Synthesis of a spirobifluorene-bridged allylsilane precursor for periodic mesoporous organosilica

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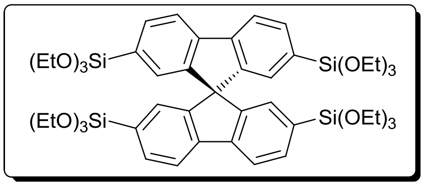
List of Supporting Information:

General Methods

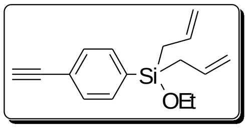
Unless otherwise noted, all materials including dry solvents were obtained from commercial suppliers and used without further purification. Rhodium complex, $[Rh(cod)(MeCN)_2]BF_4$ was prepared according to procedure reported in the literature.[1] Diethyl ether was distilled from sodium/benzophenone ketyl.[2] All air- and moisture-sensitive manipulations were carried out using standard vacuum line, Schlenk and cannula techniques. All work-up and purification procedures were carried out with reagent-grade solvents in air.

Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F_{254} precoated plates (0.25 mm). The developed chromatogram was analyzed by UV lamp (254 nm) and iodine chamber. Flash column chromatography was performed with E. Merck silica gel 60 N (spherical, neutral 100-210 μm). Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-EX270 (^{1}H 270 MHz, and ^{13}C 67.8 MHz) and JEOL JNM EX400 (^{1}H 400 MHz, and ^{13}C 100 MHz) spectrometer. Chemical shifts for ^{1}H NMR are expressed in parts per million (ppm) relative to tetramethylsilane (δ 0.0 ppm). Chemical shifts for ^{13}C NMR are expressed in parts ppm relative to $CDCl_3$ (δ 77.0 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signal), coupling constant (Hz), and integration. High resolution mass spectroscopy (HR MS) was recorded with JEOL JMS-700 spectrometer. Mass spectra were also recorded on a Bruker Daltonics Autoflex mass spectrometer with matrix-assisted laser desorption/ionization (MALDI). UV-vis absorption spectra were obtained on a JASCO V-670 spectrometer. X-ray diffraction (XRD) measurements were performed on a Rigaku RINT-TTR diffractometer with Cu-Kα radiation (50 kV, 300 mA). Nitrogen adsorption−desorption isotherms were measured using a Quantachrome Autosorb-1 sorptometer at −196 °C. Prior to measurements, all samples were outgassed at 80 °C for 2 h. Brunauer−Emmett−Teller (BET) surface areas were calculated from the linear section of the BET plot (P/P_0 = 0.05−0.2). Pore volumes were estimated by the *t*-plot method. Pore size distributions were determined using the density functional theory (DFT) method (the DFT kernel used: N_2 at 77K on silica, cylindrical pore, NLDFT equilibrium model).



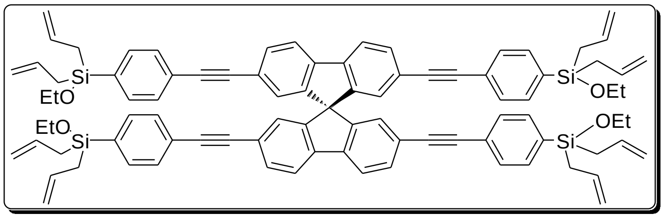
Attempted Synthesis of 2,2′,7,7′-Tetrakis(triethoxysilyl)-9,9′-spirobifluorene

A dry and nitrogen flushed 30 mL Schlenk flask, was charged with 2,2′,7,7′-tetraiodo-9,9′-spirobifluorene (150 mg, 0.183 mmol), tetra-*n*-butylammonium iodide (270.4 mg, 0.732 mmol), triethylamine (0.2 mL, 1.464 mmol), and $[Rh(cod)(CH_3CN)_2]BF_4$ (7 mg, 0.0183 mmol) in anhydrous DMF (7.5 mL) and toluene (7.5 mL) was added dropwise triethoxysilane (0.2 mL, 1.098 mmol) at 0 °C. The mixture was stirred at 80 °C under nitrogen atmosphere for 2 h. The mixture was concentrated under reduced pressure, treated with diethyl ether (25 mL) and passed through a short pad of Celite.® Evaporation of the solvent from the filtrate afforded a complex mixture in which the target compound was not detected.



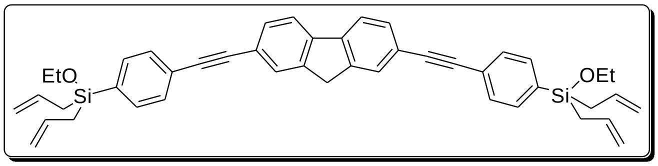
Synthesis of 4-Diallylethoxysilyl-ethynylbenzene (**3**)

To NaOH (296 mg, 7.4 mmol) in toluene (40 mL) was added **2**[3] (2.3 g, 7.4 mmol), synthesized from 1,4-diiodobenzene in 3 steps. The mixture was refluxed for 30 min and evaporated. The evaporated residue was subjected to silica gel column chromatography (hexane/AcOEt = 10 : 1) to afford **2** (1.7 g, 88%) as colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.21 (t, J = 7.1 Hz, 3H), 1.91−1.94 (m, 4H), 3.11 (s, 1 H), 3.76 (q, J = 7.0 Hz, 2H), 4.89−4.97 (m, 8H), 5.74−5.83 (m, 4H), 7.49 (d, J = 8.7 Hz, 2H), 7.53 (d, J = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.3, 21.1, 59.4, 78.0, 83.6, 115.0, 123.4, 131.2, 132.8, 133.9, 136.3; MALDI-HRMS m/z cald. for $C_{42}H_{45}N_2O_2Si_2$ $[M+H]^+$: 665.3020; found: 665.3000.



Synthesis of 2,2′,7,7′-Tetrakis(diallylethoxysilylphenylethynyl)spirobifluorene (5)

To a mixture of $Pd_2(dba)_3$ (10 mg, 0.0106 mmol), PPh_3 (6 mg, 0.0212 mmol), and CuI (4 mg, 0.0212 mmol) were added a solution of **3** (223 mg, 0.869 mmol) in toluene (2.5 mL) and **4**^{4} (100 mg, 0.212 mmol) in Et_3N (10 mL) and toluene (2.5 mL). The reaction mixture was stirred at 100 °C for 24 h. The reaction mixture was then diluted with CH_2Cl_2, washed with H_2O and brine, dried over $MgSO_4$, and concentrated. The residue was chromatographed on silica gel (hexane/EtOAc=5:1 as eluent) to give tetrakis(diallylethoxysilylphenylethynyl)spirobifluorene (**5**, 158 mg, 56%) as yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.19 (t, J = 6.8 Hz, 12H), 1.89−1.91 (m, 16H), 3.74 (q, J = 6.8 Hz, 8H), 4.89−4.95 (m, 16H), 5.72−5.83 (m, 8H), 6.95–6.96 (m, 4H), 7.41 (d, J = 8.0 Hz, 8H), 7.49 (d, J = 8.0 Hz, 8H), 7.59–7.61 (m, 4H), 7.84–7.86 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.4, 21.1, 38.7, 59.3, 90.2. 90.5, 114.9, 122.8, 124.3, 127.3, 128.3, 130.6, 130.9, 131.8, 132,7, 132.8, 133.8, 135.2, 135.5, 141.2. Anal. Calcd for $C_{89}H_{88}O_4Si_4$: C, 80.13; H, 6.65: found: C, 79.89; H, 6.53.



Synthesis of 2,7-Bis(diallylethoxysilylphenylethynyl)fluorene (6)

To a mixture of $Pd_2(dba)_3$ (11 mg, 0.012 mmol), PPh_3 (6 mg, 0.024 mmol), and CuI (5 mg, 0.024 mmol) were added a solution of **3** (128.2 mg, 0.5 mmol) in toluene (2.5 mL) and diiodofluorene (100 mg, 0.24 mmol) in Et_3N (10 mL) and toluene (2.5 mL). The reaction mixture was stirred at 100 °C for 24 h. The reaction mixture was then diluted with CH_2Cl_2, washed with H_2O and brine, dried over $MgSO_4$, and concentrated. The residue was chromatographed on silica gel (hexane/EtOAc=5:1 as eluent) to give 2,7-bis(diallylethoxysilylphenylethynyl)fluorene (**6**, 97 mg, 61%) as yellow solid. ^1H NMR ($CDCl_3$, 400 MHz) δ 1.23 (t, J = 7.2 Hz, 6H), 1.94−1.96 (m, 8H), 3.78 (q, J = 7.0 Hz, 4H), 3.93 (s, 2H), 4.91−4.98 (m, 8H), 5.77−5.85 (m, 4H), 7.54–7.58 (m, 10H), 7.72–7.76 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.4, 21.1, 36.5, 59.4, 89.7, 91.0, 115.0, 120.1, 121.6, 124.7, 128.2, 130.7, 132.9, 133.9, 135.5, 141.3, 143.5; Anal. Calcd for $C_{45}H_{46}O_2Si_2$: C, 80.07; H, 6.87: found: C, 79.70; H, 6.55.

Preparation of Organosilica Films

***5**-Brij76 film*: To a solution of **5** (25 mg) and Brij76 (20 mg) in tetrahydrofuran (1.0 g) was added 2 M hydrochloric acid (100 μL). The reaction mixture was stirred at rt for 24 h, then heated at 60 °C for 4 h. The resulting sol mixture was spin-coated onto quartz substrates (4000 rpm, 30 s) or dropped onto glass substrates. After moderate evaporation of solvents in air, the thin films were dried under vacuum. Removal of the template surfactants was carried out by immersing the film-coated substrates in ethanol at 60 °C for 12 h, followed by drying at rt.

***6*-Brij76 film**: To a solution of **6** (25 mg) and Brij76 (20 mg) in tetrahydrofuran (1.0 g) was added 2 M hydrochloric acid (100 μL). The reaction mixture was stirred at rt for 24 h, then heated at 60 °C for 10 h. The resultant sol mixture was spin-coated onto quartz substrates (4000 rpm, 30 s) or dropped onto glass substrates. After moderate evaporation of solvents in air, the thin films were dried under vacuum. Removal of the template surfactants was carried out in a similar way to that used for **5**-Brij76 film.

UV-vis Absorption Spectra of 5-Brij76 and 6-Brij76 Films

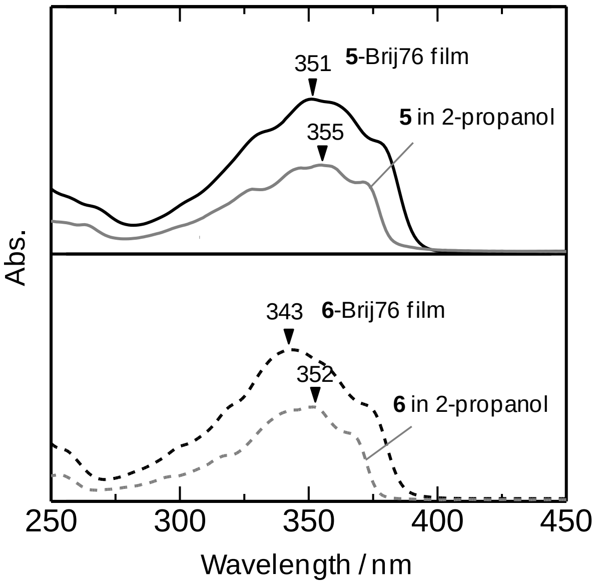


Fig. S1 UV-vis absorption spectra of **5**-Brij76 and **6**-Brij76 films and the solutions of the precursors in 2-propanol.

Nitrogen Adsorption–Desorption Measurements

For the nitrogen adsorption–desorption measurement, the as-made **5**-Brij76 film was exposed to a vapor of trichlorosilane (40 °C, 2 h) to reinforce the organosilica framework. The surfactant template was extracted with a mixed solution of ethanol and 36% hydrochloric acid (200/1, v/v) at 60 °C for 6 h. The extracted organosilica sample was peeled off the substrate and then subjected to the measurement. Fig. S2 shows the nitrogen adsorption–desorption isotherms of the peeled-off sample. The BET surface area, pore diameter and pore volume were calculated to be 188 $m^2\ g^{-1}$, 4.1 nm and 0.08 $cm^3\ g^{-1}$, respectively. The small surface area, the broad pore size distribution and the small pore volume are probably due to the partial collapse of the mesostructure by extracting the template surfactant and peeling off the substrate. Considering the pore diameter (4.1 nm) and *d*-spacing value of the XRD peak (5.4 nm), the thickness of the pore wall is estimated to be ca. 1.3–2.0 nm, which corresponds to one or two layers of the spirobifluorene–silica hybrid; therefore the collapse of the mesostructure is due to the shortage of crosslinking points in the pore wall.

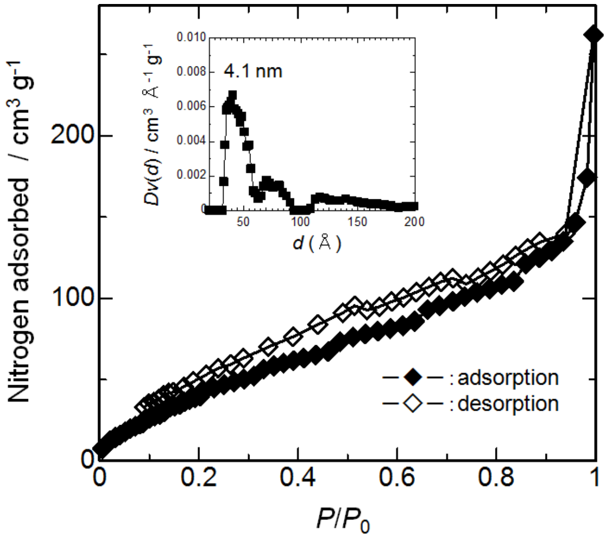


Fig. S2 Nitrogen adsorption–desorption isotherms of the extracted **5**-Brij76 film. Inset shows the pore size distribution calculated by the DFT method.

References

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