Electronic Supplementary Information

Styrylsilane coupling reagents for immobilization of organic functional groups on silica and glass surfaces

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1. General

Flash column chromatography was performed using E. Merck 230-400 mesh silica gel. Column chromatography was monitored using analytical thin-layer chromatography (TLC) carried out on 0.25 Merck silica gel plates (60 F-254) using UV light as a visualizing agent, p-anisaldehyde solution, and KMnO₄ solution as staining solutions, and heat as developing agent. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Advance II/DPX 400 (400 MHz ¹H, 100 MHz ¹³C) spectrometer with chemical shifts reported relative to residual deuterated solvent peaks. ¹H NMR spectra was referenced to residual CDCl₃ (for ¹H, δ = 7.26 ppm) as internal standard, and was reported as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, m = multiplet). ¹³C NMR spectra was referenced to the residual CDCl₃ (77.26 ppm). Fluorescence spectra were obtained on a Perkin Elmer LS 55. Infrared spectra were obtained using a Nicolet Impact 400 spectrometer. Contact angle was measured using a Bioin Scientific ThetaLite 100. Elemental analysis was obtained on a Perkin Elmer 2400 Series II at YCRF of Yonsei University facility. Analytical GPC was performed on a JASCO HPLC equipped with KF-404HQ columns (ID. 4.6 X L. 250nm, Shodex, Tokyo, Japan) using THF as the eluent at a flow rate of 1.0 ml/min.

2. Materials

Reagent grade chemicals (vinyltrimethylsilane (1h), trifluoromethanesulfonic acid (TfOH, 3a), 3b-3g, dichloromethylsilane (5), 11-chloroundec-1-ene (6), allyl chloride, LiAlH₄ (8), benzylmagnesium chloride (2.0M solution in THF), phenylacetylene(10)) were purchased from Aldrich Chemical Company and Alfa Aesar and used as received without further purification unless otherwise stated. Polybutadiene (12) was purchased from Aldrich (CAS No. 9003-17-2) and its molecular weight (Mw) is determined to be 2,950 with PDI(Mw/Mn) = 1.65. Silica ball (2, particle/pore size: 10 μm/10 nm and surface area: 310 m²/g) was purchased from Fuji Silysia Chemical, and glass (microscope slides) was purchased from Marienfeld. H₂PtCl₆.xH₂O (7) was purchased from Pressure Chemical corporation. RhCl(PPh₃)₃ (11) was prepared by using reported procedures.¹ 1-(propargyloxymethyl)pyrene (16) was prepared by etherification of 1-pyrenylmethanol and propargyl bromide with sodium hydride.

3. Experimental

- Representative procedure for immobilization of various alkenylsilane 1 onto silica surface (Table 1 and Table 2)
To a 1 mL pressure vial were added styrylsilane (1a, 0.08 mmol), silica (2, 20 mg), acid catalyst (3a, 0.004 mmol) and dichloromethane (0.1 mL). The mixture was stirred at room temperature for 6 h, filtered, and washed thoroughly with dichloromethane, H2O and acetone. Functional group-immobilized silica 4h (1.11 mmol/g) was obtained after drying in vacuo.

- Loading extent of functionalized silica by washing process

To a 2.5 mL pressure vial were added styrylsilane (1i, 0.8 mmol), silica (2, 200 mg), TfOH (3a, 0.04 mmol) and dichloromethane (1 mL) (Scheme S1). The reaction was carried out with stirring at room temperature for 6 h. After the reaction, the reaction mixture was filtered, washed thoroughly with dichloromethane, H2O and acetone, and dried in vacuo to give functionalized silica 4s-w-1 (washing process 1), whose loading extent was determined as 0.70 mmol/g by elemental analysis. The silica 4s-w-1 was rewashed with dichloromethane, H2O and acetone, and dried in vacuo to give 4s-w-2 (washing process 2), whose loading extent was determined as 0.69 mmol/g. Finally, the silica 4s-w-2 was washed with sat. aq NaHCO3 solution, sat. aq NH4Cl solution, dichloromethane, H2O and acetone (washing process 3), and dried in vacuo to give functionalized silica 4s-w-3, whose loading extent was determined as 0.71 mmol/g. These experimental results show that the sample of functionalized silica 4s-w-1 was not contaminated by other non-covalent organic species.

**Scheme S1.** Loading extent of functionalized silica by washing process.

<table>
<thead>
<tr>
<th>entry</th>
<th>functionalized silica</th>
<th>washing solvent</th>
<th>loading extent (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4s-w-1</td>
<td>CH2Cl2 / acetone / H2O</td>
<td>0.70 mmol/g</td>
</tr>
<tr>
<td>2</td>
<td>4s-w-2</td>
<td>CH2Cl2 / acetone / H2O</td>
<td>0.69 mmol/g</td>
</tr>
<tr>
<td>3</td>
<td>4s-w-3</td>
<td>sat. aq NaHCO3 / sat. aq NH4Cl and CH2Cl2 / acetone / H2O</td>
<td>0.71 mmol/g</td>
</tr>
</tbody>
</table>

- 13C CP-MAS NMR spectrum of functionalized silica

When 13C CP-MAS NMR spectra of functionalized silica 4s-w-1 (Figure S1b) was compared with that of the styryl silane compound 1i (Figure S1a), carbon signals of styryl group in 1i were completely disappeared with remaining the thirteen carbon atoms of 11-chloroundecyl and methyl groups without showing any organic carbon species. This result shows that the surface structure proposed for 4s-w-1 is right with high purity.
- Preparation of 1a–1g (Table 1)

A 2-neck round bottomed flask pre-equipped with reflux condenser was charged with chlorodimethylsilane (3 g, 33 mmol) and 10% H₂PtCl₆•xH₂O (16.4 mg, 0.03 mmol) in 2-propanol (0.1 mL) solution. The resulting solution was stirred for 30 min. Then, phenylacetylene (3.88 g, 38 mmol) was added dropwise and the resulting mixture was stirred at room temperature for 12 h. Unreacted chlorodimethylsilane was removed by distillation under reduced pressure to give crude (E)-chlorodimethyl(styryl)silane, which was used for the next step without further purification. Benzylmagnesium chloride (2.0M solution in THF, 19 ml, 38mmol) was added dropwise to the crude (E)-chlorodimethyl(styryl)silane and the resulting solution was stirred at room temperature for 30 min. Saturated NH₄Cl (aq.) was added, and the mixture was extracted with diethyl ether. The organic layer was dried over anhydrous MgSO₄, filtered, and concentrated in vacuo. Compound 1a (colorless liquid, 5.76 g, 72% yield) was obtained by using column chromatography (n-hexane). Compound 1b-1f were also prepared by using corresponding acetylene derivatives instead of phenylacetylene.

(E)-benzyldimethyl(styryl)silane (1a) [CAS No. 941318-08-7]; Obtained as a colorless liquid (5.76 g, 72% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.45 (d, J = 7.2 Hz, 2H), 7.37 (t, J = 7.2 Hz, 2H), 7.29 (t, J = 7.2 Hz, 1H), 7.25 (t, J = 7.2 Hz, 2H), 7.12 (t, J = 7.2 Hz, 1H), 7.07 (d, J = 6.8 Hz, 2H), 6.89 (d, J = 19.2 Hz, 1H), 6.47 (d, J = 19.2 Hz, 1H), 2.25 (s, 2H), 0.17 (s, 6H); ¹³C NMR (100MHz, CDCl₃) δ 144.9, 140.1, 138.4, 128.8, 128.5, 128.4, 128.3, 127.6, 126.6, 124.3, 26.4, -3.1; IR (neat): 3059, 3024, 2991, 2922, 1941, 1878, 1803, 1745, 1601, 1573, 1493, 1449, 1247, 1206, 1154, 989, 833, 790, 760, 737, 698, 622 cm⁻¹.
(E)-benzyldimethyl(pent-1-en-1-yl)silane (1b); Obtained as a colorless liquid (2.15 g, 31% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.26 (t, $J = 7.2$ Hz, 2H), 7.12 (t, $J = 7.2$ Hz, 1H), 7.06 (d, $J = 7.2$ Hz, 2H), 6.08 (dt, $J = 18.8, 6.4$ Hz, 1H), 5.66 (d, $J = 18.8$ Hz, 1H), 2.18-2.12 (m, 4H), 1.52-1.43 (m, 2H), 0.98-0.94 (m, 3H), 0.09 (s, 6H); $^{13}$C NMR (100MHz, CDCl$_3$) δ 148.7, 140.5, 128.5, 128.3, 128.0, 124.1, 39.1, 26.5, 22.1, 13.9, -3.0; IR (neat): 3061, 3025, 2958, 2873, 1936, 1862, 1797, 1738, 1616, 1601, 1493, 1452, 1378, 1248, 1206, 1153, 1056, 989, 832, 698, 615 cm$^{-1}$; ESI-MS (negative) calcd for C$_{14}$H$_{21}$Si [M-H]$^-$ 217.1418, found 217.1414.

(E)-benzyldimethyl(oct-4-en-4-yl)silane (1c); Obtained as a colorless liquid (5.78 g, 70% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.26 (t, $J = 7.6$ Hz, 2H), 7.12 (t, $J = 7.2$ Hz, 1H), 7.06 (d, $J = 7.2$ Hz, 2H), 5.77 (t, $J = 6.8$ Hz, 1H), 2.21 (s, 2H), 2.19-2.12 (m, 4H), 1.50-1.34 (m, 4H), 1.01-0.96 (m, 6H), 0.09 (s, 6H); $^{13}$C NMR (100MHz, CDCl$_3$) δ 142.1, 140.7, 139.2, 128.5, 128.2, 124.0, 32.4, 30.8, 26.2, 23.8, 22.9, 14.8, 14.2, -3.1; IR (neat): 3061, 2958, 2929, 2871, 1935, 1862, 1792, 1601, 1493, 1453, 1377, 1247, 1206, 1153, 1056, 901, 830, 759, 697, 618 cm$^{-1}$; ESI-MS (positive) calcd for C$_{17}$H$_{28}$SiNa [M+Na]$^+$ 283.1852, found 283.1953.

(E)-benzyl(1,2-diphenylvinyl)dimethylsilane (1d); Obtained as a white solid (5.9 g, 57% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.34-7.19 (m, 5H), 7.11-6.96 (m, 10H), 6.79 (s, 1H), 2.22 (s, 2H), 0.11 (s, 6H); $^{13}$C NMR (100MHz, CDCl$_3$) δ 145.5, 142.7, 140.0, 138.9, 137.4, 129.7, 128.9, 128.6, 128.4, 128.2, 127.8, 127.4, 126.0, 124.3, 25.2, -3.3; IR (CH$_2$Cl$_2$): 3058, 3023, 2957, 2894, 1945, 1866, 1804, 1746, 1599, 1571, 1492, 1448, 1406, 1247, 1206, 1154, 1057, 954, 903, 829, 759, 697, 627 cm$^{-1}$; Anal. Calcd for C$_{23}$H$_{24}$Si: C, 84.09; H, 7.36; found C, 82.89; H, 9.51.

(E)-benzyl(4-fluorostyryl)dimethylsilane (1e) [CAS No. 1329431-30-2]; Obtained as a colorless liquid (1.9 g, 90% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.44 (dd, $J = 8.4, 5.2$ Hz, 2H), 7.30 (d, $J = 7.6$ Hz, 2H), 7.15 (t, $J = 7.6$ Hz, 1H), 7.10-7.05 (m, 4H), 6.87 (d, $J = 19.2$ Hz, 1H), 6.40 (d, $J = 19.2$ Hz, 1H), 2.28 (s, 2H), 0.21 (s, 6H); $^{13}$C NMR (100MHz, CDCl$_3$) δ 162.9 (d, $J_{C-F} = 245.9$ Hz), 143.6, 140.0, 134.6, 128.5, 128.2, 127.2, 124.3, 115.6 (d, $J_{C-F} = 21.4$ Hz), 26.3, -3.1; IR (neat): 3081, 3060, 2993, 2956, 2797, 1940, 1887, 1765, 1601, 1506, 1451, 1410, 1248, 1227, 1155, 1092, 986, 904, 831, 747, 699, 619 cm$^{-1}$.

(E)-benzyl(4-methoxystyryl)dimethylsilane (1f) [CAS No. 1329431-28-8]; Obtained as a colorless liquid (226 mg, 20% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.37 (d, $J = 8.8$ Hz, 2H), 7.22 (t, $J = 7.2$ Hz, 2H), 7.09 (t, $J = 7.2$ Hz, 1H), 7.04 (d, $J = 7.2$ Hz, 2H), 6.88 (d, $J = 8.8$ Hz, 2H), 6.80 (d, $J = 19.2$ Hz, 1H), 6.26 (d, $J = 19.2$ Hz, 1H), 3.83 (s, 3H), 2.21 (s, 2H), 0.13 (s, 6H); $^{13}$C NMR (100MHz, CDCl$_3$) δ 159.8, 144.3, 140.2, 131.4, 128.5, 128.3, 127.9, 124.6, 124.2, 114.1, 55.5, 26.5, -3.1; IR (neat): 3060,
- **Preparation of trimethyl(1-phenylvinyl)silane (1g)** [CAS No. 1923-01-9]

A 10 mL flask, fitted with a rubber septum, was placed in an ice bath (0°C) and purged with nitrogen. A solution of FeCl₃ (8.1 mg, 0.05 mmol, 5 mol%) in dry THF (4 mL) was added via syringe followed by TMEDA (30 μL, 20 mol%). The mixture was stirred at 0°C (ice bath) for 10 min. Then, (1-bromovinyl)trimethylsilane (1M solution in THF, 1 mmol) and phenylmagnesium bromide (in 1 M solution in THF, 1 mmol) were added. After 30 min at 0 °C, the solution was diluted with saturated aqueous NaHCO₃ (2 mL) and extracted with diethyl ether. The combined organic layers were dried over anhydrous MgSO₄, filtered, and concentrated in vacuo. Trimethyl(1-phenylvinyl)silane (colorless liquid, 150 mg, 85% yield) was obtained by using column chromatography (n-hexane). ^1H NMR (400 MHz, CDCl₃) δ 7.35-7.31 (m, 2H), 7.27-7.21 (m, 3H), 5.86 (d, J = 3.2 Hz, 1H), 5.64 (d, J = 3.2 Hz, 1H), 0.2 (s, 9H); ^13C NMR (100MHz, CDCl₃) δ 153.7, 145.0, 128.4, 127.4, 126.9, 126.5, 0.6; IR (neat): 3057, 3031, 2957, 2898, 1943, 1870, 1597, 1571, 1488, 1405, 1248, 1072, 1028, 931, 859, 838, 777, 759, 737, 699 cm⁻¹.

- **Large scale production of (E)-(11-chloroundecyl)dimethyl(styryl)silane (1i) (Scheme 2)**

A 2-neck round bottomed flask pre-equipped with a reflux condenser was charged with chlorodimethylsilane (15 g, 158 mmol) and 10% H₂PtCl₆•xH₂O (123 mg, 0.24 mmol) in 2-propanol (0.2 mL) solution. The resulting solution was stirred for 30 min. Then, 11-chloroundec-1-ene (13 g, 79 mmol) was added dropwise and the resulting mixture was stirred at room temperature for 12 h. After the reaction, unreacted chlorodimethylsilane was removed by distillation under reduced pressure to give crude chloro(11-chloroundecyl)dimethylsilane, which was used for the next step without further purification. Chloro(11-chloroundecyl)dimethylsilane was added slowly to LiAlH₄ (4.5 g, 118.5 mmol) was added to diethyl ether (250 ml) at 0 °C. Resulting solution was stirred at room temperature for 1 h, diluted by slowly adding H₂O, and extracted with diethyl ether. The combined organic layers were dried over anhydrous MgSO₄, filtered, and concentrated in vacuo to give (11-chloroundecyl)dimethylsilane (9, colorless liquid, 17 g, 86% overall yield). ^1H NMR (400 MHz, CDCl₃) δ 3.87-3.85 (m, 1H), 3.50 (t, J = 6.8 Hz, 2H), 1.79-1.72 (m, 2H), 1.44-1.40 (m, 2H), 1.3-1.27 (m, 14H), 0.56 (t, J = 6.0 Hz, 2H), 0.05 (s, 6H); ^13C NMR (100MHz, CDCl₃) δ 45.2, 33.5, 32.9, 29.9, 29.8, 29.7, 29.6, 29.2, 27.1, 24.6, 14.4, -4.2;

A 2-neck round bottomed flask pre-equipped with a reflux condenser was charged with (11-chloroundecyl)dimethylsilane (9, 17 g, 68 mmol) and RhCl(PPh₃)₃ (377 mg, 0.4 mmol) in THF (5 ml). The resulting solution was stirred for 30 min. Then, phenylacetylene (10, 8.3 g, 81.6 mmol) was added
dropwise and the resulting mixture was stirred at room temperature for 12 h, diluted with saturated NH₄Cl (aq.), and extracted with diethyl ether. The organic layer was dried over anhydrous MgSO₄, filtered, and concentrated in vacuo. (E)-(11-Chloroundecyl)dimethyl(styryl)silane (1i, colorless liquid, 20.8 g, 75% overall yield) was obtained by using column chromatography (n-hexane).

1H NMR (400 MHz, CDCl₃) δ 7.48 (d, J = 7.2 Hz, 2H), 7.36 (t, J = 7.2 Hz, 2H), 7.28 (t, J = 7.2 Hz, 1H), 6.91 (d, J = 19.2 Hz, 1H), 6.51 (d, J = 19.2 Hz, 1H), 3.56 (t, J = 6.8 Hz, 2H), 1.82-1.75 (m, 2H), 1.46-1.43 (m, 2H), 1.36-1.31 (m, 14H), 0.67 (t, J = 7.2 Hz, 2H), 0.18 (s, 6H); 13C NMR (100 MHz, CDCl₃) δ 144.1, 138.5, 128.8, 128.7, 128.1, 126.5, 45.4, 33.8, 32.9, 29.8, 29.7, 29.6, 29.5, 29.1, 27.1, 24.1, 15.9, -2.8; IR (neat): 3078, 3059, 3028, 2988, 2925, 2853, 1941, 1875, 1801, 1604, 1573, 1494, 1464, 1446, 1288, 1247, 1215, 1070, 1028, 988, 842, 737, 689, 653 cm⁻¹; ESI-HRMS (negative) calcd for C₂₁H₃₄ClSi [M-H]⁻ 349.2124, found 349.2051.

Preparation of 1j–1q (Scheme 3 and Table 2)

Preparation of (E)-12-(dimethyl(styryl)silyl)dodecanenitrile (1j)
A solution of (E)-(11-chloroundecyl)dimethyl(styryl)silane (1i, 2 g, 5.7 mmol) and sodium cyanide (559 mg, 11.4 mmol) in DMF (10 ml) was stirred at 120 °C for 4 h, diluted by addition of saturated NH₄Cl aqueous solution, and extracted with diethyl ether. The combined organic layers were dried over anhydrous MgSO₄, filtered through Celite pad, and subjected to column chromatography (n-hexane:ethyl acetate = 10:1) to give 1j (1.77 g, yield: 91 %). 1H NMR (400 MHz, CDCl₃) δ 7.44 (d, J = 7.2 Hz, 2H), 7.33 (t, J = 7.2 Hz, 2H), 7.25 (t, J = 7.2 Hz, 1H), 6.87 (d, J = 19.2 Hz, 1H), 6.44 (d, J = 19.2 Hz, 1H), 2.33 (t, J = 6.8 Hz, 2H), 1.68-1.61 (m, 2H), 1.45-1.41 (m, 2H), 1.31-1.21 (m, 14H), 0.63 (t, J = 6.8 Hz, 2H), 0.13 (s, 6H); 13C NMR (100 MHz, CDCl₃) δ 144.0, 138.5, 128.8, 128.7, 128.1, 126.5, 120.1, 33.8, 29.7, 29.5, 29.4, 28.9, 28.8, 25.5, 24.1, 17.3, 15.9, -2.8; IR (neat): 3078, 3059, 3023, 2988, 2925, 2853, 1941, 1875, 1801, 1604, 1573, 1494, 1464, 1446, 1288, 1247, 1215, 1070, 1028, 988, 842, 737, 689, 653 cm⁻¹; ESI-HRMS (negative) calcd for C₂₂H₃₄ClSi [M-H]⁻ 340.2466, found 340.2481.

Preparation of (E)-12-(dimethyl(styryl)silyl)dodecanal (1k)
The solution of (E)-12-(dimethyl(styryl)silyl)dodecanenitrile (1j, 200 mg, 0.6 mmol) in dichloromethane was cooled to -78 °C, and 1.0 M DIBAL-H in dichloromethane (0.7 ml) was slowly added. Then temperature was raised to -40 °C and the mixture was stirred for 1 h. Silica gel and water were added, and the mixture was stirred for 1 h at 0 °C. The organic layer was separated, dried over anhydrous MgSO₄ and K₂CO₃, and filtered through Celite pad. The filtrate was concentrated in vacuo to give a residue that was subjected to column chromatography (n-hexane:ethyl acetate = 10:1) to give 1k (120 mg, yield: 59 %). 1H NMR (400 MHz, CDCl₃) δ 9.76 (t, J = 2.0 Hz, 1H), 7.44 (d, J = 7.2 Hz, 2H), 7.33 (t, J = 7.2 Hz, 2H), 7.24 (t, J = 6.8 Hz, 2H), 6.87 (d, J = 19.2 Hz, 1H), 6.46 (d, J = 19.2 Hz, 1H), 2.43-2.39 (m, 2H), 1.62 (t, J = 7.6
Hz, 2H), 1.31-1.26 (m, 16H), 0.63 (t, J = 6.4 Hz, 2H), 0.13 (s, 6H); 13C NMR (100 MHz, CDCl3) δ 203.3, 144.1, 138.6, 128.9, 128.7, 128.1, 126.5, 44.1, 33.8, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 24.1, 22.3, 15.9, -2.8; IR (neat) 3078, 3059, 3023, 2855, 1941, 1875, 1800, 1727, 1687, 1604, 1573, 1494, 1464, 1410, 1366, 1337, 1287, 1247, 1143, 988, 842, 742, 689, 631 cm⁻¹; Anal. Calcd for C22H36OSi: C, 77.68; H, 10.53; found C, 77.64; H, 12.06.

- Preparation of (E)-11-(dimethyl(styryl)silyl)undecyl acetate (II)
A solution of (E)-(11-chloroundecyl)dimethyl(styryl)silane (II, 1.0 g, 2.85 mmol) and sodium acetate (468 mg, 5.7 mmol) in DMF (5 mL) was stirred at 120 °C for 12 h. After addition of saturated NH₄Cl aqueous solution, organic layer was extracted using diethyl ether. The organic layer was dried over anhydrous MgSO₄, filtered through Celite pad, giving a filtrate that was concentrated in vacuo. The resulting residue was subjected to column chromatography (n- hexane:ethyl acetate = 10:1) to give II (854 mg, yield: 80 %). 1H NMR (400 MHz, CDCl3) δ 7.46 (d, J = 7.2 Hz, 2H), 7.34 (t, J = 7.2 Hz, 2H), 7.26 (t, J = 7.2 Hz, 1H), 6.90 (d, J = 19.2 Hz, 1H), 6.49 (d, J = 19.2 Hz, 1H), 4.07 (t, J = 6.8 Hz, 2H), 2.06 (s, 3H), 1.67-1.60 (m, 2H), 1.35-1.30 (m, 16H), 0.66 (t, J = 6.8 Hz, 2H), 0.17 (s, 6H); 13C NMR (100 MHz, CDCl3) δ 171.4, 144.1, 138.5, 128.8, 128.7, 128.1, 126.5, 64.8, 33.8, 29.8, 29.7, 29.6, 29.5, 29.4, 28.8, 26.1, 24.1, 21.2, 15.9, -2.8; IR (neat) 3059, 3024, 2924, 2854, 1742, 1604, 1573, 1494, 1465, 1447, 1387, 1365, 1245, 1126, 1030, 989, 842, 805, 778, 741, 723, 690, 632 cm⁻¹; ESI-HRMS (positive) calcd for C23H38O2SiNa [M+Na]+ 397.2533, found 397.2496.

- Preparation of (E)-11-(dimethyl(styryl)silyl)undecan-1-ol (1m)
To a solution of (E)-11-(dimethyl(styryl)silyl)undecyl acetate (II, 300 mg, 0.8 mmol) in diethylether (10 ml) was added LiAlH₄ (52 mg, 1.36 mol) carefully. The resulting mixture was stirred for 1 h, diluted by slow addition of H₂O and extracted with diethyl ether. The combined organic layers were dried over anhydrous MgSO₄, filtered through Celite pad, and purified by column chromatography (n-hexane:ethyl acetate = 5:1) to give 1m (234 mg, yield: 88 %). 1H NMR (400 MHz, CDCl3) δ 7.44 (d, J = 7.2 Hz, 2H), 7.33 (t, J = 7.6 Hz, 2H), 7.23 (t, J = 7.2 Hz, 1H), 6.87 (d, J = 19.2 Hz, 1H), 6.47 (d, J = 19.2 Hz, 1H), 3.63 (t, J = 6.8 Hz, 2H), 1.59-1.53 (m, 2H), 1.42 (m, 2H), 1.31-1.26 (m, 14H), 0.63 (t, J = 6.4 Hz, 2H), 0.13 (s, 6H); 13C NMR (100 MHz, CDCl3) δ 171.4, 144.1, 138.5, 128.8, 128.7, 128.1, 126.5, 64.8, 33.8, 29.8, 29.7, 29.6, 29.5, 29.4, 28.8, 26.1, 24.1, 21.2, 15.9, -2.8; IR (neat) 3059, 3024, 2924, 2854, 1742, 1604, 1573, 1494, 1465, 1447, 1387, 1365, 1245, 1126, 1030, 989, 842, 805, 778, 741, 723, 690, 632 cm⁻¹; ESI-HRMS (negative) calcd for C21H35OSi [M-H]⁻ 331.2462, found 331.2466.

- Preparation of (E)-(11-azidoundecyl)dimethyl(styryl)silane (1n)
(E)-(11-chloroundecyl)dimethyl(styryl)silane (II, 2 g, 5.7 mmol) and sodium azide (556 mg, 8.55 mmol)
was dissolved in DMF (10 ml), and the reaction mixture was stirred at 80 °C for 4 hours. After addition of saturated NH₄Cl aqueous solution and diethyl ether, organic layer was extracted 3 times. The collected organic layer was dried over anhydrous MgSO₄, filtered through Celite pad, giving a filtrate that was concentrated *in vacuo*. The residue was subjected to column chromatography (n-hexane:ethyl acetate = 10:1) to give **1n** (1.88 g, yield: 92 %). ¹H NMR (400 MHz, CDCl₃) δ 7.44 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 1H), 6.87 (d, *J* = 19.2 Hz, 1H), 6.47 (d, *J* = 19.2 Hz, 1H), 3.25 (t, *J* = 6.8 Hz, 2H), 1.63-1.56 (m, 2H), 1.31-1.27 (m, 16H), 0.63 (t, *J* = 6.4 Hz, 2H), 0.13 (s, 6H); ¹³C NMR(100 MHz, CDCl₃) δ 144.1, 138.6, 128.8, 128.7, 128.1, 126.5, 51.7, 33.8, 29.8, 29.7, 29.6, 29.4, 29.0, 26.9, 24.1, 15.9, -2.8; IR (neat) 3060, 3024, 2926, 2854, 2095, 1942, 1876, 1671, 1604, 1573, 1522, 1494, 1464, 1409, 1348, 1249, 1067, 988, 841, 741, 690 cm⁻¹; Anal. Calcd for C₂₁H₃₅N₃Si: C, 70.53; H, 9.86; N, 11.75; found C, 70.01; H, 11.55; N, 9.81.

- Preparation of (E)-2,5-dioxopyrrolidin-1-yl 1-(11-(dimethyl(styryl)silyl)undecyl)-1H-1,2,3-triazole-4-carboxylate (1o)

A mixture of propiolic acid (3 g, 43.4 mmol), N-hydroxysuccinimide (5.0 g, 43.4 mmol), N,N′-dicyclohexylcarbodiimide (9 g, 43.4 mmol) in ethyl acetate (EA; 80 mL) was stirred at 4 °C for 8 h. The mixture was filtered through a pad of Celite to remove dicyclohexylurea, and the filtrate was then concentrated *in vacuo*. The resulting crude compound, 2,5-dioxopyrrolidin-1-yl propiolate, was used in the next step without further purification. (E)-(11-azidoundecyl)dimethyl(styryl)silane (**1n**, 1.79 g, 5 mmol) and a mixture of CuSO₄·5H₂O (123 mg, 0.5 mmol) and sodium ascorbate (198 mg, 1 mmol) in water were added to a solution of crude 2,5-dioxopyrrolidin-1-yl propiolate (1.25 g, 7.5 mmol) in THF. The mixture was stirred at room temperature for 12 h, diluted with saturated aqueous NH₄Cl, and extracted with diethyl ether. The combined organic layers were dried over anhydrous MgSO₄, filtered through a pad of Celite, giving a filtrate that was concentrated *in vacuo*. The resulting residue was subjected to column chromatography (n-hexane:ethyl acetate = 1:1) to give **1o** (1.65 g, yield: 63 %). ¹H NMR (400 MHz, CDCl₃) δ 8.26 (s, 1H), 7.43 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 6.86 (d, *J* = 19.2 Hz, 1H), 6.46 (d, *J* = 19.2 Hz, 1H), 4.43 (t, *J* = 7.2 Hz, 2H), 2.90 (s, 4H), 1.95-1.91 (m, 2H), 1.32-1.25 (m, 16H), 0.62 (t, *J* = 6.8 Hz, 2H), 0.13 (s, 6H); ¹³C NMR(100 MHz, CDCl₃) δ 169.2, 156.0, 144.0, 138.6, 134.8, 129.2, 128.9, 128.7, 128.1, 126.5, 51.2, 33.7, 30.3, 29.7, 29.5, 29.1, 26.5, 25.8, 24.1, 15.9, -2.8; IR (CH₂Cl₂) 3133, 3058, 3019, 2984, 2923, 2853, 1926, 1777, 1743, 1604, 1572, 1533, 1493, 1466, 1446, 1370, 1306, 1247, 1210, 1159, 1081, 1060, 991, 966, 909, 842, 814, 742, 691, 651, 609 cm⁻¹; Anal. Calcd for C₂₈H₄₀N₄O₄Si: C, 64.09; H, 7.68; N, 10.68 found C, 64.29; H, 7.92; N, 10.47.

- Preparation of (E)-(3-chloropropyl)dimethyl(styryl)silane (1p)
A 2-neck round bottomed flask pre-equipped with reflux condenser was charged with chlorodimethylsilane (10 g, 105.7 mmol) and 10% H₂PtCl₆•xH₂O (164 mg, 0.3 mmol) in 2-propanol (0.2 ml) solution. The resulting solution was stirred for 30 min. Then, allyl chloride (16 g, 211.4 mmol) was added dropwise and the resulting mixture was stirred at room temperature for 12 h. After the reaction, unreacted allyl chloride and chlorodimethylsilane were removed by distillation under reduced pressure to give crude chloro(3-chloropropyl)dimethylsilane, which was used for the next step without further purification. LiAlH₄ (6 g, 158 mmol) was added to diethyl ether (250 ml) and then chloro(11-chloroundecyl)dimethylsilane was added slowly to the mixture of LiAlH₄ in diethyl ether at 0 °C. Resulting solution was stirred at room temperature for 2 h, diluted by slowly adding H₂O, and extracted with diethyl ether. The combined organic layers were dried over anhydrous MgSO₄, filtered, and concentrated in vacuo to give (3-chloropropyl)dimethylsilane (colorless liquid, 3.5 g, 30% overall yield).

A 2-neck round bottomed flask pre-equipped with reflux condenser was charged with (3-chloropropyl)dimethylsilane (3.2 g, 23.4 mmol) and RhCl(PPh₃)₃ (130 mg, 0.14 mmol) in THF (5 ml). The resulting solution was stirred for 30 min. Then, phenyl acetylene (10, 2.87 g, 28 mmol) was added dropwise and the resulting mixture was stirred at room temperature for 12 h, diluted with saturated NH₄Cl (aq.), and extracted with diethyl ether. The organic layer was dried over anhydrous MgSO₄, filtered, and concentrated in vacuo. (E)-(3-chloropropyl)dimethyl(styryl)silane (1p, colorless liquid, 4.84 g, 87% overall yield) was obtained by using column chromatography (n-hexane). ¹H NMR (400 MHz, CDCl₃) δ 7.48 (d, J = 7.2 Hz, 2H), 7.37 (t, J = 7.2 Hz, 2H), 7.29 (t, J = 7.2 Hz, 1H), 6.93 (d, J = 19.2 Hz, 1H), 6.48 (d, J = 19.2 Hz, 1H), 3.55 (t, J = 6.8 Hz, 2H), 1.89-1.81 (m, 2H), 0.80-0.75 (m, 2H), 0.21 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 144.8, 138.2, 128.7, 128.3, 127.6, 126.6, 48.2, 27.8, 13.6, -3.0; IR (neat): 3059, 3024, 2989, 2954, 2898, 1946, 1876, 1730, 1703, 1646, 1604, 1493, 1446, 1332, 1310, 1287, 1249, 1215, 1173, 1070, 1029, 990, 910, 843, 778, 743, 690 cm⁻¹; ESI-HRMS (negative) calcd for C₁₃H₁₈ClSi [M-H]⁻ 237.0872, found 237.0909.

**Preparation of (11-chloroundecyl)(methyl)di((E)-styryl)silane (1q)**

A 2-neck round bottomed flask pre-equipped with reflux condenser was charged with dichloromethylsilane (6.07 g, 52.8 mmol) and 10% H₂PtCl₆•xH₂O (41 mg, 0.08 mmol) in 2-propanol (0.1 mL) solution. The resulting solution was stirred for 30 min. Then, 11-chloroundec-1-ene (5 g, 26.4 mmol) was added dropwise and the resulting mixture was stirred at room temperature for 12 h. After the reaction, unreacted dichloromethylsilane was removed by distillation under reduced pressure to give crude dichloro(11-chloroundecyl)(methyl)silane, which was used for the next step without further purification. LiAlH₄ (2 g, 56 mmol) was added to diethyl ether (250 ml) and then dichloro(11-chloroundecyl)(methyl)silane was added slowly to the mixture of LiAlH₄ in diethyl ether at 0 °C. Resulting solution was stirred at room temperature for 2 h, diluted by slowly adding H₂O, and extracted...
with diethyl ether. The combined organic layers were dried over anhydrous MgSO₄, filtered, and concentrated \textit{in vacuo} to give (11-chloroundecyl)(methyl)silane (colorless liquid, 2.7 g, 44% overall yield). A 2-neck round bottomed flask pre-equipped with reflux condenser was charged with (11-chloroundecyl)(methyl)silane (2.7 g, 11.6 mmol) and \([\text{Cp}^*\text{RhCl}_2]\)₂ (86 mg, 0.14 mmol) in THF (5 ml). The resulting solution was stirred for 30 min. Then, phenyl acetylene (10, 3 g, 29 mmol) was added dropwise and the resulting mixture was stirred at room temperature for 12 h, diluted with saturated NH₄Cl (aq.), and extracted with diethyl ether. The organic layer was dried over anhydrous MgSO₄, filtered, and concentrated \textit{in vacuo}. (11-chloroundecyl)(methyl)di((E)-styryl)silane (1q, colorless liquid, 1.58 g, 31% overall yield) was obtained by using column chromatography (n-hexane). \(^1\)H NMR (400 MHz, CDCl₃) δ 7.46 (d, \(J = 7.2\) Hz, 4H), 7.34 (t, \(J = 7.2\) Hz, 4H), 7.26 (t, \(J = 7.6\) Hz, 2H), 6.95 (d, \(J = 19.2\) Hz, 1H), 6.52 (d, \(J = 19.2\) Hz, 1H), 3.52 (t, \(J = 6.8\) Hz, 2H), 1.79-1.72 (m, 2H), 1.41-1.26 (m, 16H), 0.79 (t, \(J = 7.2\) Hz, 2H), 0.30 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl₃) δ 145.5, 138.4, 128.7, 128.3, 127.0, 126.6, 45.3, 33.8, 32.8, 29.7, 29.6, 29.5, 29.1, 27.0, 24.0, 14.8, -4.2; IR (neat): 3078, 3058, 3023, 2989, 2923, 2853, 1943, 1876, 1803, 1705, 1602, 1573, 1493, 1463, 1446, 1408, 1334, 1288, 1251, 1215, 1197, 1175, 1070, 1028, 989, 933, 912, 837, 799, 733, 690, 652 cm\(^{-1}\); ESI-HRMS (positive) calcd for C₂₈H₄₀ClSi [M+H]\(^+\) 439.2582, found 439.2583.

- Preparation of 14–18 (Scheme 4)

- Preparation of dimethylsilanyl impregnated polybutadiene 13
A 2-neck round bottomed flask pre-equipped with a reflux condenser was charged with polybutadiene (12, 2 g, 31.4 mmol vinyl group of polybutadiene) and 10% H₂PtCl₆•xH₂O (48.7 mg, 0.09 mmol) in 2-propanol (0.2 mL) solution. The solution was stirred for 30 min. Then, chlorodimethylsilane (3 g, 31.4 mmol) was added dropwise and the resulting mixture was stirred at room temperature for 12 h. Unreacted chlorodimethylsilane was removed by distillation under reduced pressure to give crude chlorosilane contained polybutadiene, which was used for the next step without further purification. Crude chlorosilane-impregnated polybutadiene was added slowly to LiAlH₄ (1.8 g, 47 mmol) in diethyl ether (250 ml) at 0 °C. The resulting solution was stirred at room temperature for 2 h, diluted by slow addition of H₂O, and extracted with diethyl ether. The combined organic layers were dried over anhydrous MgSO₄, filtered through Celite pad. After evaporating the solvent from filtrate, the residue was washed throughly with methanol and dried to give dimethylsilanyl group-impregnated polybutadiene 13 (colorless liquid, 3 g, 76% overall yield).

- Preparation of styryl and chloroalkyl group-impregnated polybutadiene 14
A 2-neck round bottomed flask pre-equipped with a reflux condenser was charged with dimethylsilanyl
group-impregnated polybutadiene 13 (3 g, 23.9 mmol) and RhCl(PPh₃)₃ (133 mg, 0.14 mmol) in THF (5 ml). The resulting solution was stirred for 30 min. Then, phenyl acetylene (10, 1.05 ml, 9.56 mmol) and 11-chloroundec-1-ene (6, 9 ml, 47.8 mmol) were added dropwise and the resulting mixture was stirred at room temperature for 12 h, diluted with saturated NH₄Cl (aq.), and extracted with diethyl ether. The organic layer was dried over anhydrous MgSO₄, filtered, and concentrated in vacuo. The precipitate was then washed throughly with methanol and dried to give styryl and chloroalkyl group-impregnated polybutadiene 14 (5.18 g, 92% overall yield). ¹H NMR (400 MHz, CDCl₃) δ 7.41 (br s, 2H), 7.30 (br s, 3H), 6.89-6.84 (br m, 1H), 6.48-6.44 (br m, 1H), 5.37 (br s), 3.53 (br s, 3H), 1.95-1.77 (br m), 1.41-1.28 (br m) 0.48-0.03 (br m) -0.04 (br s); ¹³C NMR (100MHz, CDCl₃) δ 144.2, 138.5, 128.7, 128.1, 126.5, 45.3, 34.0, 32.9, 29.9, 29.7, 29.2, 27.1, 24.2, 15.5, -2.8, -3.1; IR (CH₂Cl₂): 3078, 3059, 3023, 2853, 2853, 1940, 1875, 1800, 1726, 1604, 1573, 1494, 1447, 1412, 1338, 1288, 1247, 1214, 1178, 1070, 1028, 988, 839, 769, 690 cm⁻¹. Mₚ/Mₙ = 2.45.

- Preparation of styryl and azido group-impregnated polybutadiene 15
Styryl and chloroalkyl group-impregnated polybutadiene 14 (2.1 g, 7.2 mmol) and sodium azide (420 mg, 10.8 mmol) were dissolved in DMF and the resulting mixture was stirred at 80 °C for 4 hours. After addition of saturated NH₄Cl aqueous solution and diethyl ether, organic layer was extracted 3 times. The collected organic layer was dried over anhydrous MgSO₄, filtered, and concentrated in vacuo. The precipitate was then washed throughly with methanol and dried to give styryl and azido group-impregnated polybutadiene 15 (1.4 g, yield: 81 %). ¹H NMR (400 MHz, CDCl₃) δ 7.40 (br s, 2H), 7.30-7.23 (br m, 3H), 6.89-6.84 (br m, 1H), 6.47-6.43 (br m, 1H), 5.36 (br s), 3.24 (br s, 3H), 2.09-1.94 (br m), 1.58-1.27 (br m), 0.47-0.03 (br m), -0.05 (br s); ¹³C NMR (100MHz, CDCl₃) δ 144.3, 138.6, 128.7, 128.1, 126.6, 51.7, 34.1, 29.9, 29.8, 29.4, 29.1, 27.0, 24.2, 15.5, 7.2, -2.8, -3.1; IR (CH₂Cl₂): 3059, 3023, 2921, 2853, 2095, 1604, 1573, 1494, 1449, 1412, 1348, 1247, 1179, 1069, 988, 837, 773, 689 cm⁻¹. Mₚ/Mₙ = 2.93.

- Preparation of styryl and pyrenyl group-impregnated polybutadiene 17
Styryl and azido group-impregnated polybutadiene 15 (500 mg, 1.06 mmol) and a mixture of CuSO₄·5 H₂O (27 mg, 0.11 mmol) and sodium ascorbate (43 mg, 0.22 mmol) in water were added to a solution of crude 1-(propargyloxymethyl)pyrene 16 in THF. The mixture was stirred at room temperature for 12 hours, diluted with saturated aqueous NH₄Cl, and extracted with diethyl ether. The combined organic layers were dried over anhydrous MgSO₄, filtered, and concentrated in vacuo. The precipitate was then washed throughly with methanol and dried to give styryl and pyrenyl group-impregnated polybutadiene 17 (600 mg, yield: 76 %). ¹H NMR (400 MHz, CDCl₃) δ 8.29 (br s), 8.11-7.99 (br m), 7.37-7.26 (br m), 6.86-6.81 (br m), 6.44-6.40 (br m), 5.30 (br s), 4.78 (br s), 4.20 (br s), 1.91-1.19 (br m), 1.19-1.07 (br s).
0.44-0.01 (br m), -0.08 (br s); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 144.3, 138.5, 131.6, 131.4, 131.2, 130.9, 129.6, 128.7, 128.1, 127.9, 127.7, 127.6, 127.4, 126.5, 126.1, 125.4, 124.7, 123.6, 122.5, 71.2, 64.0, 50.5, 34.1, 30.4, 29.9, 29.7, 29.2, 26.7, 24.2, 15.5, -2.8, -3.1; IR (neat): 3024, 2919, 2852, 1604, 1573, 1493, 1447, 1247, 1072, 844, 774, 709 cm$^{-1}$; $M_w/M_n = 1.78$.

- **Polymer 17 immobilized glass preparation (18)**
  A glass slide was treated by Piranha solution (H$_2$SO$_4$ : H$_2$O$_2$ = 7 : 3, 5 mL) for 1 h. Reaction of styryl and pyrenyl group-impregnated polybutadiene 17 with glass slide was performed in the presence of 5 mol% of 3a at room temperature in dichloromethane during 12 h. After the reaction, modified glass slide was washed with dichloromethane. The contact angles of glass slide after treatment of Piranha solution and surface-modified glass slide (18) were measured to be 7° and 112°, respectively.

- **The nitrobenzene detecting ability of 18 (Fig. 2)$^3$**

- **Fluorescence spectra of 18 at different concentration of nitrobenzene (Fig. 2a)**
  Before addition of nitrobenzene, the fluorescence spectrum of 18 (2 mL CH$_2$Cl$_2$) was recorded (excitation at 330 nm). To 18, 2 mL of 1.2 mM nitrobenzene in CH$_2$Cl$_2$ was added, and the fluorescence spectra of 18 was measured again. Then 18 was washed thoroughly with dichloromethane to give recovered 18. This procedure was repeated by increasing the concentration of nitrobenzene from 1.2 mM to 14.4 mM.

- **Fluorescence intensity change during sensing and recycling of 18 (Fig. 2b)**
  Before addition of nitrobenzene, the fluorescence spectrum of 18 (2 mL CH$_2$Cl$_2$) was recorded (excitation at 330 nm). And then, after 2 mL of 14.4 mM nitrobenzene in CH$_2$Cl$_2$ was added, the fluorescence spectrum was measured. After 18 was washed with dichloromethane thoroughly, the fluorescence spectrum was measured. This procedure was repeated three times.
4. $^1$H and $^{13}$C NMR spectra

Figure S2. $^1$H NMR spectrum of 1a.

Figure S3. $^{13}$C NMR spectrum of 1a.
Figure S4. $^1$H NMR spectrum of 1b.

Figure S5. $^1$H NMR spectrum of 1b.
Figure S6. $^1$H NMR spectrum of 1c.

Figure S7. $^{13}$C NMR spectrum of 1c.
Figure S8. $^1$H NMR spectrum of 1d.

Figure S9. $^{13}$C NMR spectrum of 1d.
Figure S10. $^1$H NMR spectrum of 1e.

Figure S11. $^{13}$C NMR spectrum of 1e.
Figure S12. $^1$H NMR spectrum of 1f.

Figure S13. $^{13}$C NMR spectrum of 1f.
Figure S14. $^1$H NMR spectrum of $1g$.

Figure S15. $^{13}$C NMR spectrum of $1g$. 
Figure S16. $^1$H NMR spectrum of 1i.

Figure S17. $^{13}$C NMR spectrum of 1i.
Figure S18. $^1$H NMR spectrum of 1j.

Figure S19. $^{13}$C NMR spectrum of 1j.
Figure S20. $^1$H NMR spectrum of 1k.

Figure S21. $^{13}$C NMR spectrum of 1k.
Figure S22. $^1$H NMR spectrum of 11.

Figure S23. $^{13}$C NMR spectrum of 11.
Figure S24. $^1$H NMR spectrum of 1m.

Figure S25. $^{13}$C NMR spectrum of 1m.
Figure S26. $^1$H NMR spectrum of 1n.

Figure S27. $^{13}$C NMR spectrum of 1n.
Figure S28. $^1$H NMR spectrum of 1o.

Figure S29. $^{13}$C NMR spectrum of 1o.
Figure S30. $^1$H NMR spectrum of 1p.

Figure S31. $^{13}$C NMR spectrum of 1p.
Figure S32. $^1$H NMR spectrum of 1q.

Figure S33. $^{13}$C NMR spectrum of 1q.
Figure S34. $^1$H NMR spectrum of 14.

Figure S35. $^{13}$C NMR spectrum of 14.
Figure S36. $^1$H NMR spectrum of 15.

Figure S37. $^{13}$C NMR spectrum of 15.
Figure S38. $^1$H NMR spectrum of 17.

Figure S39. $^{13}$C NMR spectrum of 17.
5. Reference