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Synthesis of novel highly heat-resistant fluorinated silane coupling agents

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Abstract

Novel fluorinated silane coupling agents with a biphenyl structure, C_nF_{2n+1}–$(C_6H_4)_2$–$CH_2CH_2Si(OCH_3)_3$ (n = 4, 6, and 8), were synthesized with the aim to improve the heat-resistance, oxidation-resistance, and acid-resistance of the surface modified with a common fluorinated silane coupling agent. Alcohols, Rf–$(C_6H_4)_2$–$CH(OH)CH_3$, were obtained by reducing the intermediates, Rf–$(C_6H_4)_2$–$COCH_3$, the products of the reaction of 4-acetyl-4′-bromobiphenyl with perfluoroalkyl iodides in the presence of copper powder. The reaction of the alcohols with phosphorus tribromide gave olefins, Rf–$(C_6H_4)_2$–$CH{=}CH_2$, which were then allowed to react with tetramethoxysilane in the presence of hexachloroplatinate(IV) catalyst to yield novel fluorinated silane coupling agents with a biphenyl structure. The coupling agents with four and six carbon atoms in their fluorocarbon chains were obtained as a colorless liquid while that with 8 carbon atoms was a white gel. Evaluations were made of the coupling agents using surfaces modified with them in terms of water contact angles, heat-resistance, oxidation-resistance, and acid-resistance. The agents behaved similarly to the conventional fluorinated silane coupling agents with respect to water contact angles, oxidation-resistance, and acid-resistance, whereas the former showed an extremely higher heat-resistance (up to 350 °C). In addition, C_6H_5–C_6H_4–$CH_2CH_2Si(OCH_3)_3$ and CH_3–$(C_6H_4)_2$–$CH_2CH_2Si(OCH_3)_3$ with no fluoroalkyl group were synthesized and the heat-resistance of glass surfaces modified with these compounds was examined.

Keywords: Highly heat-resistant silane coupling agent; Synthesis; Fluorocarbon chain; Biphenyl structure

1. Introduction

Materials have in many cases adsorbed water and hydroxyl groups on their surface in the atmospheric air. Silane coupling agents react with these hydroxyl groups to form a siloxane network tightly bound to the material surface. If an organic group with a certain function is introduced in silane coupling agent molecules, the function of the group can be fixed on the material surface. For example, when a fluoroalkyl group is introduced, the surface becomes water and oil repellent [1–10] and the introduction of an antibacterial quaternary ammonium group makes the surface antibacterial [11].

Fluorinated compounds are those unique compounds which possess many excellent properties including high lubricativity, noncombustibility, and chemical inactivity, in addition to water repellency and oil repellency. In recent years, fluorinated compounds have been used as highly functional and performable materials because of their superb characteristics.

We have so far synthesized many fluorinated silane coupling agents, Rf–$CH_2CH_2SiX_3$ (Rf = fluoroalkyl group; X = Cl, OCH_3, NCO), and demonstrated that the glass surfaces modified with these agents are highly water and oil repellent, acid resistant, and oxidation resistant [1–8,10,12–14]. We have also attempted to modify the surface of dental materials with $F(CF_2)_{10}$–$CH_2CH_2Si(OCH_3)_3$ and found that the modified surface exhibits water and oleic acid contact angles higher than those on the nonmodified surface [9]. The results have led us to investigate the surface modification of dentures to make them

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contamination-resistant. Thus, surface-modified dentures were worn in a heavy smoker's oral cavity for 4 months and they were found to remain uncontaminated. A resin composite modified with $F(CF_2)_{10}$–$CH_2CH_2Si(OCH_3)_3$ was resistant to coloration by tea extract, tobacco extract, and Oil Orange (Sudan 1 Olive), while resin composites for dental use are prone to coloration by many colorants in foods and tobacco smoke [15–17].

Nevertheless, the surfaces modified with these fluorinated silane coupling agents lose their acquired resistance to heat, oxidation, and many substances including acid, water, and various contaminants because the ethylene part (–CH_2CH_2–) of the agents is gradually broken down by oxidation [3,6,7] to release the fluoroalkyl chain from the modified surface. The heat-resistance of the glass surface modified with the conventional fluorinated silane coupling agent is about the same as that of poly(tetrafluoroethylene) (PTFE), the working heat resistant temperature of which is reported to be 260 °C, while the value obtained by the present authors is around 280 °C [12].

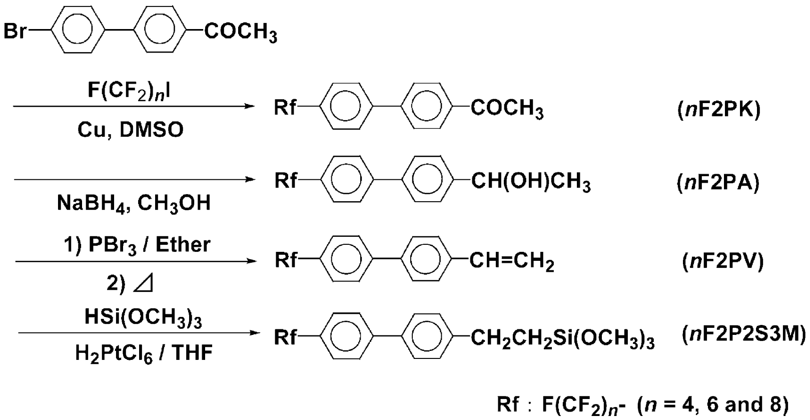
We synthesized fluorinated aromatic silane coupling agents, C_nF_{2n+1}–$C_6H_4SiX_3$ ($n = 4$, 6, and 8; X = Cl, OCH_3, and NCO) with a structure in which the ethylene part of the conventional fluorinated silane coupling agents is replaced by a benzene ring in our recent works aiming at improving the heat resistance and oxidation-resistance of the surface modified with fluorinated silane coupling agents and verified that the glass surface modified with the synthesized agents is heat resistant up to about 300 °C [10,13].

The present paper deals with the synthesis of novel silane coupling agents, Rf–$(C_6H_4)_2$–$CH_2CH_2Si(OCH_3)_3$, with a biphenyl ring introduced in their molecules, and evaluations of the surface modifiability of the agents synthesized, in which a dramatic improvement in the heat-resistance is noticed.

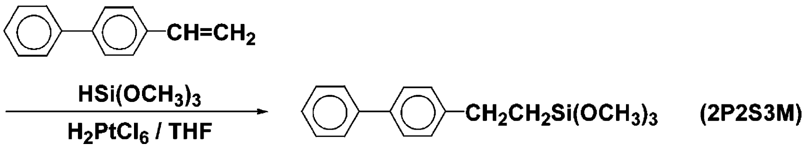
2. Results and discussion

2.1. Synthesis

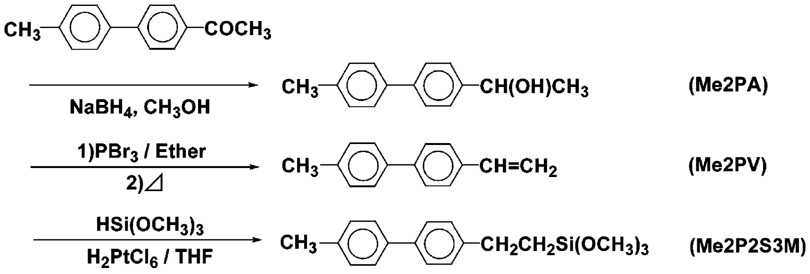
The systheses of *n*F2P2S3M, 2P2S3M, and Me2P2S3M were performed according to Schemes 1–3, respectively. All of these synthesized silane coupling agents were found to be mixtures of α and β adducts [18]. The abundance ratio of α adduct to β adduct was calculated using the integration ratio of



Scheme 1.



Scheme 2.



Scheme 3.

^{1}H NMR spectrum. Thus, each agent was synthesized three times and the three integration ratios of ^{1}H NMR spectra obtained were averaged. The averaged value gave the adduct abundance ratio for each agent. The synthesized agents were all stable in a nitrogen atmosphere, whereas their solutions became turbid immediately when they were brought to contact with moisture in the air to indicate that the agents are easily hydrolyzed. The separation of the adducts was impossible because their boiling points are very close to each other. Hence, the modification of glass surfaces was conducted using their mixtures as synthesized.

2.2. Determination of optimum modifying agent concentration

Fig. 1 shows the results of contact angles measurements on the glass surface modified with the $F(CF_2)_4$–$(C_6H_4)_2$–$CH_2CH_2Si(OCH_3)_3$ (4F2P2S3M) solution in HFE-7100. Here, the ordinate is for the contact angles of water on the modified glass surface and the abscissa is for the concentration of the modifying agent used. The contact angles remained almost constant above 15 mM and hence the minimum and sufficient modifying agent concentration was determined to be 15 mM. The same concentration was then adopted for 6F2P2S3M and 8F2P2S3M based on this result. Glass surface modifications were also made using solutions in HFE-7100 of 2P2S3M and Me2P2S3M, both with no fluorocarbon chain, at the same concentration. The values of water contact angles on the glass surfaces modified with 8F2P2S3M, 6F2P2S3M, and 4F2P2S3M were 111°, 110°, and 106°, respectively.

2.3. Determination of optimum modification time

Fig. 2 shows the relationship between modification time and water contact angles for the glass surface modified with $F(CF_2)_4$–$(C_6H_4)_2$–$CH_2CH_2Si(OCH_3)_3$ solution in HFE-7100. Here, the ordinate is for the water contact angles on the modified glass surface and the abscissa is for modification time. Two hours modification time was found to be long enough for the surface to acquire a sufficient water repellency and this modification time was also used for 6F2P2S3M and 8F2P2S3M. In addition, glass surface modification was performed using 2P2S3M and Me2P2S3M for the same modification time and the results were compared with each other.

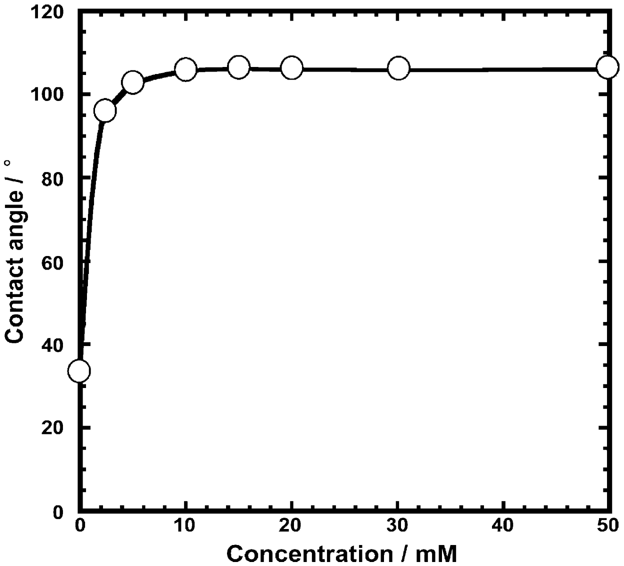


Fig. 1. Relationship between water contact angles on the glass surfaces modified with 4F2P2S3M and its concentration.

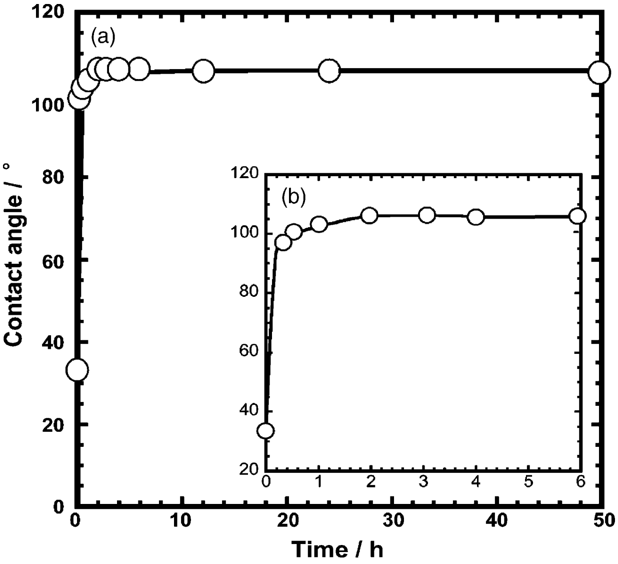


Fig. 2. Relationship between water contact angles on the glass surfaces modified with 4F2P2S3M and modification time.

2.4. Evaluation of heat-resistance of modified glass surface

Glasses modified under the optimum modifying conditions mentioned above were treated by heating at 350 °C in an oven for gas chromatography. Fig. 3 shows the relation between water contact angles and heating time for the modified glass surfaces. Here, the ordinate is for water contact angles and the abscissa is for heating time.

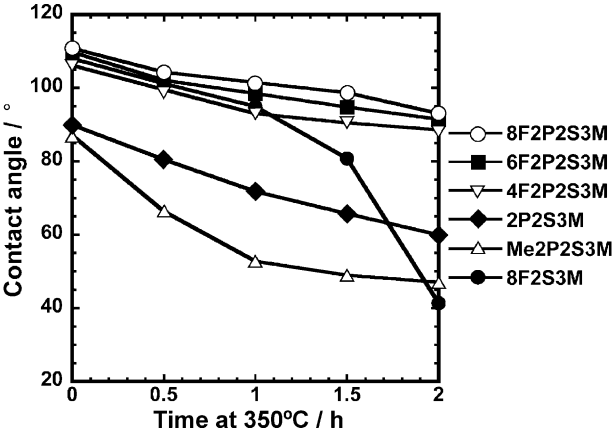


Fig. 3. Relationship between water contact angles on the modified glass surfaces and heating time at 350 °C.

The water contact angles on the glass surface modified with *n*F2P2S3M was over 90° even after the glass was heated for 2 h at 350 °C, independently of the fluorocarbon chain length of the coupling agent, which shows a high heat-resistance of the modified surface layer. Gradual decrease in the contact angles was observed up to 2 h heating on the glass surfaces modified with 2P2S3M and Me2P2S3M, both with no fluorocarbon chain, but not appreciably after 2 h heating though the water repellency of the surfaces before heat treatment (initial water repellency) was lower than that of the surfaces modified with the fluorinated coupling agents. This finding also indicates that the surface modified with these coupling agents is heat-resistant. The heat-resistance of the glass surface modified with $F(CF_2)_4–CH_2CH_2Si(OCH_3)_3$ (8F2S3M) having no biphenyl ring was lower than that of the surfaces modified with the coupling agents with a biphenyl ring as evidenced by a steep decrease in the contact angles on the former surface with increasing heating time (Fig. 3).

2.5. Evaluations of oxidation-resistance and acid-resistance of modified glass surfaces

Figs. 4 and 5 show the relationships of water contact angles with immersion time lengths in hot conc. nitric acid and hydrochloric acid, respectively. Here, the ordinate is for water contact angles and the abscissa is for immersion time length in hot conc. nitric acid (Fig. 4) or that in hot conc. hydrochloric acid (Fig. 5). The water contact angles on the glass surface modified with 8F2P2S3M was higher than 110° even after 2 h acid treatment. Similarly, the surfaces modified with 6F2P2S3M and 4F2P2S3M exhibited values of water contact angles slightly lower than that on the surface modified with 8F2P2S3M. This demonstrates that the surfaces modified with these fluorinated coupling agents are highly oxidation- and acid-resistant. The surfaces modified with 2P2S3M and Me2P2S3M were also oxidation- and acid-resistant because the water contact angles on these surfaces decreased slowly with increasing treating time though the initial water contact angles on the surfaces was low when compared with that on the surfaces modified with the fluorinated coupling agents. The glass surface modified with 8F2S3M showed an oxidation and acid-resistance lower than that of the surfaces modified with the fluorinated coupling agents with a biphenyl ring (Figs. 4 and 5).

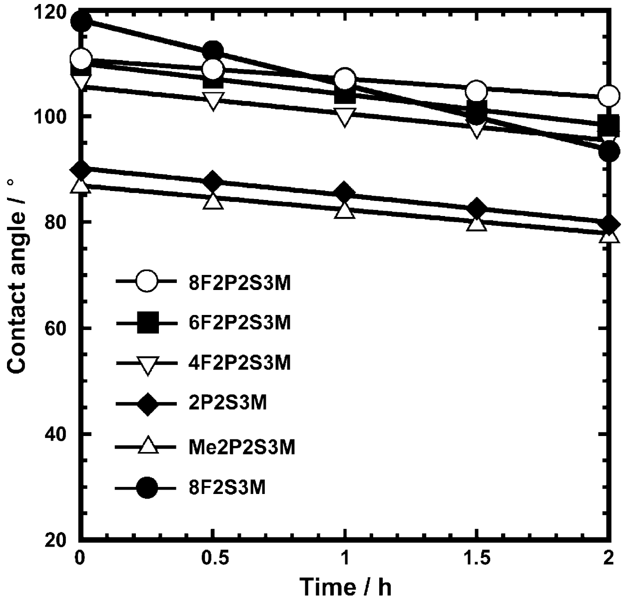


Fig. 4. Relationship between water contact angles on the modified glass surfaces and treating time in hot concentrated nitric acid.

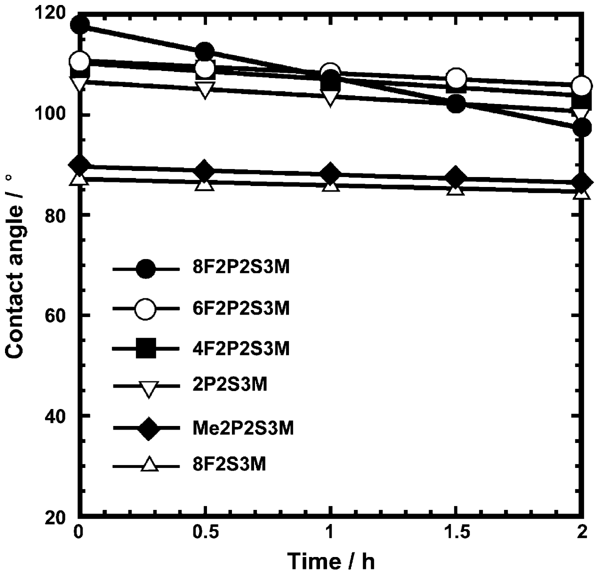
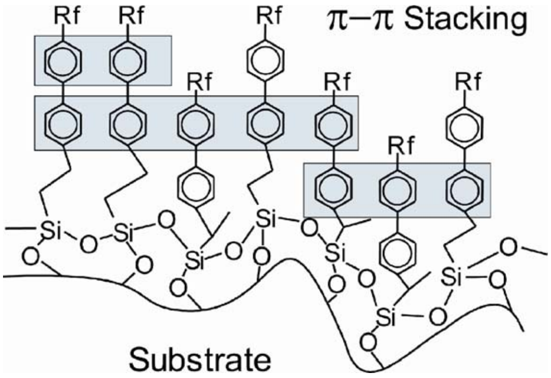


Fig. 5. Relationship between water contact angles on the modified glass surfaces and treating time in hot concentrated hydrochloric acid.

The experimental finding described above suggests that *n*F2P2S3M acquire the property to protect the ethylene spacer against oxidation through the introduction of two bulky oxidation-resistant phenylene groups into their molecules as spacer, whereas oxidation causes the bond cleavage of the ethylene spacer part of the conventional silane coupling agents, $Rf–CH_2CH_2SiX_3$ [4,7,10,11]. The improved heat-resistance and acid-resistance of the newly synthesized coupling agents may be ascribed to the π–π interaction (π–π stacking, see Scheme 4) between the aromatic rings introduced in the molecules on the modified surface where a durable siloxane network is formed [8,13].



Scheme 4.

3. Conclusions

Novel fluorinated silane coupling agents with a biphenyl structure introduced in their molecules were synthesized to improve the heat-resistance of silane layers formed on the substrate surface. The synthesized coupling agents were used to modify the glass surface and evaluations were performed of the water repellency, heat-resistance, oxidation-resistance, and acid-resistance of the modified glass surface.

The glass surface modified with the coupling agents exhibited a water repellency slightly lower than that modified with the conventional fluorinated silane coupling agents because of the presence of two aromatic rings in the molecules while the former was as oxidation-resistant and acid-resistant as the latter. The former was highly heat-resistant even at 350 °C.

4. Experimental

4.1. Materials

The following chemicals were used as supplied: copper bronze powder, potassium hydroxide (both from Kanto Chemical), 4-acetyl-4′-bromobiphenyl, 4-acetyl-4′-methylbiphenyl (both from Tokyo Chemical), sodium borohydride, phosphorus tribromide, magnesium sulfate, dichloromethane (all from Nakarai Tesk), perfluorobutyl iodide, perfluorohexyl iodide, perfluorooctyl iodide (all from Daikin Fine Chemical), and 4-vinylbiphenyl (Aldrich Chemical).

Trimethoxysilane (Tokyo Chemical) was purified by distillation in the presence of calcium hydride. Hexachloroplatinate(IV) hexahydrate (Kojima Chemical) was dissolved in THF in a nitrogen atmosphere and its concentration was adjusted to 0.1 M. Dimethylsulfoxide (DMSO, Nakarai Tesk) was purified by vacuum distillation after being dehydrated with calcium chloride and calcium hydride. Diethyl ether, tetrahydrofuran, and benzene (all from Kanto Chemical) were purified by distillation after being dehydrated with calcium hydride and metallic sodium. (Perfluoro-*i*-butyl) methyl ether (HFE-7100) (Sumitomo 3M) was distilled over calcium hydride after being dehydrated with calcium chloride and the fraction obtained at 61 °C was used. Methanol (Kanto Chemical) was purified by distillation before use after being dehydrated with calcium hydride and magnesium ribbon.

Glass plates (microslide glass, 1.3 mm thick, 76 mm × 26 mm) were purchased from Matsunami Glass Inc., Ltd.

4.2. Measurements

Measurements of ^{1}H MNR and ^{19}F NMR spectra, FT-IR spectrum, and mass spectrum were conducted using a Bruker DPX 400 (^{1}H: 400 MHz, ^{19}F: 376 MHz), Avatar 360 FT-IR spectrometer (Nicolet), and JOEL JMS-SX102A, respectively. Static contact angles measurements were performed with a CA-X contact angles meter (Kyowa Interface Science) using water drops (0.9 μl). The values of contact angles in Figs. 1–5 were the averages of those obtained at 20 different points for each sample.

4.3. Synthesis of silane coupling agents

Fluorinated silane coupling agents with a biphenyl structure were synthesized along the reaction path shown in Scheme 1. A silane coupling agent with a biphenyl structure and no fluoroalkyl group and a biphenyl-type silane coupling agent with a methyl group were synthesized according to Schemes 2 and 3, respectively.

4.3.1. Synthesis of $F(CF_2)_4–(C_6H_4)_2–COCH_3$ (4F2PK)

4-Acetyl-4′-bromobiphenyl (15.0 g, 54.6 mmol), copper bronze powder (19.0 g, 298 mmol), perfluorobutyl iodide (27.3 g, 78.8 mmol), and DMSO (110 ml) as solvent were taken into a 300 ml round bottom flask equipped with a reflux condenser and the mixture was refluxed for 24 h in a nitrogen atmosphere. Excess copper bronze powder was separated by filtration after the refluxing finished and 200 ml water was added to the filtrate to cause precipitation of $Cu(OH)_2$. The precipitate was removed by filtration and the product in the filtrate was extracted into diethyl ether. Diethyl ether was removed by distillation at a reduced pressure after the ether layer was washed with water and dehydrated using magnesium sulfate and the residue was purified by vacuum distillation to give 4F2PK as a white solid (20.2 g, yield 89%). b.p.: 123–125 °C/11 Pa. ^{1}H NMR ($CDCl_3$) δ: 2.67 (s (singlet), 3H, CH_3), 7.66–8.07 (m (multiplet), 8H, biphenyl ring protons). IR (cm^{-1}): 1132 (vs), 1202 (vs) (νC–F), 1687 (s) (νC=O). MS (*m*/*z* (rel. int.)): 414 (31, M^+); 399 (100, $[M - CH_3]^+$); 245 (7, $[M - F(CF_2)_3]^+$); 202 (20, $[CF_2C_6H_4C_6H_4]^+$); 152 (25, $[C_6H_4C_6H_4]^+$).

4.3.2. Synthesis of $F(CF_2)_6–(C_6H_4)_2–COCH_3$ (6F2PK) and $F(CF_2)_8–(C_6H_4)_2–COCH_3$ (8F2PK)

The synthesis was carried out in a way similar to that for 4F2PK.

6F2PK was obtained as a white solid (28.1 g, yield 93%) when 16.2 g (58.7 mmol) of 4-acetyl-4′-bromobiphenyl, 31.0 g (487 mmol) of copper bronze powder, and 31.6 g (70.8 mmol) of perfluorohexyl iodide were used as reactants. b.p.: 140–142 °C/11 Pa. ^{1}H NMR ($CDCl_3$) δ: 2.69 (s, 3H, CH_3), 7.68–8.07 (m, 8H, biphenyl ring protons). IR (cm^{-1}): 1140 (vs), 1198 (vs) (νC–F), 1687 (s) (νC=O). MS (*m*/*z* (rel. int.)): 514 (27, M^+); 499 (100, $[M - CH_3]^+$); 245 (8, $[M - F(CF_2)_3]^+$); 202 (20, $[CF_2C_6H_4C_6H_4]^+$); 152 (25, $[C_6H_4C_6H_4]^+$).

8F2PK was obtained as a white solid (47.0 g, yield 84%) when 25.0 g (102 mmol) of 4-acetyl-4′-bromobiphenyl, 37.7 g (593 mmol) of copper bronze powder, and 74.1 g (136 mmol) of perfluorooctyl iodide were used as reactants. b.p.: 156–158 °C/20 Pa. ^{1}H NMR ($CDCl_3$) δ: 2.66 (s, 3H, CH_3), 7.69–8.07 (m, 8H, biphenyl ring protons). IR (cm^{-1}): 1147 (vs), 1198 (vs) (νC–F), 1680 (s) (νC=O). MS (*m*/*z* (rel. int.)): 614 (27, M^+); 599 (100, $[M - CH_3]^+$); 245 (8, $[M - F(CF_2)_3]^+$); 202 (20, $[CF_2C_6H_4C_6H_4]^+$); 152 (25, $[C_6H_4C_6H_4]^+$).

4.3.3. Synthesis of $F(CF_2)_4–(C_6H_4)_2–CH(OH)–CH_3$ (4F2PA)

4F2PK (5.40 g, 13.0 mmol), sodium borohydride (0.47 g, 12.4 mmol), and THF (50 ml) as solvent were taken into a

100 ml round bottom flask. Methanol (50 ml) was slowly added drop-wise into the flask in an ice bath and the mixture was refluxed for 2 h under heating after being stirred for 30 min at room temperature. Methanol was removed by distillation at a reduced pressure after the refluxing finished and a white solid obtained was dissolved in diethyl ether. Water was added to the ether solution and the ether layer was taken out, washed with water, and dehydrated with magnesium sulfate. 4F2PA was obtained as a white solid (5.13 g, yield 95%) when diethyl ether was removed by vacuum distillation. ^{1}H NMR ($CDCl_3$) δ: 1.58 (d, $J = 6.48$ Hz, 3H, CH_3), 1.82 (s, 1H, OH), 4.96–5.03 (q (quartet), $J = 6.48$ Hz, 1H, CH), 7.50–7.73 (m, 8H, biphenyl ring protons). IR (cm^{-1}): 1123(vs), 1190 (vs) (νC–F), 2877 (w), 2975 (w) (νC–H), 3386 (w) (νO–H). MS (m/z (rel. int.)): 416 (44, M^+); 401 (100, $[M - CH_3]^+$); 247 (4, $[M - F(CF_2)_3]^+$); 214 (11, $[CF_2C_6H_4C_6H_4CH]^+$); 203 (23, $[C_6H_4C_6H_4]^+$).

4.3.4. *Synthesis of* $F(CF_2)_6{-}(C_6H_4)_2{-}CH(OH)CH_3$ *(6F2PA),* $F(CF_2)_8{-}(C_6H_4)_2{-}CH(OH)CH_3$ *(8F2PA), and* $CH_3{-}(C_6H_4)_2{-}CH(OH)CH_3$ *(Me2PA)*

The synthesis was performed in a manner similar to that for 4F2PA.

6F2PA was obtained as a white solid (5.26 g, yield 98%) when 5.35 g (10.4 mmol) of 6F2PK, 0.42 g (11.1 mmol) of sodium borohydride, and 40 ml of methanol were used as reactants. ^{1}H NMR ($CDCl_3$) δ: 1.55 (d, $J = 6.44$ Hz, 3H, CH_3), 1.85 (s, 1H, OH), 4.93–5.01 (q, $J = 6.44$ Hz, 1H, CH), 7.50–7.72 (m, 8H, biphenyl ring protons). IR (cm^{-1}): 1143 (vs), 1198 (vs) (νC–F), 2873 (w), 2979 (w) (νC–H), 3370 (w) (νO–H). MS (m/z (rel. int.)): 516(50, $[M]^+$); 501(100, $[M - CH_3]^+$); 247(4, $[M - F(CF_2)_3]^+$); 214(11, $[CF_2C_6H_4C_6H_4CH]^+$); 203 (23, $[C_6H_4C_6H_4]^+$).

8F2PA was obtained as a white solid (12.6 g, yield 88%) when 14.3 g (10.4 mmol) of 8F2PK, 0.42 g (11.1 mmol) of sodium borohydride, and 40 ml of methanol were used as reactants. ^{1}H NMR ($CDCl_3$) δ: 1.55 (d, $J = 6.48$ Hz, 3H, CH_3), 1.84 (s, 1H, OH), 4.93–5.01 (q, $J = 6.48$ Hz, 1H, CH), 7.49–7.71 (m, 8H, biphenyl ring protons). IR (cm^{-1}): 1147 (vs), 1149 (vs) (νC–F), 2850 (w), 2975 (w) (νC–H), 3315 (w) (νO–H). MS (m/z (rel. int.)): 616(44, $[M]^+$); 601(100, $[M - CH_3]^+$); 247(4, $[M - F(CF_2)_3]^+$); 214(11, $[CF_2C_6H_4C_6H_4CH]^+$); 203(23, $[C_6H_4C_6H_4]^+$).

Me2PA was obtained as a white solid (1.93 g, yield 93%) when 2.05 g (9.75 mmol) of 4-acetyl-4′-methylbiphenyl, 0.43 g (11.4 mmol) of sodium borohydride, and 50 ml of methanol were used as reactants. ^{1}H NMR ($CDCl_3$) δ: 1.56 (d, $J = 6.44$ Hz, 3H, $CH{-}CH_3$), 1.80 (s, 1H, OH), 2.42 (s, 3H, Ph-CH_3), 4.97–5.03 (q, $J = 6.44$ Hz, 1H, CH), 7.27–7.59 (m, 8H, biphenyl ring protons). IR (cm^{-1}): 1188 (w), 2853 (m) (νPh-CH), 2916 (m), 2959 (m), 3030 (m) (νC–H), 3347 (vs) (νO–H). MS (m/z (rel. int.)): 212 (81, $[M]^+$); 197 (100, $[M - CH_3]^+$); 169 (72, $[CH_3C_6H_4C_6H_4]^+$); 165 (26, $[C_6H_4C_6H_4CH]^+$); 152 (27, $[C_6H_4C_6H_4]^+$).

4.3.5. *Synthesis of* $F(CF_2)_4{-}(C_6H_4)_2{-}CH{=}CH_2$ *(4F2PV)*

4F2PA (2.04 g, 4.90 mmol) and diethyl ether (5 ml) were taken into a 100 ml round bottom flask cooled with ice, into which phosphorus tribromide (0.9 g, 3.32 mmol) was slowly added dropwise, and the mixture was stirred for 2 h at room temperature in a nitrogen atmosphere. Ice water was then added to the reactant solution and the product was extracted with diethyl ether. The ether layer was washed with water and dehydrated with magnesium sulfate. After diethyl ether was removed by distillation at a reduced pressure, the residue was distilled in a vacuum to leave 4F2PV as a white solid (1.58 g, yield 81%). b.p.: 120–123 °C/11 Pa. ^{1}H NMR ($CDCl_3$) δ: 5.32 (d, $J = 10.8$ Hz, 1H, $=CH_2$ (*trans*)), 5.83 (d, $J = 17.5$ Hz, 1H, $=CH_2$ (*cis*)), 6.73–6.82 (q, $J = 10.8$ Hz, 1H, $=CH{-}$), 7.51–7.73 (m, 8H, biphenyl ring protons). IR (cm^{-1}): 916 (m), 987 (m) (σC–H), 1128 (vs), 1194 (vs) (νC–F). MS (m/z (rel. int.)): 398 (70, $[M]^+$); 379 (6, $[M - F]^+$); 229 (100, $[CF_2C_6H_4C_6H_4{-}CH{=}CH_2]^+$).

4.3.6. *Synthesis of* $F(CF_2)_6{-}(C_6H_4)_2{-}CH{=}CH_2$ *(6F2PV),* $F(CF_2)_8{-}(C_6H_4)_2{-}CH{=}CH_2$ *(8F2PV), and* $CH_3{-}(C_6H_4)_2{-}CH{=}CH_2$ *(Me2PV)*

The synthesis was conducted in a way similar to that for 4F2PV.

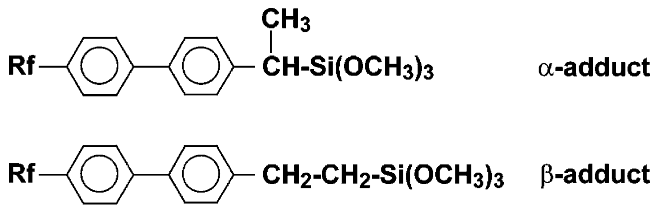
6F2PV was obtained as a white solid (20.9 g, yield 75%) when 28.9 g (55.9 mmol) of 6F2PA and 7.58 g (28.0 mmol) of phosphorus tribromide were used as reactants. b.p.: 126–128 °C/10 Pa. ^{1}H NMR ($CDCl_3$) δ: 5.32 (d, $J = 11.0$ Hz, 1H, $=CH_2$(*trans*)), 5.83 (d, $J = 17.6$ Hz, 1H, $=CH_2$(*cis*)), 6.73–6.81 (q, $J = 11.0$ Hz, 1H, $=CH{-}$), 7.52–7.73 (m, 8H, biphenyl ring protons). IR (cm^{-1}): 917 (m), 991 (m) (σC–H), 1143 (vs), 1202 (vs) (νC–F). MS (m/z (rel. int.)): 498 (47, $[M]^+$); 479 (6, $[M - F]^+$); 229 (100, $[CF_2C_6H_4C_6H_4CH{=}CH_2]^+$).

8F2PV was obtained as a white solid (7.34 g, yield 60%) when 12.6 g (20.5 mmol) of 8F2PA and 2.77 g (10.2 mmol) of phosphorus tribromide were used as reactants. b.p.: 130–133 °C/13 Pa. ^{1}H NMR ($CDCl_3$) δ: 5.31 (d, $J = 10.9$ Hz, 1H, $=CH_2$(*trans*), 5.84 (d, $J = 17.6$ Hz, 1H, $=CH_2$(*cis*)), 6.73–6.82 (q, $J = 10.9$ Hz, 1H, $=CH{-}$), 7.53–7.73 (m, $J = 8.06$ Hz, 8H, biphenyl ring protons). IR (cm^{-1}): 913 (m), 991 (m) (σC–H), 1151 (vs), 1202 (vs) (νC–F). MS (m/z (rel. int.)): 598 (78, $[M]^+$); 579 (13, $[M - F]^+$); 229 (100, $[CF_2C_6H_4C_6H_4CH{=}CH_2]^+$).

Me2PV was obtained as a white solid (2.26 g, yield 48%) when 5.12 g (24.1 mmol) of Me2PA and 4.32 g (16.0 mmol) of phosphorus tribromide were used as reactants. b.p.: 90–93 °C/18 Pa. ^{1}H NMR ($CDCl_3$) δ: 2.42 (s, 3H, Ph-CH_3), 5.29 (d, $J = 10.3$ Hz, 1H, $=CH_2$(*trans*)), 5.80 (d, $J = 17.6$ Hz, 1H, $=CH_2$(*cis*)), 6.71–6.83 (q, $J = 10.3$ Hz, 1H, $=CH{-}$), 7.27–7.57 (m, 8H, biphenyl ring protons). IR (cm^{-1}): 897 (s), 987 (s) (σC–H), 1136 (w), 2853 (m) (νPh-CH), 2971 (m), 3026 (m), 3084 (m) (νC–H). MS (m/z (rel. int.)): 194 (100, $[M]^+$); 178 (18, $[M - CH_3]^+$); 165 (20, $[C_6H_4C_6H_4CH]^+$); 152 (13, $[C_6H_4C_6H_4]^+$).

4.3.7. *Synthesis of* $F(CF_2)_4{-}(C_6H_4)_2{-}CH_2CH_2Si(OCH_3)_3$ *(4F2P2S3M)*

4F2PV (2.30 g, 5.77 mmol), 5 ml of benzene as solvent, and 0.2 ml of 0.1 M hexachloroplatinate(IV) solution in THF as catalyst were taken into a 50 ml round bottom flask equipped



Scheme 5.

with a reflux condenser and trimethoxysilane (0.91 g, 7.45 mmol) was slowly added dropwise into the reactant mixture. The mixture was stirred for 50 h at 50 °C in a nitrogen atmosphere and excess trimethoxysilane and the solvent were removed by distillation at a reduced pressure after the mixture was cooled down to room temperature. The residue was then purified by vacuum distillation to give 4F2P2S3M as a colorless liquid (0.60 g, yield 20%). b.p.: 120–123 °C/11 Pa. The product was found to be a 3:2 mixture of α and β adducts (see Scheme 5) on the basis of the integration ratio of ^{1}H NMR spectrum. Spectra measurements were performed using the α, β-mixture. ^{1}H NMR (CDCl$_3$) δ: 1.06–1.11 (m, 0.8H, –CH_2–Si), 1.29–1.31 (m, 1.8H, CH_3–CH–Si), 2.70–2.77 (q, $J = 7.56$ Hz, 0.6H, CH$_3$–CH–Si), 2.79–2.85 (m, 0.8H, –CH_2–CH$_2$–Si), 3.51–3.65 (m, 9H, OCH$_3$), 7.29–7.73 (m, 8H, biphenyl ring protons). IR (cm^{-1}): 1089 (vs) (νSi–O), 1030 (vs), 1257 (vs) (νC–F), 2843 (m) (νC–H). MS (m/z (rel. int.)): 520 (100, $[M]^+$); 488 (13, $[M-\mathrm{OCH_3}]^+$); 398 (36, $[M-\mathrm{Si(OCH_3)_3}]^+$); 385 (18, β $[M-\mathrm{CH_2Si(OCH_3)_3}]^+$); 121 (88, $[\mathrm{Si(OCH_3)_3}]^+$); 91 (26, $[\mathrm{Si(OCH_3)_2}]^+$).

4.3.8. Synthesis of $F(CF_2)_6$–$(C_6H_4)_2$–$CH_2CH_2Si(OCH_3)_3$ (6F2P2S3M), $F(CF_2)_8$–$(C_6H_4)_2$–$CH_2CH_2Si(OCH_3)_3$ (8F2P2S3M), (C_6H_5)–(C_6H_4)–$CH_2CH_2Si(OCH_3)_3$ (2P2S3M) and CH_3–$(C_6H_4)_2$–$CH_2CH_2Si(OCH_3)_3$ (Me2P2S3M)

The synthesis was carried out in a way similar to that for 4F2P2S3M.

6F2P2S3M was obtained as a colorless liquid (0.78 g, yield 60%) when 6F2PV (1.04 g, 2.09 mmol), 0.2 ml of 0.1 M hexachloroplatinate(IV) solution in THF, and trimethoxysilane (0.5 ml, 4.09 mmol) were used as reactants. b.p.: 126–128 °C/10 Pa. The product was found to be a 2:1 of α and β adducts on the basis of the integration ratio of ^{1}H NMR spectrum. ^{1}H NMR (CDCl$_3$) δ: 0.99–1.03 (m, 0.67H, –CH_2–Si), 1.79–1.88 (m, 2H, CH_3–CH–Si), 2.60–2.69 (q, $J = 7.56$ Hz, 0.66H, CH$_3$–CH–Si), 2.71–2.78 (m, 0.67H, –CH_2–CH$_2$–Si), 3.40–3.61 (m, 9H, OCH$_3$), 7.22–7.68 (m, 8H, biphenyl ring protons). IR (cm^{-1}): 1085 (vs) (νSi–O), 1014 (vs), 1257 (vs) (νC–F), 2843 (m) (νC–H). MS (m/z (rel. int.)): 620 (100, $[M]^+$); 588 (18, $[M-\mathrm{OCH_3}]^+$); 498 (51, $[M-\mathrm{Si(OCH_3)_3}]^+$); 485 (21, β $[M-\mathrm{CH_2Si(OCH_3)_3}]^+$); 121 (88, $[\mathrm{Si(OCH_3)_3}]^+$); 91 (26, $[\mathrm{Si(OCH_3)_2}]^+$).

8F2P2S3M was obtained as a colorless viscous liquid (0.76 g, yield 60%) when 8F2PV (1.26 g, 2.11 mmol), 0.2 ml of 0.1 M hexachloroplatinate(IV) solution in THF, and trimethoxysilane (0.26 g, 2.13 mmol) were used as reactants. b.p.: 130–133 °C/10 Pa. The product was found to be a 2:5 mixture of α and β adducts on the basis of the integration ratio of ^{1}H NMR spectrum. ^{1}H NMR (CDCl$_3$) δ: 0.96–1.02 (m, 1.43H, –CH_2–Si), 1.12–1.32 (m, 0.86H, CH_3–CH–Si), 2.61–2.71 (q, $J = 7.59$ Hz, 0.28H, CH$_3$–CH–Si), 2.72–2.81 (m, 1.43H, –CH_2–CH$_2$–Si), 3.37–3.63 (m, 9H, OCH$_3$), 7.22–7.74 (m, 8H, biphenyl ring protons). ^{19}F NMR (CDCl$_3$) δ: −126.44 (m, 2F, h); −123.72 (m, 2F, g); −120.51 (m, 6F, d, e and f); −121.30 (m, 2F, c); −110.11 (m, 2F, b); −78.40 (m, 3F, a) for $CF_3{}^a$–$CF_2{}^b$–$CF_2{}^c$–$CF_2{}^d$–$CF_2{}^e$–$CF_2{}^f$–$CF_2{}^g$–$CF_2{}^h$–$C_6H_4C_6H_4$–$CH_2CH_2Si(OCH_3)_3$. IR (cm^{-1}): 1089 (vs) (νSi–O), 1147 (vs), 1202 (vs) (νC–F), 2843 (m) (νC–H). MS (m/z (rel. int.)): 720 (17, $[M]^+$); 688 (2, $[M-\mathrm{OCH_3}]^+$); 598 (66, $[M-\mathrm{Si(OCH_3)_3}]^+$); 585 (16, β $[M-\mathrm{CH_2Si(OCH_3)_3}]^+$); 121 (88, $[\mathrm{Si(OCH_3)_3}]^+$); 91 (26, $[\mathrm{Si(OCH_3)_2}]^+$). HRMS(EI) (m/z (rel. int.)): obsd. 720.0985 (26.1, M^+ (calcd. 720.0988 for $C_{25}H_{21}O_3F_{17}Si_1$)).

2P2S3M was obtained as colorless liquid (1.43 g, yield 85%) when 4-vinylphenyl (1.00 g, 5.55 mmol), 0.2 ml of 0.1 M hexachloroplatinate(IV) solution in THF, and trimethoxysilane (0.73 g, 5.97 mmol) were used as reactants. b.p.: 110–113 °C/11 Pa. The product was found to be a 7:3 mixture of α and β adducts on the basis of the integration ratio of ^{1}H NMR spectrum. ^{1}H NMR (CDCl$_3$) δ: 0.99–1.01 (m, 0.6H, –CH_2–Si), 1.19–1.23 (m, 2.1H, CH_3–CH–Si), 2.55–2.66 (q, $J = 7.60$ Hz, 0.7H, CH$_3$–CH–Si), 2.68–2.78 (m, 0.6H, –CH_2–CH$_2$–Si), 3.40–3.64 (m, 9H, OCH$_3$), 7.19–7.56 (m, 9H, biphenyl ring protons). IR (cm^{-1}): 2842 (s), 2873 (s), 2932 (s), 2965 (s), 3026 (s) (νC–H), 1515 (m), 1601 (m) (νC–C), 1082 (s) (νSi–O). MS (m/z (rel. int.)): 302 (100, $[M]^+$); 270 (23, $[M-\mathrm{OCH_3}]^+$); 180 (82, $[M-\mathrm{Si(OCH_3)_3}]^+$); 167 (56, β $[M-\mathrm{CH_2Si(OCH_3)_3}]^+$); 121 (52, $[\mathrm{Si(OCH_3)_3}]^+$); 91 (22, $[\mathrm{Si(OCH_3)_2}]^+$). HRMS(EI) (m/z (rel. int.)): obsd. 302.1339 (25.8, M^+ (calcd. 302.1338 for $C_{17}H_{22}O_3Si_1$)).

Me2P2S3M was obtained as a colorless liquid (0.80 g, yield 15%) when Me2PV (2.26 g, 11.6 mmol), 0.2 ml of 0.1 M hexachloroplatinate(IV) solution in THF, and trimethoxysilane (1.42 g, 11.6 mmol) were used as reactants. b.p.: 82–85 °C/20 Pa. The product was found to be a 1:2 mixture of α and β adducts on the basis of the integration ratio of ^{1}H NMR spectrum. ^{1}H NMR (CDCl$_3$) δ: 1.06–1.10 (m, 1.33H, –CH_2–Si), 1.29–1.33 (m, 1H, CH_3–CH–Si), 2.42 (s, 3H, Ph-CH$_3$), 2.70–2.75 (q, $J = 7.60$ Hz, 0.34H, CH$_3$–CH–Si), 2.79–2.85 (m, 1.33H, –CH$_2$–CH$_2$–Si), 3.62–3.67 (m, 9H, OCH$_3$), 7.26–7.57 (m, 8H, biphenyl ring protons). IR (cm^{-1}): 2912 (vs), 2963 (vs), 3018 (vs) (νC–H), 2850 (s), 1187 (s) (νPh-CH), 1093 (vs) (νSi–O). MS (m/z (rel. int.)): 316 (100, $[M]^+$); 285 (7, $[M-\mathrm{OCH_3}]^+$); 195 (65, $[M-\mathrm{Si(OCH_3)_3}]^+$); 181 (77, β $[M-\mathrm{CH_2Si(OCH_3)_3}]^+$); 165 (23, $[M-\mathrm{CH_3}, -\mathrm{CH_2Si(OCH_3)_3}]^+$); 121 (50, $[\mathrm{Si(OCH_3)_3}]^+$); 91 (23, $[\mathrm{Si(OCH_3)_2}]^+$). HRMS(EI) (m/z (rel. int.)): obsd. 316.1497 (79.6, M^+ (calcd. 316.1495 for $C_{18}H_{24}O_3Si_1$)).

4.4. Modification of glass surfaces

The optimum modifying agent concentration and modification time were determined using 4F2P2S3M solution in HFE-7100 before evaluating the characteristics of the glass surfaces modified with each of the synthesized aromatic silane coupling agents, 8F2P2S3M, 6F2P2S3M, 4F2P2S3M, 2P2S3M, and Me2P2S3M.

Glass plates were immersed in 4F2P2S3M solutions in HFE-7100 at given concentrations prepared in a nitrogen atmosphere and their surfaces were modified at the boiling point of the solution for up to 24 h. The modified plates were immersed in distilled water for several minutes to convert the hydrolyzable groups (methoxy groups) on the surface to hydroxyl groups after being washed with the solvent. They were then heated at 150 °C for 30 min in an oven (air) to construct a siloxane network on their surface and the contact angles of water was measured on each of the surfaces [3,6,7]. The optimum concentration of modifying agent solution that gives the highest contact angles (15 mM) was thus determined. The optimum modification time (2 h) was also determined by measuring the contact angles of water on each of the surfaces modified for given periods of time at the optimum modifying agent concentration. The glass plates used were those immersed in a 1 N KOH solution for 2 h, thoroughly washed with distilled water, and stored in a desiccator.

4.5. Evaluations of heat-resistance, oxidation-resistance, and acid-resistance of modified glass surfaces

Modified glass plates were prepared using the optimum modifying agent concentration and modification time determined in Section 4.4. The evaluation of the heat-resistance of the modified glass surfaces was made by measuring the contact angles of water on them after the plates were heated at 350 °C for given periods of time. Also, the plates were immersed in concentrated nitric acid or hydrochloric acid at 80 °C for given periods of time, thoroughly washed with distilled water, and dried at room temperature. The oxidation-resistance and acid-resistance were evaluated using the values of water contact angles on these glass surfaces.

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