyl Tetraesters 2

The first step was connection of dimethyl malonate with the $-(CH_2)_{s}$ - spacer (s = 0, 1, 2, 3). Based on the method described by Li *et al.*¹⁵⁾, direct connection (dimerization) of dimethyl malonate to $\mathbf{1}_{s=0}$ was carried out *via* oxidative coupling of the enolate. Connections with other spacers(s = 1, 2, 3), were performed using the method described by Newkome *et al.*¹⁶⁾, and the connection of malonate with ω , ω '-dibromoalkane with K₂CO₃ as the base was examined. As Newkome *et al.* reported, $\mathbf{1}_{s=1}$ and $\mathbf{1}_{s=3}$ were obtained in

good yields, but hardly any $\mathbf{1}_{s=2}$ was obtained, because of preferential cyclopropane formation. We changed the molar ratio of dimethyl malonate to dibromoethane to 10:1, and $\mathbf{1}_{s=2}$ was obtained in $\sim 20\%$ yield, with dimethyl 1,1-cyclopropanedicarboxylate (60%) as the major product.

Next, diallylation at the connecting points (diallyl tetraesters 2) was carried out in THF, using NaH as the base. Compounds $2_{s=1}$, $2_{s=2}$, and $2_{s=3}$ were obtained in good yields, but $2_{s=0}$ was not produced as a major product, probably because the adjacent dianion (enolate) intermediate of $1_{s=0}$ is unstable. Therefore, in the case of $2_{s=0}$, allylation was carried out twice.

3.2 Radical Addition of Perfluoroalkyl lodide to 2

Radical addition of C_4F_9I to dially tetraester $2_{s=3}$, using AIBN as the initiator, was performed using various molar ratios, reaction temperatures, and times. The results are summarized in Table 2. In most cases, both the diiodo tetraester $\mathbf{3a}_{s=3}$ and unexpected monoiodo monolactone triester $6a_{s=3}$ were produced (Fig. 2), and the ratio of $3a_{s=3}$ to $6a_{s=3}$ increased with increasing amount of C_4F_9I used. This shows that C_4F_9I also acted as a solvent (bp 69°C) and lowered the reaction temperature. As run 7 shows, a prolonged reaction time resulted in a decrease in the amount of $3a_{s=3}$, even at low reaction temperatures. These results suggest that monoiodo monolactone triester $6a_{s=3}$ was thermally derived from $3a_{s=3}$ via intramolecular cyclization, as shown in Fig. 3. Heating the isolated $\mathbf{3}_{s=3}$ at 80°C for 1 h in the absence of a solvent gave a mixture of $6a_{s=3}$ and dilactone diester $7a_{s=3}$.

After isolation, $\mathbf{3}_{s=3}$ was reduced using Zn/HI, to give the bis (nonafluorononyl) tetraester. However, the obtained products were a complex mixture containing monolactone and dilactone esters. Similar reductions with Zn/HCl have been reported to afford lactone derivatives¹⁸, therefore



	C ₄ F ₉ –I	bath temp.	Time (h)	conversion (%)	ratio of products (%)*		
run	(equiv.)	(°C)			3a _{s=3}	$6a_{s=3}$	$7a_{s=3}$
1	2	80	8	64	~3	72	25
2	3	80	8	83	13	87	trace
3	4	80	8	92	20	80	trace
4	6	80	8	95	45	55	_
5	10	80	8	83	58	42	_
6	4	70	8	82	36	64	_
7	4	70	24	92	9	91	_
8	10	70	8	98	70 (62)**	30 (24)**	-

Table 2 Reaction conditions and results of the radical addition of C_4F_9 -I to $2_{s=3}$.

*: determined by NMR, **: isolated yield.



Fig. 2 Obtained products by the radical addition of C_4F_9 -I to diallyl tetraester $2s_{=3}$.



Fig. 3 Proposed mechanism for lactonization of γ-iodo diester.

other reductants were examined. Bu₃SnH was best, but the yield of $4_{s=3}$ was less than 50%. Subsequent hydrolysis and decarboxylation gave the malonic acid-based gemini surfactant 1,5-bis (nonafluoroheptyl) heptanedioic acid $4_{s=3}^{14}$.

The initial strategy for synthesis of malonic acid-based gemini surfactants was successful, but it should be noted that the reaction temperature for radical addition of Rf–I has a profound effect on the yields of diiodo derivatives.

3.3 Synthesis of Dilactone Diesters 7

 γ -Butyrolactone is hydrophilic and soluble in water; it is hydrolyzed to γ -hydroxybutyrate under basic conditions, e.g., in NaOH solution, and under acidic conditions it forms an equilibrium mixture of γ -butyrolactone and γ -hydroxybutyric acid. As γ -hydroxybutyrate is more hydrophilic than γ -butyrolactone itself, dilactone derivatives are promising as novel gemini surfactants under basic conditions. We therefore investigated the synthesis of dilactones (Scheme 2).

As shown above, high reaction temperatures and lengthy heating times result in thermal lactonization of iodo diesters. In the case of C_4F_9I , the bath temperature was kept at 90°C for 72 h, and in the cases of C_6F_1I and $C_8F_{17}I$, DTBPO was used instead of AIBN, and the reaction temperature was 120°C. In all cases, 10 times the molar amount of Rf–I was used, to ensure complete consumption of diallyl tetraester **2**. The results are summarized in **Table 3**. Radical addition of Rf–I and cyclization to dilactone diesters **7** proceeded smoothly, except in the cases of $\mathbf{2}_{s=0}$ and $\mathbf{2}_{s=1}$. For these compounds, with short spacers, several byproducts, including dehydrogeniodide products, were observed, probably because of steric hindrance in the Rf–I adducts.

In the case of $7_{s=0}$, stepwise synthesis was used (Scheme 3). First, the monoallyl tetraester ($5_{s=0}$) was reacted with Rf–I(C₄F₉, C₆F₁₃, and C₈F₁₇) to obtain the corresponding fluoroalkylated monolactone triesters $8_{s=0}$ in ~90% yields. A second allylation of $8_{s=0}$ was carried out, giving two monoallyl monolactone triesters, $9_{s=0}$ and $9'_{s=0}$, in nearly 70% yields (total). ¹H NMR spectroscopy showed that they were stereoisomers, with RfCH₂ substituted at the γ -position of the butyrolactone ring, in a ratio of ~2:1. Although it was



Scheme 2

run	Df	c.	initiator	bath temp.	Time	yield (%)
Tull	KI	3	minator	(°C)	(h)	7
1		0	AIBN	90	72	Complex mixture
2	CE	1	AIBN	90	72	18
3	$C_4 F_9$	2	AIBN	90	48	72
4		3	AIBN	90	24	90
5		0	DTBPO	120	8	Complex mixture
6		1	DTBPO	120	8	24
7	$C_{6}F_{13}$	2	DTBPO	120	8	97
8		3	AIBN	90	8	82
9		3	DTBPO	120	8	100
10		0	DTBPO	120	8	Complex mixture
11		1	DTBPO	120	8	21
12	$C_8 F_{17}$	2	DTBPO	120	8	100
13		3	AIBN	90	8	83
14		3	DTBPO	120	8	100

Table 3 Reaction conditions and results of the radical addition of Rf–I to 2.

possible to isolate these two isomers by silica column chromatography, a mixture of two isomers was directly subjected to a second Rf–I radical addition and lactonization. The yields of $7_{s=0}$ containing C₄F₉, C₆F₁₃, and C₈F₁₇ were 13%, 21%, and 31%, respectively.

3.4 Synthesis of Gemini Dilactones 11

Similar to the synthesis of malonic acid-based gemini compounds¹⁴⁾, dilactone diesters **7** were hydrolyzed under alkaline conditions using excess KOH; after acidification, the precipitates were collected. The IR spectra showed that the products were mixtures of butyrolactones and γ -hydroxybutyric acids. After drying, the resulting solid was dissolved in AcOH and heated under reflux for more than 48 h. Although, as expected, the yields were low(20–60%), decarboxylation and lactonization proceeded simultaneously to afford gemini dilactones **11**.

3.5 Synthesis of 1+1 type Perfluoroalkylated Lactones 15

The corresponding 1 + 1 surfactants, i.e., perfluoroalkylated lactones 15, were synthesized as shown in Scheme 5. Radical addition of Rf–I to monoallyl malonates 12^{14} proceeded quantitatively to give γ -iodo diesters **13**. Unfortunately, even prolonged heating in the presence of Rf–I did not convert the γ -iodo diesters to lactone monoesters **14**. This is probably because steric hindrance in the 1 + 1 lactones would be lower than in the gemini structure. When γ -iodo diesters **13** were heated at 140°C for 24 h, the lactone monoesters **14** were obtained in moderate yields. Lactone monoesters **14** were hydrolyzed under alkaline conditions, and subsequent decarboxylation in AcOH gave the target 1 + 1 perfluorinated lactones **15** in good yields.

3.6 Surface Tension Measurements

Unlike unsubstituted γ -butyrolactone, perfluoroalkylated 1 + 1 and gemini lactone surfactants are insoluble in water. Therefore, to change the butyrolactone framework to the more hydrophilic hydroxybutyrate, alkaline conditions were used to prepare sample solutions. As expected, all the 1 + 1 lactone surfactants **15** were soluble in aqueous NaOH and KOH solutions; the gemini dilactone surfactants **11c**, Rf = C₈F₁₇ and *s* = 0–3, were hardly soluble in aqueous NaOH and KOH solutions, **11b**_{*s*=0} and **11b**_{*s*=1} were partially soluble in KOH solution, and **11a** were all soluble in KOH



solution. In contrast, when TBAH was used as the alkaline reagent, 11a, 11b, and even $11c_{s=3}$ were soluble in water.

Figure 4 shows the IR spectra of lactone 15b(neat, NaCl), γ -hydroxybutyrate (in aqueous TBAH solution, using a microCIRCLE[®]-cell from Spectra-Tech with a ZnSe crystal), and γ -hydroxybutyric acid(solid, KBr). As the figure shows, the strong peak at 1770 cm⁻¹(chart A) attributable to γ -lactone disappeared in TBAH solution; a new peak was observed at 1606 $\text{cm}^{-1}(\text{chart B})$, which can be attributed to COO^- of γ -hydroxybutyrate, indicating that the lactone ring was completely opened by hydrolysis using TBAH. On acidification, the precipitated solid showed a C = O stretching peak at 1687 $\text{cm}^{-1}(\text{chart C})$, but no lactone peak, which means that simple acidification did not cause recyclization to the lactone. The surface properties, i.e., CMC, effectiveness of surface tension reduction (γ_{CMC}), efficiency of surface tension reduction (pC_{20}) : negative logarithm of the surfactant concentration required to reduce the surface tension of the solvent, i.e., water by 20 mN/ $m^{18)}$, maximum surface excess concentration (Γ_{CMC}), and the Gibbs occupied minimum area (A_G) of the fluoroalkylated lactone surfactants were therefore investigated at 25° in aqueous TBAH solution.

3.6.1 1+1 Lactone Surfactants

The results for 1 + 1 lactone surfactants **15** in aqueous TBAH solution are shown in **Fig. 5** and **Table 4**. A definite CMC can be observed and the γ_{CMC} values were 23, 16, and 13 mN/m for Rf = C₄F₉, C₆F₁₃, and C₈F₁₇, respectively; these values are almost the same as those of semifluoroalkylated fatty acids in KOH solution. Similar to hydrocarbon monomeric surfactants, both CMC and γ_{CMC} became smaller with increasing carbon number of the fluoroalkyl group (C₄F₉> C₆H₁₃>C₈F₁₇).

The adsorbed amount of a surfactant $(\Gamma_{\rm CMC})$ can be calculated using the Gibbs adsorption equation, $\Gamma = -(1/vRT)$ $(d\gamma/d\ln C)^{19}$. Here, γ denotes the surface tension, R is the gas constant (8.31 J mol⁻¹ K⁻¹), T is the absolute temperature, and C is the surfactant concentration. The value of vused in this study was 2, because the concentration of TBAH was not high and the volume of tetrabutylammonium counter ions adsorbed at the air/water interface would be large. In our previous $\mathrm{work}^{20)}, A_\mathrm{G}$ values for $\mathrm{Rf-(CH_2)}_n COOK(Rf = C_4F_9, C_6F_{13}, C_8F_{17}; n = 3-10)$ were in the range 0.35-0.45 nm² per molecule. Contrary to our expectations, all the $A_{\rm G}$ values for 15 were twice as large as those for Rf– $(CH_2)_n$ -COOK; this may be because of the large volume of tetrabutylammonium counter ions at the air/water interface. With regard to the effect of fluoroalkyl length on the $A_{\rm G}$ value, **Table 4** also shows that $A_{\rm G}$ increased with increasing fluoroalkyl length; this is the opposite trend to the CMC and $\gamma_{\rm CMC}$ values. Further investigation is necessary to clarify these results.

3.6.2 Gemini Dilactone Surfactants

As in the case of 1 + 1 surfactants, sample solutions were



Fig. 4 IR spectra of 1 + 1 lactone surfactant with semifluoroalkyl group, **15b** (Rf = C₆F₁₃): A, γ -butyrolactone form (NaCl); B, γ -hydroxybutyrate form in 0.01M TBAH solution (microCIRCLE[®]-cell); C, recovered γ -hydroxybutyric acid form by acidification of sample B (KBr).

prepared using TBAH solution. Figure 6 shows the IR spectra of lactone $11c_{s=3}$ (KBr, chart D) and γ -hydroxybutyrate (in TBAH solution, chart E). As can be seen, the strong γ -lactone peak at 1764 cm⁻¹ disappeared in TBAH solution, and a COO⁻ peak was observed at 1607

cm⁻¹, clearly indicating that the two lactone rings were completely opened by hydrolysis. These surfactants with bis (γ -hydroxybutyrate) structures are called dilactone gemini surfactants. The surface properties (CMC, γ_{CMC} , and $A_{\rm G}$) of the dilactone gemini surfactants were investigated in aqueous TBAH solution at 25°C. The results are shown in **Figs. 7-9** and **Table 5**.

Figure 7a and 7b show the surface tension versus concentration curves of all the dilactone gemini surfactants prepared from $11a (C_4F_9)$ and $11b (C_6F_{13})$, respectively, with 15a and 15b, respectively, in aqueous TBAH solution at 25°C. The CMC values of 11a were all around 2.0×10^{-3} mol/L and were one order of magnitude smaller than that of 15a. In addition, the $\gamma_{\rm CMC}$ values of 11a were smaller than that of 15a. In the case of 11b, all the CMC values were around 2.0×10^{-5} mol/L, and were two orders of magnitude smaller than that of 15b, but the $\gamma_{\rm CMC}$ values were comparable to that of 15b. These results show that the gemini structure is effective in decreasing the surface tension of water.

In terms of the effect of spacer length on surface activity, the CMC, γ_{CMC} , and A_{G} values were almost the same, regard-



Fig. 5 Surface tension-concentration curves of 1 + 1 lactone surfactants with semifluoroalkyl group in aqueous TBAH solution at 25° C. \Box : **15a** (Rf = C₄F₉), \bigtriangleup : **15b** (Rf = C₆F₁₃), \blacktriangledown : **15c** (Rf = C₈F₁₇).

less of the spacer length. Similar independence of the spacer length was observed in the surface tension-concentration curves and surface pressure-area isotherms of hydrocarbon-type malonic gemini surfactants (Akedo, Y.; Oida, T; Kawase, T., unpublished data). It was therefore expected that the effect of spacer length on the surface activities of dilactone gemini surfactants would be small.



Fig. 6 IR spectra of gemini dilactone surfactant with semifluoroalkyl group, $11c_{s=3}$ (Rf = C₈F₁₇): D, bis(γ -butyrolactone) form (KBr); E, bis(γ hydroxybutyrate) form in 0.01M TBAH solution (microCIRCLE[®]-cell).

Table 4Surfactant properties of semifluoroalkylated 1 + 1 lactone
surfactants in aqueous TBAH solution at 25° C.

1+1 type	CMC (mol/L)	$\gamma_{\rm CMC}$ (mN/m)	pC_{20}	$\Gamma_{\rm CMC}$ (µmol/m ²)	$A_{\rm G}$ (nm ² /molecule)
15a	1.8×10^{-2}	23	3.4	1.9	0.90
15b	2.0×10^{-3}	16	4.5	1.8	0.95
15c	4.7×10^{-4}	13	5.7	1.4	1.19



Fig. 7 Effects of spacer length on surface tensions of gemini dilactone surfactants with semifluoroalkyl group in aqueous TBAH solution at 25° C. **a**: **11a** (Rf = C₄F₉, *s*=0, 1, 2, 3), **b**: **11b** (Rf = C₆F₁₃, *s*=0, 1, 2, 3).

Surface tension measurements were only performed for $11c_{s=3}$, because it was soluble in aqueous TBAH solution, whereas $11c_{s=0}$ to $11c_{s=2}$ were only slightly soluble. As shown in Fig. 8, as expected, the CMC of $11c_{s=3}$ was one order of magnitude smaller than that of 15c. However, the γ_{CMC} value was, unexpectedly, higher than that of 15c.

The effect of fluoroalkyl length on the surface activity was also investigated. It is widely accepted that an increase in surfactant hydrophobicity reduces the CMC and $\gamma_{\rm CMC}$. For malonic gemini surfactants with RfCH₂CH₂CH₂ and s = 3 in 0.01 mol/L KOH solution¹⁴⁾, the CMC values were 9.0×10^{-4} , 5.0×10^{-5} , and 5.0×10^{-5} mol/L for Rf = C₄F₉, C₆F₁₃, and C₈F₁₇, respectively, which accords with the common



Fig. 8 Effect of fluoroalkyl length on surface tensions of gemini dilactone surfactants in aqueous TBAH solution at 25°C. \Box : 11 $\mathbf{a}_{s=3}$ (Rf = C₄F₉), $\mathbf{\nabla}$: 11 $\mathbf{b}_{s=3}$ (Rf = C₆F₁₃), \oplus : 11 $\mathbf{c}_{s=3}$ (Rf = C₈F₁₇).



Fig. 9 Comparison of surface tension-concentration curves of gemini dilactone surfactant $11b_{s=3}$ (\bigcirc) and malonic-based gemini surfactant 4 (\bigcirc : Rf = C_6F_{13} , s=3) in aqueous TBAH solution at 25°C.

effect of hydrophobicity. However, as can be seen in Fig. 8, the order of the CMC values of dilactone gemini surfactants was different, namely $C_4F_9>C_8F_{17}>C_6F_{13}$. However, the A_G value of $11c_{s=3}$ was smaller than those of 15c and other dilactone gemini surfactants, possibly because of the relatively high interactions between long fluoroalkyl groups.

The IR spectra (**Figs. 4** and **6**) show that the lactone rings were completely opened by TBAH to γ -hydroxybutyrate, which is more hydrophilic than a simple carboxylate anion. The fluoroalkylated malonic gemini $4_{s=3}$ (C₆F₁₃CH₂CH₂CH₂, s=3) was also dissolved in aqueous TBAH solution, for comparison with $11b_{s=3}$ (Fig. 9). Contrary to expectations,

	Rf	S	CMC (mol/L)	γ _{смс} (mN/m)	$A_{\rm G}$ (nm ² /molecule)
		0	1.2×10^{-3}	20	1.57
11.0	СE	1	4.5×10^{-3}	24	1.85
118	C_4F_9	2	3.7×10^{-3}	22	1.59
		3	2.0×10^{-3}	23	1.58
		0	1.5×10^{-5}	22	1.20
1116	CE	1	2.0×10^{-5}	22	1.44
110	$C_{6}\Gamma_{13}$	2	2.2×10^{-5}	22	0.91
		3	2.0×10^{-5}	19	1.22
$11c_{s=3}$	$C_8 F_{17}$	3	6.5×10^{-5}	20	0.48
Malonic gemini, 4	$C_{6}F_{13}$	3	2.0×10^{-4}	18	1.20

Table 5 Surfactant properties of semifluoroalkylated gemini dilactone surfactants in aqueous TBAH solution at 25°C.

the CMC of $11b_{s=3}$ was one order of magnitude smaller than that of the malonic gemini surfactant, but their γ_{CMC} and A_{G} values were almost the same. The reason for this result is not clear, and further investigation is ongoing.

3.7 Recovery of Gemini Dilactone Surfactants

In view of potential environmental problems, the recovery of these surfactants was investigated (**Scheme 6**).

In the case of 1 + 1 lactone **15c**, acidification gave a precipitate that showed a C = O stretching peak at 1687 cm⁻ but no lactone peak in the IR spectrum (Fig. 4). This C = Opeak can be attributed to γ -hydroxybutyric acid. After isolation, the resulting solid was heated in AcOH(100°C, 3 h) and 15c was recovered quantitatively, which clearly shows that simple acidification did not cause recyclization to the lactone. Acidification of a TBAH solution of $11c_{s=3}$ also gave a precipitate, but the IR spectrum had two C = Ostretching peaks, at 1764 and 1692 cm⁻¹, attributable to lactone and γ -hydroxybutyric acid structures, respectively (Fig. 10, chart F). In the case of dilactone gemini surfactants, simple acidification achieved spontaneous recyclization of γ -hydroxybutyric acid to the lactone, although the conversion was not complete ($\sim 80\%$). In addition, heating the precipitate at 100° in AcOH for 4 h completely converted to the lactone (chart G), and the recovery was quantitative. The difference between the recoveries of gemini surfactants and 1+1 surfactants can be explained in terms of steric hindrance at the connecting point: lactonization (recyclization) reduces steric hindrance at the connecting point, but in 1+1 surfactants, such hindrance can be neglected.

4 CONCLUSION

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Novel γ -butyrolactone monomeric (1+1) and dimeric



(gemini) surfactants containing semifluoroalkyl groups (Rf– $(CH_2)_3$ -; Rf = C₄F₉, C₆F₁₃, C₈F₁₇) as the hydrophobic group and $-(CH_2)_s$ -(s = 0, 1, 2, 3) as the spacer were successfully synthesized, and their surfactant properties were studied based on surface tension measurements.

All the monomeric semifluoroalkylated γ -butyrolactones were soluble in aqueous NaOH, KOH, and TBAH solutions, as the γ -hydroxybutyrate form. Dilactone gemini surfactants with longer Rf groups were poorly soluble in NaOH and KOH solution, but when TBAH was used, most gemini surfactants were soluble in water in the bis(γ -hydroxybutyrate) form. The CMC and pC_{20} values showed the excellent efficiency of the gemini structures in reducing the surface tension; the CMC values were one order of magnitude lower than those of the corresponding 1 + 1 surfactants. However, the $\Gamma_{\rm CMC}$ values of the gemini surfactants were slightly larger than those of the corresponding 1 + 1 surfactants.

The best way to solve the problems caused by fluorosurfactants would be a reduction in their use. Fluoroalkylated gemini surfactants have good prospects because their CMCs are more than one order of magnitude lower than those of the corresponding 1 + 1 surfactants. Moreover, persistence in the environment is also of great importance.



Fig. 10 IR spectra of gemini dilactone surfactant $11c_{s=3}$ (Rf = C₈F₁₇): F, just recovered by acidification of sample D in Fig. 6 (a mixture of γ -hydroxybutyric acid form (right) and γ -butyrolactone form (left)) (KBr); G, after treated with heating in AcOH at 100°C for 4h (KBr).

Our γ -butyrolactone monomeric and dimeric (gemini) surfactants were easily and quantitatively recovered, simply by acidification, in the γ -hydroxybutyric acid form for monomeric surfactants, or as a mixture of γ -butyrolactone and γ -hydroxybutyric acid forms for gemini surfactants. It is reasonable to conclude that γ -butyrolactone gemini surfactants with semifluoroalkyl groups are prospective candidates as fluorosurfactants.

Supporting Information

This material is available free of charge via the Internet at http://dx.doi.org/jos.64.10.5650/jos.ess.14193

References

- Kissa, E. Fluorinated Surfactants and Repellents, 2nd ed. Surfactant Science Series, Vol. 97, Marcel Dekker Inc. New York (2001).
- Lehmler, H. J. Synthesis of environmentally relevant fluorinated surfactants-a review. *Chemosphere* 58, 1471-1496 (2005).
- Salager, J-L. Surfactants-Types and Uses. FIRP Booklet # 300-A. Universidad de los Andes Laboratory of Formulation, Interfaces Rheology, and Processes. p. 44. URL: http://www.nanoparticles.org/pdf/Salager-E300A.pdf.
- Houde, M; Martin, J. W.; Letcher. R. J.; Solomon, K. R.; Muir, D. C. Biological monitoring of polyfluoroalkyl substances: A review. *Environ. Sci. Technol.* 40, 3463-3473 (2006).
- 5) Calafat, A. M.; Wong, L. Y.; Kuklenyik, Z.; Reidy, J. A.; Needham, L. L. Polyfluoroalkyl chemicals in the U. S. population: data from the National Health and Nutrition Examination Survey (NHANES) 2003-2004 and comparisons with NHANES 1999-2000. *Environ Health Perspect.* **115**, 1596-1602 (2007).
- 6) Hori, H.; Nagaoka, Y.; Murayama, M.; Kutsuna, S. Efficient decomposition of perfluorocarboxylic acids and alternative fluorochemical surfactants in hot water. *Environ. Sci. Technol.* 2, 7438-7443 (2008).
- More environmentally friendly alternatives to PFOScompounds and PFOA, *Danish Environmental Protection Agency, Environmental* Project No. 1013 (2005).
- Menger, F. M.; Littau, C. A. Gemini-surfactants: synthesis properties. J. Am. Chem. Soc. 113, 1451-1452 (1991).
- Menger, F. M.; Littau, C. A. Gemini surfactants: a new class of self-assembling molecules. J. Am. Chem. Soc. 115, 10083-10090 (1993).
- Menger, F. M.; Keiper, J. S. Gemini surfactants. Angew. Chem. Int. Ed. 39, 1906-1920 (2000).
- Zana, R. Dimeric and oligomeric surfactants. Behavior at interfaces and in aqueous solution: a review. Adv. Colloid. Interface Sci. 97, 203-251 (2002).
- 12) Zana, R. Dimeric (Gemini) surfactants: effect of the spacer group on the association behavior in aqueous solution. J. Colloid. Interface Sci. 248, 203-220 (2002).
- 13) Kawase, T.; Iidzuka, J.; Oida, T. A Novel Synthesis of SO₃H Type Gemini Surfactant Having Semifluoroalkyl Group As Hydrophobic Group. J. Oleo Sci. 59, 483-493 (2010).
- 14) Kawase, T.; Ankyu, T.; Oida, T. Synthesis and Surface Properties of CO₂H Type Gemini Surfactant Having Semifluoroalkyl Group as Hydrophobic Group. *Ten*side Surfactants Detergents 49, 498-507 (2012).
- 15) Li, Y.; Wang, Q.; Dong, L.; Guo, X.; Wang, W.; Xie, J.;

Chang, J. Asymmetric synthesis of (+) - and (-) -wuweizisu C stereoisomers and their chemosensitizing effects on multidrug-resistant cancer cells. *Synthesis* **20**, 3383-3390 (2009).

- 16) Newkome, G. R.; Baker, G. R.; Arai, S.; Saunders, M. J.; Russo, P. S.; Theriot, K. J.; Moorefield, C. N.; Rogers, L. E.; Miller, J. E. Cascade molecules. Part 6. Synthesis and characterization of two-directional cascade molecules and formation of aqueous gels. *J. Am. Chem. Soc.* **112**, 8458-8465(1990).
- Brace, N. O. Long Chain Alkanoic and Alkenoic Acids with Perfluorolakyl Terminal Segments. J. Org. Chem. 27, 4491-4498 (1962).
- 18) Brace, N. O. Radical addition of R_FI to alkenylsuccinic anhydrides and gem-substituted alkenyl triesters: Zinc and radical induced, or spontaneous radical cyclization, of the δ -iodoalkanoic esters to γ -lactones. J. Fluorine Chem. **123**, 237-248 (2003).
- Rosen, M. J. Surfactants and Interfacial Phenomena, 3rd ed., John Wiley and Sons New York (2004).
- 20) Kawase, T.; Ohshita, S.; Yoshimasu, C.; Oida, T. A novel design of water- and oil-repellent surface modifier having double-fluoroalkyl groups *Contact Angle*, *Wettability and Adhesion*, Koninklijke Brill, Vol. 6, 173-189 (2009).