

Substituent Effects at the Benzyl Position and Aromatic Ring of Silane-Coupling Agents Containing 2-Nitrobenzyl Esters on Photosensitivity and Hydrophobic Surface of a Self-Assembled Monolayer (SAM)

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Abstract

Silane-coupling agents with 2-nitrobenzyl esters containing alkyl substituents at the benzyl position and alkoxy and/or fluoroalkoxy groups of the aromatic ring were synthesized to prepare a self-assembled monolayer (SAM) on quartz glass, silicon wafer and thermally oxidized silicon wafer. The resulting photosensitive SAMs before and after photoirradiation were characterized by contact angle measurement, UV spectroscopy, X-ray photoelectron spectroscopy (XPS), and X-ray reflectivity (XRR). Photosensitivity of the SAM was influenced by substituents at the benzyl position and aromatic ring as well as the irradiation conditions in air or solution and substrates employed. Silane-coupling agents with bulky substituent at the benzyl position and double fluoroalkoxy chains are preferable in terms of the photosensitivity and hydrophobic surface.

Silane-coupling agents, organosilicon compounds with alkyl and hydrolysable chlorosilyl or alkoxysilyl groups are employed for modification of inorganic surfaces such as Si wafer, indium tin oxide (ITO), titanium dioxide (TiO₂) and zinc oxide (ZnO).^{1–4} Silane-coupling agents containing several functional groups such as amino, mercapto, cyano, and azido groups are commercially available. However, silane-coupling agents containing carboxy and sulfo groups are not known and few hydroxy groups are found because these functional groups are reactive and therefore incompatible with hydrolyzable group at the other terminal of the coupling agent. We reported a silane-

coupling agent containing 2-nitrobenzyl ester as a photodegradable protecting group of carboxylic acid.⁵ The 2-nitrobenzyl group was developed by Patchornik et al.⁶ and can be cleaved by UV light under neutral condition as a protecting group. Different types of photodegradable protecting groups such as nitrophenethyl, coumarinylmethyl, and quinolinylmethyl groups were reported in the past.7 Among many photodegradable groups studied, 2-nitrobenzyl derivatives have gained a great deal of attention in the field of biologically active compounds and those applications.8 We have used silane-coupling agents containing 2-nitrobenzyl ester as described above to apply for patterning of cells.⁹ These substrates are improved and employed for further applications.¹⁰ Another representative molecule to form SAM is thiol to bind noble metals such as Au through sulfide bonds. Various functional groups at the other terminal of thiol compounds are known to be used for the introduction of photocleavable protecting groups.¹¹ Many examples of photosensitive SAMs from thiols (Thiol-SAM) on Au substrate are reported, especially in the application of biotechnology as well as photosensitive SAMs based on silane coupling agents (Si-SAM).¹² Thiol-SAM is thermally rather unstable and therefore thermally stable Si-SAM should be much more preferable for application to electronics.¹³ In recent years, Si-SAMs have attracted much attention due to application to electronics fields such as photolithography¹⁴ and organic thin film transistors (OTFTs).^{15,16} Photosensitive SAM from compounds bearing a chlorosilyl group and long alkyl or fluoroalkyl chain connected with 2nitrobenzyl ester have been used in attempt to pattern micro-

fluidic devices, resulting in lowering photosensitivity.^{17,18} We have also employed a silane coupling agent bearing 2-nitrobenzyl sulfonate with a long fluoroalkyl chain for fabrication of an electrode for organic thin-film transistors on flexible plastic substrate.¹⁹ A large hydrophobic-hydrophilic difference between 4-fluoroalkoxy-2-nitrobenzyl sulfonate and the photogenerated sulfonic acid was obtained, but photosensitivity of the sulfonate was pretty low. Si-SAM is preferable for electronics application as described above, however the photosensitivity might not be enough for electronics applications compared to conventional photolithography with resist materials. In this paper, silane-coupling agents 1a-1n containing 2nitrobenzyl ester with alkyl groups at the benzyl position and alkoxy and/or fluoroalkoxy groups at 4- and 5-positions of the aromatic ring were synthesized to form and characterize the photosensitive SAMs to improve the photosensitivity with the large hydrophobic-hydrophilic deference before and after photoirradiation as shown in Figure 1.

Experimental

Reagents and Materials. Most of the reagents and solvents described herein were purchased either from Wako (Osaka, Japan), TCI (Tokyo, Japan) or Sigma-Aldrich (St. Louis, MO). Quartz glasses were purchased from Kogakugiken (Kanagawa, Japan). Silicon wafers were provided by Enatek (Tokyo, Japan). Silicon wafers with a thermally-oxidized film (thickness of 150 nm) were purchased from Yamanaka semiconductor (Kyoto, Japan).

Synthesis of 1a–1n. Silane-coupling agents **1a–1n** were synthesized according to Schemes 1–4.

1-[2-Nitro-4,5-di(1*H***,1***H***,2***H***,2***H***,3***H***,3***H***-perfluoroheptyloxy)phenyl]ethyl 5-(Trimethoxysilyl)pentanoate (1g):** A solution of 1-[2-nitro-4,5-di(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroheptyloxy)phenyl]ethyl 4-pentenoate (**2g**) (3.00 g, 3.74 mmol) in dry THF (2 mL) was added to trimethoxysilane (4.57 g, 37.4







Scheme 1. Synthesis of photosensitive silane-coupling agents 1a, 1i, 1j, 1k, and 1l.



Scheme 2. Synthesis of photosensitive silane-coupling agents 1b, 1c, and 1d.

mmol) in the presence of Karstedt's catalyst (10 drops). The solution was stirred at room temperature for 4 h under a nitrogen atmosphere and concentrated using a rotary evaporator. The crude product was purified by silica gel column chromatography (hexane/ethyl acetate/tetramethoxysilane, 6:1:0.07) to yield 2.25 g (2.43 mmol, 65%) of **1g** as a yellowish solid. ¹H NMR (400 MHz, CDCl₃): δ 7.56 (s, 1H), 6.99 (s, 1H), 6.45 (q, J = 6.5 Hz, 1H), 4.20–4.10 (m, 4H), 3.57 (s, 9H), 2.42–2.26 (m, 6H), 2.22–2.12 (m, 4H), 1.65 (q, J = 7.7 Hz, 2H), 1.60 (d, J = 6.5 Hz, 3H), 1.47–1.39 (m, 2H), 0.660–0.620 (m, 2H). Anal. Calculated for C₃₀H₃₅F₁₈NO₉Si: C, 39.01; H, 3.82; N, 1.52\%. Found: C, 38.98; H, 3.37; N, 1.53\%. **1b–1f** and **1h–11** were synthesized in a similar way to synthesis of **1g**.

1-(4,5-Dimethoxy-2-nitrophenyl)ethyl 5-(Trimethoxy-silyl)pentanoate (1a): Yield: 65%, ¹H NMR (400 MHz, CDCl₃): δ 7.58 (s, 1H), 7.01 (s, 1H), 6.47 (q, J = 6.4 Hz, 1H), 3.98 (s, 3H), 3.94 (s, 3H), 3.55 (s, 9H), 2.39–2.32 (m, 2H), 1.70–1.60 (m, 5H), 1.48–1.40 (m, 2H), 0.66–0.62 (m, 2H). Anal. Calculated for C₃₀H₃₅F₁₈NO₉Si: C, 50.10; H, 6.77; N, 3.25%. Found: C, 49.98; H, 6.77; N, 3.27%.

1-[2-Nitro-4,5-di(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroheptyloxy)phenyl]-2-methylpropyl 5-(Trimethoxysilyl)pentenoate (1m): Yield: 67%, ¹H NMR (400 MHz, CDCl₃): δ 7.57 (s, 1H), 6.87 (s, 1H), 6.30 (q, *J* = 5.8 Hz, 1H), 4.17–4.08 (m, 4H), 3.55 (s, 9H), 2.39–2.26 (m, 6H), 2.21–2.12 (m, 5H), 1.66 (q, *J* = 7.6 Hz, 2H), 1.47–1.39 (m, 2H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.97 (d, *J* = 6.8 Hz, 3H) 0.67–0.61 (m, 2H). Anal. Calculated for $C_{32}H_{39}F_{18}NO_9Si$: C, 40.38; H, 4.13; N, 1.47%. Found: C, 40.45; H, 3.86; N, 1.50%.

1-[2-Nitro-4,5-di(1*H***,1***H***,2***H***,2***H***,3***H***,3***H***-perfluoroheptyloxy)phenyl]-2,2-dimethylpropyl 5-(Trimethoxysilyl)pentenoate (1n): Yield: 67%, ¹H NMR (400 MHz, CDCl₃): δ 7.54 (s, 1H), 6.90 (s, 1H), 6.63 (s, 1H), 4.13–4.10 (m, 4H), 3.55 (s, 9H), 2.41–2.23 (m, 6H), 2.21–2.14 (m, 4H), 1.68 (q, J = 7.6 Hz, 2H), 1.49–1.42 (m, 2H), 0.96 (s, 9H), 0.66–0.62 (m, 2H). Anal. Calculated for C₃₃H₄₁F₁₈NO₉Si: C, 41.04; H, 4.28; N, 1.45%. Found: C, 40.74; H, 4.07; N, 1.40%.**

1-[2-Nitro-4,5-di(1H,1H,2H,2H,3H,3H-perfluoroheptyloxy)phenyl]ethyl 4-Pentenoate (2g): To a solution of 1-[2nitro-4,5-di(1H,1H,2H,2H,3H,3H-perfluoroheptyloxy)phenyl]ethan-1-ol (1.31 g, 2.21 mmol), 4-pentenoic acid (0.37 g, 3.70 mmol), 4-dimethylaminopyridine (0.27 g, 2.21 mmol) in dry THF (6 mL) at 0 °C under a nitrogen atmosphere was added dropwise a solution of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (0.803 g, 4.19 mmol) in dry THF (3 mL). The solution was stirred at room temperature overnight. After concentrating the solution using a rotary evaporator, H₂O (40 mL) and 2 M HCl (10 mL) were added, and the solution was extracted with ethyl acetate ($40 \text{ mL} \times 2$). The organic layer was washed with 5% NaHCO₃ (50 mL \times 3) and dried over MgSO₄. The solvent was removed under reduced pressure to yield 1.28 g (1.60 mmol, 88%) of 2g as a yellowish solid. ¹H NMR (400 MHz, CDCl₃): δ 7.58 (s, 1H), 6.99 (s, 1H), 6.45 (q, J = 6.4 Hz, 1H), 5.83-5.76 (m, 4H), 5.07-4.98 (m, 2H),



Scheme 3. Synthesis of photosensitive silane-coupling agents 1e and 1f.

4.20–4.10 (m, 4H), 2.51–2.28 (m, 8H), 2.22–2.13 (m, 4H), 1.60 (d, J = 6.5 Hz, 3H). **2a–2f** and **2h–2n** were synthesized in a similar way to synthesis of **2g**.

1-[2-Nitro-4,5-di(1H,1H,2H,2H,3H,3H-perfluoroheptyloxy)phenyl]ethan-1-ol (3g): Sodium tetrahydroborate (0.14 g, 3.70 mmol) was added to a solution of 2-nitro-4,5-di(1H,1H,2H,2H,3H,3H-perfluoroheptyloxy)acetophenone (1.37 g, 1.91 mmol) in THF (6 mL) and methanol (2 mL) at 0 °C. The solution was stirred at 0 °C for 20 min and then at room temperature for 3.5 h. After concentrating the solution using a rotary evaporator, H₂O (40 mL) and 2 M HCl (10 mL) were added, and the solution was extracted with chloroform $(40 \text{ mL} \times 2)$. The organic layer was dried over MgSO₄, and the solvent was removed under a reduced pressure to yield 1.31 g (1.82 mmol, 95%) of **3g** as a yellow solid. ¹H NMR (400 MHz, CDCl₃): δ 7.57 (s, 1H), 7.30 (s, 1H), 55.7 (g, J = 6.2 Hz, 1H), 4.24-4.08 (m, 4H), 2.39-2.29 (m, 4H), 2.23-2.12 (m, 5H), 1.55 (d, J = 6.2 Hz, 3H). **3a–3f** and **3h–3n** were synthesized in a similar way to synthesis of 3g.

2-Nitro-4,5-di(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroheptyloxy)acetophenone (4g): To a solution of 3,4di(1*H*,1*H*,2*H*,3*H*,3*H*-perfluoroheptyloxy)acetophenone (2.14 g, 3.18 mmol) in diethyl ether (10 mL), HNO₃ (15 mL) was carefully added dropwise at 0 °C. The solution was subsequently stirred at 0 °C for 5 h. The solution was added to ice water (100 mL) and the solution was extracted with ethyl acetate (40 mL \times 2). The organic layer was washed with 5% NaHCO₃ (50 mL \times 3) and dried over MgSO₄. After concentrating the solution using a rotary evaporator, the residue was purified by recrystallization with ethanol to yield 1.38 g (1.92 mmol, 60%) of **4g** as yellow needle crystals. ¹H NMR (400 MHz, CDCl₃): δ 7.60 (s, 1H), 6.75 (s, 1H), 4.14 (m, 2H), 4.13 (m, 2H), 2.50 (s, 3H), 2.33–2.27 (m, 4H), 2.22–2.17 (m, 4H). **4h** was synthesized in a similar way to that of **4g**.

3,4-Di(1H,1H,2H,2H,3H,3H-perfluoroheptyloxy)acetophenone (5g): Potassium carbonate (1.08 g, 7.81 mmol) was added to a solution of 3,4-dihydroxyacetophenone (0.59 g, 3.88 mmol) in N,N-dimethylformamide (3 mL). The solution was stirred at room temperature for 5 h. A solution of 1-iodo-1H,1H,2H,2H,3H,3H-perfluoroheptane (3.10 g, 7.76 mmol) in DMF (5 mL) was added dropwise to the solution. The solution was refluxed at 60 °C overnight. After the solvent was removed under reduced pressure, water (60 mL) and 2 M HCl (10 mL) were added, and the solution was extracted with chloroform $(40 \text{ mL} \times 3)$. The organic layer was washed with saturated NaCl $(100 \text{ mL} \times 2)$ and dried over MgSO₄. The resulting material was finally concentrated under reduced pressure to yield 2.14 g (3.18 mmol, 82%) of 5g as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.58 (dd, J = 2.0, 8.4 Hz, 1H), 7.52 (d, J = 2.0 Hz, 1H), 6.88 (d, J = 8.5 Hz, 1H), 4.14 (m, 2H), 4.13 (m, 2H), 2.56 (s, 3H), 2.34–2.32 (m, 4H), 2.19–2.15 (m, 4H). 4b-4f and 5h, 5m, 5n were synthesized in a similar way to that of 5g.

5-Hydroxy-4-methoxy-2-nitroacetophenone (5e): 5-Benzyloxy-4-methoxy-2-nitroacetophenone 1.23 g (4.09 mmol) was added to trifluoroacetic acid (12 mL). The solution was stirred at room temperature for 21 h. After concentrating the solution using a rotary evaporator, 1 M NaOH (21 mL) and 1 M



Scheme 4. Synthesis of photosensitive silane-coupling agents 1g, 1h, 1m, and 1n.

HCl (3 mL) were added, and the solution was extracted with chloroform (40 mL × 4). The organic layer was dried over MgSO₄. After concentrating the solution using a rotary evaporator, the residue was purified by recrystallization with ethyl acetate. The solvent was removed under reduced pressure to yield 0.70 g (3.31 mmol, 81%) of **5e** as a dark yellow solid. ¹H NMR (400 MHz, CDCl₃): δ 7.65 (s, 1H), 6.86 (s, 1H), 6.28 (s, 1H), 4.03 (s, 3H), 2.50 (s, 3H).

The purity of all compounds were comparable from ¹H NMR spectra in Supporting Information.

Compounds of 2a, 3a, 3i, 3j, 3k, 3l, 4a, 4i, 4j, 4k, 4l, 5j, 5k, 5l, 5h, 7m, and 7n were synthesized according to known methods.

Preparation of SAMs and Photodeprotection. The formation and photodeprotection of SAM were carried out according to Figure 2. Silicon wafers and quartz glasses were cleaned and hydroxy terminated with a UV-ozone cleaner (UV253, Filgen, Japan). The substrates were soaked in dry toluene containing silane coupling agents **1a–1n** (1 mM) at

100 °C for 3 h. The modified substrates were rinsed with methanol, sonicated in methanol for 10 min and then in chloroform for 10 min, and finally dried with nitrogen. Characterization was performed by contact angle measurements, UV, XRR, and XPS. The modified substrates were irradiated with an ultrahigh pressure mercury lamp (USH-500SH, Ushio, Japan) through PYREX glass ($\lambda > 300$ nm) and water (for cutting off IR) or copper sulfate solution ($\lambda > 320$ nm). The light intensity was 50 mW cm⁻², as determined with a UIT-201 power meter equipped with a UVD-365PD (Ushio, Japan). All irradiated SAMs were rinsed with chloroform and then sonicated in chloroform for 10 min, and finally dried with nitrogen.

Characterization. Water contact angle measurements were conducted at room temperature using a DropMaster 700 contact angle meter (Kyowa Interface Science, Japan). The pure water was placed onto the surface and monitored with a camera. The captured images were analyzed using FAMAS software (Kyowa Interface Science) to determine the contact angle. The contact



Figure 2. The formation of SAM on substrate using silane-coupling agent containing 2-nitrobenzyl ester, and photodeprotection of SAM using UV irradiation to generate carboxy-functionalized SAMs.

angles reported in this study are the average of more than three values taken at different points on the surface. UV-vis spectra of the substrates were measured with a V-570 (JASCO, Japan). Quartz glass plates were used for this experiment. The surface density of the SAM, Γ (molecules cm⁻²), can be estimated from the UV absorbance using $\Gamma = 1/2[A_{\lambda}\varepsilon_{\lambda}^{-1}N_{\rm A}] \times 10^{-3}$, where A_{λ} is the absorbance of the surface layer at a given wavelength, ε_{λ} is the molar extinction coefficient of the precursor in 0.1 mM ethanol solution (M⁻¹ cm⁻¹) at λ , and N_A is Avogadro's number.20 The thickness has been investigated by XRR (UltimaIV, Rigaku, Japan) with monochromatized Cu Ka radiation at 40 kV and 40 mA. The measurement profile was analyzed using GlobalFit software (Rigaku) with multilayer model of organic layer/oxidized silicon layer/silicon substrate. XPS spectra were obtained using a X-ray photoelectron scope (JPS-9010MC, JEOL, Japan) with a monochromated Mg Ka source (10 kV, 10 mA).

Acid–Base Responsiveness. The modified silicon wafer with 1m was irradiated, and alternately dipped in 5% NaHCO₃ aqueous solution and 2 M HCl aqueous solution. Change of wettability was estimated by contact angle measurement.

Photodegradation in Acidic Solution. The modified silicon wafer with **1m** was irradiated in 0.1 M HCl 2-propanol. Characterization was performed by contact angle measurements and XPS.

SAMs on Different Substrates. SAMs were prepared on quartz glass, silicon wafer and silicon wafers with a thermally-oxidized film (thickness of 150 nm). They were characterized by contact angle measurement and compared to one another.

Patterning of SAM. Photoirradiation (light intensity 50 mW cm⁻², exposure time 120 s, exposure dose 6 J) of SAM of **1a** was carried out with a photomask composed of Cr patterns on quartz glass in air. The patterned substrate was immersed in 5% NaHCO₃ aqueous solution for 1 h. And then the substrate was stained with amine-modified fluorescent microspheres (Thermo Fisher Scientific, USA) aqueous solution for 1 h. The patterned surface was observed by fluorescence microscope (BX-FLA, OLYMPUS, Japan).

Results and Discussion

Synthesis. Synthetic routes for **1a**, **1i**, **1j**, **1k**, and **1l** are shown in Scheme 1. 1,2-Dimethoxybenzene was acylated by the corresponding acid anhydrides with iodine to obtain **5i**, **5j**, **5k**, and **5l**. Commercially available **5a** and the synthesized **5i**,

5j, 5k, and 5l were nitrated by 70% HNO₃ to afford nitro compounds 4a, 4i, 4j, 4k, and 4l which were reduced by NaBH₄ to afford alcohols 3a, 3i, 3j, 3k, and 3l. The resulting alcohols were condensed with 4-pentenoic acid in the presence of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide/hydrochloride and 4-dimethylaminopyridine to get esters 2a, 2i, 2j, 2k, and 21. Finally the precursors were hydrosilvlated with trimethoxysilane with Karstedt's catalyst to obtain silane coupling agents 1a, 1i, 1j, 1k, and 1l. Synthetic routes for 1b, 1c, and 1d are shown in Scheme 2. 4-Hydroxy-3-methoxyacetophenone was benzylated with benzyl bromide in the presence of K₂CO₃, and nitrated with fuming HNO₃ in acetic acid, and debenzylated with trifluoroacetic acid, to nitro ketone. The ketone reacted with the corresponding iodides in the presence of K₂CO₃ in DMF to get ethers which were reduced with NaBH₄ to alcohols 4b, 4c, and 4d. The esterification and hydrosilylation were carried out similar to Scheme 1 to get final products 1b, 1c, and 1d. Synthetic routes for 1e and 1f are shown in Scheme 3. Instead of 4-hydroxy-3-methoxyacetophenone in Scheme 2, 3-hydroxy-4-methoxyacetophenone was employed as a starting material using similar procedures to get alcohols 4e and 4f. The esterification and hydrosilylation were carried out similar to Scheme 1 to get final products 1e and 1f. Synthetic routes for 1g, 1h, 1m, and 1n are shown in Scheme 4. Acylation of 1,2-dimethoxybenzene with the corresponding acid anhydrides was carried out followed by demethylation with LiCl in DMF to obtain 4-acyl-1,2-dihydroxybenzenes. Dihydroxy compounds were etherified with the corresponding iodides, nitrated with 70% HNO3, and reduced with NaBH₄ to the corresponding alcohols 4g, 4h, 4m, and 4n. The esterification and hydrosilylation were carried out similar to Scheme 1 to get final products 1g, 1h, 1m, and **1n**. The yields of ether synthesis using K_2CO_3 were 69–91%. Diethyl ether was used for nitration of fluoroalkoxy compounds as solvent. Yields of nitration were around 50% probably because of a side reaction such as deacylation. Reduction of ketones with NaBH₄ proceeded in high yields. Condensation of alcohols with 4-pentenoic acid gave the desired esters in high yields. Yields of hydrosilylation were 22-76%. Hydrogenation of the starting material as a side reaction resulted in low yields. In addition, to prevent the trimethoxysilyl group of the desired product from reacting and immobilizing to silica gel for column chromatography, a small amount of tetramethoxysilane was added to an eluent of column chromatography, however

it was very difficult for the trimethoxysilyl group to avoid hydrolysis and/or reaction with silica gel completely, resulting in low yields.²¹

Characterization. Results of contact angle measurement of photosensitive SAMs on silicon wafer prepared from 1a-1n before and after photoirradiation as well as exposure dose required for constant contact angles lowered are shown in Table 1. Contact angles of SAMs from 1a-1n are 67-108°, different from one another depending on the substituents of 1a-1n. The contact angle after complete photoreaction should be the same value if the carboxylic acid was generated quantitatively. However, the contact angles were almost 50-60°, suggesting that photoreaction was incomplete, side reaction occurred, and/or decomposed products stayed on the surface. With increase in length of alkoxy and fluoroalkoxy chains at the 4-position of the aromatic ring, the contact angle of water on the photosensitive SAM of 1a-1n increased, but the exposure dose required for a constant contact angle decreased by photoirradiation increase, that is, the photosensitivity was lowered. Introduction of alkoxy and fluoroalkoxy chains at the 5-position of the 2-nitrobenzyl group (1e and 1f) improved the photosensitivity. From the contact angle values, the hydrophobicity of SAM from 1d with long fluoroalkoxy chain is higher than that of 1b and 1f bearing alkoxy chain. Compounds 1g and 1h bearing double fluoroalkoxy and alkoxy chains at 4- and 5-positions retained a comparable hydrophobicity and improved the photosensitivity. It was also proved that the substituent at benzyl position affected photosensitivity of SAM. Ethyl-substituted compound **1i** with two methoxy groups at the aromatic ring was necessary for exposure dose of the cleavage of benzyl ester on the SAM larger than that for SAM from 1a. SAM of propyl-substituted 1j had a photosensitivity higher than of 1a. Isopropyl-substituted 1k offered a SAM with higher sensitivity, while SAM of t-butyl-substituted 11 was comparable to that of 1a. Silane coupling agents 1m and 1n bearing double fluoroalkoxy chains substituted with isopropyl and t-butyl groups at the benzyl position gave hydrophobic SAM (contact angle around 100°) which displayed a photosensitivity four times that of methyl-substituted compound 1g. It was

 Table 1. Contact angle of water on SAMs with 1a-1n

 before and after photoirradiation, and the UV dose for completing photolysis of SAMs

Compound	Contact an	gle/degree	Exposure dose
Compound	Modified	Irradiated	$/\mathrm{Jcm^{-2}}$
1a	67	51	12
1b	93	61	540
1c	85	73	180
1d	108	61	360
1e	89	55	24
1f	81	56	12
1g	108	57	60
1h	97	58	36
1i	66	50	16
1j	75	53	9
1k	73	54	7.5
11	71	51	12
1m	98	52	15
1n	100	52	15

found from the results described above that fluoroalkoxy chain and double substituents at 4- and 5-positions of the 2nitrobenzyl group are preferable to alkoxy chain and a single substituent at 4- or 5-position for the hydrophobicity of photosensitive SAM and that short-chain substituents at the 4and 5-positions of the aromatic ring and a bulky substituent are desirable for the photosensitivity.

Concerning 1a, 1g, and 1k-1n, thickness of the photosensitive SAM on Si wafer before and after photoirradiation and surface density of the SAM on quartz glass were measured by XRR and UV spectroscopy as shown in Table 2. Film thickness of SAMs prepared from 1a, 1k, and 1l was 1.2 nm comparable with the calculated values of 1.5 nm from ChemBioDraw Ultra 12.0. On the other hand, the measured film thickness of SAMs with double fluoroalkoxy chains from 1g, 1m, and 1n was comparable with those of SAMs from 1a, 1k, and 1l and almost one half as much as the calculated values. It can be seen that the SAMs from 1a, 1k, and 1l are formed with nearly perpendicular and relatively dense orientation, while SAMs from 1g, 1m, and 1n are poorly oriented and much less dense leading to thickness much smaller than the calculated one. This is also supported from the fact that the densities of 1a, 1k, and 1l of SAM on quartz glass were calculated from the UV absorbance based on the 2-nitrobenzyl moiety to be about 3×10^{14} molecules cm⁻² nearly one and half fold greater than those of 1g, 1m, and 1n. Elemental ratio of C1s, N1s, and F1s normalized with Si2p_{3/2} based on Si-Si at 99 eV was determined from XPS measurement of Si wafer modified with 1g. 1m. and 1n before and after photoirradiation, shown in Table 3. Peaks of N1s assigned to nitro group and F1s were detected to confirm the substrates were modified with 1g, 1m, and 1n. After irradiation, the peak of N1s of nitro group disappeared and the peak of F1s decreased to less than 10% indicating that photoreaction proceeded to cleave nitrobenzyl ester and form carboxylic acid. Remaining peaks of F1s and N1s other than nitro group were probably due to reduction as a side reaction of nitro to amino group without scission of the ester bond²² or due to damages of X-ray in XPS measurement.²³ Figure 3 shows C1s XPS spectra of the SAM (1m) before (a) and after (b) photoirradiation. The peaks of fluoroalkyl, ether, carbonyl and neutral carbons were characterized and confirmed reduction of the fluoroalkyl peaks after the UV irradiation.

Acid–base response of carboxylic acid formed on the surface of SAM by photoirradiation was investigated by measurement of contact angle on the surface shown in Figure 4. The contact

 Table 2. Results of XRR measurement and surface density of SAMs

		Thickr			
Compound	Modified		Irradi	iated	Surface density $/molecules cm^{-2}$
	Found	Calcd	Found	Calcd	/ molecules em
1a	1.2	1.5	1.1	0.8	2.9×10^{14}
1k	1.2	1.5	1.1	0.8	2.7×10^{14}
11	1.2	1.5	0.83	0.8	3.0×10^{14}
1g	1.1	2.1	0.83	0.8	1.9×10^{14}
1m	1.1	2.1	0.91	0.8	1.9×10^{14}
1n	1.3	2.1	0.92	0.8	1.7×10^{14}

Compound C1s		s	N1s (NO ₂)		F1s		Si2p (Si–Si)	
Compound	Mod.	Irr.	Mod.	Irr.	Mod.	Irr.	Mod.	Irr.
1g	0.50	0.39	0.018 (0.0077)	0.0084 (0.0)	0.47	0.037	1	1
1m	0.58	0.44	0.016 (0.0066)	0.0087 (0.0)	0.54	0.043	1	1
1n	0.75	0.73	0.021 (0.0090)	0.0075 (0.0)	0.66	0.016	1	1

Table 3. Normalized XPS peak area of the C1s, N1s, and F1s spectra to the Si2p (Si–Si) peak, of SAMs before and after UV irradiation



Figure 3. C1s XPS spectra of the SAM (1m) before (a) and after (b) photoirradiation.



Figure 4. Change of contact angle of water on SAMs (1m) by acid-base response.

angle of 51° on the substrate after photoirradiation was lowered to 21° by immersion of the substrate into 5% NaHCO₃, which was recovered to 39° by immersion in 2 M HCl. This response was repeatedly observed confirming that the carboxylic acid was generated by photoirradiation of SAM from **1m**. The large difference of contact angle of about 80° was obtained by basic solution treatment of generated carboxylic acid surface between the ester and sodium salt.

Photoirradiation of SAM from **1m** in air and in acidic solution was carried out as shown in Table 4. Exposure dose in acidic solution required for getting a constant contact angle was decreased to half as much as that in air. Photoreaction was extremely improved in acidic solution. This is also supported from elemental ratios determined by XPS spectra of N1s and F1s on the substrate of SAM from **1m** normalized with Si2p_{3/2} (Si–Si) shown in Table 5. Elemental ratio of N1s and F1s after irradiation in acidic solution decreased clearly as well as those irradiated in air. This is consistent with the literature²² which

Table 4. Change of contact angle of water on SAMs (1m) by irradiation in air and HCl 0.1 M 2-propanol solution

	Contact ar	ngle/degree	Exposure dose	
	Modified	Irradiated	$/\mathrm{Jcm^{-2}}$	
In air	98	51	18	
In solution	101	48	9	

Table 5. Normalized XPS peak area of the C1s, N1s, and F1s spectra to the Si peak, of SAMs (**1m**) before and after UV irradiation in air or HCl 0.1 M 2-propanol solution

	Cla	N1c	E1a	Si2p	
	018	1115	115	Si-O	Si–Si
Before irradiation	0.58	0.016	0.54	0.38	1
Irradiation in air	0.44	0.0087	0.043	0.39	1
Irradiation in solution	0.46	0.0059	0.014	0.42	1

indicates side reaction of reduction of nitro to amino was inhibited.

Contact angles of SAMs from **1m** on different substrates, naturally and thermally oxidized Si wafers and quartz glass were measured before and after photoirradiation shown in Table 6. It was found that SAMs from **1m** on thermally oxidized Si wafer and quartz glass were photolyzed much faster than that on naturally oxidized Si wafers (as shown in Figure 5). The mechanism for this is not understood, but significant difference was obtained between different types of substrates.

Photoirradiation of SAM of **1a** with a photomask was carried out to fabricate the pattern of carboxylic acid generated

on the substrate surface. The patterned surface was stained with amine-modified fluorescent microspheres as shown in Figure 6. Immobilization of amine-modified fluorescent microspheres on the acid generated on the irradiated part with line width of

 Table 6. Contact angle measurement for SAMs (1m) on different substrate

Substrate	Contact an	gle/degree	Exposure dose
Substrate	Modified	Irradiated	$/\mathrm{Jcm^{-2}}$
Naturally oxidized Si	98	51	15.0
Thermally oxidized Si	98	56	1.5
Quartz glass	100	53	2.5



Figure 5. Change of contact angle of water on irradiated SAM (1m) on natural oxidation silicon, thermal oxidation silicon and quartz glass.

 $20\,\mu m$ was observed by fluorescence microscope and scanning electron microscope (Figures 6c and 6d).

Conclusion

Silane coupling agents 1a-1n with 2-nitrobenzyl esters containing alkyl substituents at benzyl position and alkoxy and/or fluoroalkoxy groups at 4- and 5-positions of the aromatic ring were synthesized. The photosensitivity of SAMs from the silane-coupling agents was affected by the substituents at the benzyl position and aromatic ring, density of SAMs, environments and substrates. The highest sensitivity was given by 1k with methoxy groups at the aromatic ring and isopropyl group at the benzyl position. Fluoroalkoxy chains were better than alkoxy ones and double chains better than single chain for hydrophobicity of SAM. The significant change of contact angle from 101 to 21° was obtained by basic solution treatment of generated carboxylic acid surface. It was suggested by XPS measurement that side reaction was highly depressed during photolysis of the SAM in an acidic solution, leading to the rate of photolysis was about twice as much as that in air. SAMs formed on quartz glass and thermally oxidized Si exhibited to highly improve the photosensitivity compared to that on naturally oxidized Si. Finally, we demonstrate selective deposition of amine-modified fluorescent particles to generated carboxylic acid surface by UV irradiation.

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Figure 6. (a) The procedures of photopatterning of SAM; (b) photomask; (c) fluorescence microscope image of patterned SAM with amine-modified fluorescent microspheres; (d) SEM image of patterned SAM with amine-modified fluorescent microspheres.

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Supporting Information

¹HNMR spectra of synthesized all compounds. XRR and XPS data of SAMs. This material is available on http://dx.doi.org/10.1246/bcsj.20150316.

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