Electronic Supplementary Information

One-Step Co-condensation Method for Synthesis of Well-Defined Functionalized Mesoporous SBA-15 Using TrimethallyIsilanes as

Organosilane Sources

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1. General

Flash column chromatography was performed using E. Merck 230-400 mesh silica gel. Column Chromatography were 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 and *p*-anisaldehyde solution, 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 deuteriated solvent peaks. Infrared spectra were obtained using a Nicolet Impact 400 spectrometer. ¹H NMR spectra were referenced to tetramethylsilane (δ 0.00 ppm) as an internal standard and are reported as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). ¹³C NMR spectra were referenced to the residual CDCl₃ (77.16 ppm). Transmission Electron Microscope datas were recorded by JEM-2010 (120 kV) and Scanning Electron Microscope datas were recorded by JEOL-6701F. Elemental analyses were provided by the Organic Chemistry Research Center, Sogang University and Yonsei Center for Research Facilities. Solid state CP-MAS ¹³C spectra (spin rate = 7 kHz), solid state CP-MAS and MAS ²⁹Si spectra (spin rate = 5 kHz) and powder XRD measurements with CuK α radiation (D8 Advance, Bruker) were provided by the National Instrumentation Center for Environmental Management (NICEM), Seoul National University. Fluorescence data were recorded on a Hitachi F-4500 spectrometer. BET analyses of surface area, pore size and pore volume were provided by Yonsei Center for Research Facilities.

2. Materials

Most commercially available reagent grade chemicals were used as received without further purification unless otherwise stated [magnesium turning, 3-chloro-2-methylpropene, allyl chloride, 10-undecen-1-ol, trichlorosilane, tetraethoxysilane (TEOS), pluronic P123, CuSO₄·5H₂O, (+)sodium ascorbate, triphenylphosphine, dabsyl chloride, benzaldehyde, malononitrile and cyclohexane, purchased from Aldrich Chemical Company; sodium azide and carbon tetrachloride, purchased from Samchun chemical Co.; *N*,*N*-dimethylformamide, purchased from Burdick & Jackson; conc. HCl aqueous solution, purchased from SK chemical Co.]. Dichloromethane and THF were distilled by reported procedure.¹ 1-Ethynylpyrene (CAS No. 34993-56-1) was prepared by Pd(II)/Cu(II)-catalyzed Sonogashira reaction of 1-bromopyrene with trimethylsilylacetylene and subsequent basic deprotection of trimethylsilyl group.

3. Preparations of Organic Precursors

Preparation of 11-chloroundecyltrimethallylsilane: A 2-neck round bottomed flask preequipped with reflux condenser was charged with trichlorosilane (11 g, 79.47 mmol) and 10% H₂PtCl₆•6H₂O (40 mg, 0.08 mmol) in 2-propanol (0.2 mL) solution. The resulting solution was stirred for 30 min. Then, 11-chloroundecene (11 g, 52.98 mmol) was added dropwise and the resulting mixture was stirred at room temperature for 12 h. After the reaction, unreacted reagents (11-chloroundecene and trichlorosilane) were removed by distillation under reduced pressure to give crude 11-chloroundecyltrichlorosilane, which was used for the next step without further purification. The crude 11-chloroundecyltrichlorosilane was added dropwise to methallylmagnesium chloride solution in THF (made by the reaction of methallyl chloride with Mg in THF) and the resulting solution was stirred at 0 °C for 5 h. 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. 11-Chloroundecyltrimethallylsilane (colorless liquid, 7 g, 36% overall yield) was obtained by using column chromatography (nhexane, $R_f = 0.6$). ¹H NMR (400 MHz, CDCl₃) δ 4.59 (d, J=37.48 Hz, 6H), 3.52 (t, J=6.8 Hz, 2H), 1.74 (s, 9H), 1.63 (s, 6H), 1.43-1.27 (m, 18H), 0.65-061 (m, 2H); ¹³C NMR (100MHz, CDCl₃) δ 143.4, 109.6, 45.3, 34.0, 32.9, 29.7, 29.4, 29.1, 27.1, 25.8, 24.3, 23.8, 13.4; IR (neat): 3075, 2925, 2854, 1637, 1447, 1373, 1279, 1169, 1000, 974, 827, 838 cm⁻¹; Anal. Calcd for C₂₃H₄₃ClSi: C, 72.10; H, 11.31; found: C, 72.12; H, 11.35.

Preparation of 11-azidoundecyltrimethallylsilane (1d, CAS No. 928139-84-8): The title compound was prepared by using nucleophilic substitution reaction of 11-chloroundecyltrimethallylsilane with sodium azide in DMF (colorless liquid, 7.6 g, 86 % yield). ¹H NMR (400 MHz, CDCl₃) δ 4.59 (d, *J*=37.84 Hz, 6H), 3.24 (t, *J* = 13.88 Hz, 2H), 1.73 (s, 9H), 1.63 (s, 6H), 1.35-1.27 (m, 18H), 0.65-0.61 (m, 2H); ¹³C NMR (100MHz, CDCl₃) δ 143.3, 109.6, 51.6, 34.0, 29.7, 29.6, 29.4, 29.3, 29.0, 26.9, 25.7, 24.3, 23.8, 13.8; IR (neat): 3076, 2925, 2860, 2100, 1637, 1450, 1274, 1166, 873 cm⁻¹; Anal. Calcd for C₂₃H₄₃N₃Si: C, 70.89; H, 11.12; N, 10.78; found: C, 70.8617; H, 11.1947; N, 10.8487.

3-Chloropropyltrimethallylsilane (CAS No. 928139-38-2) and 3-azidopropyltrimethallylsilane (**1c**, CAS No. 928139-43-9) were prepared by using the same procedures for preparing 11-chloroundecyltrimethallylsilane and 11-azidoundecyltrimethallylsilane, respectively.

11-aminoundecyltrimethallylsilane: A round-bottomed flask (10 mL) was charged with 11azidoundecyltrimethallylsilane (1.35 g, 3.5 mmol) and THF (5 mL), and triphenylphosphine (1 g, 3.8 mmol) and distilled water (100 mg, 5.25 mmol) was added to the solution. The mixture was stirred at room temperature for 12 h and concentrated in vacuo. Pure 11aminoundecyltrimethallylsilane was obtained by using column chromatography (dichloromethane/methanol=9/1, $R_f=0.2$) (68% isolated yield). ¹H NMR(400 MHz, CDCl₃ δ): 4.62-4.53 (d, J=38.2 Hz, 6H), 2.68-2.65(t, J=6.8 Hz, 2H), 1.72(s, 9H), 1.62(s, 6H), 1.44-1.39(m, 2H), 1.33-1.22(m, 16H), 0.63-0.59(m, 2H); ¹³C NMR(100 MHz, CDCl₃ δ): 143.5, 109.6, 42.4, 34.0, 29.89, 29.86, 29.80, 29.7, 29.4, 27.1, 25.8, 24.3, 23.8, 13.4; IR spectrum (neat) 3300, 3074, 2965, 2922, 2851, 2725, 1747, 1637, 1574, 1493, 1454, 1373, 1313, 1279, 1168, 999, 973, 871, 837, 781, 732 cm⁻¹; Anal. Calcd for C₂₃H₄₅NSi: C, 75.96; H, 12.47; N, 3.85; found: C, 70.53; H, 13.85; N, 3.86.

Preparation of 4-(pyren-1-yl)-1-(11-(tris(2-methylallyl)silyl)undecyl)-1H-1,2,3-triazole (1a): CuSO₄•5H₂O (84 mg, 0.34 mmol) and sodium ascorbate (133 mg, 0.67 mmol) were dissolved in H₂O (5 mL). The resulting mixture was added to a solution of 11azidoundecyltrimethallylsilane **1d** (1.31 g, 3.37 mmol) and 1-ethynylpyrene (769 mg, 3.37 mmol) in THF/H₂O (10 mL/5 mL). The mixture was stirred at 80 °C for 24 h. Saturated NH₄Cl solution (aq.) was added and the mixture was extracted with diethyl ether. The organic layer was dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. Pure **1a** was obtained by using column chromatography (*n*-hexane:ethyl acetate=4:1, R_f=0.2) (pale yellow solid, 1.4 g, 66% yield). Mp: 86-87 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.70 (d, *J* = 9.28 Hz, 1H), 8.21-8.14 (m, 4H), 8.09-7.97 (m, 4H), 7.83 (s, 1H), 4.62 (d, *J*=37.44 Hz, 6H), 4.41 (t, *J* = 7.28 Hz, 2H), 2.00-1.92 (m, 2H), 1.76 (s, 9H), 1.66 (s, 6H), 1.34-1.27 (m, 16H), 0.67-0.63 (m, 2H); ¹³C NMR (100MHz, CDCl₃ δ): 147.4, 143.4, 131.5, 131.3, 131.0, 128.6, 128.2, 127.9, 127.4, 127.2, 126.1, 125.5, 125.5, 125.4, 125.2, 125.1, 124.9, 124.8, 122.8, 109.5, 50.6, 34.0, 30.5, 29.7, 29.6, 29.4, 29.2, 26.7, 25.8, 24.2, 23.8, 13.3; IR (KBr): 3076, 3045, 2920, 2850, 1635, 1604, 1585, 1461, 1436, 1371, 1278, 1168, 1058, 871 cm⁻¹; Anal. Calcd for C₄₁H₅₃N₃Si: C, 79.95; H, 8.67; N, 6.82; found: C, 80.55; H, 9.14; N, 7.11.

DABS-aminoundecyltrimethallylsilane (1b): A 20 mL round-bottom flask was charged with dabsyl chloride (400 mg, 1.24 mmol), triethylamine (160 mg, 1.57 mmol), 11aminoundecyltrimethallylsilane (573 mg, 1.58 mmol) and acetonitrile (6 mL). The mixture was stirred at room temperature for 12 h. Saturated NaHCO₃ (aq) solution was added to the mixture, which was then extracted with dichloromethane. The organic layer was dried over anhydrous MgSO₄, filtered through celite pad and concentrated *in vacuo* giving a residue that was subjected to column chromatography (*n*-hexane:ethyl acetate = 1:1, R_f = 0.7) to give (76% isolated yield). ¹H NMR(400 MHz, CDCl₃ δ): 7.96-7.88 (m, 6H), 6.76-6.74 (d, *J*=8.8 Hz, 2H), 4.62-4.53 (d, *J*=39.2 Hz, 6H), 4.53 (br s, 1H), 3.11 (s, 6H), 2.98-2.93 (q, *J*=6.8 Hz, 2H), 1.72 (s, 9H), 1.62 (s, 6H), 1.47-1.42 (m, 2H), 1.32-1.20 (m, 16H), 0.62-0.58 (m, 2H); ¹³C NMR(100 MHz, CDCl₃ δ) 155.8, 153.2, 143.7, 143.5, 139.5, 128.2, 125.9, 122.8, 111.6, 109.6, 43.5, 40.5, 34.0, 29.8, 29.7, 29.6, 29.4, 29.3, 26.7, 25.8, 24.2, 23.8, 13.4; IR spectrum (neat) 3281, 3072, 2966, 2922, 2853, 1755, 1637, 1607, 1519, 1444, 1422, 1391, 1370, 1325, 1278, 1229, 1162, 1141, 1089, 1000, 871, 843, 820, 700, 640 cm⁻¹; Anal. Calcd for C₃₇H₅₈N₄O₂SSi: C, 68.26; H, 8.98; N, 8.61; found: C, 68.23; H, 10.85; N, 8.71.

*1-mesityl-3-(11-(tris(2-methylallyl)silyl)*undecyl)-*1H-imidazol-3-ium chloride (1e)*: A 10mL round-bottom flask was charged with 1-mesityl-1H-imidazole (573 mg, 3.08 mmol), 11-

chloroundecyltrimethallylsilane (1.41 g, 3.69 mmol) and acetonitrile (4mL). The mixture was stirred at 120 °C for 24 h. After the reaction, the solvent was evaporated and the mixture was decanted with hexane for several times to give (pale yellow sticky oil, 1.6 g, 91% isolated yield). ¹H NMR (400 MHz, CD₂Cl₂ δ): 10.88 (s, 1H), 7.84 (s, 1H), 7.27 (s, 1H), 7.02 (s, 2H), 4.61-4.52 (d, *J*=35.2 Hz, 6H), 4.58 (t, *J*=7.2 Hz, 2H), 2.33 (s, 3H), 2.06 (s, 6H), 1.95 (m, 2H), 1.71 (s, 9H), 1.62 (s, 6H), 1.33-1.24 (m, 16H), 0.64-0.60 (m, 2H); ¹³C NMR (100MHz, CD₂Cl₂ δ): 143.8, 141.5, 139.4, 134.8, 131.4, 130.1, 123.6, 123.0, 109.6, 50.5, 34.3, 30.8, 30.0, 29.9, 29.7, 29.5, 26.6, 25.8, 24.4, 24.0, 21.3, 17.8, 13.6 ppm; IR spectrum (neat): 3074, 2923, 2854, 1636, 1566, 1547, 1487, 1454, 1373, 1279, 1204, 1165, 1069, 1035, 1000, 973, 935, 871, 839, 781, 670 cm⁻¹; Anal. Calcd for C₃₅H₅₇ClN₂Si: C, 73.83; H, 10.09; N, 4.92; found: C, 73.16; H, 10.85; N, 5.02.

Dissociation of methallylsilyl group under acidic SBA-15 synthetic condition:

In order to demonstrate that dissociation of all methallyl groups of trimethallylsilane derivatives (1) occurs under acidic reaction conditions, 3-chloropropyltrimethallylsilane was used as a substrate. NMR analysis showed that treatment of 3-chloropropyltrimethallylsilane (0.1 mmol) with 2 M HCl in CD₃CN, leads to complete loss of all resonance associated with the methallylsilane group within 5 min (Figure S1). This result shows that organotrimethallylsilane derivatives can be successfully applied to the synthesis of organic group-functionalized SBA-15 under SBA-15 synthetic condition.

Representative Procedure for One-Step Preparation of Functional SBA-15:

The composition of the reagents used in the syntheses of all SBA-15 samples described in this manuscript was a molar ratio of x TEOS : 100-x organotrimethallylsilanes (1) : 6.1 HCl : 0.017 P123 : 165 H₂O. A solution of pluronic P123 (500 mg) in distilled water (4 mL) was stirred at 35 °C for 4 h. Then, 2 M HCl solution (15 mL) was added, and the mixture was

stirred vigorously for 1 h at ambient temperature and 40 °C for additional 1 h. After adding TEOS dropwise, the mixture was stirred for 3 h. A solution of trimethallylsilane derivative was added slowly (In the cases of using solid trimethallylsilane derivatives, they were dissolved in small amounts of dichloromethane or acetone.), and the mixture was stirred vigorously for 21 h, transferred to a hydrothermal reactor, and let stand at 100 °C for 48 h. The mixture was washed with excess H₂O, ethanol, acetone and diethyl ether thoroughly to give a powder, which was dispersed in ethanol, and the resulting slurry was stirred at 80 °C for 24 h. The mixture was filtered, and the precipitate was washed with ethanol and acetone thoroughly. The resulting powder was dried *in vacuo* to obtain organic group-functionalized SBA-15.

Preparation of amine functionalized SBA-15 (**Pr-NH**₂**@**Si and **Und-NH**₂**@**Si) by using Staudinger reaction on silica: Azide functionalized SBA-15, **Und-N**₃**@**Si (100 mg, 0.052 mmol N₃ groups), was dispersed in 5 mL THF and H₂O (9.36 mg, 0.52 mmol) and triphenylphosphine (68 mg, 0.26 mmol) was added. The mixture was stirred at room temperature for 12 h. The resulting slurry was filtered, and the precipitate was washed with dichloromethane and acetone thoroughly. The resulting solid was dried *in vacuo* to give 11-aminoundecyl group functionalized SBA-15 (**Und-NH**₂**@**Si). For preparing **Pr-N**₃**@**Si, the reaction was carried out at 55 °C. Conversion of the azide to the amine group was determined by monitoring the 2110 cm⁻¹ peak in the FT-IR spectrum (Figure S2).

Knoevenagel reaction using amine-group functionalized SBA-15 (**Pr-NH**₂**@**Si or Und-NH₂**@**Si): Benzaldehyde (53 mg, 0.5 mmol) and malononitrile (34 mg, 0.51 mmol) were added to a slurry of amine functionalized SBA-15 (**Pr-NH**₂**@**Si or Und-NH₂**@**Si), 10 mg) dispersed in cyclohexane (1 mL). The mixture was stirred at room temperature. The reaction progress was monitored by using gas chromatography.

Preparation of palladium functionalized SBA-15 (Pd-NHC@Si):

TMCS (Trimethylsilylchloride, 2.3 mL, 18.1 mmol) was added to a mixture of imidazolium group functionalized SBA-15 (**Imid@Si**, 0.3 g) in dry toluene (10 mL) at 70 °C. The mixture was maintained for 24 h. Pd(OAc)₂ (11.2 mg, 0.05 mmol) was added to the slurry of imidazolium group functionalized SBA-15-site isolated (0.1 g) dispersed in acetonitrile (0.7 mL) and the mixture was stirred at 83 °C for 24 h. The **Pd-NHC@Si** was obtained as a beige powder by filtration through paper. ICP-AES analysis: calculated 11% Pd, found 2.9% Pd (original data was shown as 29383.854 mg/kg of Pd onto the surface).

Suzuki reaction using palladium functionalized SBA-15 (Pd-NHC@Si):

Phenylboronic acid (24.5 mg, 0.2 mmol), 4-iodotoluene (21.8 mg, 0.1 mmol), potassium carbonate (27.5 mg, 0.2 mmol) and palladium functionalized SBA-15 (**Pd-NHC@Si**, 20 mg) were dispersed in a water:2-methoxyethanol = 1:3 solution. The mixture was stirred at room temperature for 1 h and subjected to centrifugation to give recovered **Pd-NHC@Si**, which was reused in a next recycle reaction as a catalyst.

Figure of experimental section (Figure S1-S4)



Figure S1. NMR monitoring of dissociation of methallyl groups under acidic conditions. Dichlorobenzene (DCB) was used as an internal standard.



Figure S2. ¹³C NMR spectrum of 1a (upper) and ¹³C CP-MAS solid state NMR spectrum of Pyr@Si(15%) (lower). Peaks marked *m*, which correspond to the methallyl group in 1a are not present in the spectrum of Pyr@Si(15%).



Figure S3. FT-IR data for Pr-NH₂@Si and Und-NH₂@Si synthesized from Pr-N₃@Si and Und-N₃@Si.



Figure S4. ¹³C NMR spectrum of **1e** (upper) and ¹³C CP-MAS solid state NMR spectrum of **Imid@Si** (lower). Peaks marked *m*, which correspond to the methallyl group in **1e** are not present in the spectrum of **Imid@Si**.



Figure S5. ²⁹Si CP-MAS (top) and MAS (bottom) solid state NMR spectrum of **Imid@Si**. Peaks marked Q_3 and Q_4 correspond to the silanol group and the silicate group, respectively. Peaks marked T_3 correspond to the functional group-impregnated silane group in **Imid@Si**.

Results of elemental analysis of functionalized SBA-15

sample	Loading rate	Elemental analysis		
	(mmol g ⁻¹)	C (%)	H (%)	N (%)
Pyr@Si(1%)	0.12	10.14	1.84	0.53
Pyr@Si (5%)	0.40	18.63	2.65	1.72
Pyr@Si (10%)	0.77	39.95	4.7	3.25
Pyr@Si (15%)	1.00	38.70	4.28	4.21
Dabsyl@Si(1%)	0.11	12.50	1.59	0.60
Dabsyl@Si(5%)	0.51	22.41	3.57	2.87
Dabsyl@Si(10%)	0.72	30.32	4.61	4.03
Dabsyl@Si(15%)	0.78	34.72	3.95	4.38
Pr-N ₃ @Si	0.50	8.60	2.79	2.09
Und-N ₃ @Si	0.52	14.48	2.83	2.19
Imid@Si	1.13	24.39	3.80	3.16

BET surface areas (m²/g), pore sizes (nm) and pore volumes (cm³/g) of functionalized

SBA-15 materials

	Surface area (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)
Pyr@Si(1%)	577.1	7.71	1.11
Pyr@Si (5%)	368.5	6.81	0.63
Pyr@Si (10%)	164.8	8.09	0.33
Pyr@Si (15%)	139.3	8.16	0.28
Dabsyl@Si(1%)	505.2	8.42	1.06
Dabsyl@Si(5%)	535.1	8.56	1.14
Dabsyl@Si(10%)	395.3	8.31	0.82
Dabsyl@Si(15%)	242.3	10.9	0.66

Pr-N ₃ @Si	409.6	6.43	0.66
Und-N ₃ @Si	385.9	6.64	0.64
Imid@Si	368.8	7.01	0.65

SEM and TEM images of functionalized SBA-15

- SEM images of **Pyr@Si(15%)**



- TEM images of **Pyr@Si(X%)** [**X**=1, 5, 10 and 15]



- TEM images of **Dabsyl@Si(X%)** [**X**=1, 5, 10 and 15]



- TEM images of Pr-N₃@Si and Und-N₃@Si



- TEM images of Imid@Si



XPS of Pd-NHC complex functionalized SBA-15 (Pd-NHC@Si)

- XPS of Pd-NHC complex functionalized SBA-15



- XPS of Pd-NHC complex functionalized SBA-15 after 5th recycle



¹H and ¹³C NMR spectra for new compounds

-¹H NMR of 3-Chloropropyltrimethallylsilane



-¹H NMR of 3-azidopropyltrimethallylsilane (1c)







-¹H NMR of 11-Azidoundecyltrimethallylsilane (1d)



-¹H NMR of 11-aminoundecyltrimethallylsilane







-¹H NMR of DABS-aminoundecyltrimethallylsilane (1b)









References

(1) For a book chapter, see W. L. F. Armarego and D. D. Perrin, *Purification of laboratory chemicals (4th edition)*; Butterworth Heinemann, Oxford, UK, 2001, pp. 176, 334.
(2) J. Nakazawa, B. J. Smith and T. D. P. Stack, *J. Am. Chem. Soc.*, 2012, **134**, 2750.