

Electronic Supplementary Information

Direct cross-linking of silyl-functionalized cage siloxanes *via* nonhydrolytic siloxane bond formation for preparing nanoporous materials

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1. Experimental Details

Materials

The following reagents were used as received without purification: ethanol (Junsei Chemical Co., Ltd., >99.5%), hexane (Junsei Chemical Co., Ltd., >96.0%), 6 mol L⁻¹ hydrochloric acid (FUJIFILM Wako Pure Chemical Corporation), 8 mol L⁻¹ potassium hydroxide (KOH) solution (FUJIFILM Wako Pure Chemical Corporation), pyridine (FUJIFILM Wako Pure Chemical Corporation, >99.5%), tetrahydrofuran (THF, stabilizer free, FUJIFILM Wako Pure Chemical Corporation, >99.8%), tetramethylammonium (TMA) hydroxide pentahydrate (TMAOH·5H₂O, FUJIFILM Wako Pure Chemical Corporation, >97%), and α-cyclodextrin (αCD, Tokyo Chemical Industry Co., Ltd., >98.0%).

Procedure S1. Synthesis of TMA-D4R

Tetramethylammonium silicate with a D4R structure (TMA₈Si₈O₂₀·xH₂O, **TMA-D4R**) was synthesized according to our previous report.¹ TMAOH·5H₂O (50.15 g, 276.7 mmol), H₂O (24.8 mL, 1.38 mol), ethanol (161.0 mL, 2.757 mol), and TEOS (61.4 mL, 274.9 mmol) were mixed in a 300 mL beaker. The molar ratio was TEOS:TMAOH:ethanol:H₂O = 1:1:10:10. After stirring for 3 d at room temperature, the solvents were evaporated by heating until the liquid volume was reduced to almost half. After cooling, insoluble products were recovered by filtration and dried under reduced pressure to give a white solid (58.70 g). Selective formation of the D4R silicate was confirmed by ²⁹Si NMR (99.4 MHz, methanol-*d*₄, δ = -98.99 ppm).

Procedure S2. Synthesis of D4R-SiMe₂H

D4R-SiMe₂H was synthesized according to our previous report.² **TMA-D4R** (13.26 g) was dissolved in methanol (15 mL). The solution was added to the mixture of DMSCl (20 mL) and hexane (20 mL). After stirring for 1 h at room temperature, the hexane layer was extracted, and the volatile compounds were removed at 40 °C under reduced pressure. The resulting product was washed with acetonitrile to give a white solid (1.86 g). ¹H NMR (500.16 MHz, chloroform-*d*): δ (ppm) = 0.25 (d, *J* = 2.9 Hz, 48H, SiCH₃), 4.73 (m, 8H, SiH); ¹³C NMR (125.77 MHz, chloroform-*d*): δ (ppm) = 0.06; ²⁹Si NMR (99.37 MHz, chloroform-*d*): δ (ppm) = -1.39 ((SiO)SiMe₂H), -108.65 (Si(OSi)₄). The ¹H and ²⁹Si NMR spectra are shown in Fig. S1(a) and 1A(a), respectively.

Procedure S3. Synthesis of D6R-αCD

D6R-type potassium silicate sandwiched by two αCD (K₁₂Si₁₂O₃₀·2αCD·xH₂O, **D6R-αCD**) was synthesized according to the previous report³ with a slight modification. αCD (25.33 g, 26.03 mmol) and H₂O (152 mL, 8.44 mol) were added into a beaker. The mixture was ultrasonicated using an ultrasonic stirrer (35 W, 40KHz) (USS-1, NIHONSEIKI KAISHA LTD.) for 15 min to dissolve αCD in H₂O. Then, TEOS (35.1 mL, 158 mmol) and a KOH aqueous solution (8 mol L⁻¹, 19.6 mL) were added to the mixture. The mixture was stirred in a desiccator in the presence of separated ethanol to provide an ethanol vapor in the reaction system. After stirring for 7 d, white precipitates were recovered by filtration and dried under reduced pressure to give a white solid (40.01 g). The ²⁹Si MAS NMR

spectrum of the product showed overlapped signals assigned to Q³ (Si(OSi)₃O⁻) at $\delta = -99.2$, -100.1 , and -100.5 ppm.

Procedure S4. Synthesis of D6R-SiMe₂H

D6R-SiMe₂H was synthesized according to our previous report.⁴ DMSCl (50.0 mL, 460 mmol), pyridine (30.0 mL, 372 mmol), and D6R- α CD (10.0 g, 2.6 mmol) were added to THF (100 mL) cooled in an ice bath (0 °C). The mixture was stirred at 0 °C for 2 h and then at room temperature for 1 d. After the stirring, ethanol (26.8 mL) and hexane (~50 mL) were added to the mixture and the mixture was stirred at 0 °C for several minutes in an ice bath. The precipitate was removed via filtration and the solvent was removed at 40 °C under reduced pressure. After the addition of hexane (~50 mL) to the resulting solid, the insoluble component was removed via filtration, and the solvent was removed at 40 °C under reduced pressure to form a white solid (1.81 g). ¹H NMR (500.16 MHz, chloroform-*d*): δ (ppm) = 0.24 (d, *J* = 2.3 Hz, 72H; SiCH₃), 4.74 (m, 12H, SiH); ¹³C NMR (125.77 MHz, chloroform-*d*): δ (ppm) = 0.15; ²⁹Si NMR (99.37 MHz): δ (ppm) = -2.35 ((SiO)SiMe₂H), -109.58 (Si(OSi)₄). The ¹H and ²⁹Si NMR spectra are shown in Figs. S2(a) and 1B(a), respectively.

2. Additional Data

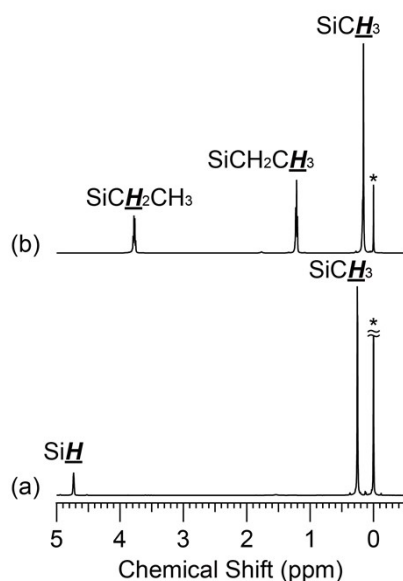


Fig. S1. ¹H NMR spectra of (a) D4R-SiMe₂H and (b) D4R-SiMe₂OEt.

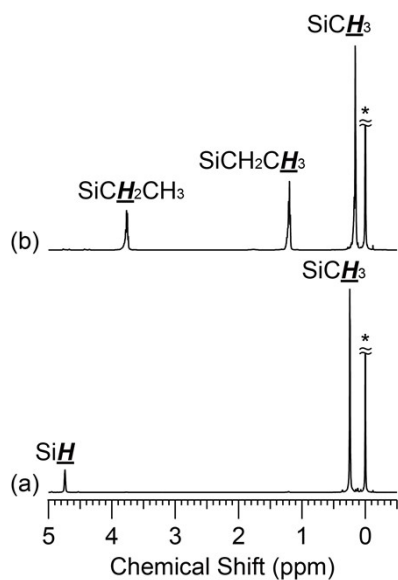


Fig. S2. ^1H NMR spectra of (a) **D6R-SiMe₂H** and (b) **D6R-SiMe₂OEt**.

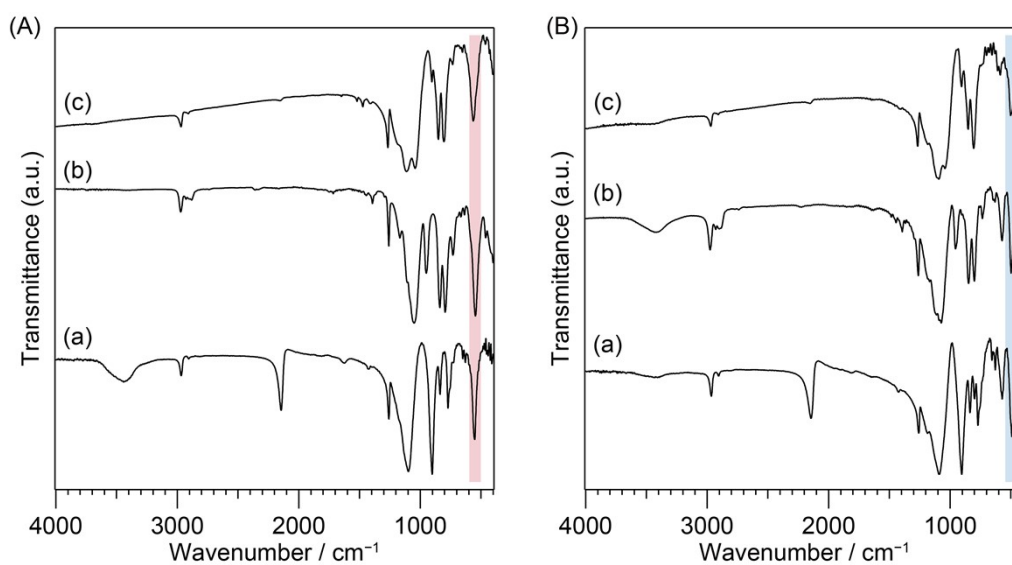


Fig. S3. (A) FT-IR spectra of (a) **D4R-SiMe₂H**, (b) **D4R-SiMe₂OEt**, and (c) **D4R-PR**. (B) FT-IR spectra of (a) **D6R-SiMe₂H**, (b) **D6R-SiMe₂OEt**, and (c) **D6R-PR**.

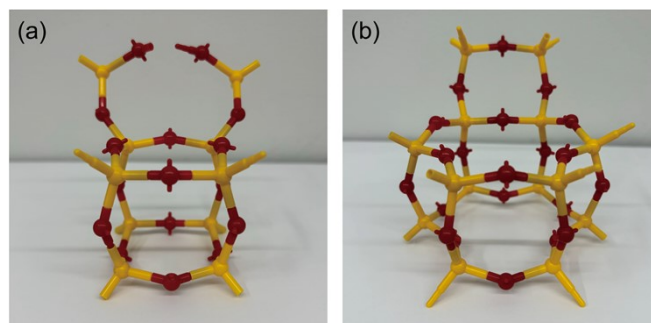


Fig. S4. Molecular models for intramolecular condensation of the adjacent silyl groups of cage siloxanes. (a) In D4R siloxane, formation of the tetrasiloxane ring cannot occur. (b) In D6R siloxane, the tetrasiloxane ring can be formed.

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