

Electronic Supplementary Information

Synthesis of a 12-Membered Cyclic Siloxane Possessing Alkoxysilyl Groups as a Nanobuilding Block and Its Use for Preparation of Gas Permeable Membrane

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1. ^{13}C NMR spectrum of 12MR-Me-TES

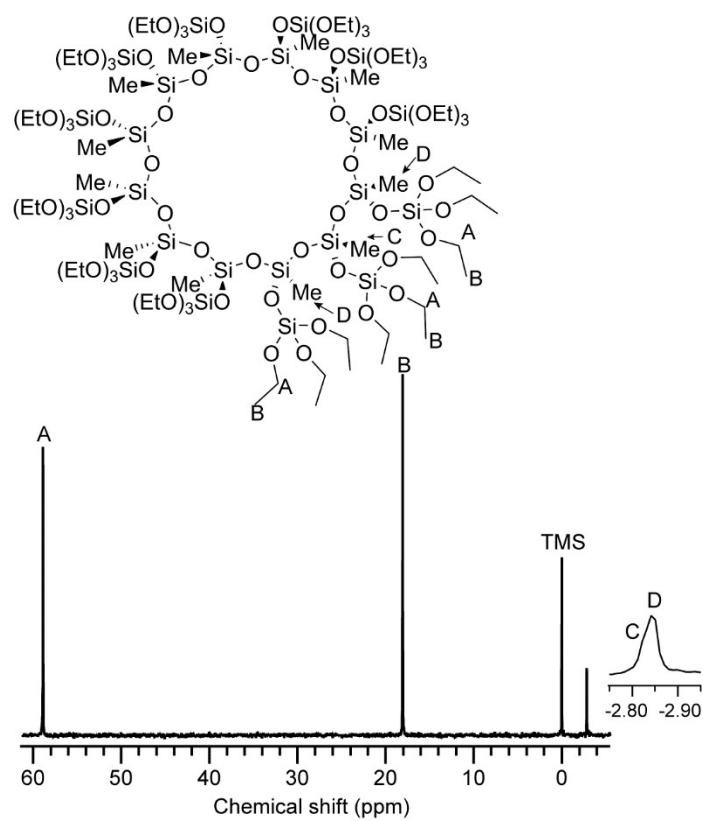


Figure S1 ^{13}C NMR spectrum of 12MR-Me-TES.

2. Solid-state NMR and FT-IR spectra of 12MR-Me-*TES*-derived gel

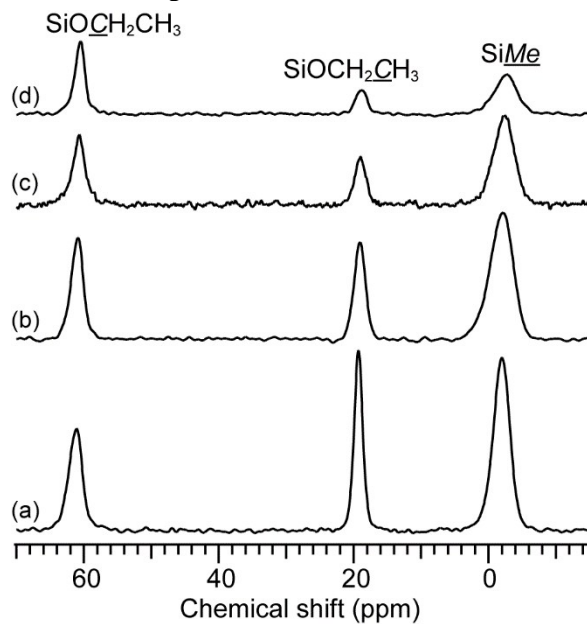


Figure S2 ^{13}C CP/MAS NMR spectra of **12MR-Me-*TES***-derived gel. (a) **12MR-gel-as**, (b) **12MR-gel-heat100**, (c) **12MR-gel-heat200**, and (d) **12MR-gel-heat300**.

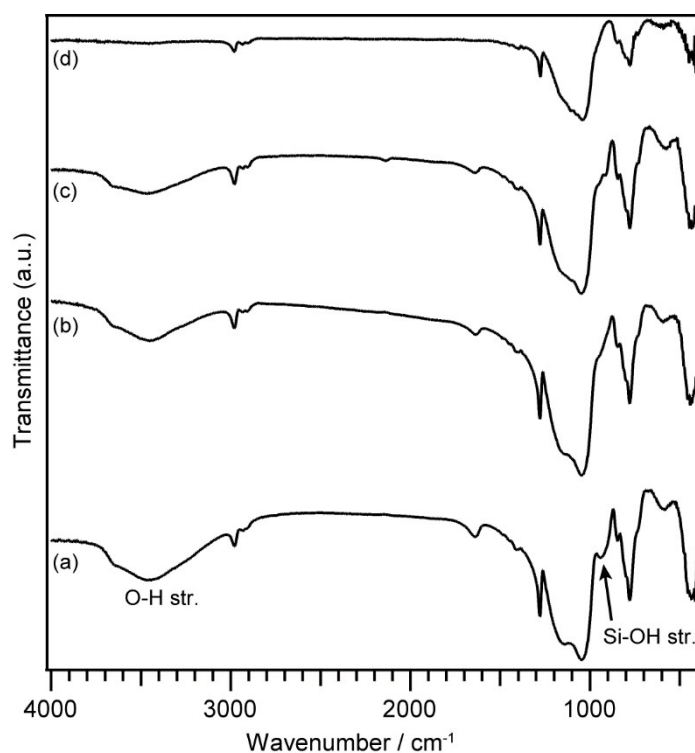


Figure S3 FT-IR spectra of **12MR-Me-*TES***-derived gel. (a) **12MR-gel-as**, (b) **12MR-gel-heat100**, (c) **12MR-gel-heat200**, and (d) **12MR-gel-heat300**.

3. Solid-state NMR spectra of 12MR-gel-as prepared with different hydrolysis time

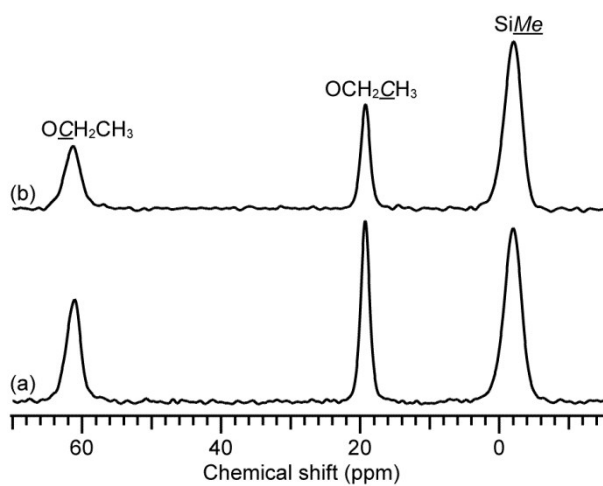


Figure S4 ^{13}C CP/MAS NMR spectra of **12MR-gel-as** prepared with different hydrolysis time. (a) 1 d and (b) 2 d.

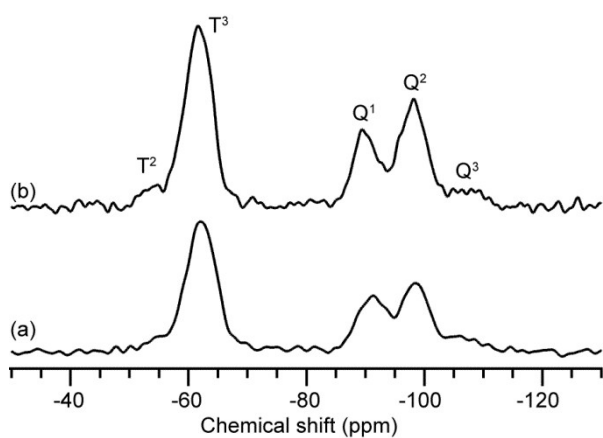


Figure S5 ^{29}Si MAS NMR spectra of **12MR-gel-as** with different hydrolysis time. (a) 1 d and (b) 2 d.

4. Solid-state NMR spectra of TEOS-MTES-derived gels

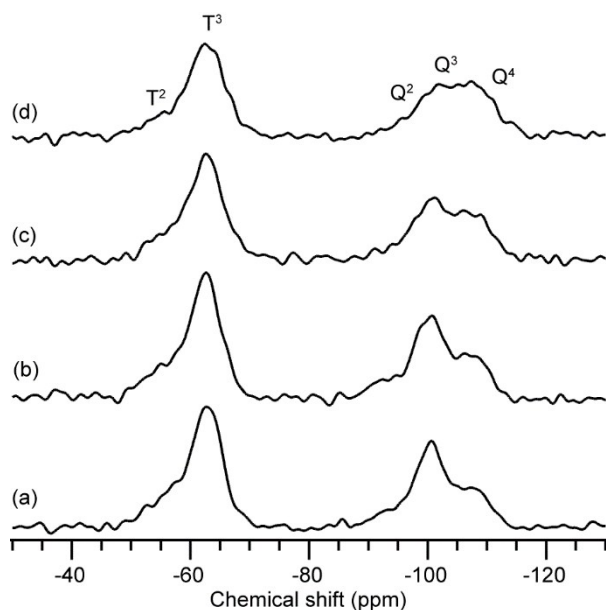


Figure S6 ^{29}Si MAS NMR spectra of TEOS-MTES-derived gel.

(a) **TEOS-MTES-gel-as**, (b) **TEOS-MTES-gel-heat100**, (c) **TEOS-MTES-gel-heat200**, and (d) **TEOS-MTES-gel-heat300**.

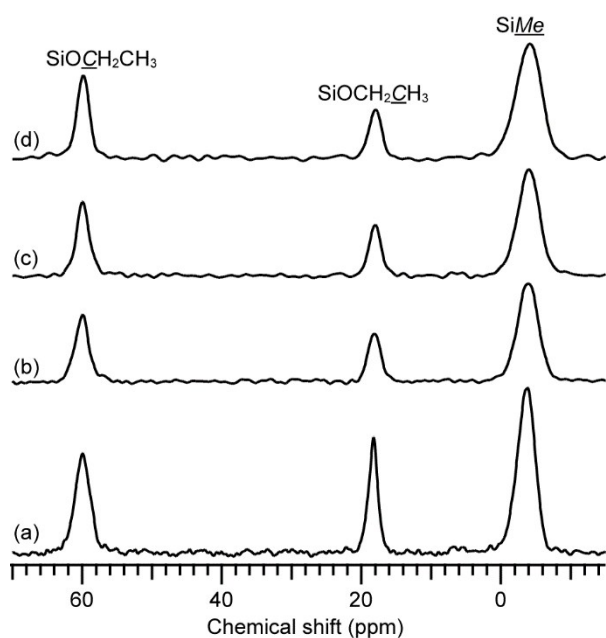


Figure S7 ^{13}C CP/MAS NMR spectra of TEOS-MTES-derived gel.

(a) **TEOS-MTES-gel-as**, (b) **TEOS-MTES-gel-heat100**, (c) **TEOS-MTES-gel-heat200**, and (d) **TEOS-MTES-gel-heat300**.

5. Characterization of $\text{Cu}_4\text{Na}_4(\text{MeSiO}_2)_{12}\cdot x(n\text{BuOH})\cdot y\text{H}_2\text{O}$

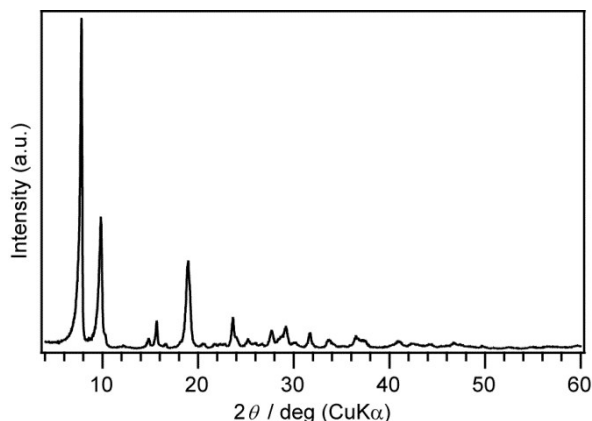


Figure S8 Powder XRD pattern of $\text{Cu}_4\text{Na}_4(\text{MeSiO}_2)_{12}\cdot x(n\text{BuOH})\cdot y\text{H}_2\text{O}$.

Experimental procedure for trimethylsilylation of $\text{Cu}_4\text{Na}_4(\text{MeSiO}_2)_{12}\cdot x(n\text{BuOH})\cdot y\text{H}_2\text{O}$

$\text{Cu}_4\text{Na}_4(\text{MeSiO}_2)_{12}\cdot x(n\text{BuOH})\cdot y\text{H}_2\text{O}$ (0.1 g) was added to a mixture of dehydrated toluene (20 mL) and dehydrated pyridine (0.58 mL, 7.2 mmol). After stirring until homogenization at room temperature under N_2 atmosphere, chlorotrimethylsilane (0.91 mL, 7.2 mmol) was added to the mixture and blue green precipitates were formed. After stirring the mixture at 40 °C for 24 h, dehydrated ethanol (0.42 mL, 7.2 mmol) was added to the mixture for alkoxylation of remaining chlorotrimethylsilane. The mixture was stirred at room temperature for 30 min, and the precipitates were removed by suction filtration with Celite®. The filtrate was evaporated to obtain a colorless viscous liquid.

Trimethylsilylated 12-membered ring siloxane: δ H (500.13 MHz; CDCl_3 ; TMS) 0.08 (s, 36H, O_3SiCH_3), 0.11 (s, 108H, $\text{OSi}(\text{CH}_3)_3$); δ C (125.76 MHz; CDCl_3 ; TMS) -2.06 (SiCH_3), -2.01 (SiCH_3), 1.81 ($\text{OSi}(\text{CH}_3)_3$), 1.84 ($\text{OSi}(\text{CH}_3)_3$); δ Si (99.36 MHz; CDCl_3 ; TMS) -67.5 (T^3 , 4Si, O_3SiMe), -67.2 , (T^3 , 8Si, O_3SiMe), 7.61 (M^1 , 8Si, OSiMe_3), 7.67 (M^1 , 4Si, OSiMe_3); MS (Electrospray ionization, 2 kV): calcd. for $\text{C}_{48}\text{H}_{144}\text{O}_{24}\text{Si}_{24}\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 1799.4 ; found: 1799.3.

6. Experimental apparatus for a single-gas permeation measurement

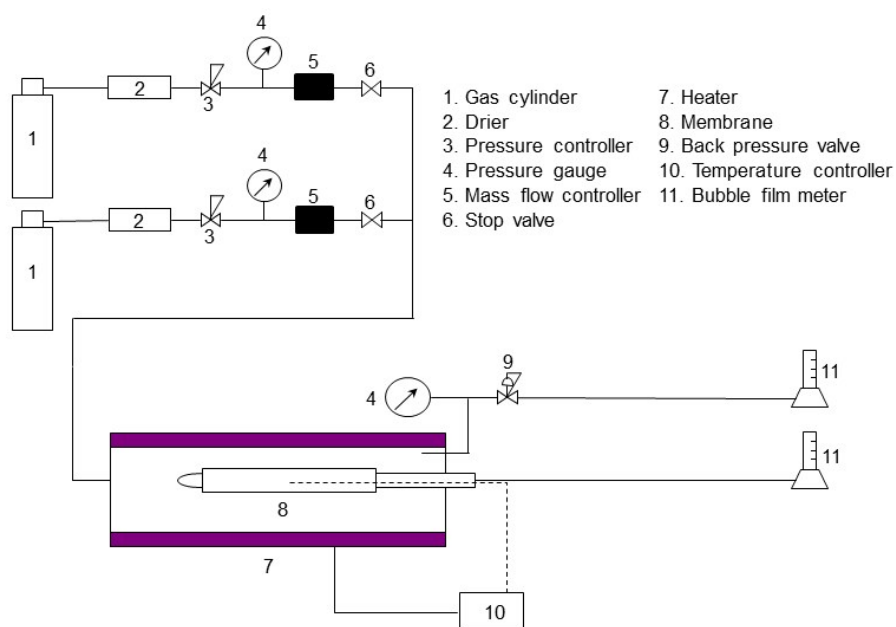


Figure S9 Experimental apparatus for a single-gas permeation measurement.