

Supporting Information

for

In Situ Selective Ligand Transformation from Si–H to Si–OH for Synergistic Assembly of Hydrogen-bonded Metal–Organic Frameworks

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General Information

All manipulations of air- and/or moisture-sensitive compounds were performed either using the standard Schlenk-line technique or in a glove box filled with argon atmosphere. Anhydrous THF, Et₂O, and hexane were dried by passing through columns of activated alumina and supported copper catalyst supplied by Shanghai MIKROUNA Co., Ltd (SolvPurer A5/G5). Trichlorosilane was distilled over calcium hydride (CaH₂) prior to use. Other chemicals were used as received.

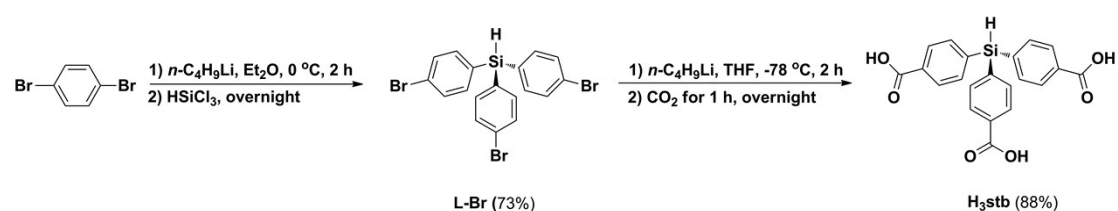
The single crystal X-ray diffraction analyses of the SiMOF-1 and SiMOF-2 were performed at 293(2) K and 150(2) K, respectively. Reflections were collected on a Bruker APEX II CCD using graphite-monochromated Mo *K*α radiation ($\lambda = 0.71073$ Å) or Cu *K*α radiation ($\lambda = 1.54178$ Å). Structures were determined by direct methods and refined by least squares on F² using the SHELX suit of programs. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were constrained in geometrical positions to their parent atoms. The solvated atoms located at the packing cavities of SiMOFs were treated as diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON.

The nuclear magnetic resonance (NMR) measurements were measured on Bruker AV600 spectrometer (600 MHz for ¹H, 151 MHz for ¹³C, and 119 MHz for ²⁹Si). Powder X-ray diffraction patterns (PXRD) were measured by a D8 ADVANCE (Bruker AXS Inc. Madison, WI, 2001) (Cu *K*α, $\lambda = 0.15418$ nm) at 45 kV and 40 mA at ambient temperature. Thermal gravimetric analyses (TGA) were carried out on a Perkin-Elmer Pyris 1 instrument, under a constant stream of dry nitrogen gas (flow rate, 20 mL min⁻¹) over a temperature range of 22 – 800 °C and at a heating rate of 5 °C min⁻¹. The Gas Chromatography–Mass Spectrometry was measured on a GCMS-QP2010 SE, SHIMADZU instrument. Fourier transform infrared (FT-IR) data were collected on a Bruker ALPHA FTIR spectrometer from 400 to 4000 cm⁻¹ at room temperature.

BET surface area measurements were carried out on a Micromeritics ASAP 2020 instrument. The N₂ sorption isotherms were recorded at 77 K and the CO₂ sorption

isotherms were recorded at 273 K and 298 K, respectively. Generally, prior to the measurements, materials are activated under dynamic vacuum (1×10^{-4} Pa) using a Micromeritic SmartVacPrep sample preparation unit. The activation procedures are as following: 1) MOFs were collected after filtration and washed by DMF and EtOH for three times respectively. 2) The collected MOFs were soaked in ethanol for 3 d and exchanged with fresh ethanol every day. 3) The ethanol solvent was removed and the MOF crystals were activated at 80 °C under dynamic vacuum (1×10^{-4} Pa) for 24 h.

Synthesis and Characterization of The Linker



L-Br (tris(4-bromophenyl)silane) was synthesized according to the literature.^[1]

Synthesis of **H₃stb** (4,4',4''-silanetriyltribenzoic acid)

4,4',4''-silanetriyltribenzoic acid (H₃stb) The synthesis of H₃stb was carried out under argon atmosphere. To a anhydrous THF solution (100 mL) of L-Br (5.0 g, 10.0 mmol) was added dropwise a *n*-butyllithium solution (2.5 M, 12.0 ml, 30.0 mmol) at -78 °C in 0.5 h. And then the mixture was stirred at this temperature for 1 h. Subsequently the yellow mixture was bubbled with dry CO₂ gas for 1 h and allowed to ambient temperature overnight. The reaction was quenched with water and adjusted the pH to 6 by aqueous HCl (1.0 M). The mixture was then extracted with ethyl acetate (4 × 20 mL). The combined organic layers were dried over MgSO₄ and evaporated to get crude product. The crude product was purified by silica gel column chromatography to afford the pure compound H₃stb (3.5 g, 88.0 %) as a white solid. ¹H NMR (600 MHz, Methanol-*d*₄) δ 8.06 (d, J = 8.1 Hz, 6 H), 7.70 (d, J = 8.1 Hz, 6 H), 5.54 (s, 1 H); ¹³C NMR (151 MHz, DMSO-*d*₆) δ 167.31, 141.02, 134.66, 132.14, 128.62.; ²⁹Si NMR (119 MHz, DMSO-*d*₆) δ -19.21. IR (cm⁻¹): 2667 (w), 2541 (w), 2121 (w), 1684 (s), 1599 (w), 1554 (w), 1418 (m), 1389 (w), 1319 (w), 1286 (s), 1187

(w), 1133 (w), 1101 (m), 1020 (w), 927 (w), 853 (w), 787 (s), 744 (s), 703 (s).

HRMS(ESI): $m/z[M+Na]^+$ calcd for $C_{21}H_{16}NaO_6Si$: 415.0614, found: 415.0608.

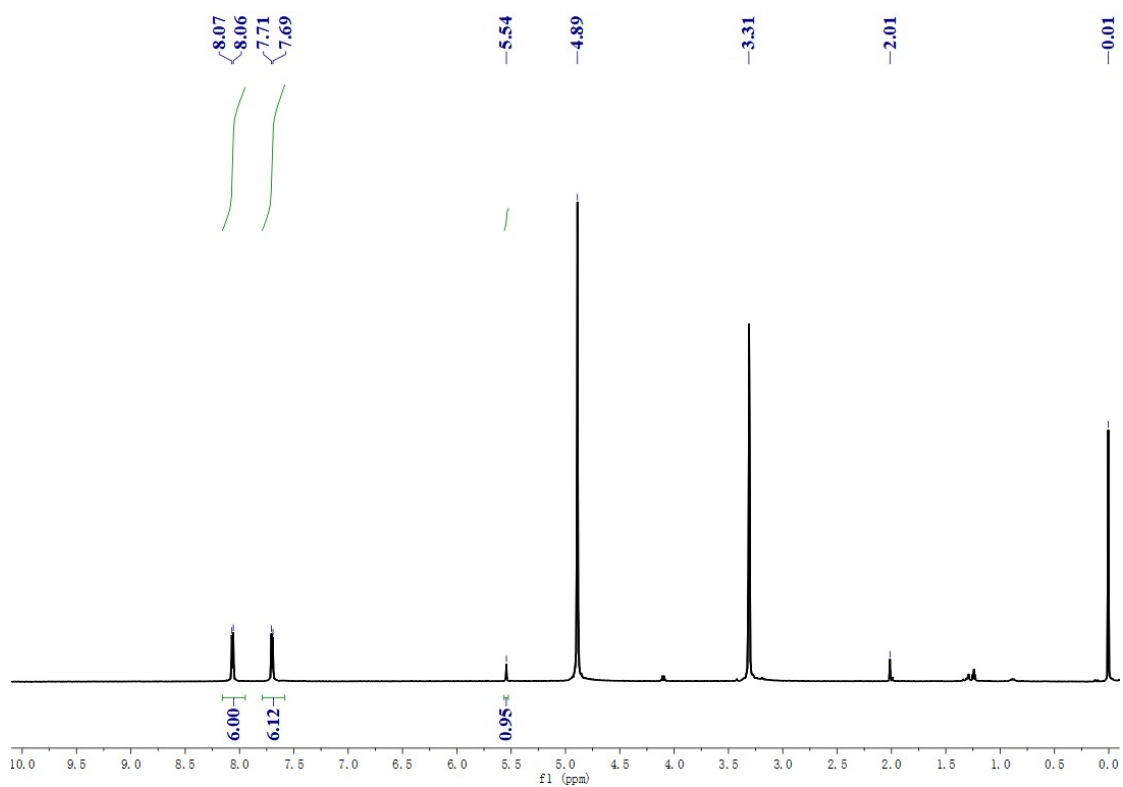


Figure S1. The 1H NMR spectrum of H_3stb (600 MHz, $Methanol-d_4$).

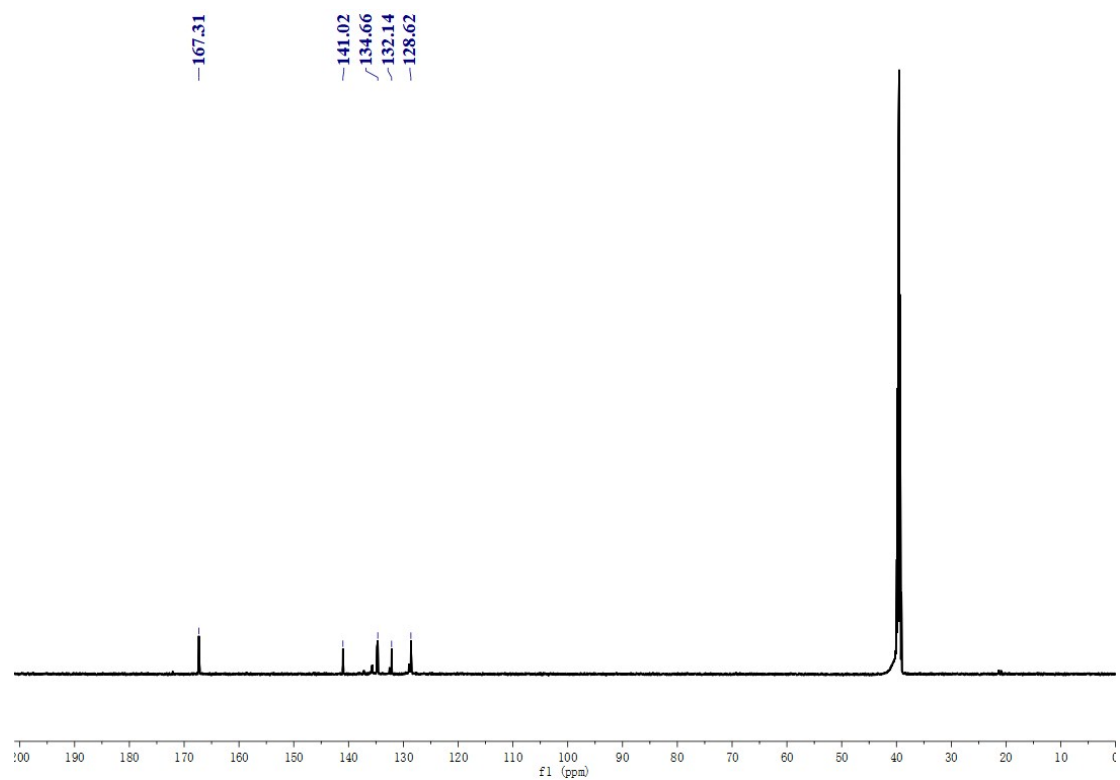


Figure S2. The ^{13}C NMR spectrum of H_3stb (151 MHz, $\text{DMSO-}d_6$).

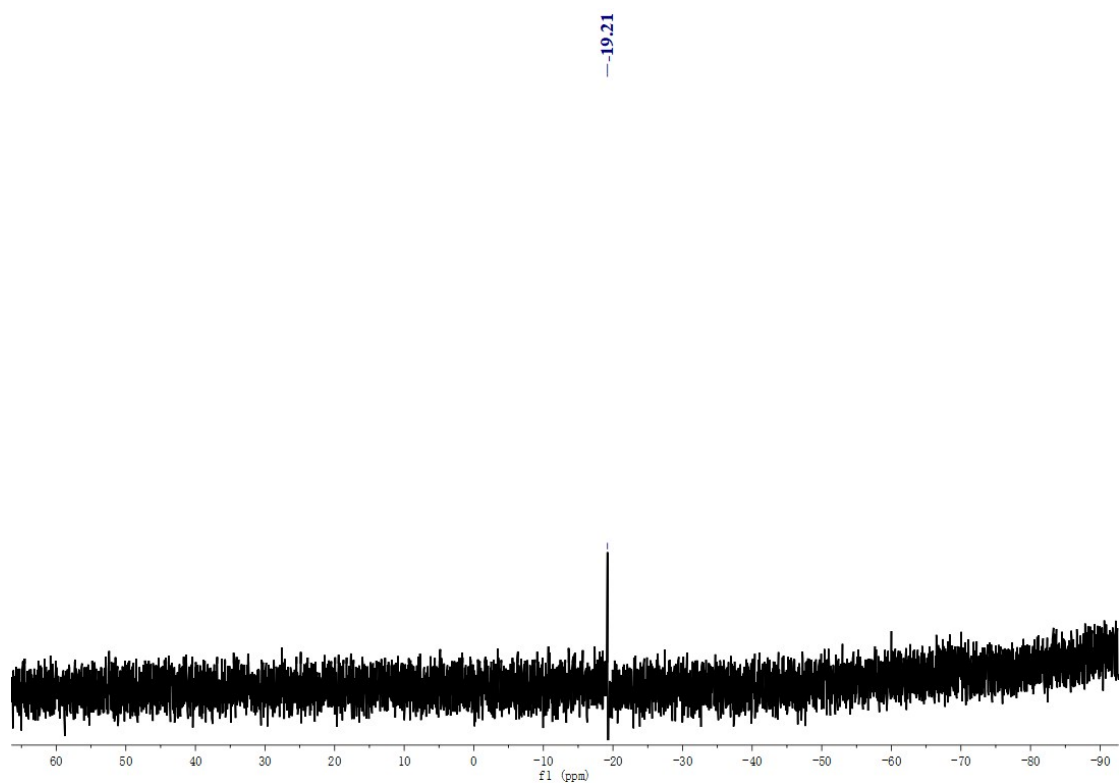


Figure S3. The ^{29}Si NMR spectrum of H_3stb (119 MHz, $\text{DMSO-}d_6$).

Synthesis and Characterization of MOFs

Synthesis of SiMOF-1

A mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ (5.6 mg, 0.020 mmol), H_3stb (4.0 mg, 0.010 mmol), DMF (1 mL), H_2O (100 μL) and con. HCl (10 μL) was put in a 5 ml glass tube. And then the sample was heated at 85 °C for 72 h. After cooling to room temperature, colorless crystals were harvested in 45% yield based on Zn. By comprehensive characterizations, the obtained SiMOF-1 was found to be the same as the reported IMP-19 synthesized from the silanol ligand.^[2] ^1H NMR (600 MHz, Methanol- d_4) of the digested SiMOF-1 by DCl (20% in D_2O) δ 8.08 (d, $J = 8.1$ Hz, 4 H), 8.04 (d, $J = 8.1$ Hz, 2 H), 7.72 (d, $J = 8.1$ Hz, 6 H).

Synthesis of SiMOF-2

A mixture of $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (7.0 mg, 0.028 mmol), H_3stb (4.0 mg, 0.010 mmol), DMF (800 μL), MeOH (1 mL) and con. HCl (10 μL) was put in a 5 ml glass tube. And then the sample was heated at 85 °C for 72 h, and subsequently cooled to room temperature. Colorless crystals were obtained in 46% yield based on H_3stb . IR (cm^{-1}): 1701 (w), 1598 (m), 1536 (m), 1102 (s), 1018 (w), 878 (w), 726 (s), 703 (m), 485 (m), 423 (m). ^1H NMR (600 MHz, Methanol- d_4) of the digested SiMOF-2 by DCl (20% in D_2O) δ 8.06 (d, $J = 8.2$ Hz, 2 H), 8.03 (d, $J = 8.2$ Hz, 4 H), 7.71 (d, $J = 8.2$ Hz, 6 H).

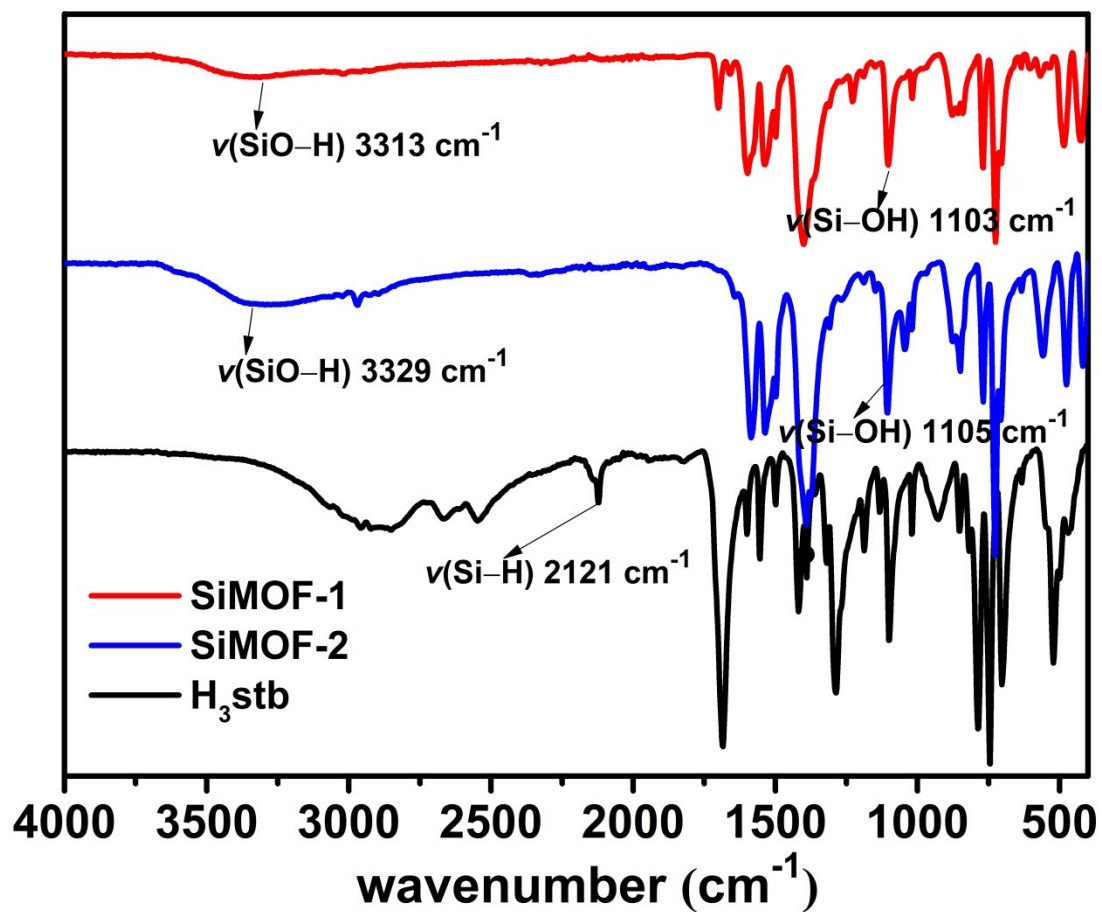


Figure S4. The FT-IR spectra of the ligand H₃stb, SiMOF-1 and SiMOF-2.

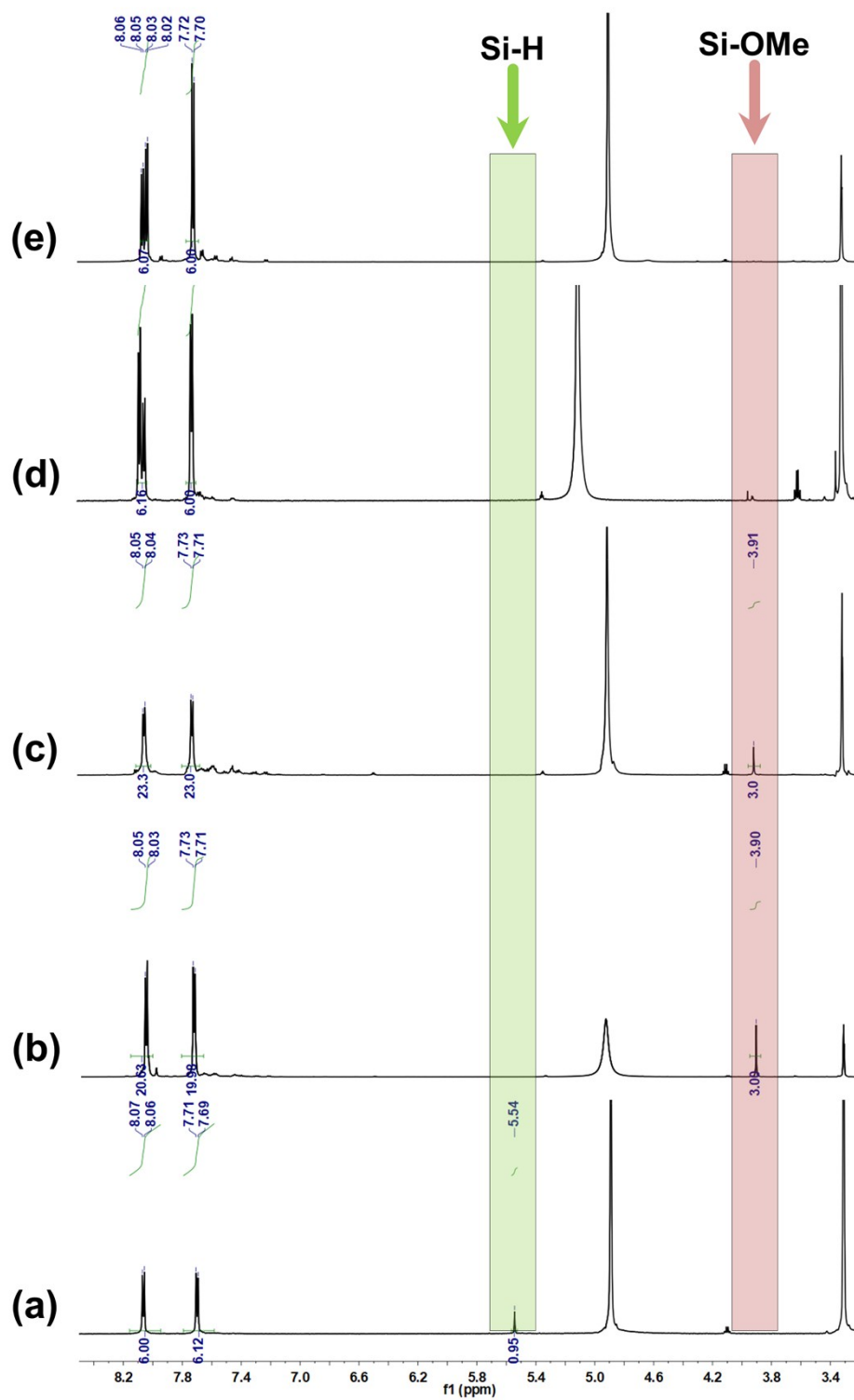


Figure S5. The ^1H NMR spectra of (a) the ligand H_3stb , (b) the mother solution of the solvothermal reaction for SiMOF-1, (c) the mother solution of the solvothermal reaction for SiMOF-2, (d) the digested SiMOF-1 by DCl (20% in D_2O) and (e) the digested SiMOF-2 by DCl (20% in D_2O).

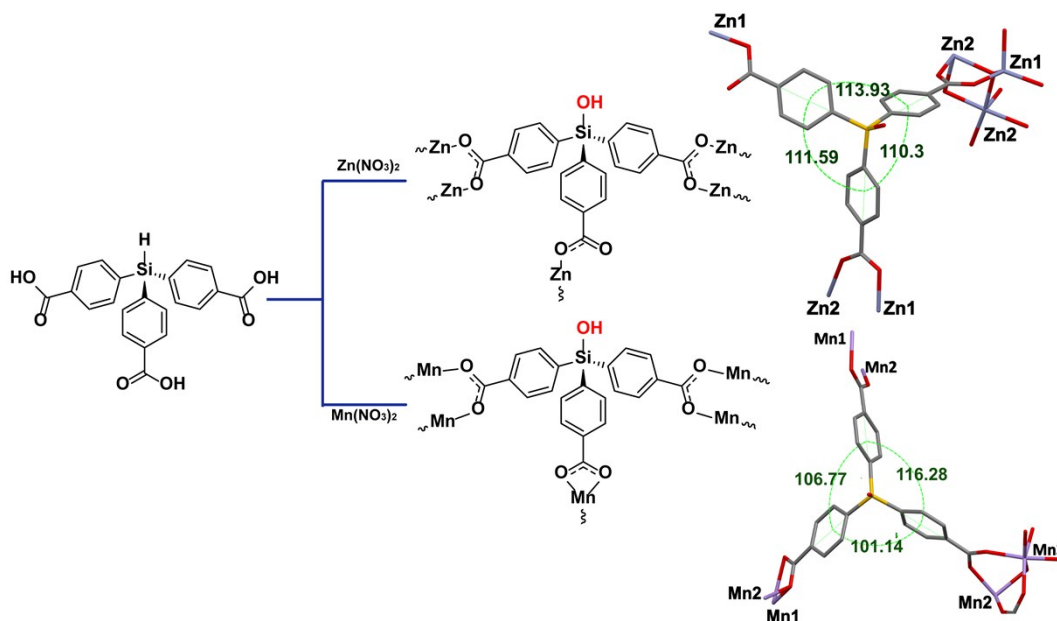


Figure S6. The syntheses of SiMOFs by *in situ* transformation from the Si–H to Si–OH ligands. (C, O, and Si, are represented by gray, red, and orange, respectively. H atoms are omitted for clarity).

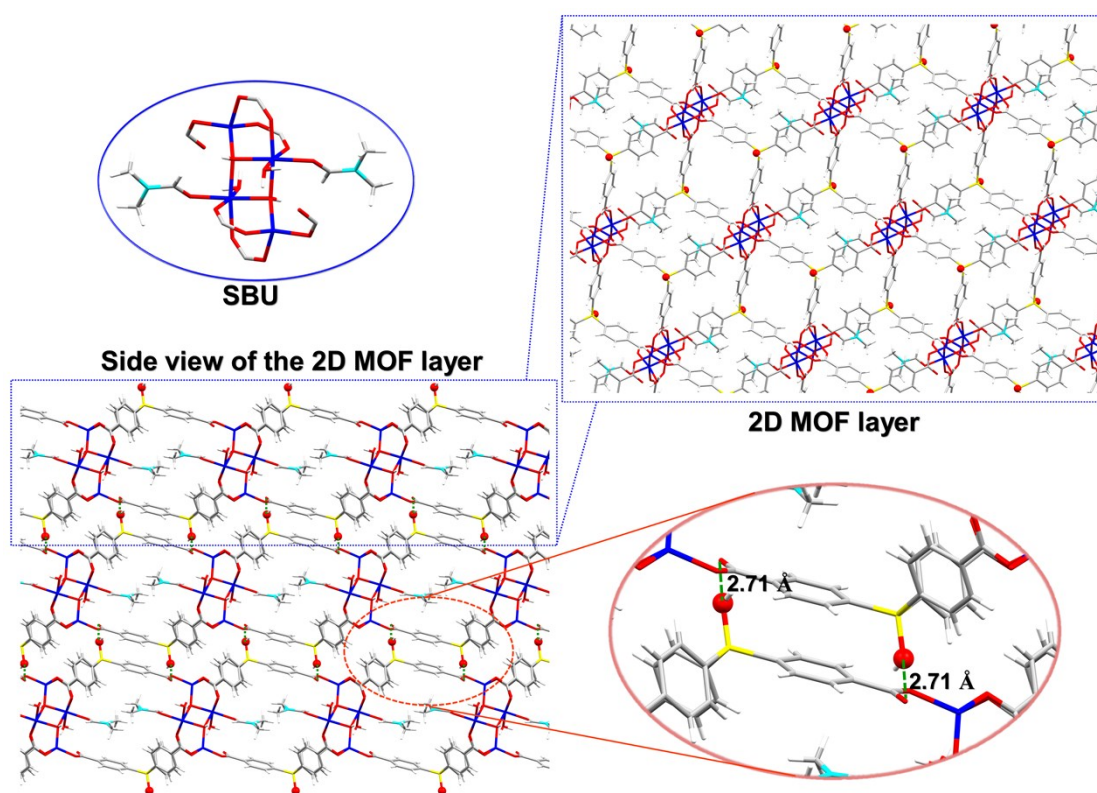


Figure S7. The crystal structure details of SiMOF-1.

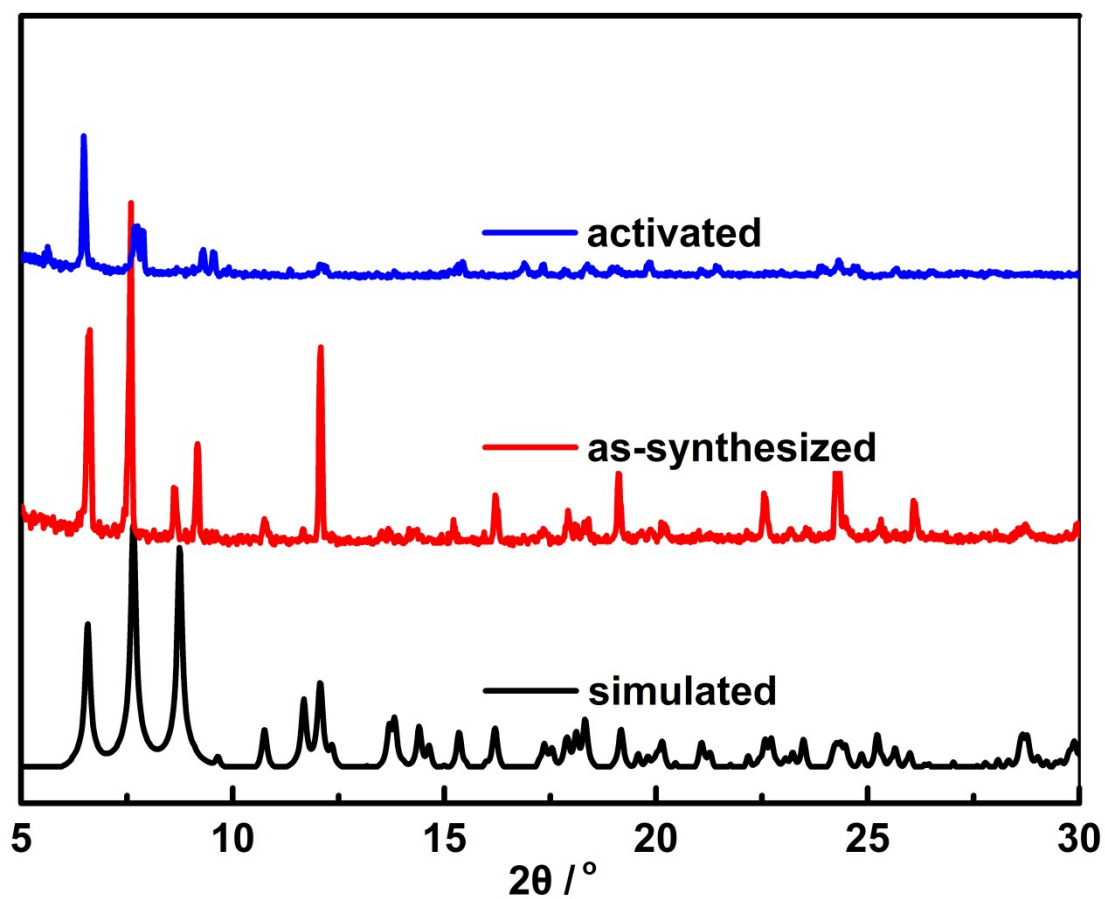


Figure S8. The PXR D patterns of the simulated (black), as-synthesized (red) and activated (blue) SiMOF-1.

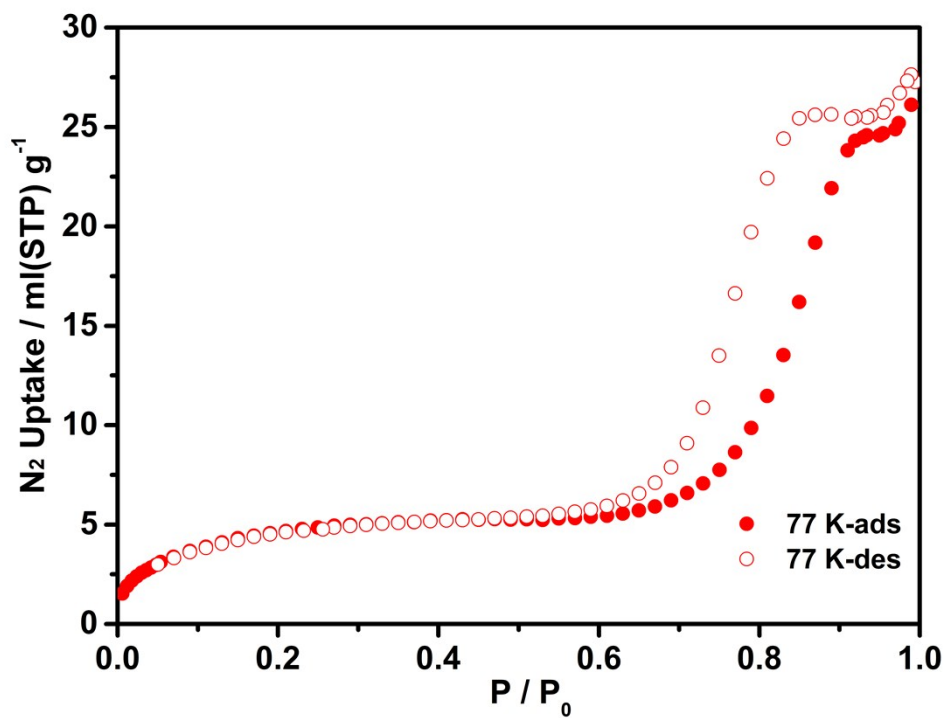


Figure S9. The N_2 sorption isotherm of SiMOF-1 at 77 K.

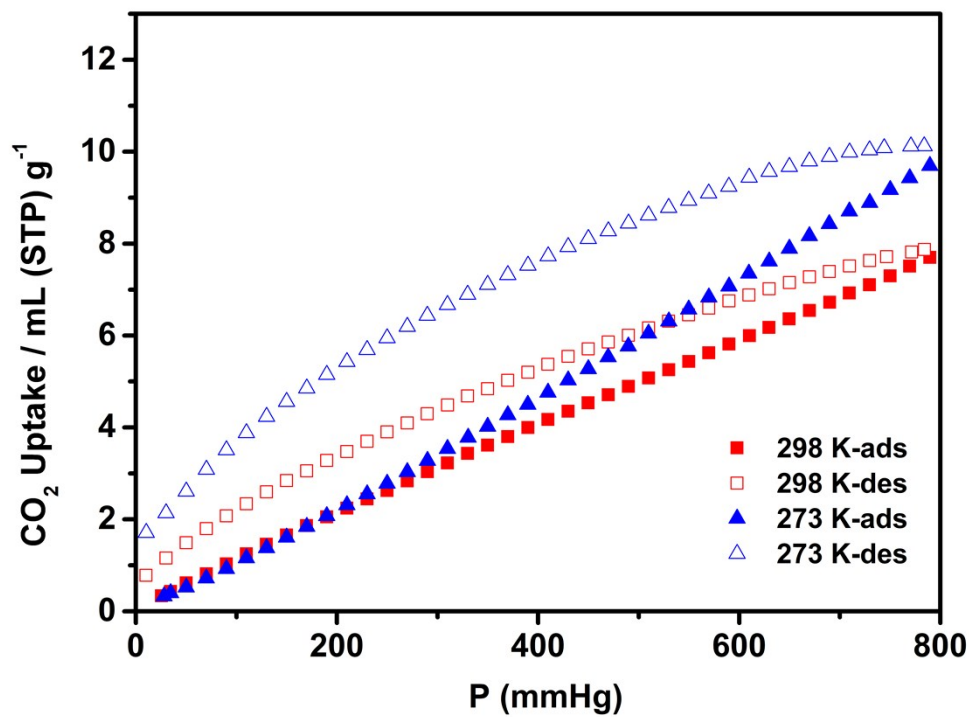


Figure S10. The CO_2 sorption isotherms of SiMOF-1 at 273 K (blue) and 298 K (red).

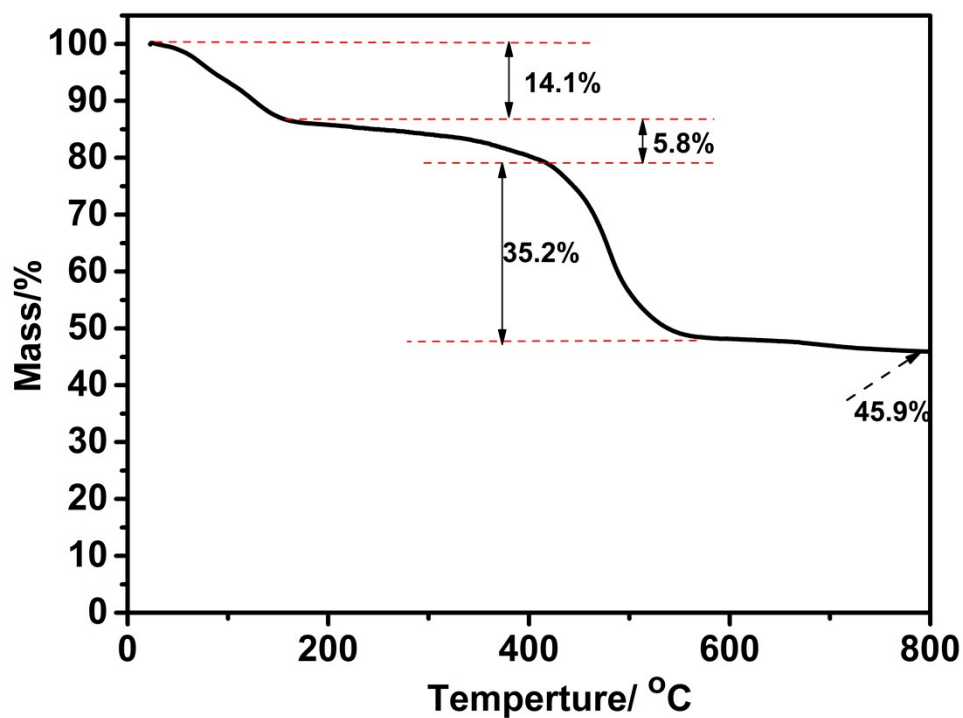


Figure S11. The TGA curve of SiMOF-2 under N₂ gas flow.

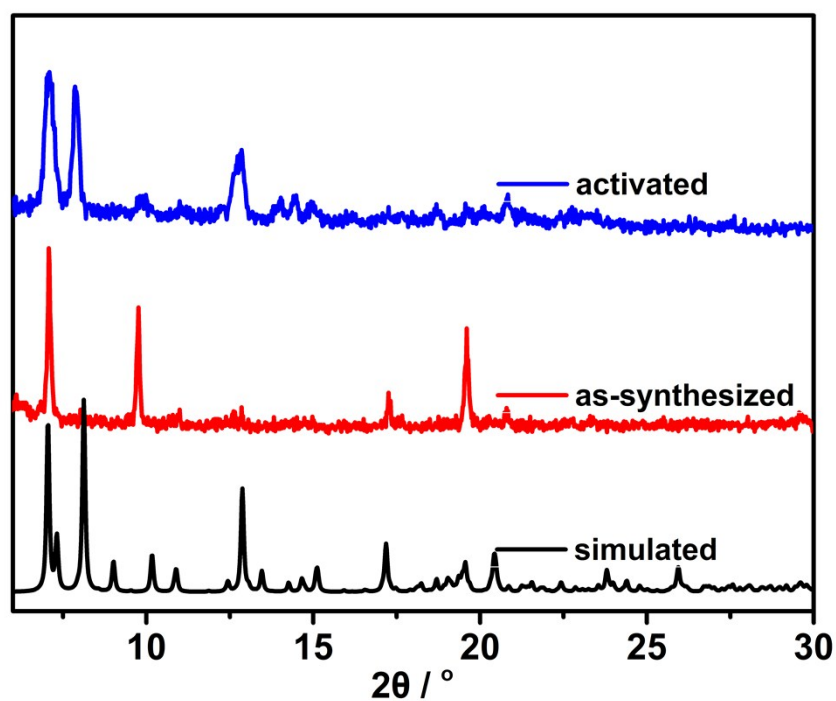


Figure S12. The PXRD patterns of the simulated (black), as-synthesized (red) and activated (blue) SiMOF-2 samples.

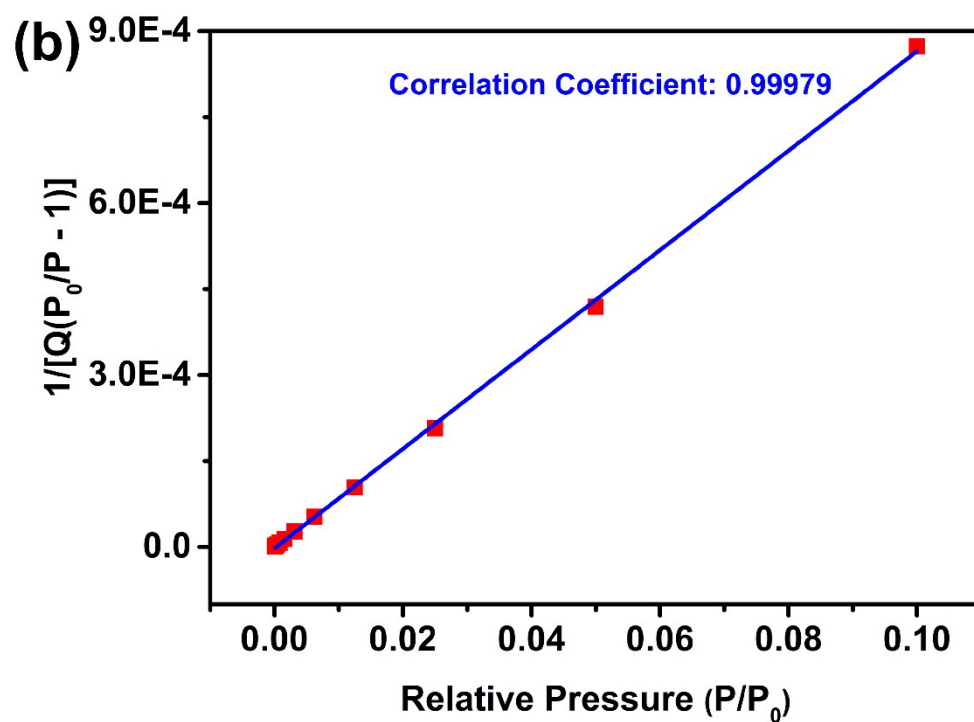
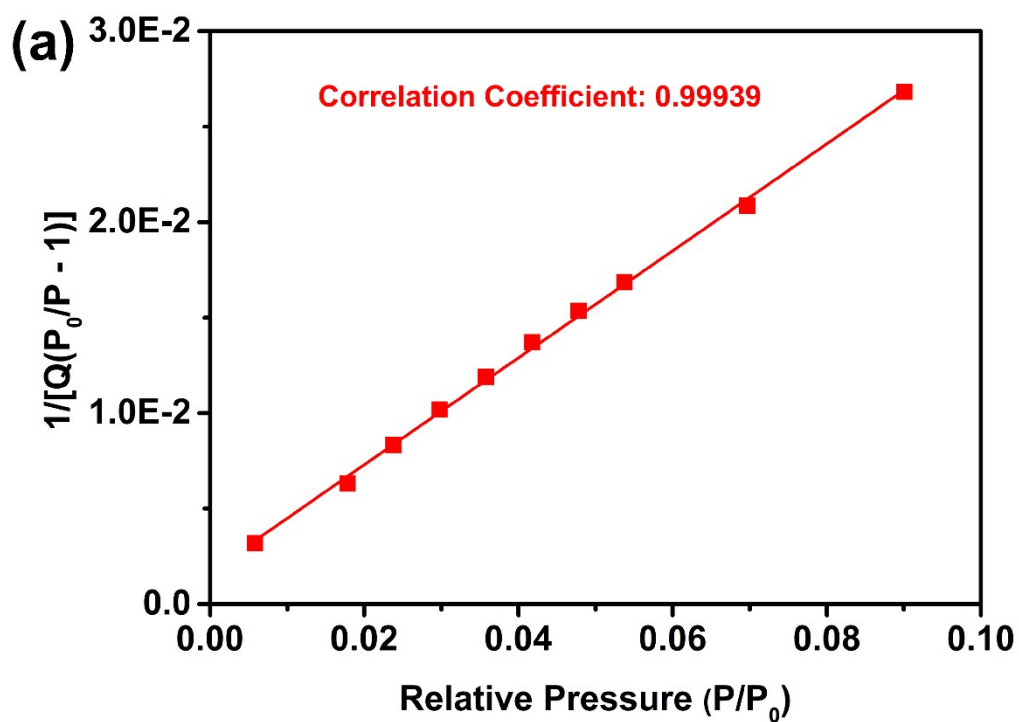


Figure S13. The plots for BET surface area calculations of (a) SiMOF-1 and (b) SiMOF-2 in the range ($P/P_0 = 0.01 - 0.1$).

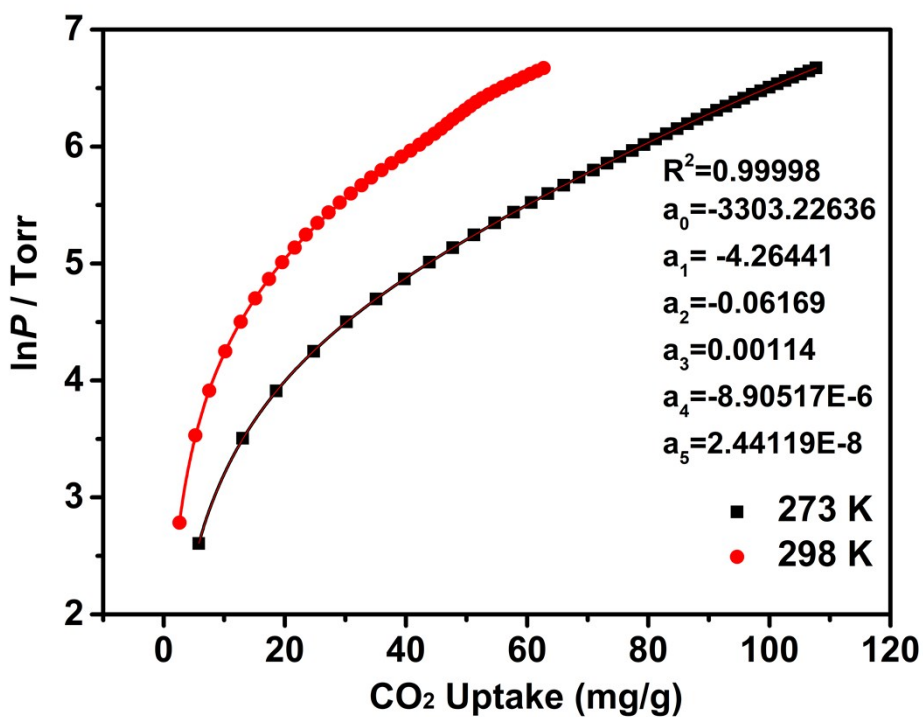


Figure S14. The CO₂ isotherms at 273 K and 298 K (symbols) and the virial equation fittings (lines) for SiMOF-2 according to the literature. [3]

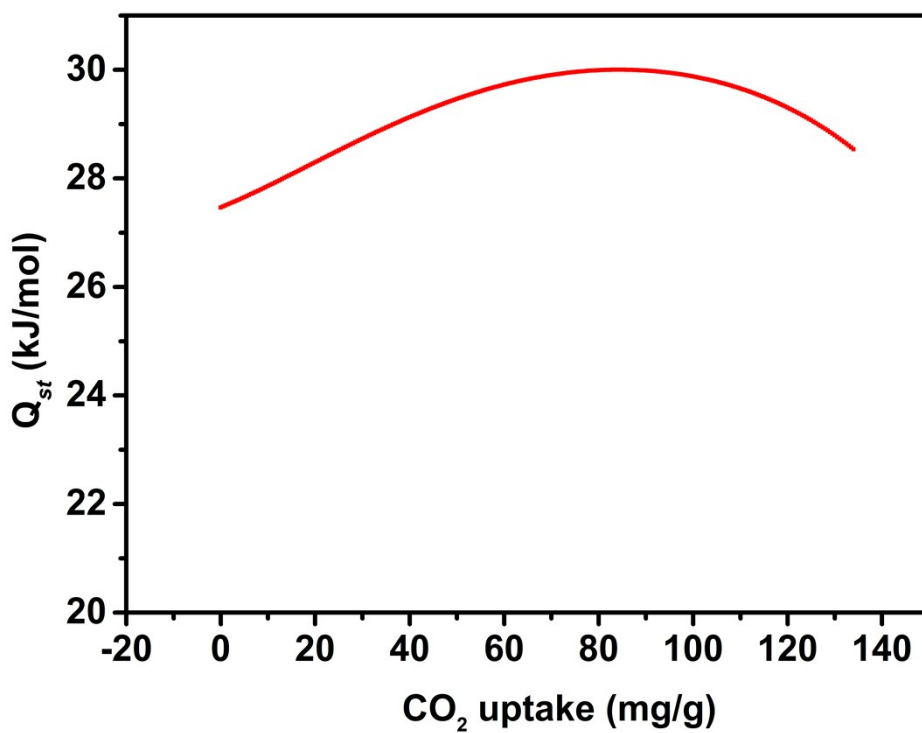


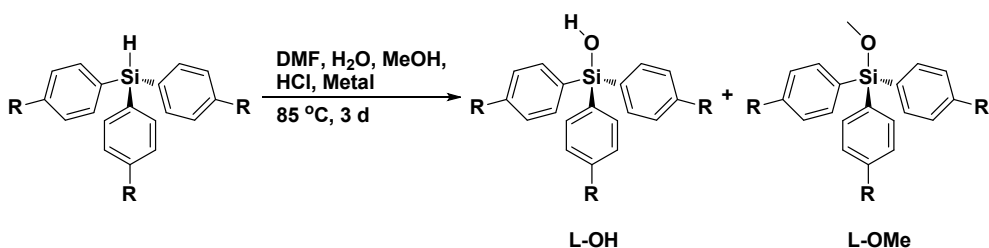
Figure S15. The isosteric heats of CO₂ sorption on SiMOF-2.

Table S1. The crystal parameters of SiMOF-1 and SiMOF-2.

Complex	SiMOF-1	SiMOF-2
Formula	$C_{24}H_{23}NO_{10}SiZn_2$	$C_{45}H_{39}NO_{18}Si_2Mn_3$
Formula weight	644.30	1102.77
Temperature (K)	293(2)	150(2)
Crystal system	Triclinic	Monoclinic
Space group	P-1	P 21/n
a/Å	12.513(3)	10.7672(2)
b/Å	13.386(3)	25.0553(5)
c/Å	14.866(3)	24.4048(5)
$\alpha/^\circ$	113.61(3)	90.0
$\beta/^\circ$	91.56(2)	98.310(1)
$\gamma/^\circ$	106.97(3)	90.0
$V/\text{Å}^3$	2152.4(9)	6514.7(2)
Z	2	4
$\rho_{\text{calc}}/\text{g cm}^{-3}$	0.994	1.124
F (000)	656	2252
Crystal size/mm ³	$0.40 \times 0.38 \times 0.34$	$0.26 \times 0.10 \times 0.08$
R_1/wR_2 ($I > 2\sigma$)	0.0612/0.1373	0.0627/0.1393
R_1/wR_2 (all data)	0.0846/0.1464	0.088/0.1497
Completeness	0.979	0.990
Goodness-of-fit on F^2	0.999	1.054

Methods and Characterizations of The Control Experiments

Entry 1 – 4: A mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ (0.020 mmol, 5.6 mg) or $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.028 mmol, 7.0 mg), HSiPh_3 (0.01 mmol, 2.6 mg), DMF (0.8 mL) MeOH (1 mL) with/without HCl (con., 10 μL) was charged into a 8 ml glass tube. The mixture was heated at 85 $^\circ\text{C}$ for 72 h, and allowed to room temperature. After evaporation of the solvent, H_2O was added and extracted with CH_2Cl_2 (3×2 mL). The combined organics were washed with brine and dried over Na_2SO_4 . After the solvent was removed, the mixture was analyzed by GC-MS.



Entry	Compound(L)	Metal	HCl (μL)
1	HSiPh_3	$\text{Zn}(\text{NO}_3)_2$	0
2	HSiPh_3	$\text{Mn}(\text{NO}_3)_2$	0
3	HSiPh_3	$\text{Zn}(\text{NO}_3)_2$	10
4	HSiPh_3	$\text{Mn}(\text{NO}_3)_2$	10

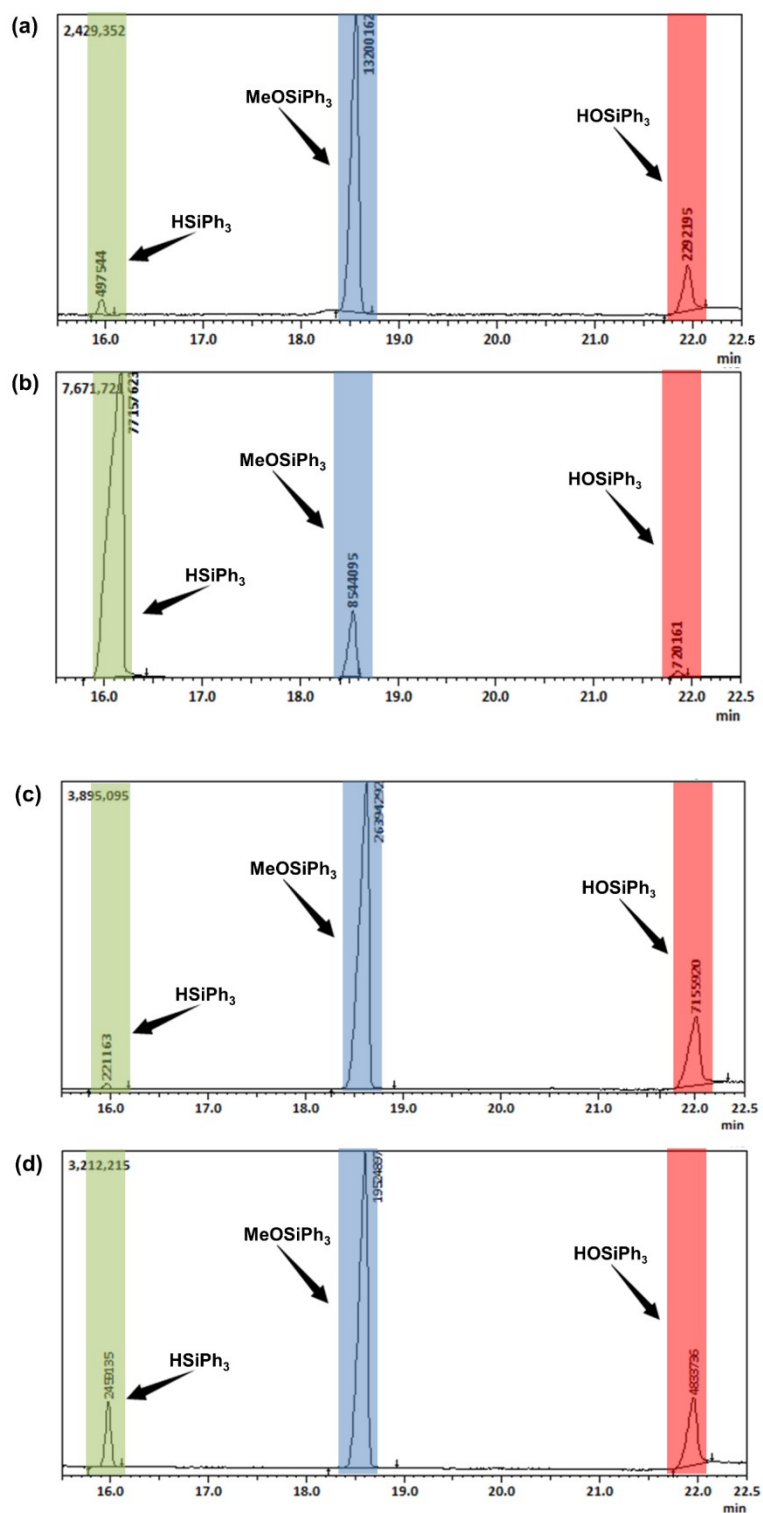


Figure S16. The GC spectra of the control experiments. (a) Entry 1. (b) Entry 2. (c) Entry 3. (d) Entry 4. There are three compounds (HSiPh_3 , MeOSiPh_3 , HOSiPh_3) in the reaction mixture and their retention times are 16.60 min, 18.63 min and 21.99 min, respectively.

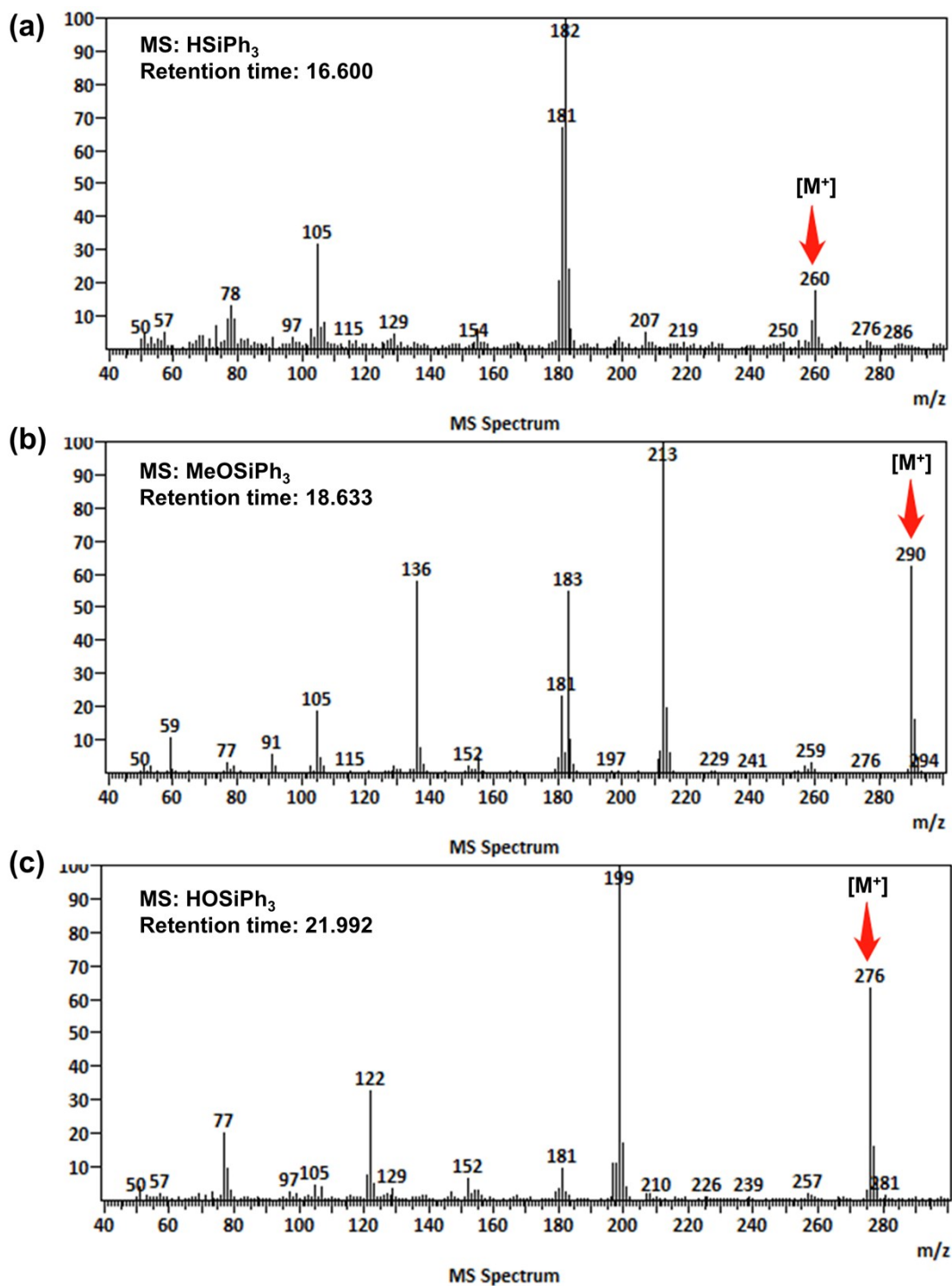


Figure S17. The Mass Spectra at the corresponding retention times for characterization of the compounds HSiPh₃, MeOSiPh₃, HOSiPh₃.

Reference

- [1] Wander, M.; Hausoul, P. J. C.; Sliedregt, L. A. J. M.; Van Steen, B. J.; Van Koten, G.; Gebbink, R. J. M. K., Synthesis of Polyaryl Rigid-Core Carbosilane Dendrimers for Supported Organic Synthesis. *Organometallics* **2009**, *28*, 4406–4415.
- [2] Delmas, L. C.; Horton, P. N.; White, A. J. P.; Coles, S. J.; Lickiss, P. D.; Davies, R. P., Siloxane-based linkers in the construction of hydrogen bonded assemblies and porous 3D MOFs. *Chem. Commun.* **2017**, *53*, 12524–12527.
- [3] Zheng, B.; Bai, J.; Duan, J.; Wojtas, L.; Zaworotko, M. J., Enhanced CO₂ Binding Affinity of a High-Uptake *rht*-Type Metal–Organic Framework Decorated with Acylamide Groups. *J. Am. Chem. Soc.* **2011**, *133*, 748–751.