Electronic Supplementary Information (ESI)

Rapid and enhanced activation of microporous coordination polymers by flowing supercritical CO_2

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Contents

I. Description of flowing SC-CO_2 activation, N_2 adsorption, PXRD and TGA

Flowing SC-CO_2 Activation. The experimental setup is shown in Figure S1. Typically, 50-150 mg solvated crystal slurries were transferred into a 4.6 mm i.d × 10 cm stainless steel column using a glass pipette, and then the column was connected to a supercritical CO_2 system with a JASCO BP-1580-81 back pressure regulator set at 100 bar. The CO_2 was pumped by a JASCO PU-1580-CO_2 delivery pump at a flow rate of 2 mL/min and the column was heated at 55 °C through a CERA column heater. After flowing of CO_2 for 2.5 h, the flow was stopped and supercritical CO_2 in the column was gradually released to atmosphere. The activated sample in the column was transferred to a sorption cell in a N_2 glove box and the surface area was measured.

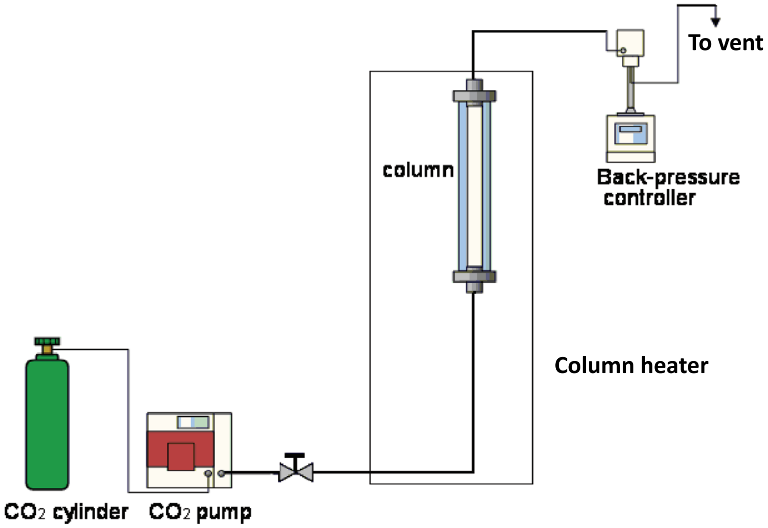

Figure S1. Experimental setup for the flowing supercritical CO_2 activation.

N_2 Adsorption Measurements. N_2 adsorption isotherms were measured by a volumetric method at 77 K in the range $5.00\times10^{-3} \leq P/P_0 \leq 1.00$ on a NOVA 4200 (UMCM-9 was measured by Autosorb-1) by Quantachrome Instruments (Boynton Beach, Florida, USA). Ultra-high purity N_2 (99.999%) was purchased from Cryogenic Gasses and used as received. Unless otherwise noted, the linear region used for the BET plot was $0.01 \leq P/P_0 \leq 0.1$, and for the Langmuir plot the range was $0.02 \leq P/P_0 \leq 0.3$.

Powder X-ray Diffraction (PXRD) Analysis. Crystals of different MCPs were coated on a Nylon loop using Paratone N mineral oil (Hampton Research) and mounted on a Rigaku R-Axis Spider diffractometer equipped with a Cu Kα X-ray source (λ = 1.5406 Å) operating at 50 kV and 40 mA. Images were collected by transmission with $\chi = 45°$, φ rotating at 10°/min, and ω

oscillating between 80° and 140°. Integration of the images was carried out using the AreaMax (2.0) software package with a step size of 0.02° in 2θ.

Thermogravimetric Analysis (TGA). Measurements of MCP samples activated by different methods were performed on a TA Q50 TGA apparatus. Approximately 1-5 mg of activated sample of different MCPs was loaded into a platinum pan and heating from room temperature to 650 °C at 5 or 10 °C/min.

II. Synthesis, Powder XRD patterns, N_2 adsorption isotherms, and TGA traces of UMCM-9

Naphthalene-2,6-dicarboxylic acid (H_2NDC) (28.7 mg, 0.132 mmol) and biphenyl-4,4'-dicarboxylic acid (H_2BPDC) (35.6 mg, 0.147 mmol) were dissolved in a mixture of 6.7 mL of N,N-diethylformamide (DEF) and 13.3 mL of N-methyl pyrrolidone (NMP). $Zn(NO_3)_2 \cdot 6H_2O$ (0.238 g, 0.800 mmol) was added to the solution. The mixture was sonicated for 15 min and heated to 85 °C. After 4 days, crystals of a single phase were obtained. After cooling to room temperature the product was isolated by decanting the mother liquor and washed with N,N-dimethylformamide (DMF) (3 × 10 mL).[S1] The DMF-solvated samples were then activated by flowing SC-CO_2.

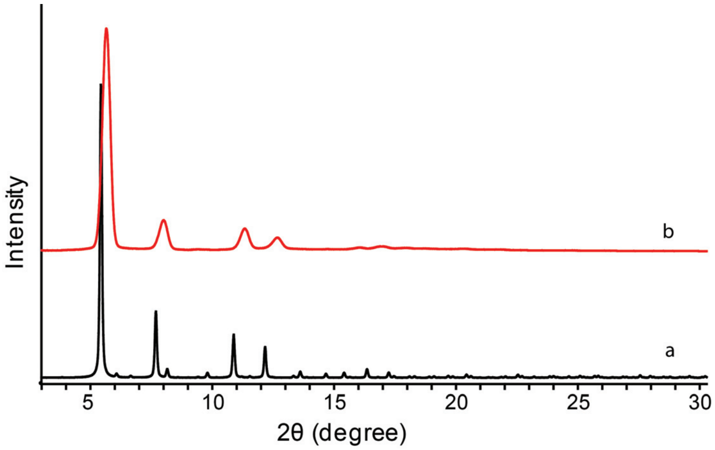

Figure S2. PXRD patterns of UMCM-9. a) Simulated, b) flowing SC-CO_2 activation from DMF.

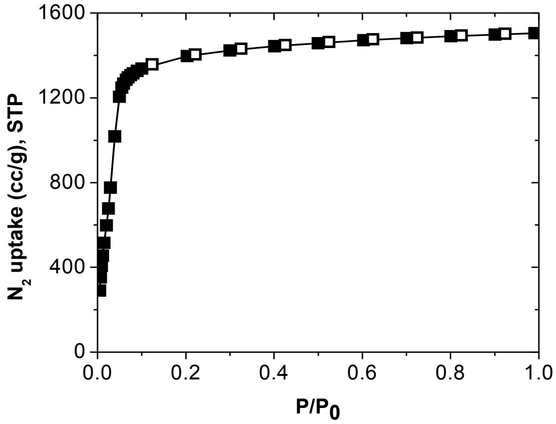

Figure S3. Nitrogen adsorption (solid) and desorption (open) isotherms at 77 K for UMCM-9 activated by flowing SC-CO_2 from DMF-solvated sample. The BET surface area is 5357 m^2/g ($0.05 \leq P/P_0 \leq 0.1$).

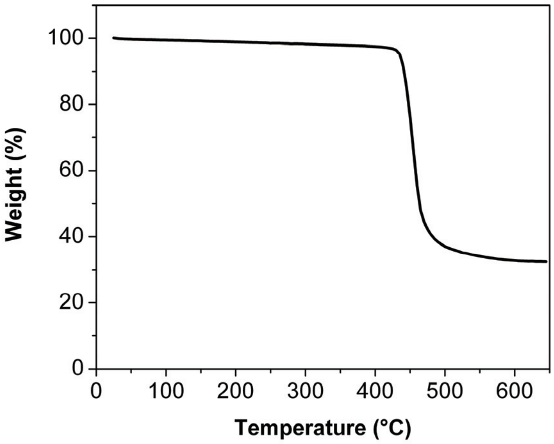

Figure S4. TGA trace at 5 °C/min of UMCM-9 activated by flowing SC-CO_2 from DMF-solvated sample.

III. Synthesis, Powder XRD patterns, N_2 adsorption isotherms, and TGA traces of FJI-1

A mixture of $Zn(ClO_4)_2 \cdot 6H_2O$ (0.223 g, 0.6 mmol), 1,3,5-benzenetribenzoic acid (H_3BTB) (0.175g, 0.4 mmol), 4,4'-bipy (0.047 g, 0.3 mmol) and fluoboric acid (48%, 100 μL) in DMF (10 mL) in a 20-mL vial was dissolved by ultrasonic waves 10 minutes and heated at 85 °C for 3 days.[S2] Then the mixture was cooled to room temperature, yielding colorless transparent cubic crystals which were collected and repeatedly washed with DMF three times (3×10 mL). The DMF-solvated crystals were then activated by flowing SC-CO_2.

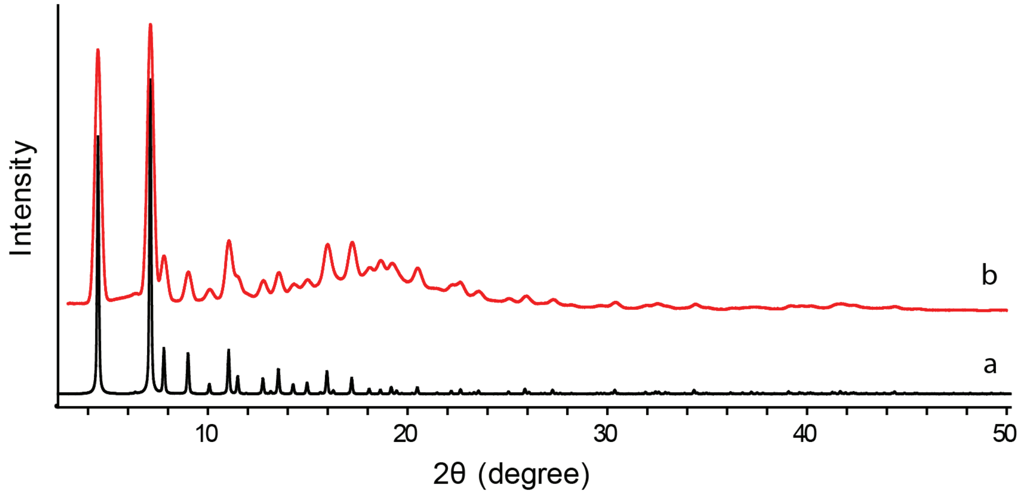

Figure S5. PXRD patterns of FJI-1. a) Simulated, b) flowing SC-CO_2 activation from DMF.

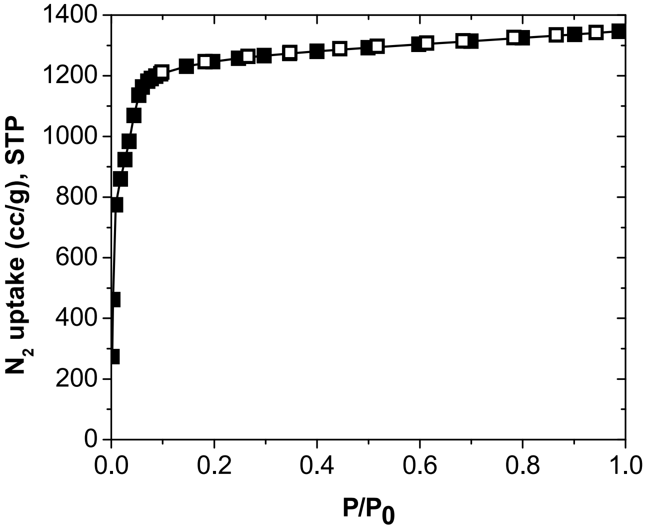

Figure S6. Nitrogen adsorption (solid) and desorption (open) isotherms at 77 K for FJI-1 activated by flowing SC-CO_2 from DMF-solvated sample. The surface area is 4813 m^2/g (BET, $0.05 \le P/P_0 \le 0.1$) and 5647 m^2/g (Langmuir, $0.05 \le P/P_0 \le 0.35$).

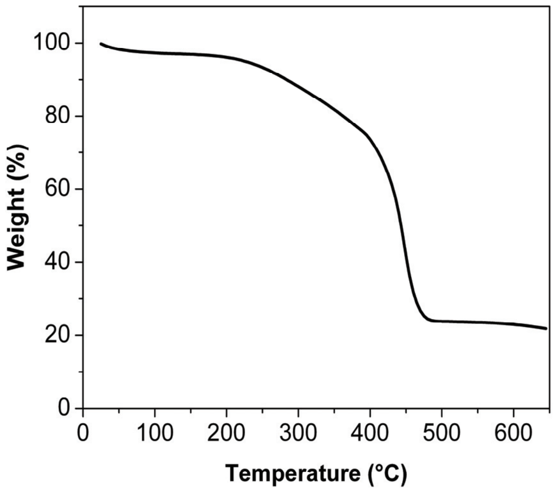

Figure S7. TGA trace at 5 °C/min of FJI-1 activated by flowing SC-CO_2 from DMF-solvated sample.

IV. Synthesis, Powder XRD patterns, N_2 adsorption isotherms, and TGA traces of IRMOF-3

IRMOF-3 was prepared according to slight modification of the published procedure.[S3] $Zn(NO_3)_2{\cdot}6H_2O$ (4.735 g, 15.92 mmol) and 2-aminobenzenedicarboxylic acid (0.960 g, 5.30 mmol) were dissolved in a 500 mL jar containing 200 mL DMF. The jar was tightly capped and heated in a 100 °C oven for 24 h. After cooling to room temperature, the solution was decanted, then the brown block crystals were washed with DMF three times (3 × 30 mL). After washing with DMF, some of the crystals were directly activated by flowing SC-CO_2. The rest were divided into several parts, transferred to 20 mL vials, exchanged DMF with different solvents (CH_2Cl_2, $CHCl_3$, and absolute ethanol) thrice in three days (3 × 10 mL), then activated by flowing SC-CO_2 and conventional evacuation. Conventional activation of IRMOF-3: $CHCl_3$-exchanged sample was evacuated at room temperature for 24 h.

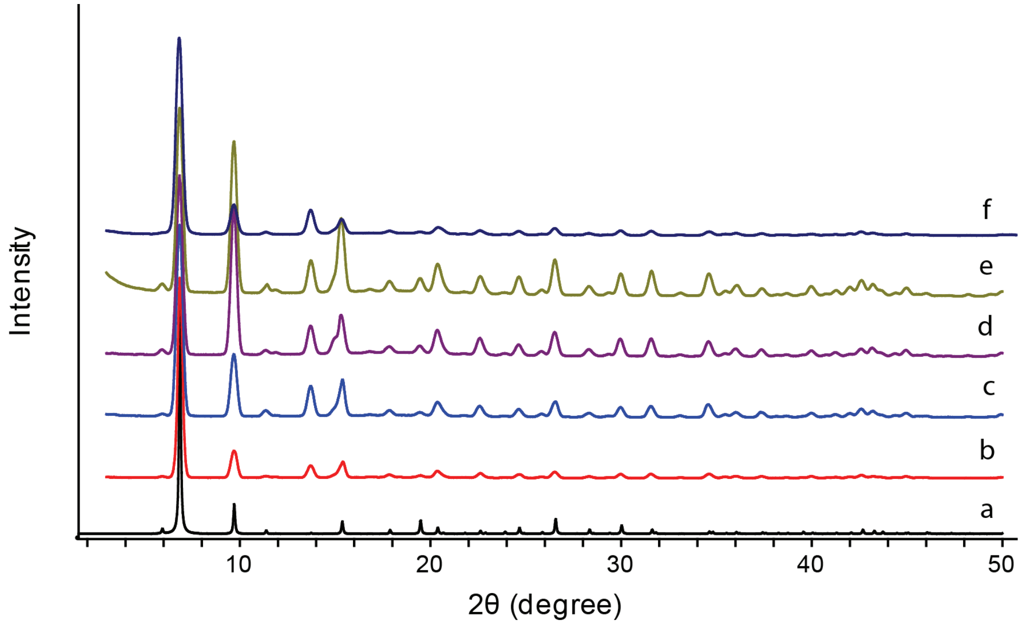

Figure S8. PXRD patterns of IRMOF-3. a) Simulated, b) flowing SC-CO_2 activation from DMF, c) flowing SC-CO_2 activation from $CHCl_3$, d) flowing SC-CO_2 activation from CH_2Cl_2, e) flowing SC-CO_2 activation from absolute ethanol, f) exchange with $CHCl_3$ then evacuation at room temperature.

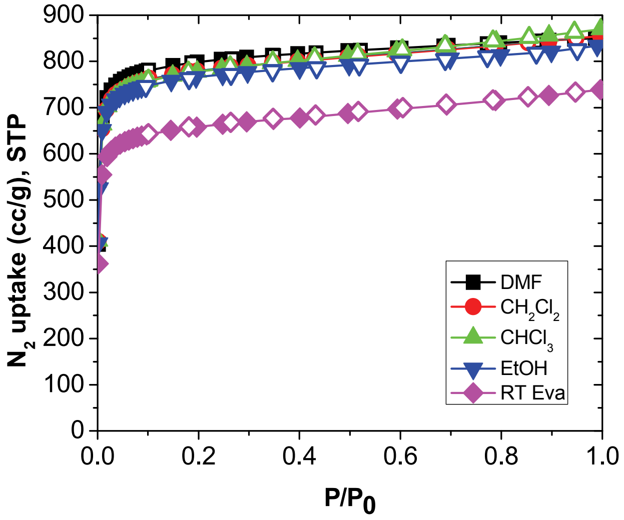

Figure S9. Nitrogen adsorption (solid) and desorption (open) isotherms at 77 K for IRMOF-3 following exchange with $CHCl_3$ then evacuation at room temperature ◆; flowing SC-CO_2 activation from different solvents, DMF ■, dichloromethane ●, chloroform ▼, and absolute ethanol ▲.

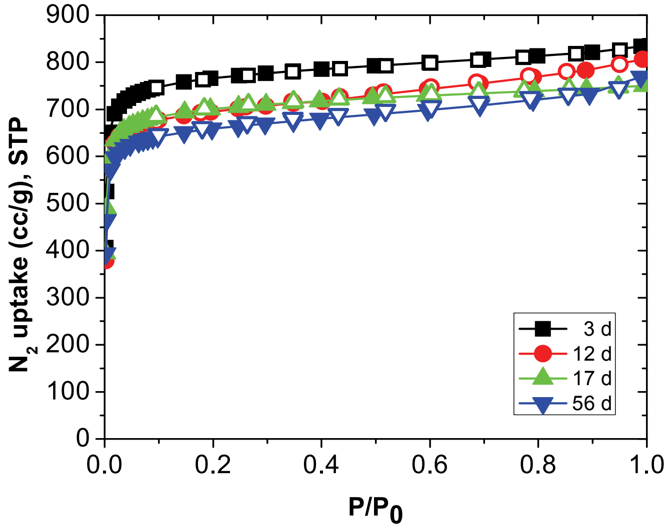

Figure S10. Nitrogen adsorption (solid) and desorption (open) isotherms at 77 K for flowing SC-CO_2 activated IRMOF-3 soaking in absolute ethanol for 3 d ■, 12 d ●, 17 d ▲, and 56 d ▼.

Table S1. BET (Langmuir) surface areas (m^2/g) of IRMOF-3 activated by flowing SC-CO_2 and conventional evacuation at room temperature.

Flowing SC-CO_2 activation				Conv. evacuation from $CHCl_3$
DMF	CH_2Cl_2	$CHCl_3$	Absolute ethanol	
3090 (3537)	3029 (3460)	3012 (3457)	2960 (3395), 3 d 2712 (3090), 12 d 2707 (3103), 17 d 2534 (2922), 56 d	2553 (2927)

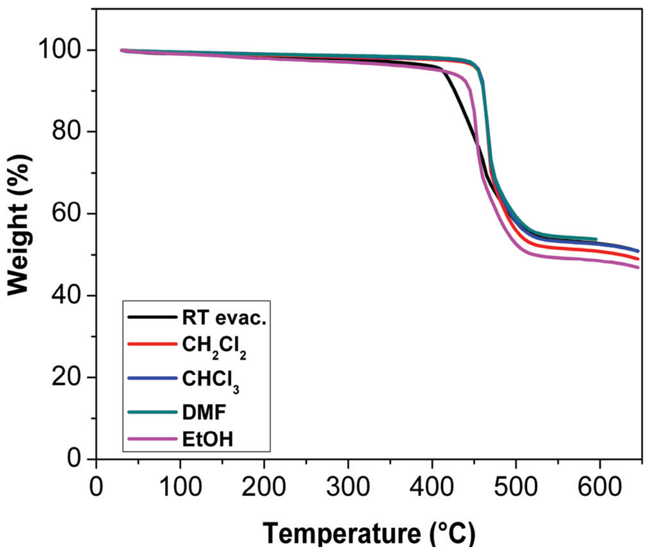

Figure S11. TGA trace at 10 °C/min of activated IRMOF-3. Exchanged with $CHCl_3$ then evacuation at room temperature (black), Flowing SC-CO_2 activation from DMF (green), dichloromethane (red), chloroform (blue), and absolute ethanol (pink) solvated samples.

V. Synthesis, Powder XRD patterns, N_2 adsorption isotherms, and TGA traces of MOF-177

Scaled up according to published procedure.[S4] $Zn(NO_3)_2 \cdot 6H_2O$ (0.736 g, 2.474 mmol) and H_3BTB (0.360 g, 0.822 mmol) were dissolved in DEF (30 mL) in a 60 mL jar, capped tightly, and heated to 100 °C for 20 h. The solution was decanted, and the clear block crystals were washed with DMF (3 × 10 mL) and then activated by flowing SC-CO_2. Conventional activation method: DMF-solvated crystals were exchanged with $CHCl_3$ thrice in three days (3 × 10 mL), evacuated to 10^{-3} Torr at room temperature for 2 h, heated at a constant rate (1 °C /min) to 120 °C for 6 h, then cooled to room temperature.

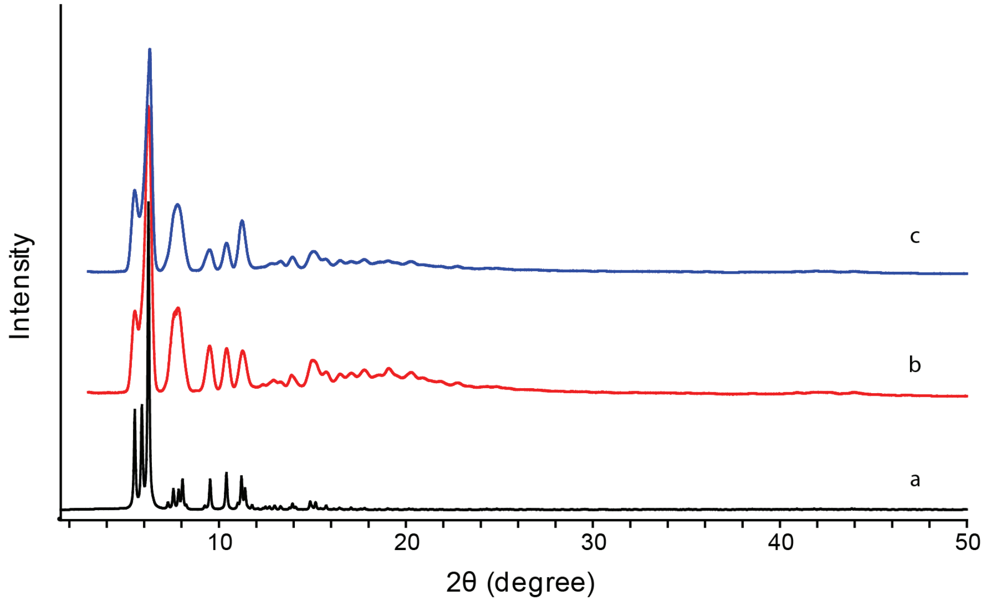

Figure S12. PXRD patterns of MOF-177. a) Simulated, b) flowing SC-CO_2 activation from DMF, c) exchange with $CHCl_3$ then evacuation at 120 °C for 6 h.

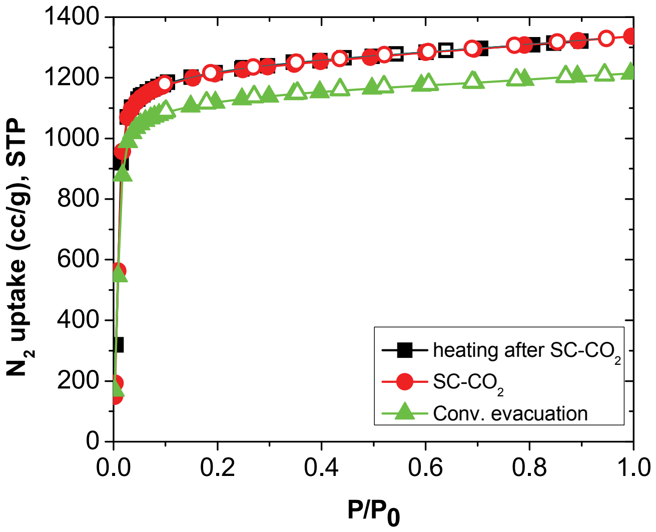

Figure S13. Nitrogen adsorption (solid) and desorption (open) isotherms at 77 K for MOF-177 activated by flowing SC-CO_2 in DMF ●, additional heating at 120 °C for 6 h after SC-CO_2 activation ■, and exchange with $CHCl_3$ then evacuation at 120 °C ▲.

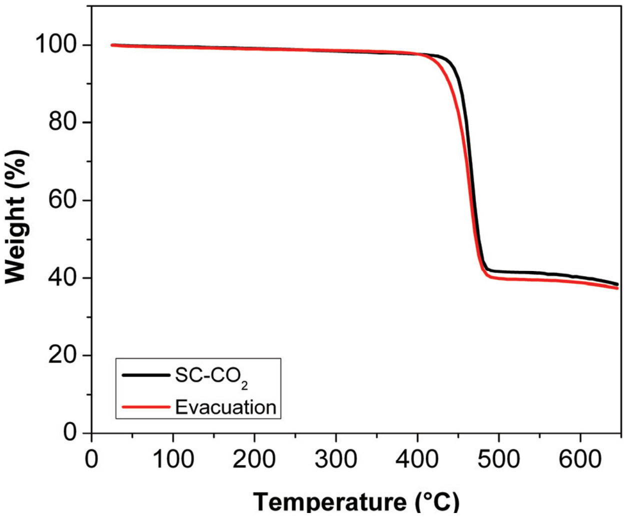

Figure S14. TGA trace at 5 °C/min of activated MOF-177 by flowing SC-CO_2 from DMF-solvated sample (black) and evacuation at 120 °C from $CHCl_3$ solvated sample (red).

VI. Synthesis, Powder XRD patterns, N_2 adsorption isotherms, and TGA traces of MOF-5

$Zn(NO_3)_2·6H_2O$ (0.90 g, 3.05 mmol) and 1,4-benzenedicarboxylic acid (H_2BDC) (0.165 g, 1.0 mmol) were dissolved in 25 mL of DEF in a 60 mL jar with a Teflon lined lid. The solution was heated in an oven at 100 °C for 24 h to yield large, cube-shaped crystals.[S5] The jar was then removed from the oven and cooled to room temperature. The crystals were transferred to a 20 mL vial and washed thrice with DMF (3 × 10 mL) within 24 h, and then activated by flowing SC-CO_2.

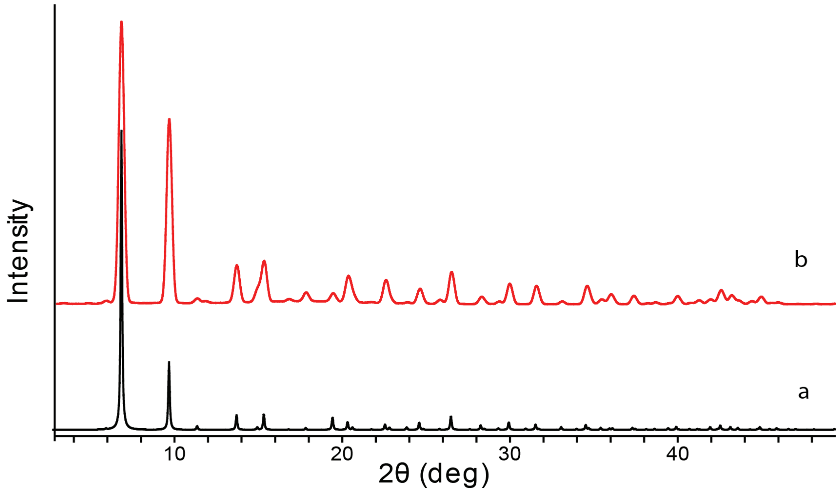

Figure S15. PXRD patterns of MOF-5. a) Simulated, b) flowing SC-CO_2 activation from DMF.

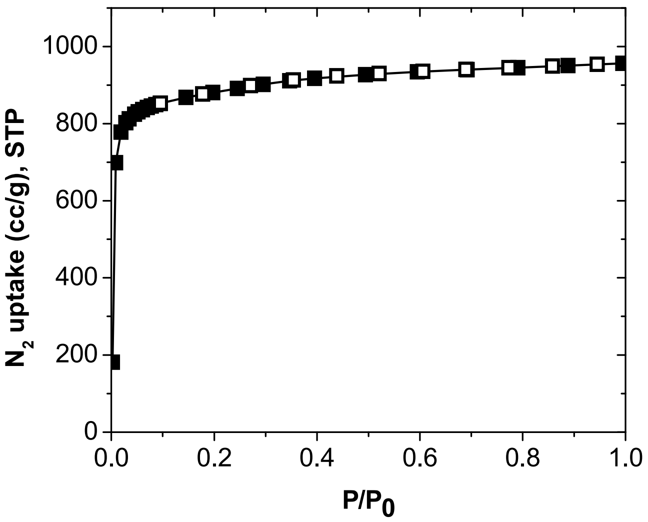

Figure S16. Nitrogen adsorption (solid) and desorption (open) isotherms at 77 K for MOF-5 activated by flowing SC-CO_2 from DMF-solvated sample.

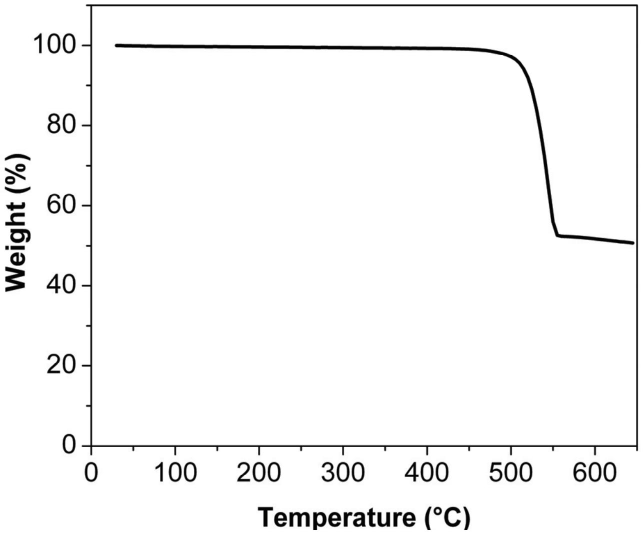

Figure S17. TGA trace at 5 °C/min of activated MOF-5 by flowing SC-CO_2 from DMF-solvated sample.

VII. Synthesis, Powder XRD patterns, N_2 adsorption isotherms, and TGA traces of UiO-66

UiO-66 was prepared according to published process[S6] with scale-up. $ZrCl_4$ (1.06 g, 4.54 mmol) and H_2BDC (0.68g, 4.54 mmol) were mixed with 200 mL DMF in a 500 mL jar and sonicated resulting a clear solution. Then the jar was sealed and placed in a pre-heated oven at 120 °C for 24

h. After cooling to room temperature the resulting solid was repeatedly washed with DMF (3 × 30 mL) and soaked in CH_2Cl_2 and absolute ethanol (10 mL) for three days with fresh solvent exchanged every 24 h. Then the samples were activated by flowing SC-CO_2.

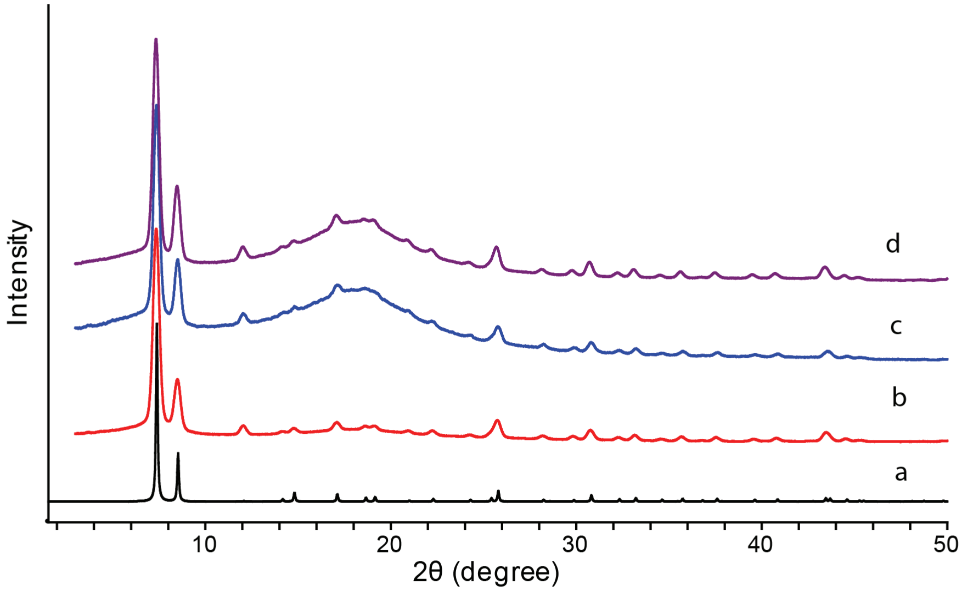

Figure S18. PXRD patterns of UiO-66. a) Simulated, b) flowing SC-CO_2 activation from DMF, c) flowing SC-CO_2 activation from dichloromethane, d) flowing SC-CO_2 activation from absolute ethanol.

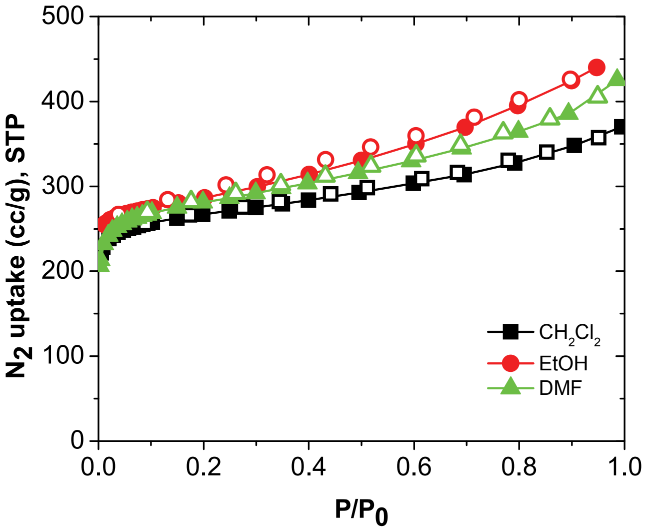

Figure S19. Nitrogen adsorption (solid) and desorption (open) isotherms at 77 K for UiO-66 activated by flowing SC-CO_2 from different solvents, dichloromethane ■, absolute ethanol ●, DMF ▲.

Table S2. BET (Langmuir) surface areas (m^2/g) of UiO-66 activated by flowing SC-CO_2 from different solvents.

Flowing SC-CO_2 Activation		
DMF	CH_2Cl_2	Absolute ethanol
1065 (1289)	1018 (1208)	1084 (1313)

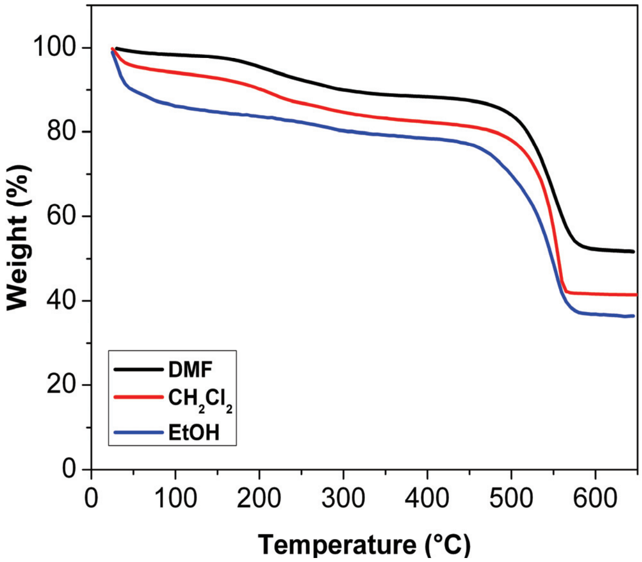

Figure S20. TGA trace at 10 °C/min of UiO-66 activated by flowing SC-CO_2 from DMF (black), dichloromethane (red), and absolute ethanol (blue) solvated samples.

VIII. Synthesis, Powder XRD patterns, N_2 adsorption isotherms, and TGA traces of MOF-74

2,5-dioxido-1,4-benzenedicarboxylic acid (H_4DOBDC) (1.25 g, 6.51 mmol) and $Zn(NO_3)_2 \cdot 6H_2O$ (5.65 g, 22.0 mmol) were added to a 500 mL jar with 250 mL of DMF and 12.5 mL H_2O. The resulting mixture was dissolved by sonication until dissolution of the solids was complete. The jar was tightly sealed with a Teflon-lined cap and placed into an oven heated at 100 °C. After 20 h the jar was removed from the oven and the hot mother liquor was decanted and washed with DMF trice (3 × 30 mL).[S7] Some of the crystals was transferred into a 20 mL vial and replaced DMF with methanol (10mL). The methanol was replaced 3 times over 6 days. The DMF-solvated and methanol exchanged samples were activated by flowing SC-CO_2 and further heated at 270 °C under dynamic vacuum for 14 h.

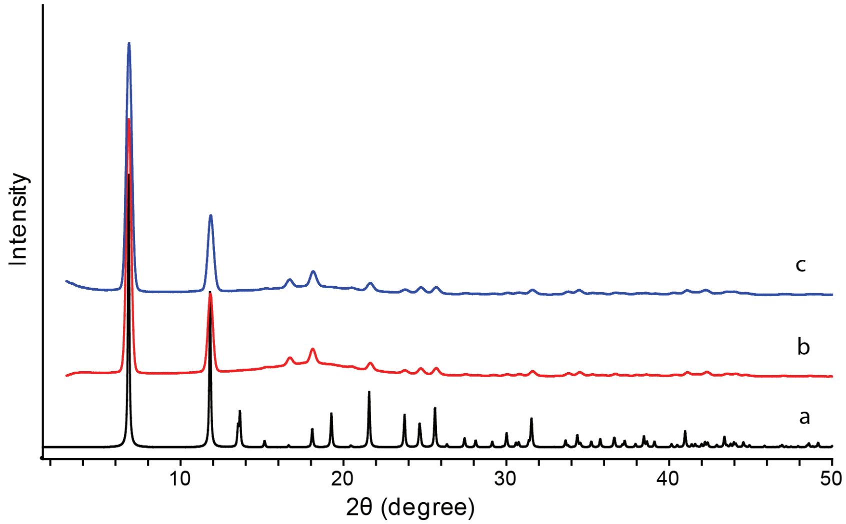

Figure S21. PXRD patterns of MOF-74. a) Simulated, b) flowing SC-CO_2 activation from DMF, c) flowing SC-CO_2 activation from methanol.

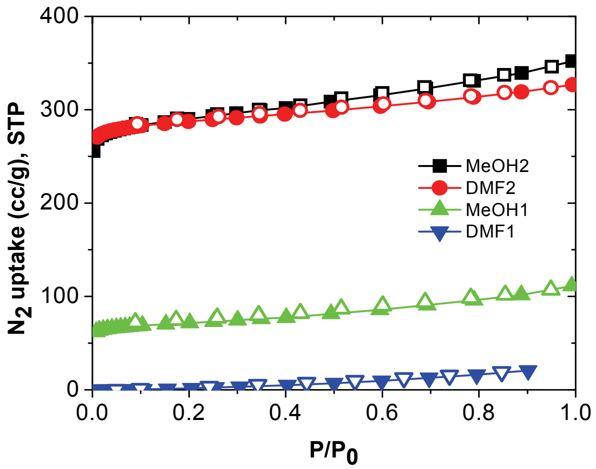

Figure S22. Nitrogen adsorption (solid) and desorption (open) isotherms at 77 K for MOF-74 activated by flowing SC-CO_2 drying from DMF ▼ and methanol ▲, and heating at 270 °C for 14 h after flowing SC-CO_2 drying from DMF ● and methanol ■.

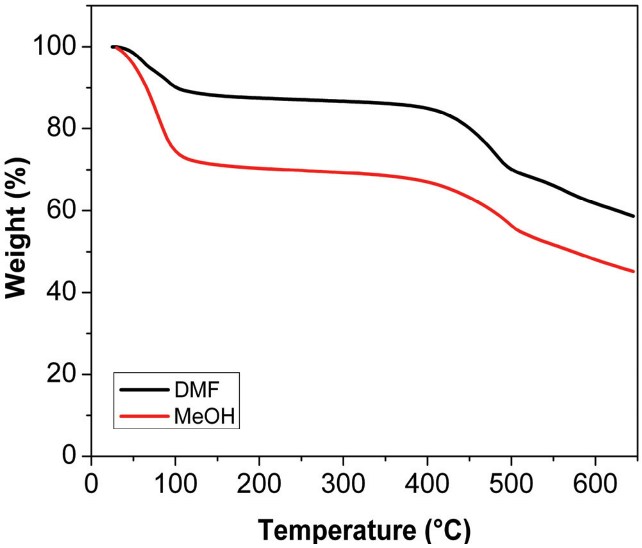

Figure S23. TGA trace at 10 °C/min of activated MOF-74 by heating at 270 °C for 14 h after flowing SC-CO_2 drying from DMF (black) and methanol (red).

IX. Synthesis, Powder XRD patterns, N_2 adsorption isotherms, and TGA traces of HKUST-1

$Cu(NO_3)_2{\cdot}2.5H_2O$ (4.2 g, 18.06 mmol) and 1,3,5-benzenetricarboxylic acid (H_3BTC) (2.1 g, 10 mmol) were stirred for 10 minutes in 210 mL of solvent consisting of DMF, ethanol and water (1:1:1) in a 500 mL jar to form a slurry. The tightly capped jar was heated at 85 °C over night.[S5] After cooling to room temperature, the solution was decanted, then the blue crystals were washed with DMF (3 × 30 mL). After washing with DMF, some of the crystals were directly activated by flowing SC-CO_2. The rest were divided into several parts, transferred to 20 mL vials, exchanged DMF with different solvents (CH_2Cl_2, $CHCl_3$, and absolute ethanol) thrice in three days (3 × 10 mL), then activated by flowing SC-CO_2 and conventional evacuation. The SC-CO_2 treated samples were further heated under vacuum at 170 °C for 24 h. Conventional activation of HKUST-1: CH_2Cl_2-exchanged sample was evacuated at room temperature to dry then heated under vacuum at 170 °C for 24 h.

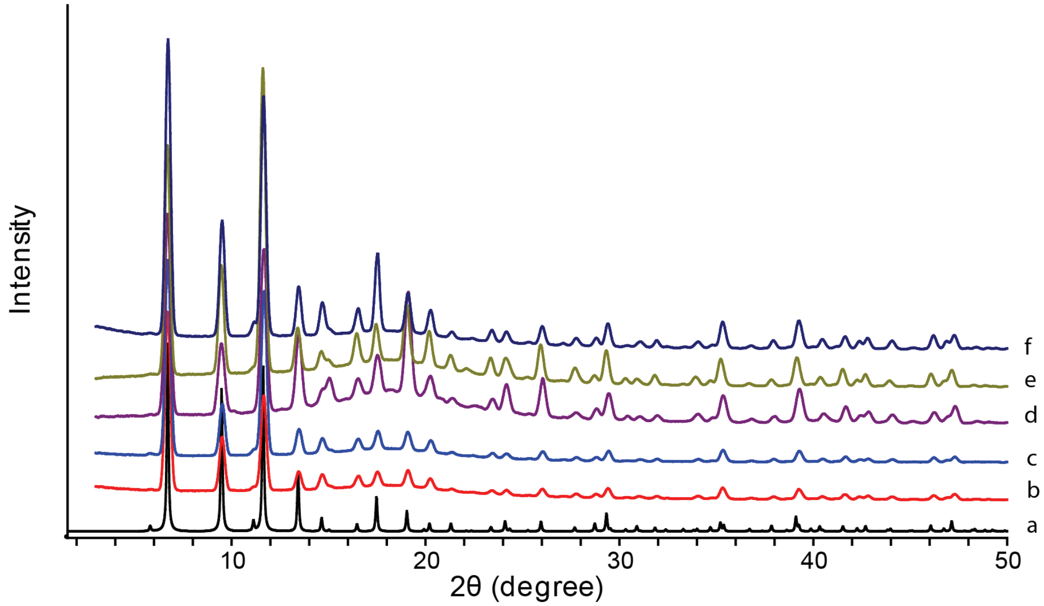

Figure S24. PXRD patterns of HKUST-1. a) Simulated, b) flowing SC-CO_2 activation from DMF, c) flowing SC-CO_2 activation from dichloromethane, d) flowing SC-CO_2 activation from chloroform, e) flowing SC-CO_2 activation from absolute ethanol, f) exchange with CH_2Cl_2 then heating at 170 °C under vacuum for 24 h.

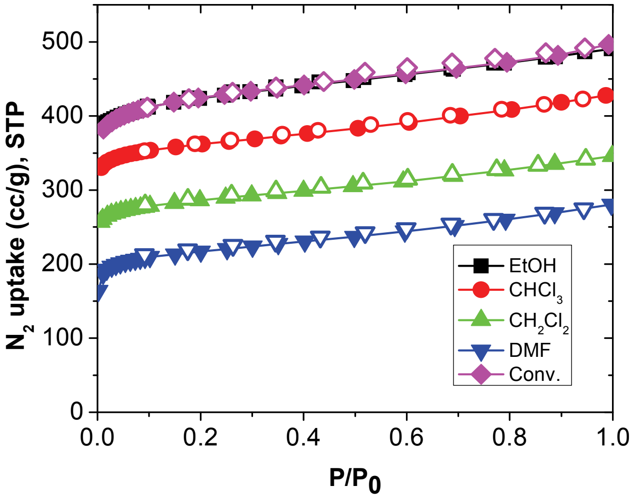

Figure S25. Nitrogen adsorption (solid) and desorption (open) isotherms at 77 K for HKUST-1 by conventional heating at 170 °C under vacuum after exchange with CH_2Cl_2 ◆; flowing SC-CO_2 activation from absolute ethanol ■, $CHCl_3$ ●, CH_2Cl_2 ▼, and DMF ▲.

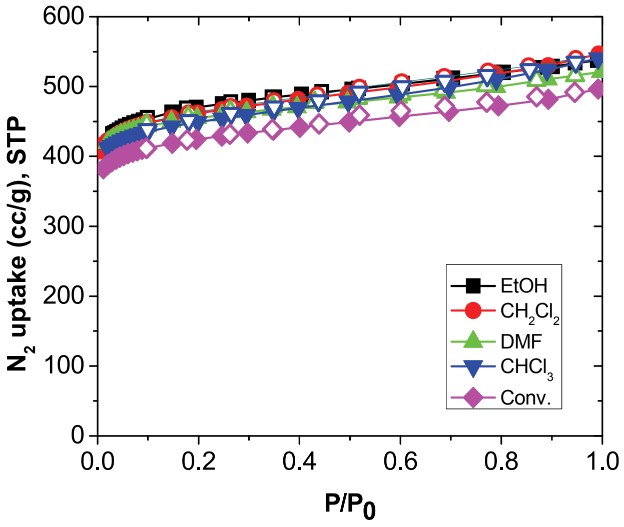

Figure S26. Nitrogen adsorption (solid) and desorption (open) isotherms at 77 K for HKUST-1 by conventional heating under vacuum at 170 °C for 24 h after exchange with CH_2Cl_2 ◆; heating under vacuum at 170 °C for 24 h after flowing SC-CO_2 activation from absolute ethanol ■, CH_2Cl_2 ●, $CHCl_3$ ▼, and DMF ▲

Table S3. BET (Langmuir) surface areas (m^2/g) of HKUST-1 activated by flowing SC-CO_2 and conventional heating.

Solvent	Flowing SC-CO_2 activation	Heating after flowing SC-CO_2 activation	Conventional heating under evacuation
DMF	830 (981)	1737 (2024)	
CH_2Cl_2	1098 (1281)	1751 (2068)	1620 (1893)
$CHCl_3$	1394 (1613)	1713 (2010)	
Ethanol	1610 (1891)	1770 (2110)	

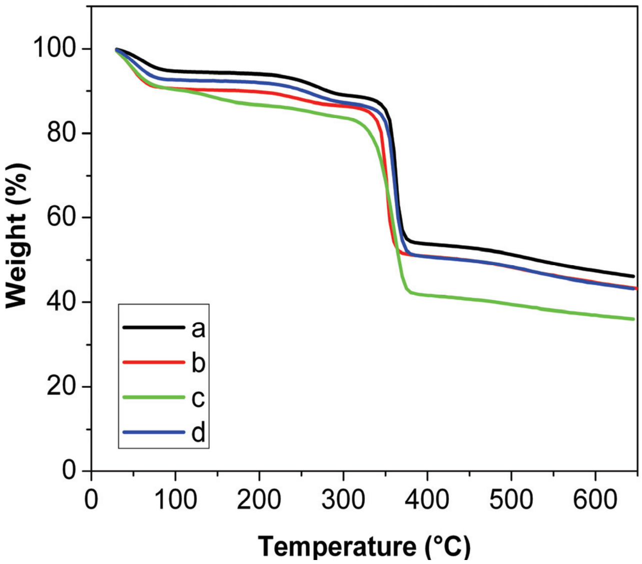

Figure S27. TGA trace of activated HKUST-1 by flowing SC-CO_2 from different solvents and conventional heating under vacuum. (a: heating after flowing SC-CO_2 from DMF (black); b: heating after flowing SC-CO_2 from CH_2Cl_2 (red); c: flowing SC-CO_2 from EtOH (green); d: Conventional activation (blue)).

X. Synthesis, Powder XRD patterns, N_2 adsorption isotherms, and TGA traces of UMCM-150

Biphenyl-3,4',5-tricarboxylic acid (0.060 g, 0.21 mmol) and $Cu(NO_3)_2 \cdot 2.5H_2O$ (0.099 g, 0.042 mmol) were dissolved in DMF/dioxane/H_2O (4:1:1, 30 mL). The solution was placed in a tightly capped 60 mL jar and heated at 75 °C for 12 h. Upon cooling the mother liquor was decanted and replaced thrice with fresh DMF and then activated by flowing SC-CO_2. Conventional activation: DMF-solvated crystals were exchanged with fresh acetone three times over a period of three days, the crystals were then activated under vacuum at ambient temperature for 20 h and further evacuated at 100 °C overnight.[S8]

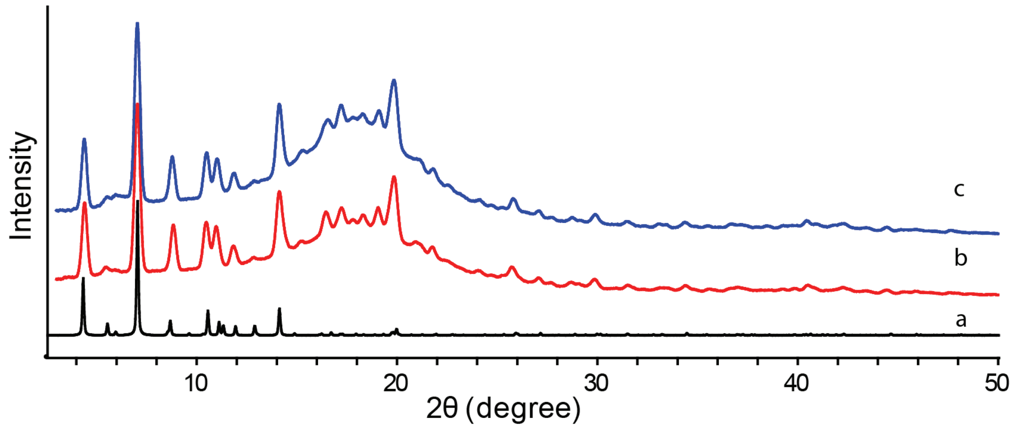

Figure S28. PXRD patterns of UMCM-150. a) Simulated, b) flowing SC-CO_2 activation from DMF, c) exchange with acetone then evacuation at 100 °C for 2 h.

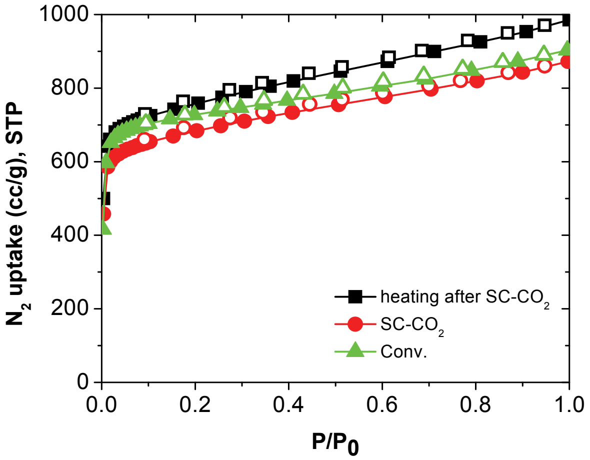

Figure S29. Nitrogen adsorption (solid) and desorption (open) isotherms at 77 K for UMCM-150 by exchange with acetone then evacuation at 100 °C ▲; flowing SC-CO_2 activation from DMF ●, and heating at 100 °C over night after flowing SC-CO_2 activation from DMF ■.

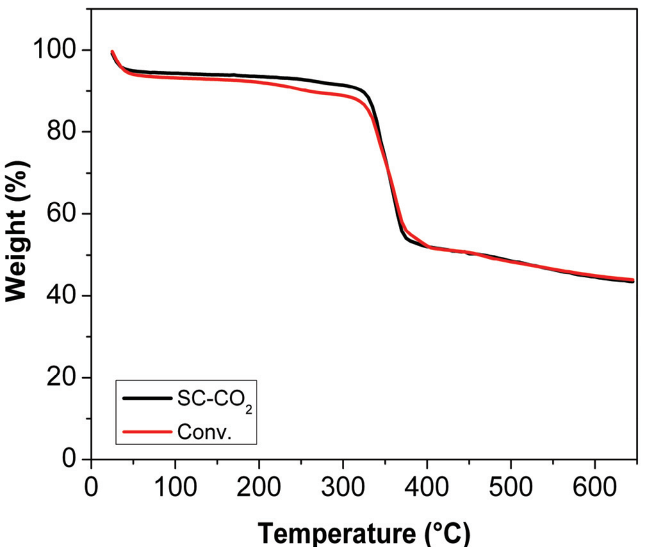

Figure S30. TGA trace at 5 °C/min of activated UMCM-150 by heating at 100 °C after flowing SC-CO_2 activation of DMF-solvated sample (black) and exchange with acetone then evacuated at 100 °C (red).

XI. Disclaimer

XII. References

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