

Synthesis of a silane coupling agent containing a 4-(perfluoroalkyl)phenyl group and its application to the surface modification of glass

Norio Yoshino *, Akihiro Sasaki, Tsuyoshi Seto

Department of Industrial Chemistry, Faculty of Engineering, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162, Japan

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Abstract

Eight silane coupling agents, $\text{CF}_3(\text{C}_6\text{H}_4)\text{C}_2\text{H}_4\text{Si}(\text{CH}_3)(\text{OCH}_3)_2$ ($\text{C}_6\text{H}_4 = p$ -phenylene) (1), $\text{C}_4\text{F}_9(\text{C}_6\text{H}_4)\text{C}_2\text{H}_4\text{Si}(\text{CH}_3)(\text{OCH}_3)_2$ (2), $\text{C}_6\text{F}_{13}(\text{C}_6\text{H}_4)\text{C}_2\text{H}_4\text{Si}(\text{CH}_3)(\text{OCH}_3)_2$ (3), $\text{C}_8\text{F}_{17}(\text{C}_6\text{H}_4)\text{C}_2\text{H}_4\text{Si}(\text{CH}_3)(\text{OCH}_3)_2$ (4), $\text{CF}_3(\text{C}_6\text{H}_4)\text{C}_2\text{H}_4\text{Si}(\text{OCH}_3)_3$ (5), $\text{C}_4\text{F}_9(\text{C}_6\text{H}_4)\text{C}_2\text{H}_4\text{Si}(\text{OCH}_3)_3$ (6), $\text{C}_6\text{F}_{13}(\text{C}_6\text{H}_4)\text{C}_2\text{H}_4\text{Si}(\text{OCH}_3)_3$ (7) and $\text{C}_8\text{F}_{17}(\text{C}_6\text{H}_4)\text{C}_2\text{H}_4\text{Si}(\text{OCH}_3)_3$ (8) have been prepared by the hydrosilylation reaction of dichloro(methyl)silane or trichlorosilane with the corresponding 4-perfluoroalkylstyrene in the presence of hydrogen hexachloroplatinate(IV), followed by reaction with sodium methoxide. These new coupling agents were freely soluble in hydrocarbon solvents. Their application for the surface modification of glass has been attempted. From measurements of the contact angles θ ($^\circ$) of water and oleic acid on a modified glass plate surface, it was found that the silane coupling agents show a high degree of surface modification. The oxidation resistance of the modified glass surface has also been investigated.

Keywords: Syntheses; Silane coupling agents; Glass surface modification; NMR spectroscopy; IR spectroscopy; Mass spectrometry

1. Introduction

The use of silane coupling agents to promote surface modification and/or adhesion are most familiar for $\text{R}_n\text{SiX}_{4-n}$ ($n = 1, 2$ and 3) organosilanes having two types of substituents, R and X. The substituent R is a non-hydrolyzable relatively inert organic group such as alkyl or a non-hydrolyzable reactive group such as epoxy, vinyl or amino alkyl. The X functionality is a hydrolyzable group, often alkoxy [1].

Recently we reported the syntheses of four silane coupling agents, (1*H*,1*H*,2*H*,2*H*-polyfluoroalkyl)dime-thoxy(methyl)silanes, and of another four silane coupling agents, (1*H*,1*H*,2*H*,2*H*-polyfluoroalkyl)tri-methoxysilanes, together with studies of the surface modification of glass using these coupling agents [2,3]. The hydrosilylation of dichloro(methyl)silane or trichlorosilane with 1*H*,1*H*,2*H*-polyfluoro-1-alkene was highly regioselective. For water and oil repellency on the modified glass surface, (1*H*,1*H*,2*H*,2*H*-hencicosafuoro-dodecyl)trimethoxysilane, $\text{C}_{10}\text{F}_{21}\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$, displayed the highest repellent ability. The modified glass surface using this coupling agent displayed the highest oxidation resistance towards hot concentrated

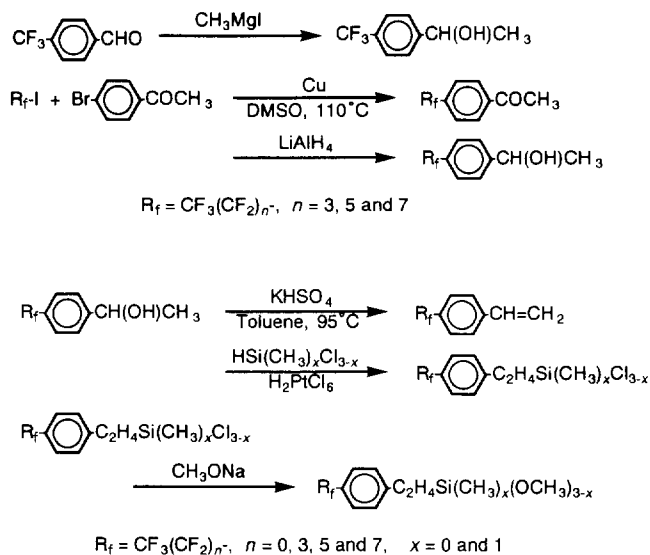
nitric acid. These results were assessed by measuring the contact angles of water and oleic acid.

In our recent paper [4], we tried to modify dental-material surfaces using (1*H*,1*H*,2*H*,2*H*-hencicosafuoro-dodecyl)trimethoxysilane, and an increase in the contact angles of water and oleic acid on the modified surface was observed. We also attempted surface modification of a denture to give stain-protecting ability and high contamination-protection ability was observed after wearing the denture in the mouth normally for four months. Although the best solvent for these coupling agents was 1,1,2-trichloro-1,2,2-trifluoroethane (F-113), its use may lead to ozone depletion in the stratosphere.

In this paper, the results of the syntheses and characterization of eight new silane coupling agents possessing an $\text{R}_f(\text{C}_6\text{H}_4)\text{C}_2\text{H}_4-$ ($\text{R}_f =$ perfluoroalkyl, $\text{C}_6\text{H}_4 = p$ -phenylene) group are reported. These coupling agents are expected to exhibit a higher solubility towards hydrocarbon solvents relative to the silane coupling agents having fluorocarbon chains which we have produced previously [2,3].

The synthetic processes employed are depicted in Scheme 1. The application of the coupling agents produced towards the surface modification of glass and the oxidation resistance of the modified glass surface

* Corresponding author.



Scheme 1. Syntheses of silane coupling agents.

towards hot nitric acid was investigated by measuring the contact angles of water and oleic acid.

2. Results and discussion

2.1. Synthesis

The syntheses of $\text{CF}_3(\text{C}_6\text{H}_4)\text{C}_2\text{H}_4\text{Si}(\text{CH}_3)\text{Cl}_2$ (**1C**), $\text{C}_4\text{F}_9(\text{C}_6\text{H}_4)\text{C}_2\text{H}_4\text{Si}(\text{CH}_3)\text{Cl}_2$ (**2C**), $\text{C}_6\text{F}_{13}(\text{C}_6\text{H}_4)\text{C}_2\text{H}_4\text{Si}(\text{CH}_3)\text{Cl}_2$ (**3C**), $\text{C}_8\text{F}_{17}(\text{C}_6\text{H}_4)\text{C}_2\text{H}_4\text{Si}(\text{CH}_3)\text{Cl}_2$ (**4C**), $\text{CF}_3(\text{C}_6\text{H}_4)\text{C}_2\text{H}_4\text{SiCl}_3$ (**5C**), $\text{C}_4\text{F}_9(\text{C}_6\text{H}_4)\text{C}_2\text{H}_4\text{SiCl}_3$ (**6C**), $\text{C}_6\text{F}_{13}(\text{C}_6\text{H}_4)\text{C}_2\text{H}_4\text{SiCl}_3$ (**7C**) and $\text{C}_8\text{F}_{17}(\text{C}_6\text{H}_4)\text{C}_2\text{H}_4\text{SiCl}_3$ (**8C**) in high yield were achieved successfully by reaction in sealed glass ampoules. It is reported that, in general, mixed products of the type Si-CHX-CH_3 (the α -addition product) and $\text{Si-CH}_2\text{-CH}_2\text{-X}$ (the β -addition product) are formed by the platinum-catalyzed addition reaction of Si-H -containing compounds with compounds having the general formula $\text{CH}_2=\text{CH-X}$, where the X group is conjugated with $\text{C}=\text{C}$ [5]. These two products were also obtained in our investigation and could not be separated by distillation. The estimated ratios of the α - and β -addition products were shown to be ca. 1:9 by comparing the proton signal intensities in the corresponding ^1H NMR spectra.

2.2. Solubilities

All the silane compounds prepared in this study were readily soluble in hydrocarbon solvents such as benzene, toluene and hexane.

2.3. Surface modification of glass plate

Figs. 1–4 show the results of contact angle measurements of water and oleic acid on the modified glass

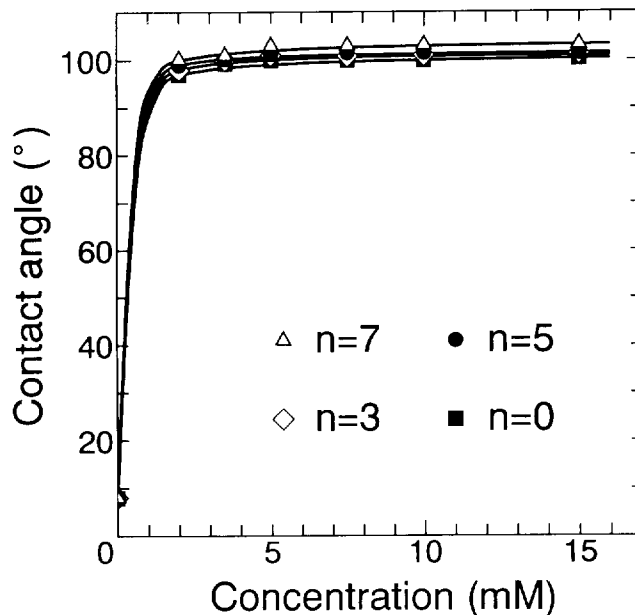


Fig. 1. Relation between the contact angle θ ($^\circ$) of water on the surface-modified glass plate and the concentration of silane coupling agents 1–4. The symbol n corresponds to the number of CF_2 groups in $\text{CF}_3(\text{CF}_2)_n(\text{C}_6\text{H}_4)\text{C}_2\text{H}_4\text{Si}(\text{CH}_3)(\text{OCH}_3)_2$ in Figs. 1–4 and 6–9.

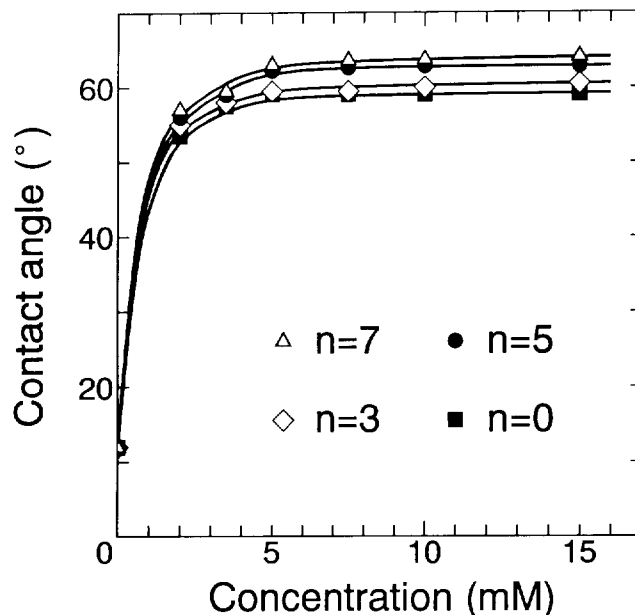


Fig. 2. Relation between the contact angle θ ($^\circ$) of oleic acid on the surface-modified glass plate and the concentration of silane coupling agents 1–4.

surfaces. These data show that the contact angles on the modified glass surface were dependent on the fluorocarbon chain length. However, the difference between the contact angle value displayed with different fluorocarbon chain lengths was smaller than for the same type of silane coupling agents without a benzene ring [2,3]. Modification of the glass surface using the coupling agents showed that the hydrophilic surface

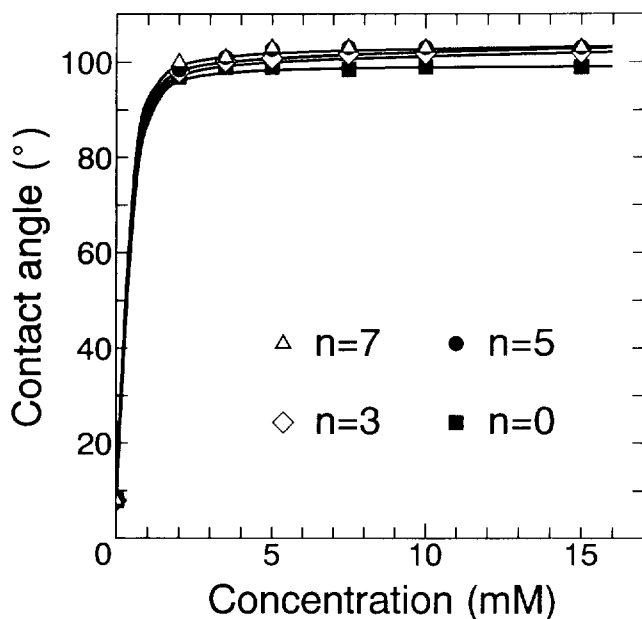


Fig. 3. Relation between the contact angle θ ($^{\circ}$) of water on the surface-modified glass plate and the concentration of silane coupling agents 5–8.

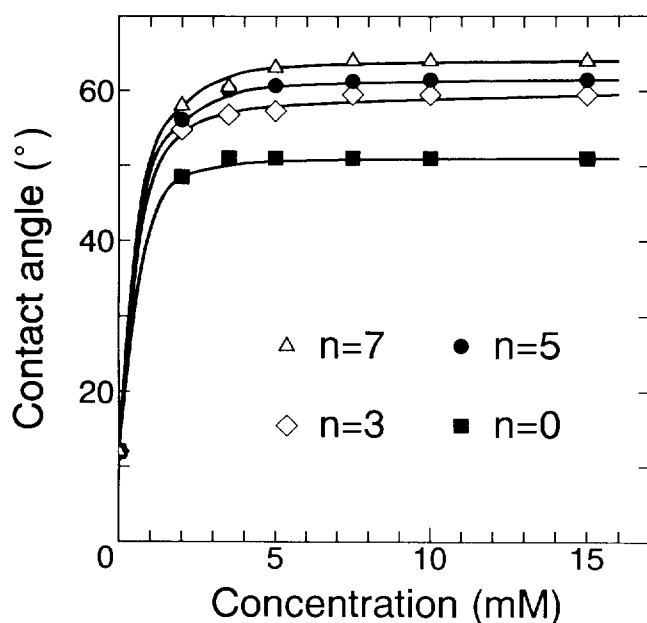


Fig. 4. Relation between the contact angle θ ($^{\circ}$) of oleic acid on the surface-modified glass plate and the concentration of silane coupling agents 5–8.

was covered effectively by the longer fluorocarbon chains. Consequently, the effect on the contact angle of the hydrocarbon moiety $\text{SiC}_2\text{H}_4(\text{C}_6\text{H}_4)-$ reduced according to the value of n in $-(\text{CF}_2)_n\text{CF}_3$. The difference between the contact angle on the glass surface modified with dimethoxy- and trimethoxy-type coupling agents with longer fluorocarbon chains was only very slight. This may be due to the steric effect of the benzene ring located in a position removed from the glass surface,

i.e. in the case of dimethoxy-type coupling agents, the effect on the contact angle of a methyl group ($\text{Si}-\text{CH}_3$) located on the surface [2] should be minimized by the adjacent benzene ring. Hence these data indicate that the thickness of the layer of coupling agent on the modified glass surface [2,3] depends on the fluorocarbon chain length. The largest contact angle for water on the modified glass surface (103.2°) was exhibited by compound **8** (Fig. 2, $n=7$). This value for the contact angle was less than that for a glass surface modified with silane coupling agents having no benzene ring but of the same fluorocarbon chain length, e.g. $\text{C}_8\text{F}_{17}\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)(\text{OCH}_3)_2$ (105°) [2] or $\text{C}_8\text{F}_{17}\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ (113°) [3]. This may also be due to the effect of the benzene ring which, in contrast to the fluorocarbon chain, cannot increase the contact angle. Alternatively, the fluorocarbon chain on the glass surface may slant from the vertical, because the rigid, straight fluoroalkyl group [6] would be bent at the CF_2 carbon (sp^3) adjacent to the benzene ring (see stabilized structure of **8** obtained by computer modeling (PM3 method) in Fig. 5). In other words, a lower contact angle value may be effected by a CF_2 chain relative to a CF_3 group.

2.4. Oxidation resistance of the modified glass surface

After oxidation of the surface-modified glass by hot concentrated nitric acid, the contact angles of water and oleic acid were again measured and are shown in Figs. 6–9. These figures show that the contact angle reduction effected by oxidation of the glass surface modified by silane coupling agents with longer fluorocarbon chains was very small, while the values for short fluorocarbon chains were reduced to an even greater extent. Thus the contact angle reduction brought about by nitric acid oxidation of the modified glass

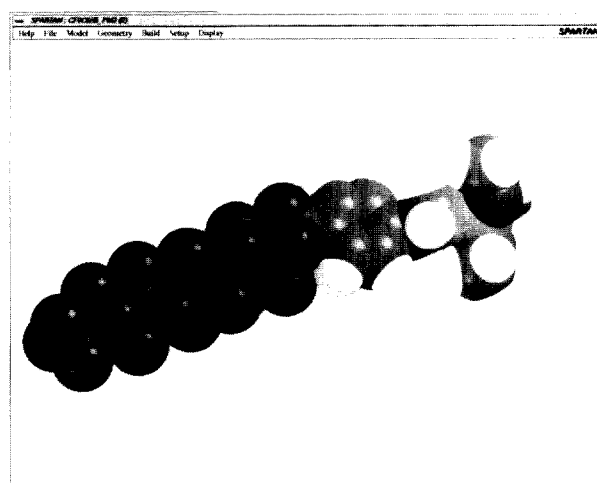


Fig. 5. Stabilized molecular structure for $\text{C}_8\text{F}_{17}(\text{C}_6\text{H}_4)\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$, as obtained by computer modeling (PM3 method).

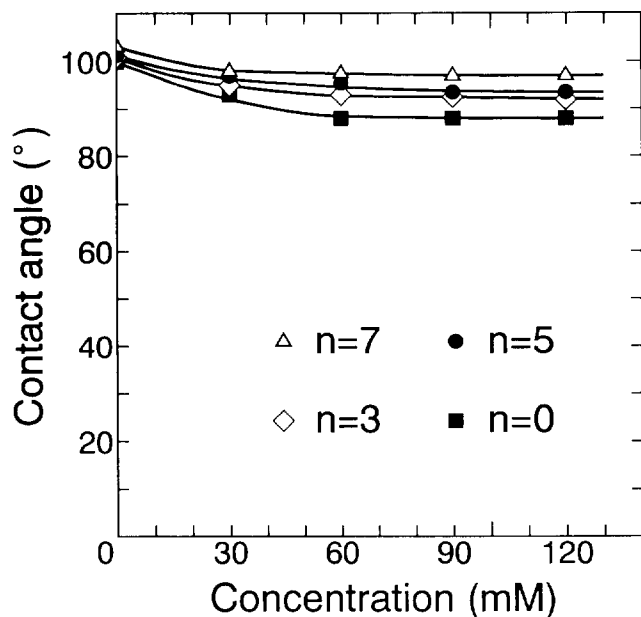


Fig. 6. Relation between the contact angle θ (°) of water on the oxidized glass surface treated with silane coupling agents 1–4 and the time allowed for oxidation in nitric acid.

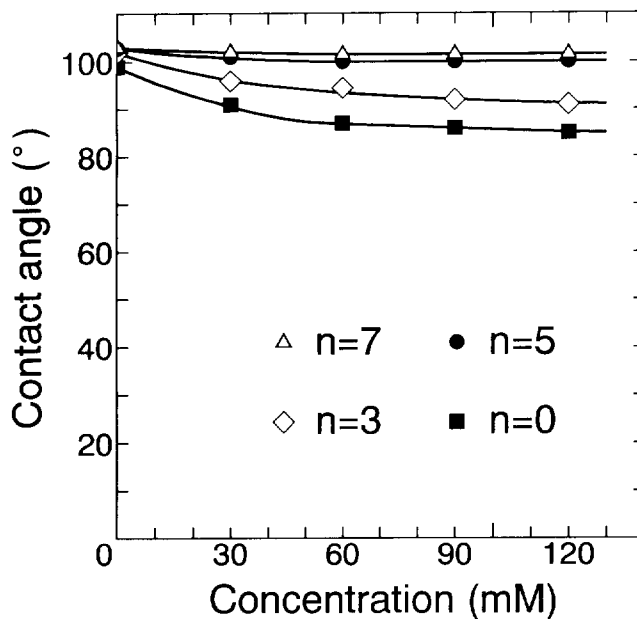


Fig. 8. Relation between the contact angle θ (°) of water on the oxidized glass surface treated with silane coupling agents 5–8 and the time allowed for oxidation in nitric acid.

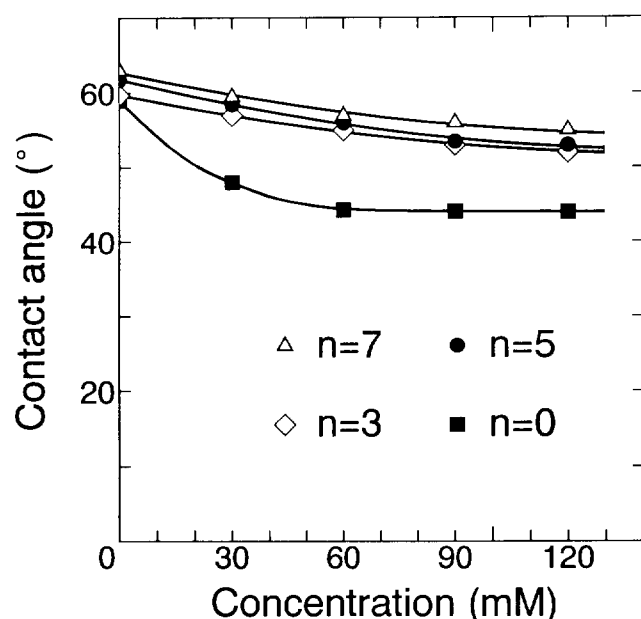


Fig. 7. Relation between the contact angle θ (°) of oleic acid on the oxidized glass surface treated with silane coupling agents 1–4 and the time allowed for oxidation in nitric acid.

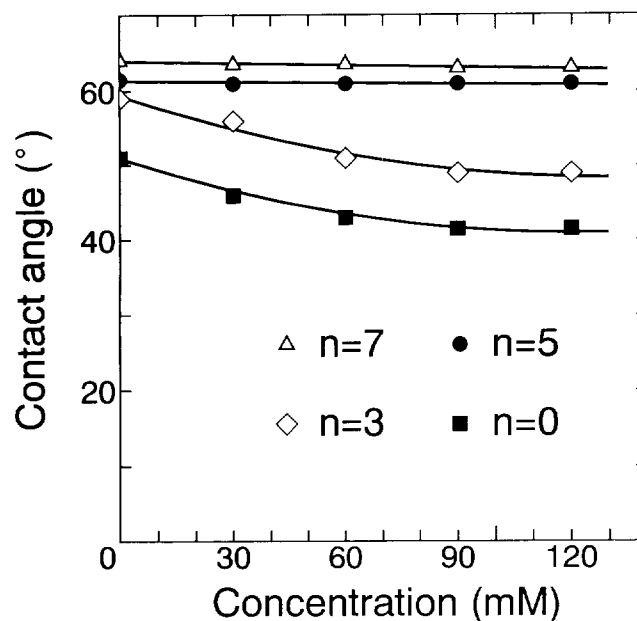


Fig. 9. Relation between the contact angle θ (°) of oleic acid on the oxidized glass surface treated with silane coupling agents 5–8 and the time allowed for oxidation in nitric acid.

surface was also dependent on the fluorocarbon chain length. However, contact angle reduction by oxidation was smaller than for glass surfaces subject to modification by coupling agents which did not possess a benzene ring [2,3]. These results show that either the fluorocarbon chains in the silane coupling agents tend to pack together and/or the fluorocarbon chains are slanted from the vertical on the glass surface, as in poly(tetrafluoroethylene).

Additional studies on the detailed structure and oxidation resistance of the modified glass surface using FT-IR-RAS and ESCA analyses are now in progress.

Finally, it should be noted that the silane coupling agents prepared in the present work were soluble in hydrocarbon solvents and the solubility will contribute to reduction of stratospheric ozone depletion by their use. The modified glass surfaces displayed high water and oil repellency, and had a high oxidation resistance.

3. Experimental details

Special precautions were adopted in order to avoid hydrolysis of the starting materials and products; all experiments were carried out under an atmosphere of purified nitrogen to preclude oxygen and moisture.

3.1. Materials

Dichloro(methyl)silane (b.p. 41 °C), trichlorosilane (b.p. 31–32 °C), 4-(trifluoromethyl)benzaldehyde (b.p. 66–67 °C/13 mmHg), perfluorobutyl iodide (b.p. 67 °C), perfluorohexyl iodide (b.p. 119 °C) and perfluorooctyl iodide (b.p. 95 °C/103 mmHg) were purchased from Tokyo Kasei Kogyo Co., Ltd. and purified by distillation. 4'-Bromoacetophenone (Tokyo Kasei Kogyo Co., Ltd.), copper bronze (Aldrich Chemical Co., Inc.), aluminum lithium hydride (Kanto Chemical Co., Inc.), potassium hydrogen sulfate (Kanto Chemical Co., Inc.), hydrogen hexachloroplatinate(IV) (Kojima Chemicals Co., Ltd.), 4-t-butylcatechol (Kanto Chemical Co., Inc.) and sodium methoxide (Kanto Chemical Co., Inc.) were used without further purification. The various solvents [methanol, diethyl ether, dimethyl sulfoxide (DMSO), toluene and 1,1,2-trichloro-1,2,2-trifluoroethane (F-113)] were purified by the usual methods. Plate glass (micro slide glass, thickness 1.3 mm, 76 mm × 26 mm) was obtained from Matsunami Glass Inc., Ltd.

3.2. Measurements

FT-IR spectra were measured using a liquid film or a KBr method with a JEOL JIR 5300 spectrophotometer. Each spectrum was recorded at a resolution of 4 cm⁻¹ with a total of 30 scans. Pulsed Fourier-transform 500 MHz ¹H NMR measurements were run in CDCl₃ with TMS as internal standard using a JEOL GSX-500 spectrometer at 25 °C: pulse repetition time, 3.277 s; number of accumulations, 32. Contact angles θ (°) were measured at 23 °C with an Elma-Kougaku Co. Goniotype apparatus. Mass spectra (MS) were measured (at 70 eV) with a Hitachi M-80A GC-MS spectrometer and the data were evaluated using a Hitachi M-003 data processing system.

3.3. Synthesis of 4'-nonafluorobutylacetophenone, C₄F₉(C₆H₄)COCH₃

Dispersions of perfluorobutyl iodide (20.7 g, 59.8 mmol), 4'-bromoacetophenone (11.0 g, 55.2 mmol), copper bronze powder (17.6 g, 276 mmol) and DMSO (50 cm³) were heated with stirring for 20 h at 110 °C in a two-necked 200-ml flask connected with a reflux condenser and a three-way stopcock. Excess copper bronze powder was removed by filtration. To the filtrate was added 50 cm³ of water and 50 cm³ of diethyl ether.

After stirring the mixture for 5 min, the ether layer was separated, washed three times with 50 cm³ water to remove DMSO and evaporated under reduced pressure. C₄F₉(C₆H₄)COCH₃ (17.3 g, yield 90.9%, b.p. 65–67 °C/0.26 mmHg) was obtained as a colorless liquid by distillation. IR (cm⁻¹): 2927 (w); 1697 (vs); 1410 (s); 1354 (s); 1302 (m); 1267 (s); 1236 (vs); 1205 (s); 1134 (s); 1111 (m); 1095 (m); 815 (m); 744 (m). ¹H NMR δ: 2.53 (3H, s, CH₃); 7.66 (2H, d, *J*=8.5 Hz, *o*-protons from C=O); 8.05 (2H, d, *J*=8.5 Hz, *m*-protons from C=O) ppm.

3.4. Syntheses of 4'-tridecafluorohexylacetophenone, C₆F₁₃(C₆H₄)COCH₃, and 4'-heptadecafluorooctylacetophenone, C₈F₁₇(C₆H₄)COCH₃

The procedures and purification techniques employed were similar to those for C₄F₉(C₆H₄)COCH₃.

C₆F₁₃(C₆H₄)COCH₃: colorless solid, yield 91.8%, b.p. 83–89 °C/0.23 mmHg, m.p. 48–49 °C. IR (cm⁻¹): 2933 (w); 1693 (vs); 1410 (s); 1365 (s); 1292 (m); 1253 (vs); 1209 (vs); 1146 (vs); 1111 (m); 1095 (m); 833 (m); 734 (m); 690 (m); 667 (m). ¹H NMR δ: 2.53 (3H, s, CH₃); 7.70 (2H, d, *J*=8.5 Hz, *o*-protons from C=O); 8.08 (2H, d, *J*=8.5 Hz, *m*-protons from C=O) ppm.

C₈F₁₇(C₆H₄)COCH₃: colorless solid, yield 90.0%, b.p. 102–106 °C/0.28 mmHg, m.p. 63.5–64 °C. IR (cm⁻¹): 2933 (w); 1686 (vs); 1410 (s); 1371 (s); 1301 (m); 1200 (vs); 1149 (vs); 1117 (m); 1095 (m); 947 (m); 844 (w); 657 (m). ¹H NMR δ: 2.54 (3H, s, CH₃); 7.79 (2H, d, *J*=8.5 Hz, *o*-protons from C=O); 8.17 (2H, d, *J*=8.5 Hz, *m*-protons from C=O) ppm.

3.5. Synthesis of 1-(4'-nonafluorobutylphenyl)ethanol, C₄F₉(C₆H₄)CH(OH)CH₃

To a dispersion of lithium aluminum hydride (1.20 g, 31.6 mmol) in diethyl ether (30 cm³), a solution of C₄F₉(C₆H₄)COCH₃ (19.3 g, 57.1 mmol) in diethyl ether (30 cm³) was added slowly with stirring over 30 min at room temperature into a two-necked 200-ml flask connected with a reflux condenser and a dropping funnel. After the reaction mixture had refluxed for 30 min, ice-cooled water was added slowly at 0 °C until the evolution of hydrogen had ceased. Dilute sulfuric acid (ca. 6 M, 1 M=1 mol dm⁻³) was then added until all the aluminum hydroxide precipitate had dissolved and the ether layer was then separated. The ether layer was washed thoroughly with an aqueous solution of sodium hydrogen carbonate and evaporated under reduced pressure. C₄F₉(C₆H₄)CH(OH)CH₃ (19.1 g, yield 98.7%, b.p. 68–69 °C/0.15 mmHg) was obtained as a colorless liquid after distillation. IR (cm⁻¹): 3346 (s); 2980 (m); 2933 (w); 2881 (w); 1618 (w); 1419 (m); 1352 (m); 1270 (s); 1236 (vs); 1205 (vs); 1134 (vs); 1092 (s); 1005 (m); 868 (m); 854 (m); 820 (m); 746 (m);

727 (m); 694 (m). $^1\text{H NMR } \delta$: 1.40 (3H, d, $J=6.7$ Hz, CH_3); 3.17 (1H, s, OH); 4.77 (1H, q, $J=6.7$ Hz, CH); 7.36 (2H, d, $J=9.3$ Hz, m -protons from CF_2); 7.56 (2H, d, $J=9.3$ Hz, o -protons from CF_2) ppm.

3.6. Syntheses of 1-(4'-tridecafluorohexylphenyl)ethanol, $\text{C}_6\text{F}_{13}(\text{C}_6\text{H}_4)\text{CH}(\text{OH})\text{CH}_3$, and 1-(4'-heptadecafluoro-octylphenyl)ethanol, $\text{C}_8\text{F}_{17}(\text{C}_6\text{H}_4)\text{CH}(\text{OH})\text{CH}_3$

The procedures and purification techniques were similar to those for $\text{C}_4\text{F}_9(\text{C}_6\text{H}_4)\text{CH}(\text{OH})\text{CH}_3$.

$\text{C}_6\text{F}_{13}(\text{C}_6\text{H}_4)\text{CH}(\text{OH})\text{CH}_3$: colorless solid, yield 98.2%, b.p. 95–98 °C/0.24 mmHg, m.p. 46–47.5 °C. IR (cm^{-1}): 3336 (s); 2978 (m); 2933 (w); 2897 (w); 1618 (w); 1452 (m); 1417 (m); 1365 (s); 1292 (s); 1236 (vs); 1196 (vs); 1147 (vs); 1124 (s); 1092 (m); 1041 (m); 1016 (s); 835 (s); 768 (m); 740 (m); 696 (s); 694 (s); 646 (m). $^1\text{H NMR } \delta$: 1.39 (3H, d, $J=7.0$ Hz, CH_3); 3.70 (1H, s, OH); 4.83 (1H, q, $J=6.2$ Hz, CH); 7.46 (2H, d, $J=9.0$ Hz, m -protons from CF_2); 7.66 (2H, d, $J=9.0$ Hz, o -protons from CF_2) ppm.

$\text{C}_8\text{F}_{17}(\text{C}_6\text{H}_4)\text{CH}(\text{OH})\text{CH}_3$: colorless solid, yield 98.0%, b.p. 102–106 °C/0.23 mmHg, m.p. 58.5–59 °C. IR (cm^{-1}): 3304 (s); 2978 (m); 2902 (w); 1618 (w); 1452 (m); 1371 (s); 1302 (s); 1227 (vs); 1200 (vs); 1147 (vs); 1117 (s); 1090 (m); 1088 (s); 846 (m); 657 (m). $^1\text{H NMR } \delta$: 1.36 (3H, d, $J=6.6$ Hz, CH_3); 4.14 (1H, s, OH); 4.96 (1H, q, $J=7.2$ Hz, CH); 7.44 (2H, d, $J=9.6$ Hz, m -protons from CF_2); 7.66 (2H, d, $J=9.6$ Hz, o -protons from CF_2) ppm.

3.7. Synthesis of 4-trifluoromethylstyrene, $\text{CF}_3(\text{C}_6\text{H}_4)\text{CH}=\text{CH}_2$

A solution of methyl iodide (24.4 g, 172 mmol in 20 cm^3 of diethyl ether) was added slowly to a dispersion of magnesium metal flakes (3.71 g, 153 mmol in 20 cm^3 of diethyl ether) from a dropping funnel and the mixture refluxed over 30 min in a 200-ml flask connected to a reflux condenser to form CH_3MgI . A solution of 4-(trifluoromethyl)benzaldehyde (25.1 g, 144 mmol in 20 cm^3 of diethyl ether) was then added slowly to the Grignard solution at room temperature and the mixture refluxed for 2 h. Ice-cooled water (30 cm^3) and 4 M hydrochloric acid (50 cm^3) were then added. $\text{CF}_3(\text{C}_6\text{H}_4)\text{CH}(\text{OH})\text{CH}_3$ (27.0 g, 98.3%) was obtained by distillation from the ether layer (b.p. 53–55 °C/0.38 mmHg). The dispersion of $\text{CF}_3(\text{C}_6\text{H}_4)\text{CH}(\text{OH})\text{CH}_3$ (27.0 g, 142 mmol), potassium hydrogen sulfate (7 g) and a polymerization inhibitor [4-*t*-butylcatechol (0.01 g)] was heated at 150 °C for 1 h with stirring in a 50-ml flask connected to a reflux condenser and distilled twice. Pure $\text{CF}_3(\text{C}_6\text{H}_4)\text{CH}=\text{CH}_2$ (18.7 g, yield 76.5%, b.p. 78–80 °C/20 mmHg) was obtained as a colorless liquid. IR (cm^{-1}): 2988 (w); 1618 (m); 1404 (m); 1325 (vs); 1167 (s); 1126 (s); 1068 (s); 1016 (m); 989 (w); 920

(w); 847 (m); 739 (w). $^1\text{H NMR } \delta$: 5.24–5.93 (2H, four peaks, $=\text{CH}_2$); 6.47–6.93 (1H, four peaks, $=\text{CH}$); 7.36 (2H, d, $J=9.6$ Hz, m -protons from CF_3); 7.54 (2H, d, $J=9.6$ Hz, o -protons from CF_3) ppm.

3.8. Synthesis of 4-nonafluorobutylstyrene, $\text{C}_4\text{F}_9(\text{C}_6\text{H}_4)\text{CH}=\text{CH}_2$

A dispersion of $\text{C}_4\text{F}_9(\text{C}_6\text{H}_4)\text{CH}(\text{OH})\text{CH}_3$ (14.4 g, 42.3 mmol), toluene (2 cm^3) and potassium hydrogen sulfate (4 g) was heated at 95 °C for 18 h with stirring in a 50-ml flask connected to a reflux condenser. After reaction had ceased, the mixture was distilled with 4-*t*-butylcatechol (0.01 g). $\text{C}_4\text{F}_9(\text{C}_6\text{H}_4)\text{CH}=\text{CH}_2$ (9.1 g, yield 78.5%, b.p. 66–69 °C/0.39 mmHg) was obtained as a colorless liquid. IR (cm^{-1}): 2985 (w); 1616 (m); 1408 (m); 1406 (m); 1352 (m); 1269 (s); 1234 (vs); 1205 (vs); 1134 (vs); 1113 (m); 1092 (m); 825 (m); 727 (m). $^1\text{H NMR } \delta$: 5.24–5.93 (2H, four peaks, $=\text{CH}_2$); 6.49–6.97 (1H, four peaks, $=\text{CH}$); 7.45 (2H, d, $J=9.0$ Hz, m -protons from CF_2); 7.62 (2H, d, $J=9.0$ Hz, o -protons from CF_2) ppm.

3.9. Syntheses of 4-tridecafluorohexylstyrene, $\text{C}_6\text{F}_{13}(\text{C}_6\text{H}_4)\text{CH}=\text{CH}_2$, and 4-heptadecafluoro-octylstyrene, $\text{C}_8\text{F}_{17}(\text{C}_6\text{H}_4)\text{CH}=\text{CH}_2$

The procedures and purification techniques were similar to those for $\text{C}_4\text{F}_9(\text{C}_6\text{H}_4)\text{CH}=\text{CH}_2$.

$\text{C}_6\text{F}_{13}(\text{C}_6\text{H}_4)\text{CH}=\text{CH}_2$: colorless liquid, yield 89.4%, b.p. 66.5–68 °C/0.36 mmHg. IR (cm^{-1}): 3097 (w); 1616 (m); 1408 (m); 1363 (m); 1288 (s); 1240 (vs); 1203 (vs); 1147 (vs); 1093 (s); 843 (m); 696 (m); $^1\text{H NMR } \delta$: 5.26–5.96 (2H, four peaks, $=\text{CH}_2$); 6.52–7.00 (1H, four peaks, $=\text{CH}$); 7.46 (2H, d, $J=9.0$ Hz, m -protons from CF_2); 7.64 (2H, d, $J=9.0$ Hz, o -protons from CF_2) ppm.

$\text{C}_8\text{F}_{17}(\text{C}_6\text{H}_4)\text{CH}=\text{CH}_2$: colorless liquid, yield 79.3%, b.p. 86–91 °C/0.23 mmHg. IR (cm^{-1}): 2987 (w); 1616 (m); 1408 (m); 1369 (m); 1298 (s); 1242 (vs); 1203 (vs); 1149 (vs); 1114 (s); 1090 (m); 920 (m); 845 (m); 703 (m); 660 (m). $^1\text{H NMR } \delta$: 5.30–6.01 (2H, four peaks, $=\text{CH}_2$); 6.59–7.07 (1H, four peaks, $=\text{CH}$); 7.52 (2H, d, $J=9.0$ Hz, m -protons from CF_2); 7.68 (2H, d, $J=9.0$ Hz, o -protons from CF_2) ppm.

3.10. Synthesis of $\text{CF}_3(\text{C}_6\text{H}_4)\text{C}_2\text{H}_4\text{Si}(\text{CH}_3)\text{Cl}_2$ (1C)

Dichloro(methyl)silane (9.73 g, 84.6 mmol), $\text{CF}_3(\text{C}_6\text{H}_4)\text{CH}=\text{CH}_2$ (9.74 g, 56.6 mmol) and a 0.1 M methanolic solution of hydrogen hexachloroplatinate(IV) (0.2 cm^3) were placed in a 200-ml glass ampoule tube with rigid exclusion of moisture. After sealing the tube under reduced pressure at -196 °C, the mixture was allowed to react at 100 °C for 50 h with stirring in an oil bath, following which the tube was broken. Compound 1C was obtained as a colorless liquid after

distillation (14.5 g, yield 89.0%, b.p. 126–129 °C/8.0 mmHg). ^1H NMR measurements showed that **1C** was the mixture of α - and β -addition products, $\text{CF}_3(\text{C}_6\text{H}_4)\text{CH}(\text{CH}_3)\text{Si}(\text{CH}_3)\text{Cl}_2$ [**1C α** (α = α -addition compound)] and $\text{CF}_3(\text{C}_6\text{H}_4)\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)\text{Cl}_2$ [**1C β** (β = β -addition compound)]. The mixture could not be separated by fractional distillation. The ratios of compounds **1C α** and **1C β** were 13.0:87.0 from ^1H NMR analysis. ^1H NMR [intensities expressed on the basis of total phenylene protons (4H)] δ : 0.67 [0.39H, s, Si-CH₃ (**1C α**)]; 0.75 [2.61H, s, Si-CH₃ (**1C β**)]; 1.46–1.50 [1.74H, m, Si-CH₂-CH₂ (**1C β**)]; 1.56 [0.39H, d, $J=7.32$ Hz, Si-CH-CH₃ (**1C α**)]; 2.69–2.74 [0.13H, q, $J=7.32$ Hz, Si-CH-CH₃ (**1C α**)]; 2.89–2.91 [1.74H, m, Si-CH₂-CH₂ (**1C β**)]; 7.31–7.56 (4H, phenylene protons) ppm.

3.11. Syntheses of $\text{C}_4\text{F}_9(\text{C}_6\text{H}_4)\text{C}_2\text{H}_4\text{Si}(\text{CH}_3)\text{Cl}_2$ (**2C**), $\text{C}_6\text{F}_{13}(\text{C}_6\text{H}_4)\text{C}_2\text{H}_4\text{Si}(\text{CH}_3)\text{Cl}_2$ (**3C**), $\text{C}_8\text{F}_{17}(\text{C}_6\text{H}_4)\text{C}_2\text{H}_4\text{Si}(\text{CH}_3)\text{Cl}_2$ (**4C**), $\text{CF}_3(\text{C}_6\text{H}_4)\text{C}_2\text{H}_4\text{SiCl}_3$ (**5C**), $\text{C}_4\text{F}_9(\text{C}_6\text{H}_4)\text{C}_2\text{H}_4\text{SiCl}_3$ (**6C**), $\text{C}_6\text{F}_{13}(\text{C}_6\text{H}_4)\text{C}_2\text{H}_4\text{SiCl}_3$ (**7C**) and $\text{C}_8\text{F}_{17}(\text{C}_6\text{H}_4)\text{C}_2\text{H}_4\text{SiCl}_3$ (**8C**)

The procedures and purification techniques were similar to those for the preparation of compound **1C**. These compounds also contained α - and β -addition products and all products were colorless liquids.

Compound **2C**: yield 76.4%, b.p. 86–90 °C/0.35 mmHg, $\alpha/\beta=9.0:91.0$. ^1H NMR δ : 0.65 [0.27H, s, Si-CH₃ (**2C α**)]; 0.73 [2.73H, s, Si-CH₃ (**2C β**)]; 1.47–1.50 [1.82H, m, Si-CH₂-CH₂ (**2C β**)]; 1.58 [0.27H, d, $J=7.32$ Hz, Si-CH-CH₃ (**2C α**)]; 2.69–2.73 [0.09H, q, $J=7.32$ Hz, Si-CH-CH₃ (**2C α**)]; 2.89–2.92 [1.82H, m, Si-CH₂-CH₂ (**2C β**)]; 7.31–7.53 (4H, phenylene protons) ppm.

Compound **3C**: yield 88.4%, b.p. 100–102 °C/0.57 mmHg, $\alpha/\beta=9.5:90.5$. ^1H NMR δ : 0.65 [0.29H, s, Si-CH₃ (**3C α**)]; 0.73 [2.71H, s, Si-CH₃ (**3C β**)]; 1.47–1.50 [1.81H, m, Si-CH₂-CH₂ (**3C β**)]; 1.58 [0.29H, d, $J=7.63$ Hz, Si-CH-CH₃ (**3C α**)]; 2.69–2.75 [0.10H, q, $J=7.63$ Hz, Si-CH-CH₃ (**3C α**)]; 2.89–2.93 [1.81H, m, Si-CH₂-CH₂ (**3C β**)]; 7.31–7.53 (4H, phenylene protons) ppm.

Compound **4C**: yield 87.1%, b.p. 114.5–116 °C/0.23 mmHg, $\alpha/\beta=10.3:89.7$. ^1H NMR δ : 0.64 [0.31H, s, Si-CH₃ (**4C α**)]; 0.72 [2.69H, s, Si-CH₃ (**4C β**)]; 1.46–1.50 [1.79H, m, Si-CH₂-CH₂ (**4C β**)]; 1.57 [0.31H, d, $J=7.63$ Hz, Si-CH-CH₃ (**4C α**)]; 2.68–2.74 [0.10H, q, $J=7.63$ Hz, Si-CH-CH₃ (**4C α**)]; 2.89–2.92 [1.79H, m, Si-CH₂-CH₂ (**4C β**)]; 7.29–7.53 (4H, phenylene protons) ppm.

Compound **5C**: yield 74.9%, b.p. 108–112 °C/11 mmHg, $\alpha/\beta=22:78$. ^1H NMR δ : 1.74–1.77 [1.56H, m, Si-CH₂-CH₂ (**5C β**)]; 1.64 [0.66H, d, $J=6.72$ Hz, Si-CH-CH₃ (**5C α**)]; 2.72 [0.22H, q, $J=6.72$ Hz, Si-CH-CH₃ (**5C α**)]; 2.95–2.98 [1.56H, m, Si-CH₂-CH₂ (**5C β**)]; 7.31–7.58 (4H, phenylene protons) ppm.

Compound **6C**: yield 90.2%, b.p. 98 °C/0.29 mmHg, $\alpha/\beta=4.9:95.1$. ^1H NMR δ : 1.75–1.79 [1.90H, m, Si-CH₂-CH₂ (**6C β**)]; 1.86 [0.15H, d, $J=6.72$ Hz, Si-CH-CH₃ (**6C α**)]; 2.72 [0.05H, q, $J=6.72$ Hz, Si-CH-CH₃ (**6C α**)]; 2.95–2.98 [1.90H, m, Si-CH₂-CH₂ (**6C β**)]; 7.31–7.60 (4H, phenylene protons) ppm.

Compound **7C**: yield 93.1%, b.p. 101–102 °C/0.29 mmHg, $\alpha/\beta=6.7:94.3$. ^1H NMR δ : 1.75–1.79 [1.89H, m, Si-CH₂-CH₂ (**7C β**)]; 1.86 [0.20H, d, $J=7.02$ Hz, Si-CH-CH₃ (**7C α**)]; 2.72 [0.07H, q, $J=7.02$ Hz, Si-CH-CH₃ (**7C α**)]; 2.95–2.98 [1.89H, m, Si-CH₂-CH₂ (**7C β**)]; 7.32–7.58 (4H, phenylene protons) ppm.

Compound **8C**: yield 90.2%, b.p. 120–123 °C/0.26 mmHg, $\alpha/\beta=7.5:92.5$. ^1H NMR δ : 1.75–1.78 [1.85H, m, Si-CH₂-CH₂ (**8C β**)]; 1.86 [0.23H, d, $J=6.71$ Hz, Si-CH-CH₃ (**8C α**)]; 2.78 [0.08H, q, $J=6.71$ Hz, Si-CH-CH₃ (**8C α**)]; 2.95–2.98 [1.85H, m, Si-CH₂-CH₂ (**8C β**)]; 7.31–7.59 (4H, phenylene protons) ppm.

3.12. Synthesis of $\text{CF}_3(\text{C}_6\text{H}_4)\text{C}_2\text{H}_4\text{Si}(\text{CH}_3)(\text{OCH}_3)_2$ (**1**)

Compound **1C** (mixture of **1C α** and **1C β**) (10.3 g, 37.3 mmol) was added slowly at 65 °C with stirring in a 100-ml flask to 35 cm³ of a 3 M methanolic solution of sodium methoxide, and the reaction mixture was then allowed to react for 1 h at 65 °C. After separation of sodium chloride, compound **1** was obtained as a colorless liquid by distillation (6.5 g, yield 65.0%, b.p. 102–105 °C/10 mmHg). The content ratios of α - and β -addition products were nearly the same as for the corresponding chloro derivatives. The mixture could not be separated by fractional distillation. IR (cm⁻¹): 2924 (m); 2823 (m); 1610 (w); 1414 (w); 1323 (vs); 1260 (m); 1189 (m); 1162 (s); 1122 (vs); 1084 (vs); 1068 (vs); 1018 (m); 906 (w); 828 (m); 779 (w). ^1H NMR [intensities expressed on the basis of total phenylene protons (4H)] δ : 0.08 [0.39H, s, Si-CH₃ (**1 α**)]; 0.13 [2.61H, s, Si-CH₃ (**1 β**)]; 0.97–1.01 [1.74H, m, Si-CH₂-CH₂ (**1 β**)]; 1.25 [0.39H, d, $J=7.63$ Hz, Si-CH-CH₃ (**1 α**)]; 2.70 [0.13H, q, $J=7.63$ Hz, Si-CH-CH₃ (**1 α**)]; 2.73–2.77 [1.74H, m, Si-CH₂-CH₂ (**1 β**)]; 3.48 [0.78H, s, OCH₃ (**1 α**)]; 3.53 [5.22H, s, OCH₃ (**1 β**)]; 7.31–7.55 (4H, phenylene protons) ppm. MS (m/z) (rel. int.): 278 (14) [M]⁺; 263 (16) [M-CH₃]⁺; 259 (19) [M-F]⁺; 231 (39) [M-CH₃-OCH₃-H]⁺; 154 (55) [M-Si(OCH₃)₂-CH₃-F]⁺; 105 (100) [M-C₄F₉-C₆H₄-C₂H₄]⁺.

3.13. Syntheses of $\text{C}_4\text{F}_9(\text{C}_6\text{H}_4)\text{C}_2\text{H}_4\text{Si}(\text{CH}_3)(\text{OCH}_3)_2$ (**2**), $\text{C}_6\text{F}_{13}(\text{C}_6\text{H}_4)\text{C}_2\text{H}_4\text{Si}(\text{CH}_3)(\text{OCH}_3)_2$ (**3**), $\text{C}_8\text{F}_{17}(\text{C}_6\text{H}_4)\text{C}_2\text{H}_4\text{Si}(\text{CH}_3)(\text{OCH}_3)_2$ (**4**), $\text{CF}_3(\text{C}_6\text{H}_4)\text{C}_2\text{H}_4\text{Si}(\text{OCH}_3)_3$ (**5**), $\text{C}_4\text{F}_9(\text{C}_6\text{H}_4)\text{C}_2\text{H}_4\text{Si}(\text{OCH}_3)_3$ (**6**), $\text{C}_6\text{F}_{13}(\text{C}_6\text{H}_4)\text{C}_2\text{H}_4\text{Si}(\text{OCH}_3)_3$ (**7**) and $\text{C}_8\text{F}_{17}(\text{C}_6\text{H}_4)\text{C}_2\text{H}_4\text{Si}(\text{OCH}_3)_3$ (**8**)

The procedures and purification techniques were similar to those for the preparation of compound **1**.

All the products were colorless liquids and contained α - and β -addition products.

Compound 2: yield 68.0%, b.p. 87.5–89 °C/0.35 mmHg. IR (cm^{-1}): 2943 (m); 2839 (m); 1616 (w); 1419 (w); 1352 (m); 1269 (s); 1236 (vs); 1196 (vs); 1134 (vs); 1090 (vs); 1003 (w); 870 (m); 825 (s); 746 (m); 736 (m); 692 (w). ^1H NMR δ : 0.12 [2.73H, s, Si-CH₃ (**2 β)**]; 0.14 [0.27H, s, Si-CH₃ (**2 α)**]; 0.99–1.02 [1.78H, m, Si-CH₂-CH₂ (**2 β)**]; 1.86 [0.33H, d, $J=6.71$ Hz, Si-CH-CH₃ (**2 α)**]; 2.72 [0.11H, q, $J=6.71$ Hz, Si-CH-CH₃ (**2 α)**]; 2.75–2.79 [1.78H, m, Si-CH₂-CH₂ (**2 β)**]; 3.48 [0.66H, s, OCH₃ (**2 α)**]; 3.52 [5.34H, s, OCH₃ (**2 β)**]; 7.31–7.50 (4H, phenylene protons) ppm. MS (m/z) (rel. int.): 428 (2) [$\text{M}]^+$; 413 (2) [$\text{M}-\text{CH}_3]^+$; 381 (5) [$\text{M}-\text{OCH}_3-\text{CH}_3-\text{H}]^+$; 323 (2) [$\text{M}-\text{Si}(\text{OCH}_3)_2-\text{CH}_3]^+$; 304 (12) [$\text{M}-\text{Si}(\text{OCH}_3)_2-\text{CH}_3-\text{F}]^+$; 105 (100) [$\text{M}-\text{C}_6\text{F}_9-\text{C}_6\text{H}_4-\text{C}_2\text{H}_4]^+$.

Compound 3: yield 76.0%, b.p. 89–92 °C/0.25 mmHg. IR (cm^{-1}): 2947 (m); 2841 (m); 1616 (w); 1419 (w); 1363 (m); 1288 (m); 1240 (vs); 1198 (vs); 1147 (vs); 1092 (vs); 1014 (w); 829 (s); 777 (m); 735 (m); 694 (w). ^1H NMR δ : 0.12 [2.72H, s, Si-CH₃ (**3 β)**]; 0.14 [0.28H, s, Si-CH₃ (**3 α)**]; 0.99–1.02 [1.70H, m, Si-CH₂-CH₂ (**3 β)**]; 1.86 [0.45H, d, $J=7.63$ Hz, Si-CH-CH₃ (**3 α)**]; 2.72 [0.15H, q, $J=7.63$ Hz, Si-CH-CH₃ (**3 α)**]; 2.75–2.79 [1.70H, m, Si-CH₂-CH₂ (**3 β)**]; 3.49 [0.89H, s, OCH₃ (**3 α)**]; 3.52 [5.11H, s, OCH₃ (**3 β)**]; 7.31–7.50 (4H, phenylene protons) ppm. MS (m/z) (rel. int.): 528 (1) [$\text{M}]^+$; 513 (2) [$\text{M}-\text{CH}_3]^+$; 481 (3) [$\text{M}-\text{OCH}_3-\text{CH}_3-\text{H}]^+$; 423 (2) [$\text{M}-\text{Si}(\text{OCH}_3)_2-\text{CH}_3]^+$; 404 (9) [$\text{M}-\text{Si}(\text{OCH}_3)_2-\text{CH}_3-\text{F}]^+$; 105 (100) [$\text{M}-\text{C}_6\text{F}_{13}-\text{C}_6\text{H}_4-\text{C}_2\text{H}_4]^+$.

Compound 4: yield 82.0%, b.p. 103–105 °C/0.33 mmHg. IR (cm^{-1}): 2945 (m); 2841 (m); 1616 (w); 1418 (w); 1369 (m); 1298 (m); 1242 (vs); 1201 (vs); 1149 (vs); 1114 (vs); 1089 (s); 827 (m); 775 (m); 731 (m); 656 (m). ^1H NMR δ : 0.12 [2.69H, s, Si-CH₃ (**4 β)**]; 0.14 [0.31H, s, Si-CH₃ (**4 α)**]; 0.99–1.02 [1.79H, m, Si-CH₂-CH₂ (**4 β)**]; 1.86 [0.31H, d, $J=7.62$ Hz, Si-CH-CH₃ (**4 α)**]; 2.72 [0.10H, q, $J=7.62$ Hz, Si-CH-CH₃ (**4 α)**]; 2.75–2.79 [1.79H, m, Si-CH₂-CH₂ (**4 β)**]; 3.49 [0.62H, s, OCH₃ (**4 α)**]; 3.52 [5.38H, s, OCH₃ (**4 β)**]; 7.31–7.50 (4H, phenylene protons) ppm. MS (m/z) (rel. int.): 628 (1) [$\text{M}]^+$; 613 (2) [$\text{M}-\text{CH}_3]^+$; 581 (2) [$\text{M}-\text{OCH}_3-\text{CH}_3-\text{H}]^+$; 523 (2) [$\text{M}-\text{Si}(\text{OCH}_3)_2-\text{CH}_3]^+$; 504 (6) [$\text{M}-\text{Si}(\text{OCH}_3)_2-\text{CH}_3-\text{F}]^+$; 105 (100) [$\text{M}-\text{C}_8\text{F}_{17}-\text{C}_6\text{H}_4-\text{C}_2\text{H}_4]^+$.

Compound 5: yield 67.6%, b.p. 135–139 °C/0.50 mmHg. IR (cm^{-1}): 2955 (m); 2852 (m); 1620 (w); 1422 (w); 1334 (s); 1200 (m); 1185 (m); 1132 (s); 1093 (vs); 1074 (s); 1024 (w); 832 (m); 766 (w); 739 (w); ^1H NMR δ : 0.97–1.03 [1.56H, m, Si-CH₂-CH₂ (**5 β)**]; 1.25 [0.66H, d, $J=7.62$ Hz, Si-CH-CH₃ (**5 α)**]; 2.70 [0.22H, q, $J=7.62$ Hz, Si-CH-CH₃ (**5 α)**]; 2.77–2.80 [1.56H, m, Si-CH₂-CH₂ (**5 β)**]; 3.60 [1.98H, s, OCH₃ (**5 α)**]; 3.57 [7.02H, s, OCH₃ (**5 β)**]; 7.26–7.54 (4H, phenylene protons) ppm. MS (m/z)

(rel. int.): 294 (11) [$\text{M}]^+$; 275 (5) [$\text{M}-\text{F}]^+$; 231 (5) [$\text{M}-\text{Si}(\text{OCH}_3)_2-\text{H}]^+$; 154 (54) [$\text{M}-\text{Si}(\text{OCH}_3)_2-\text{F}]^+$; 121 (100) [$\text{M}-\text{CF}_3-\text{C}_6\text{H}_4-\text{C}_2\text{H}_4]^+$.

Compound 6: yield 62.8%, b.p. 87–90 °C/18 mmHg. IR (cm^{-1}): 2945 (m); 2845 (m); 1616 (w); 1419 (w); 1352 (m); 1308 (w); 1271 (m); 1236 (vs); 1198 (vs); 1133 (vs); 1089 (s); 1002 (w); 871 (m); 819 (ms); 744 (m); 736 (m); 694 (m); 593 (w). ^1H NMR δ : 1.00–1.03 [1.88H, m, Si-CH₂-CH₂ (**6 β)**]; 1.44 [0.18H, d, $J=6.73$ Hz, Si-CH-CH₃ (**6 α)**]; 2.73 [0.06H, q, $J=6.73$ Hz, Si-CH-CH₃ (**6 α)**]; 2.78–2.82 [1.88H, m, Si-CH₂-CH₂ (**6 β)**]; 3.49 [0.55H, s, OCH₃ (**6 α)**]; 3.57 [8.45H, s, OCH₃ (**6 β)**]; 7.34–7.50 (4H, phenylene protons) ppm. MS (m/z) (rel. int.): 444 (7) [$\text{M}]^+$; 323 (7) [$\text{M}-\text{Si}(\text{OCH}_3)_3]^+$; 304 (7) [$\text{M}-\text{Si}(\text{OCH}_3)_3-\text{F}]^+$; 121 (100) [$\text{M}-\text{C}_6\text{F}_9-\text{C}_6\text{H}_4-\text{C}_2\text{H}_4]^+$.

Compound 7: yield 85.3%, b.p. 112–115 °C/0.38 mmHg. IR (cm^{-1}): 2945 (m); 2849 (m); 1616 (w); 1419 (w); 1366 (m); 1293 (w); 1249 (s); 1206 (vs); 1153 (vs); 1097 (vs); 1020 (w); 898 (w); 814 (m); 749 (w); 740 (w); 697 (w). ^1H NMR δ : 1.00–1.04 [1.85H, m, Si-CH₂-CH₂ (**7 β)**]; 1.44 [0.23H, d, $J=7.63$ Hz, Si-CH-CH₃ (**7 α)**]; 2.71 [0.08H, q, $J=7.63$ Hz, Si-CH-CH₃ (**7 α)**]; 2.79–2.82 [1.85H, m, Si-CH₂-CH₂ (**7 β)**]; 3.49 [0.69H, s, OCH₃ (**7 α)**]; 3.56 [8.31H, s, OCH₃ (**7 β)**]; 7.31–7.50 (4H, phenylene protons) ppm. MS (m/z) (rel. int.): 544 (5) [$\text{M}]^+$; 423 (1) [$\text{M}-\text{Si}(\text{OCH}_3)_3]^+$; 404 (6) [$\text{M}-\text{Si}(\text{OCH}_3)_3-\text{F}]^+$; 121 (100) [$\text{M}-\text{C}_6\text{F}_{13}-\text{C}_6\text{H}_4-\text{C}_2\text{H}_4]^+$.

Compound 8: yield 72.2%, b.p. 113–116 °C/0.25 mmHg. IR (cm^{-1}): 2955 (m); 2852 (m); 1618 (w); 1422 (w); 1374 (m); 1303 (m); 1252 (vs); 1206 (vs); 1157 (s); 1097 (s); 1020 (w); 828 (m); 753 (w); 740 (w); 711 (w). ^1H NMR δ : 1.00–1.03 [1.76H, m, Si-CH₂-CH₂ (**8 β)**]; 1.44 [0.35H, d, $J=7.63$ Hz, Si-CH-CH₃ (**8 α)**]; 2.71 [0.12H, q, $J=7.63$ Hz, Si-CH-CH₃ (**8 α)**]; 2.78–2.82 [1.76H, m, Si-CH₂-CH₂ (**8 β)**]; 3.49 [1.06H, s, OCH₃ (**8 α)**]; 3.56 [7.94H, s, OCH₃ (**8 β)**]; 7.31–7.50 (4H, phenylene protons) ppm. MS (m/z) (rel. int.): 644 (4) [$\text{M}]^+$; 523 (4) [$\text{M}-\text{Si}(\text{OCH}_3)_3]^+$; 504 (1) [$\text{M}-\text{Si}(\text{OCH}_3)_3-\text{F}]^+$; 121 (100) [$\text{M}-\text{C}_8\text{F}_{17}-\text{C}_6\text{H}_4-\text{C}_2\text{H}_4]^+$.

3.14. Surface modification of glass

Glass plates were allowed to react with the silane coupling agents in 100 cm³ of F-113 at various concentrations for 2 h at 47 °C (boiling point) under an atmosphere of purified nitrogen. The surface-modified glass was rinsed with fresh F-113 and dried. The glass was treated thermally in an oven at 200 °C for 1 h and the contact angles of water and oleic acid were then measured relative to these glass samples. Contact angles θ (°) were measured using 1.0×10^{-6} dm³ drops of water or oleic acid. The contact angles were evaluated

by extrapolating to zero time from a plot of the advancing contact angle vs. time [7].

3.15. Measurement of oxidation resistance of modified glass surfaces

Glass plates which had been treated with the eight types of coupling agents in a 30 mM solution of F-113 were heated in 100 cm³ of concentrated nitric acid for 30, 60, 90 and 120 min, respectively, at 100 °C. After oxidation, each sample was rinsed with water and dried at room temperature for 1 d. The contact angles for water and oleic acid were then measured as described above.

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