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Supporting Information

Superior Metal-Organic Framework Activation with Dimethyl Ether

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Supporting Information

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1. Description of dimethyl ether (DME) activation apparatus and protocol

Caution: Dimethyl ether is extremely flammable and should be handled with caution. Personal protective equipment (lab coat, goggles, and gloves) should be worn when handling to prevent frostbite.

Description of DME washing apparatus. The experimental setup is shown in Figure 1. In a typical experiment, solvated MOF is loaded (via 9'' glass pipette) into a glass column (approximately 3.5 mL volume) plugged at the bottom with 4-micron quartz wool to retain the sample. The column is then installed into the apparatus via ¼'' Swagelok fittings. For all MOFs, the column was initially filled with DME and then immediately vented. Two subsequent cycles of DME filling followed by venting were performed over the course of 8 hours

Part list. The DME washing apparatus consists of the following parts: glass column (length = 5'' and outer diameter= ¼''), stainless steel 1-piece 40G 3-way ball valve (Swagelok), stainless steel tube fittings, 1/8'' x ¼'' unions, soft coil copper tubing, CGA fitting 350 (for DME cylinder), needle valve, Teflon ferrules (for glass connections only), and a 1/8'' two-way valve (Swagelok).

Assembly. The 350 CGA fitting was attached to the DME gas cylinder (dip tube cylinder) to introduce DME through the metering valve that throttles the flow of DME into the vessel. At one end of the metering valve is a 3-way valve that opens the system to DME, nitrogen, or isolates the vessel. The two way-ball valve is connected to the column at the end of the apparatus to vent DME in and out of the column (this can optionally be substituted with a cap nut).

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Description of Activation Protocol. Once the MOF has been exchanged in DME as described above, the MOF was transferred into a glass activation bulb, placed on a Schlenk line, and dried under dynamic vacuum. While under dynamic vacuum, the vessel was evacuated at room temperature (for MOF-5, UMCM-151, Cu-DUT-23, and DUT-34) or heated at a constant temperature of 120 °C (HKUST-1and Zn-MOF-74) in an oil bath. The MOF remained under vacuum and heating for 16–24 hours. The MOF was transferred to a nitrogen glovebox until further use.

Description of NMR sample preparation by digestion. The DME-exchanged MOF was digested in 600 µL of DMSO-d_6 and 100 µL of 35 wt.% DCl in D_2O.

SUPPORTING INFORMATION

2. Materials

Solvents: dimethylformamide (DMF, Fisher Scientific, ACS grade), acetone (99.8%, Extra Dry, AcroSeal), 1,4-dioxane (ACS grade, Fisher Scientific), ethanol (EtOH, Decon Labs, 200 proof), methanol (MeOH, Fisher Scientific, ACS grade), diethylformamide (DEF, TCI America, 99%, purified by storage on activated charcoal for ~1 month followed by removal of impurities via silica gel column), dimethyl ether (DME, Airgas 99.5%), dimethyl sulfoxide-d_6 (DMSO-d_6, Sigma-Aldrich, 99.9% atom D), deuterium chloride (35 wt.% DCl in D_2O), Sigma-Aldrich, 99 atom % D). Deionized water was used for all syntheses where H_2O was required.
To minimize solvent water content, MeOH and EtOH were stored over 3Å activated sieves, whereas DEF was stored over 4Å activated sieves.

Metal Salts: copper(II) nitrate hemi(pentahydrate) ($Cu(NO_3)_2 \cdot 2.5H_2O$, Fisher Scientific, ACS reagent, 98%), magnesium acetate tetrahydrate ($Mg(OAc)_2 \cdot 4H_2O$, Fisher Scientific, 98% ACS reagent), zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$ Fisher Scientific, 99.98%).

Organic Linkers: benzene-1,3,5-tricarboxylic acid (H_3BTC, TCI, 98%), 2,5-dihydroxyterephthalic acid (H_4DOBDC, Hang Zhou Trylead Chemical Technology Corporation Ltd., 97%), benzene-1,4-dicarboxylic acid (H_2BDC, Sigma Aldrich, 98%), 1,3,5-tris(4-carboxyphenyl)benzene (H_3BTB, Alfa Aesar, 97%). All linkers were used without further purification.

Other synthesis materials: methyl 3,5-dibromobenzoate and 4-(methoxycarbonyl)phenylboronic acid (98% and 96% respectively, TCI America), tetrakis(triphenylphosphine)palladium(0), 99% (99.9+%-Pd, Strem Chemicals), pyridine (ACS grade, Fisher Scientific), potassium phosphate tribasic (97%, Fisher Scientific), potassium hydroxide (Fisher Scientific), trifluoroacetic acid (99% Acros Organics), 4-4’ bipyridine (98% Acros Organics).

3. Instrument details

Nitrogen (N_2) Sorption: N_2 isotherms were obtained using a Nova 4200e gas sorption analyzer by Quantachrome Instruments (Boynton Beach, Florida, USA). N_2 (99.999% purity) was purchased from Cryogenic Gases and used as received. Samples were loaded into a calibrated sorption tube and isotherms were measured at 77 K in the range of $5.0 \times 10^{-3} \leq P/P_o \leq 1$, collecting 45 adsorption points and 20 desorption points. Sample surface areas were calculated by using the BET method where the linear region was $0.02 \leq P/P_o \leq 0.05$. Data was collected using the NovaWin Software.

Thermogravimetric Analysis (TGA) and Infrared Spectroscopy (IR):TGA-IR data was collected using a PERSEUS TGA 209 F1 Libra® coupled to a Nicolet iS50 FTIR Spectrometer with TGA-IR module (Thermo Scientific). Samples ($5 \text{ mg} \leq x \leq 15 \text{ mg}$) were loaded into a tared alumina crucible and then samples were heated from 20 – 300 °C at a ramp rate of 5 °C/min. All data was collected and worked up in Omnic Spectra or Proteus Thermal Analysis.

Proton Nuclear Magnetic Resonance Spectroscopy (^{1}HNMR): NMR spectra were obtained using a 400 MHz spectrometer. All data was collected in NMR software VNMRJ then worked up using MestReNOVAx64.

4. MOF synthesis

MOF synthesis and activation:

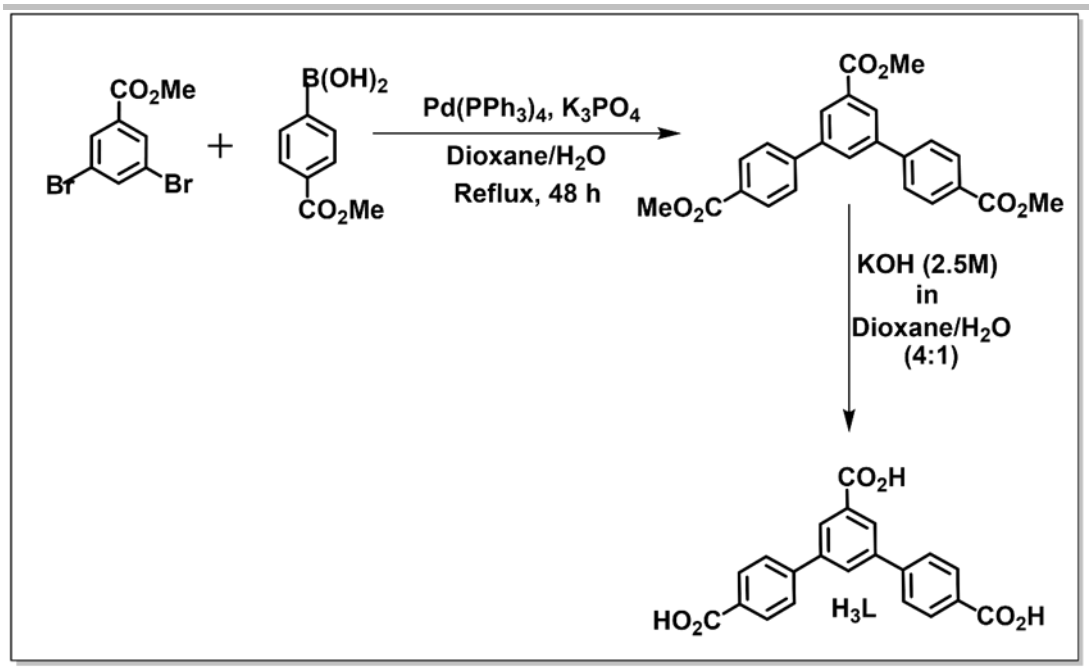
MOF syntheses followed reported literature protocols with minimal changes. Syntheses were performed in 20–60 mL vials sealed by Teflon-lined caps unless otherwise specified.

MOF-5 synthesis[1] and activation: In a 60 mL vial, 4.44 g of $Zn(NO_3)_2 \cdot 6H_2O$ and 670 mg H_2BDC were added to 50 mL of DEF. The mixture was sonicated for approximately 15 minutes to dissolve the salt and linker. Into five 20 mL scintillation vials, 10 mL of precursor solution were transferred. The vials were then placed into a preheated oven (100 °C) for 18–24 hours. After the time elapsed, the mother liquor was decanted, and the crystals were washed 3 times with DMF following the published procedure.[2] Approximately 40 mg of MOF was then transferred to the apparatus for DME activation (exchange and evacuation).

HKUST-1 synthesis[3] and activation: H_2O, EtOH, and DMF were combined in a 30 mL jar at a ratio of 1:1:1 (total volume 30 mL). To this mixture 0.6714 g of $Cu(NO_3)_2 \cdot 2.5H_2O$ and 0.3109 g of H_3BTC were added. The mixture was then sonicated (approximately 15 minutes at 30 °C) to dissolve both the salt and linker. To this cloudy blue solution, 10–15 drops of concentrated HCl were added via glass pipette which turned the solution transparent. The contents of the jar were then transferred to three 20 mL scintillation vials (10 mL/vial). The vials were then placed in an oven, set to 85 °C, for approximately 20 hours. The vials were then allowed to cool to room temperature and the mother liquor was decanted. The MOF was then combined into one vial and washed 3 times with fresh DMF and agitated on an IKA HS 260 shaker (120 rpm) to facilitate exchange. Once fully exchanged, the MOF was transferred to the DME apparatus for washing and activation during which time the material turned purple.

Zn-MOF-74 synthesis and activation: This synthesis was scaled down and modified from a previously published procedure.[4] In a 55 mL vial, 0.125 g of H_4DOBDC and 0.565 g of $Zn(NO_3)_2 \cdot 6H_2O$ were added then dissolved in 25 mL of DMF and 1.25 mL of H_2O. The mixture was sonicated for approximately 15 minutes at ~30 °C to dissolve the salt and linker. After sonicating, the solution was placed in an oven at 100 °C for ~20 hours. The vial was then removed from the oven and the hot mother liquor was decanted. The MOF was washed with MeOH 3 times over the course of 6 days. Once fully exchanged, the MOF was transferred to the DME apparatus for washing and activation.

UMCM-151 ligand synthesis: The linker for UMCM-151 was synthesized following a published procedure.[5]



Scheme S1. Synthesis of the linker (H_3L) for UMCM-151.

UMCM-151 synthesis[5] and activation: The linker (H_3L) (50.05 mg) was added to a solution of DMF/dioxane/H_2O (4:1:1, 10 mL total volume) in a 20-mL scintillation vial. To this mixture, $Cu(NO_3)_2 \cdot 2.5H_2O$ (96.04 mg) was added, and the contents were sonicated until dissolved and then heated at 80 °C for ~16 hours. Bluish green plate-like crystals were obtained, which were washed 3 times over an hour with DMF to ensure removal of unreacted linker. Multiple batches of the MOF were synthesized and stored in DMF to be treated with acetone or DME.

Conventional activation: The crystals were then exchanged with dry MeOH for 3 days, four times each day. The sample was further treated with dry acetone 3 times in 1 day. After removing acetone by decanting, the sample was dried under vacuum (0.03 Torr) at room temperature for 4 hours, and then further heated at 60 °C for 12 hours during which time the material turned green.

Supercritical CO_2 activation: After the crystals were washed in DMF, the crystals were washed repeatedly with ethanol 3 times in 1 day. Ethanol solvated crystals were then activated through flowing supercritical CO_2 activation for a period of 5 hours.[6] Following supercritical activation, the crystals were further heated under dynamic vacuum (0.01 Torr) at 80 °C for 12 hours.

DME activation: ~100 mg of MOF crystals stored in DMF were loaded into the DME exchange apparatus for exchange and activation, during which time the material turned blue.

DUT-34 synthesis and activation: DUT-34 was synthesized following a published literature with slight modifications.[7] $Cu(NO_3)_2 \cdot 2.5H_2O$ (241 mg), H_3BTB (109 mg), and benzoic acid (299 mg) were added to a screw-capped vial (20 mL). The contents were dissolved in a mixture of DMF (5 mL), EtOH (abs., 5 mL), and pyridine (65 µl) through sonication for 5 min and then heated at 80 °C for ~20 hours. Clear light blue crystals were obtained. These crystals were washed repeatedly with DMF to ensure removal of unreacted linker. Crystals were washed

with fresh DMF two times for 3 consecutive days and then exchanged with EtOH. EtOH exchange was performed 3 times in 1 day.

Conventional activation: Ethanol solvated crystals were then activated through flowing supercritical CO_2 activation for a period of 5 hours.[6] Following supercritical activation, the crystals were further heated under dynamic vacuum (0.01 Torr) at 80 °C for 12 hours.

DME activation: The material was loaded into the DME exchange apparatus (from DMF) and then exchanged and evacuated at room temperature following the procedure above during which time the material turned blue.

Cu-DUT-23 synthesis and activation: Cu-DUT-23 was synthesized following a published literature procedure.[7] In a 20 mL vial $Cu(NO_3)_2 \cdot 2.5H_2O$ (0.241 g), 2-2 bipyridine (0.042 g) and H_3BTB (0.109 g) were added. To the same reaction vial 5 mL of DMF, 5 mL of EtOH, and 50 µL of trifluoroacetic acid were added. The vial was then capped, sonicated for 5 minutes to dissolve the solids, then transferred to a heated oven at 80 °C for 20 – 24 hours. Clear light blue crystals were obtained. The mother liquor was then decanted, and the crystals were washed with fresh DMF 3 times over 2 days.

DME activation: The material was loaded into the DME exchange apparatus (for exchange and activation at 120 °C) during which time the material turned blue.

5. Characterization of dimethyl ether exchange by NMR spectroscopy

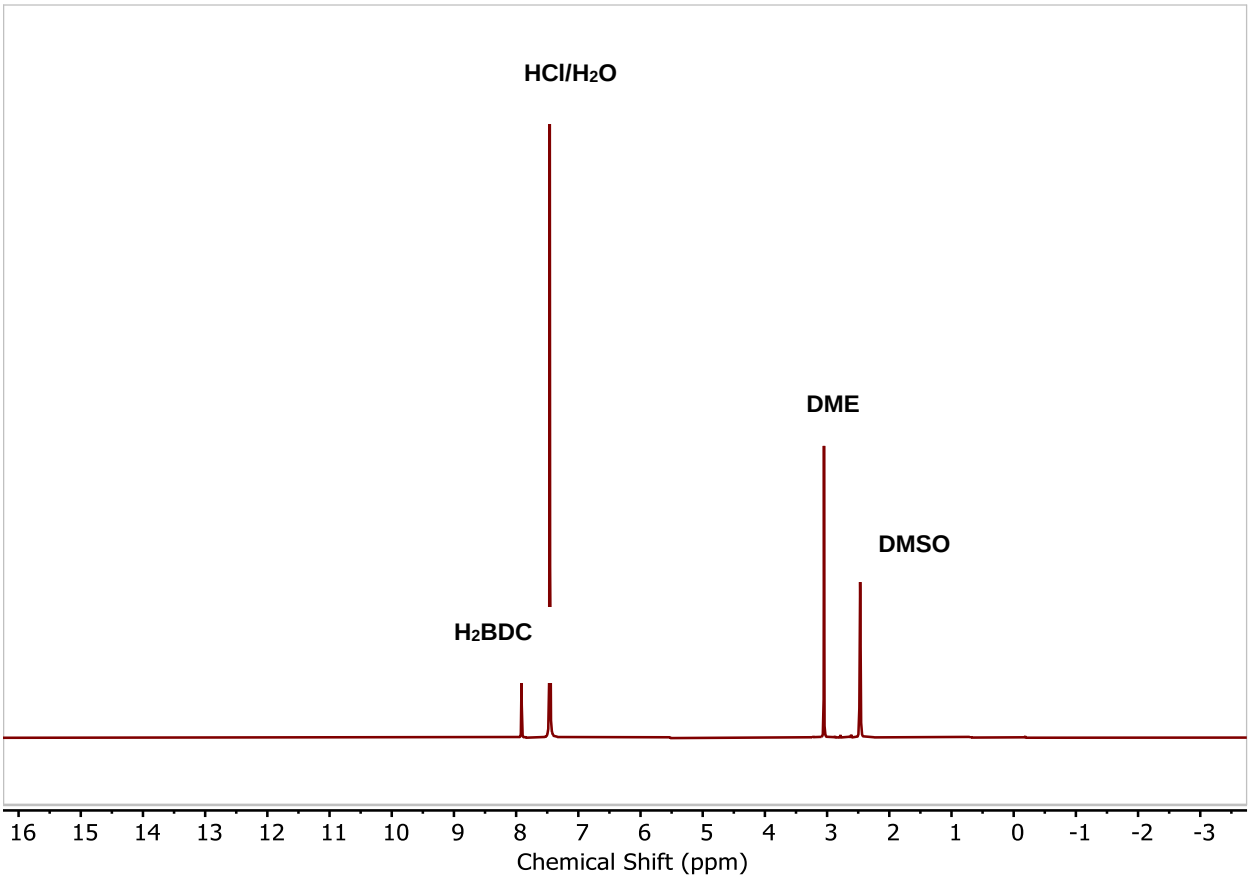


Figure S1. ^{1}H-NMR spectrum of twice DME exchanged and digested MOF-5.

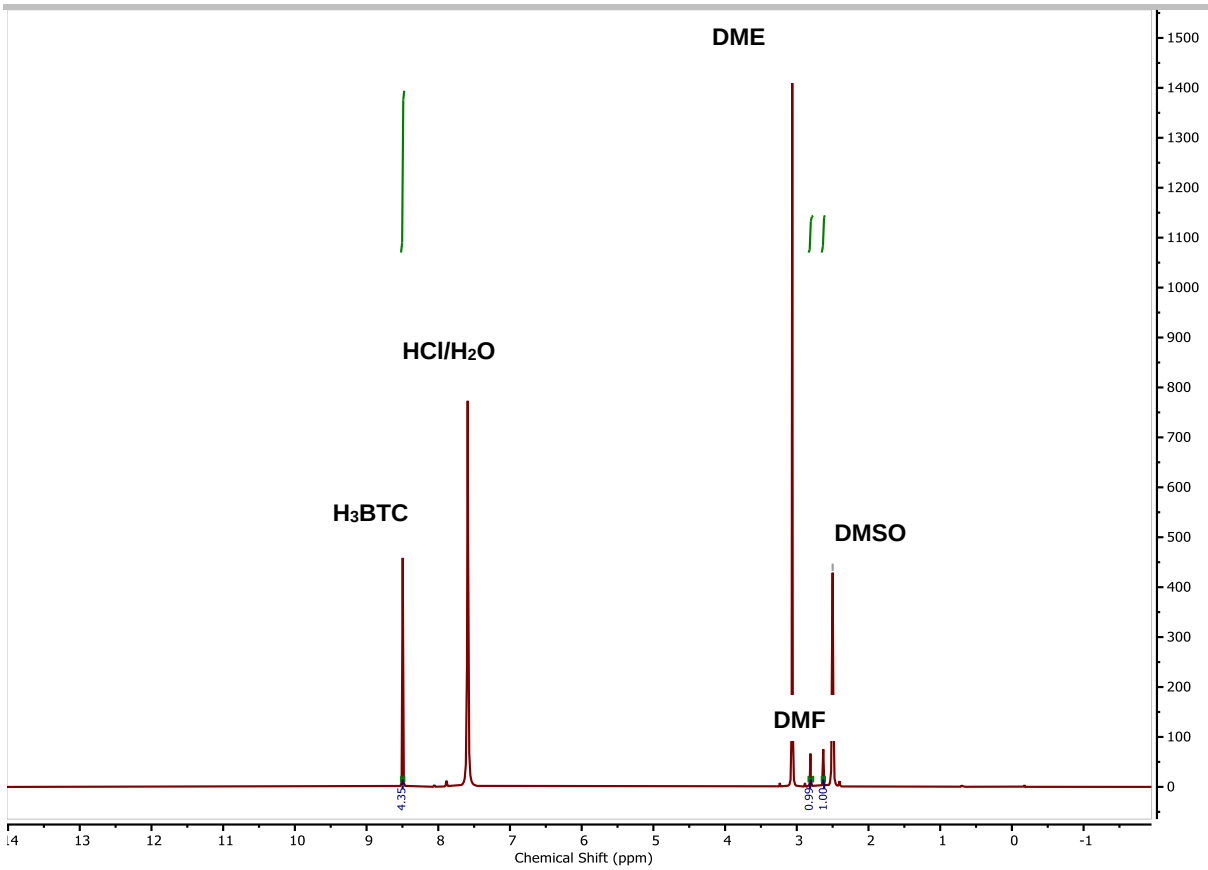


Figure S2. ^{1}H-NMR spectrum of 1-hour DME exchanged and digested HKUST-1

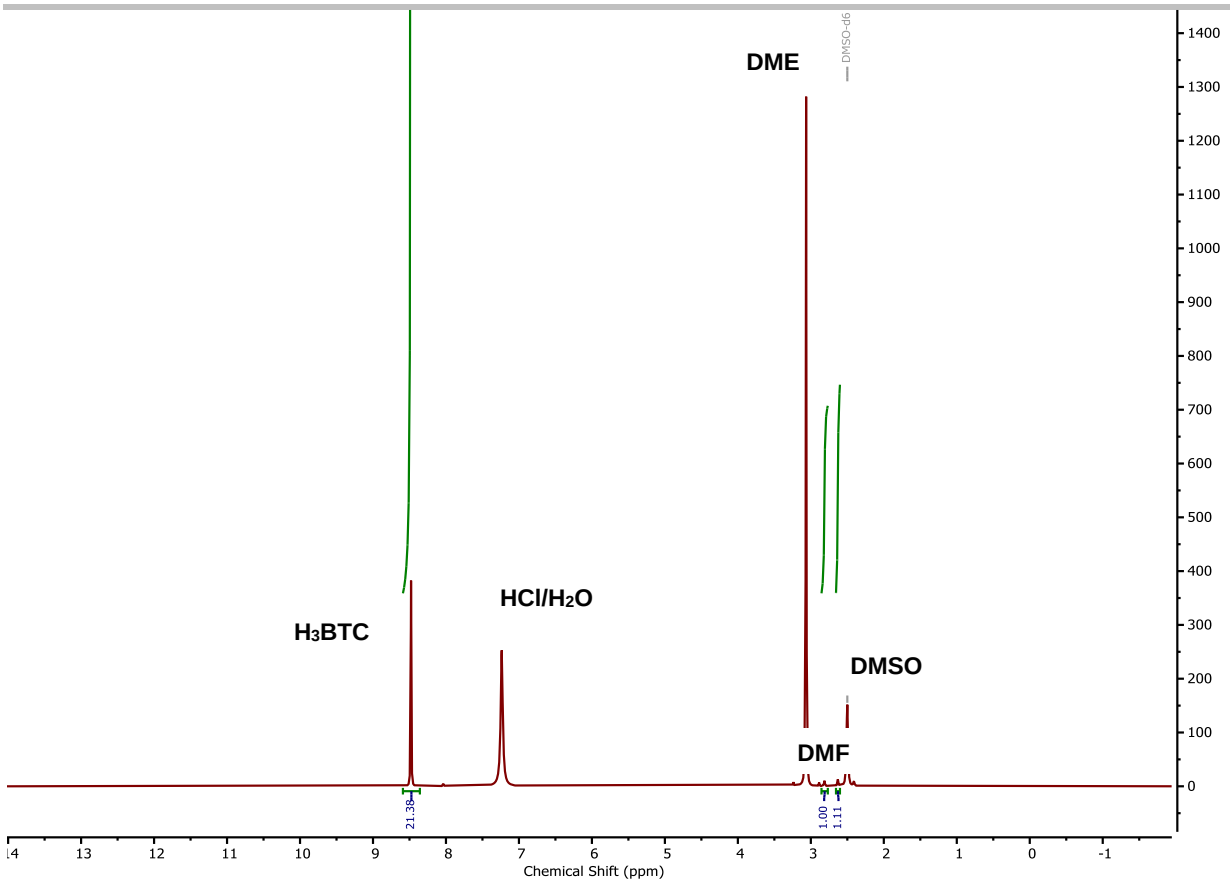


Figure S3. ^{1}H-NMR spectrum of twice DME exchanged and digested HKUST-1.

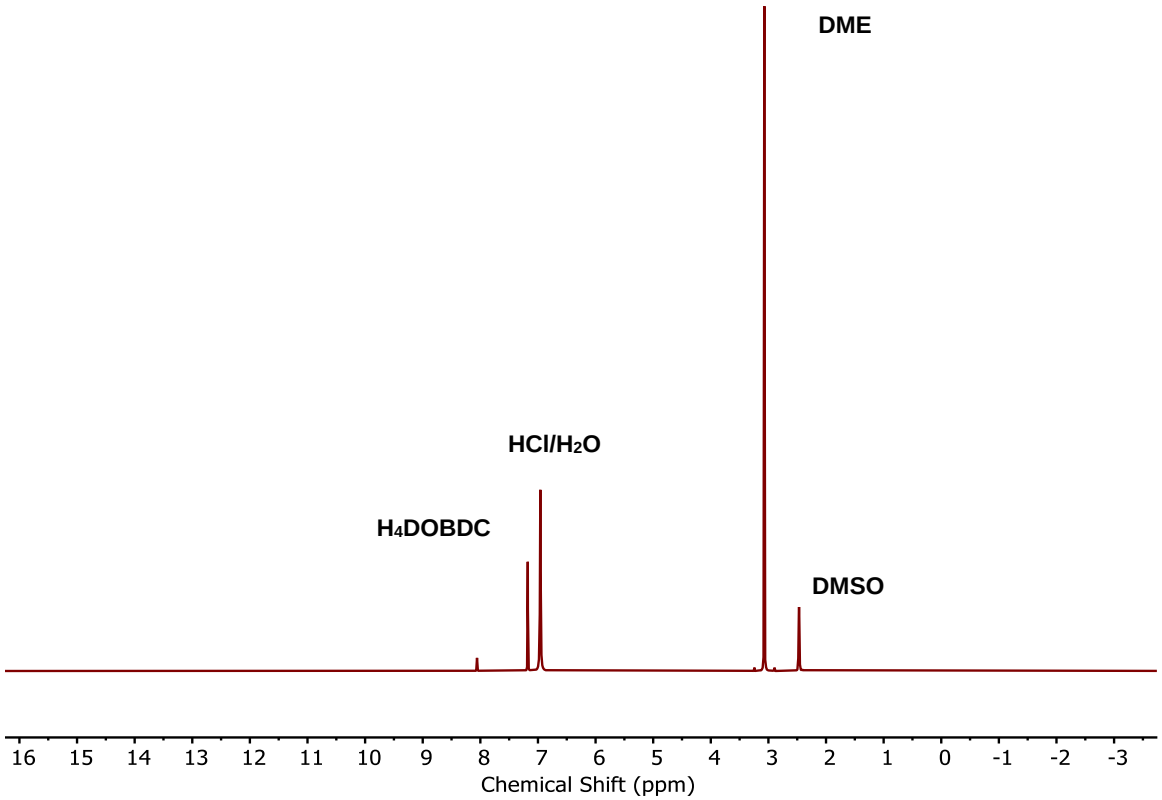


Figure S4. ^{1}H-NMR spectrum of twice DME exchanged and digested Zn-MOF-74.

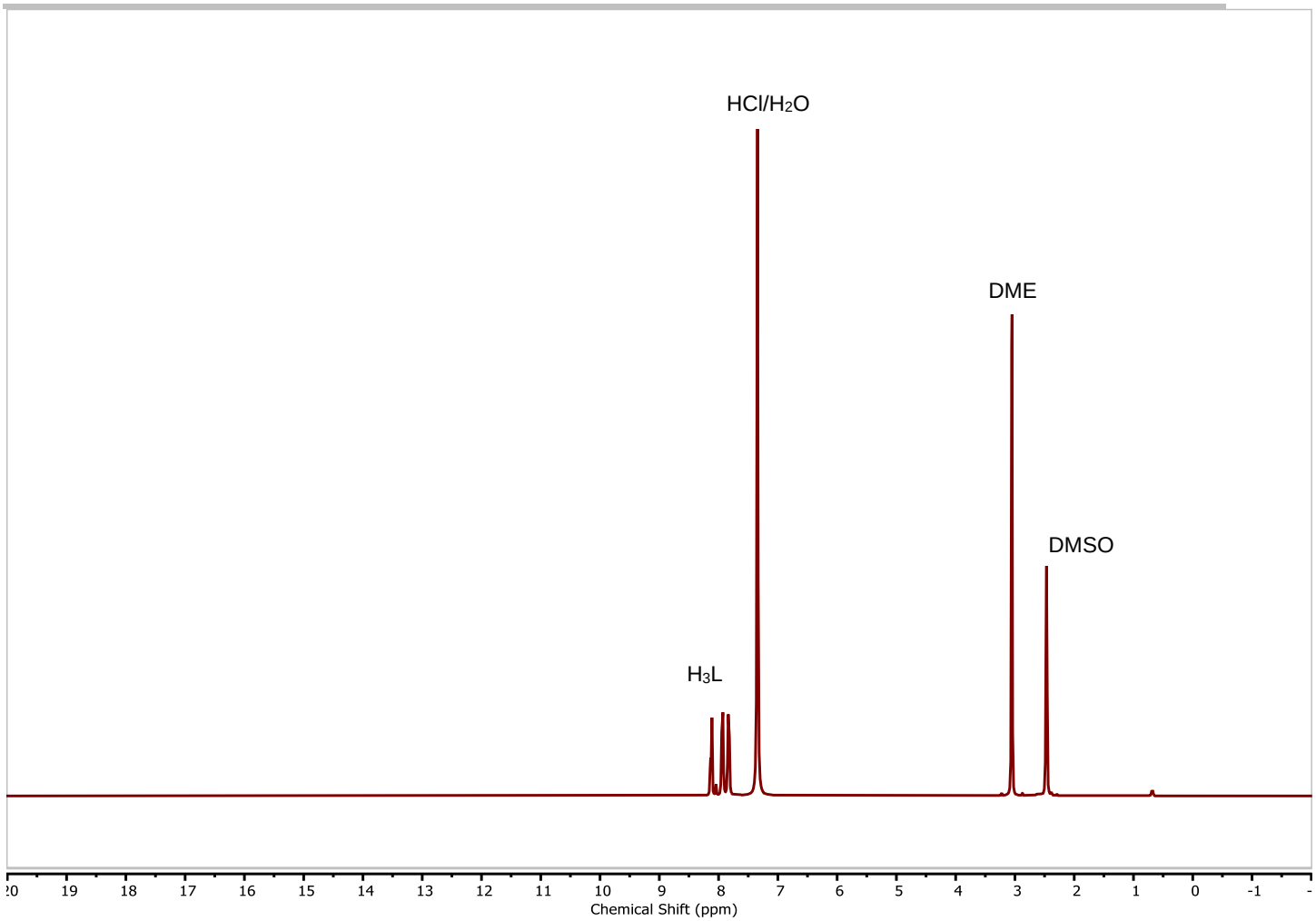


Figure S5. ^{1}H-NMR spectrum of twice DME exchanged and digested UMCM-151.

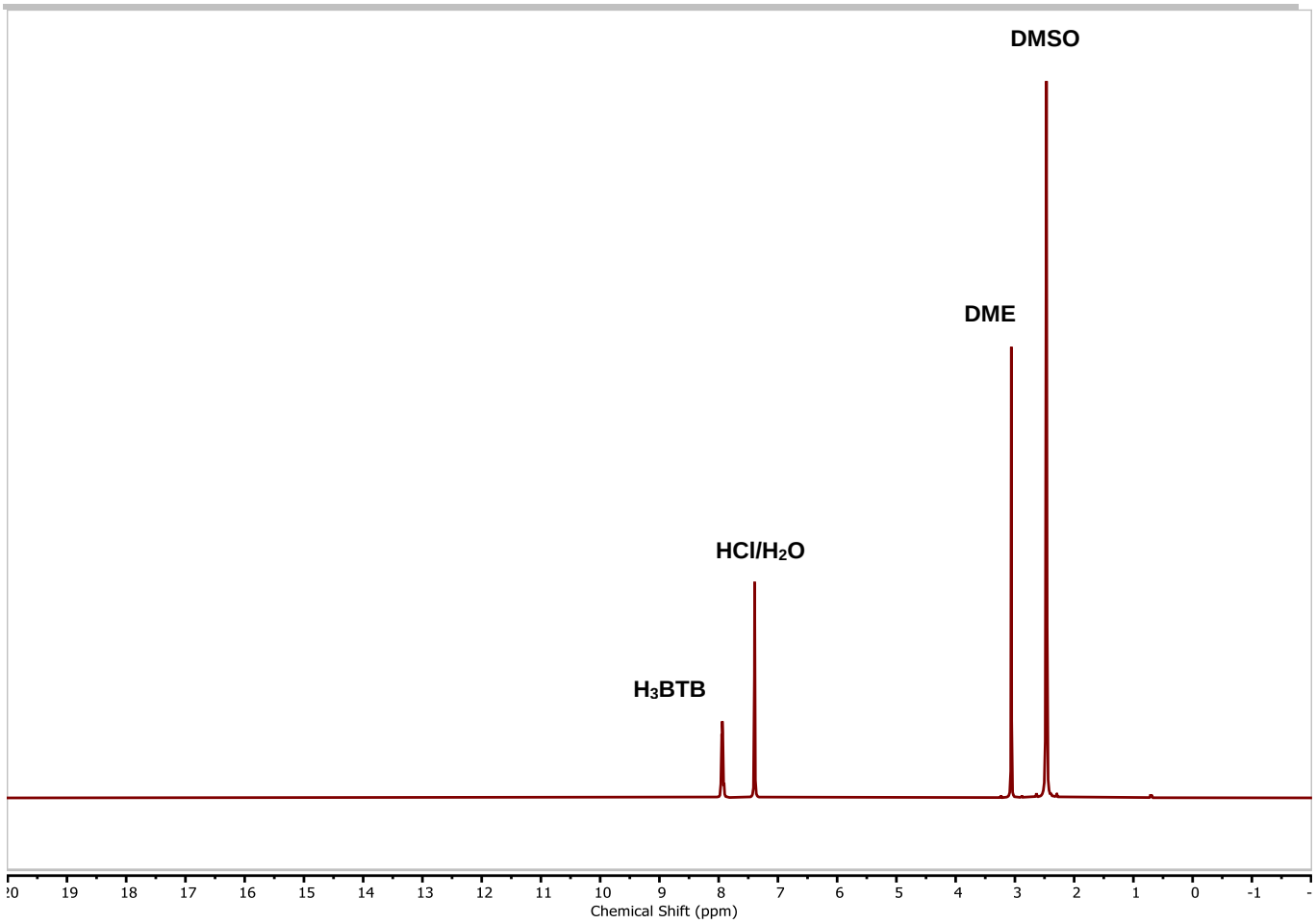


Figure S6. ^{1}H-NMR spectrum of twice DME exchanged and digested DUT-34.

6. TGA-IR data for DMF and DME exchanged HKUST-1

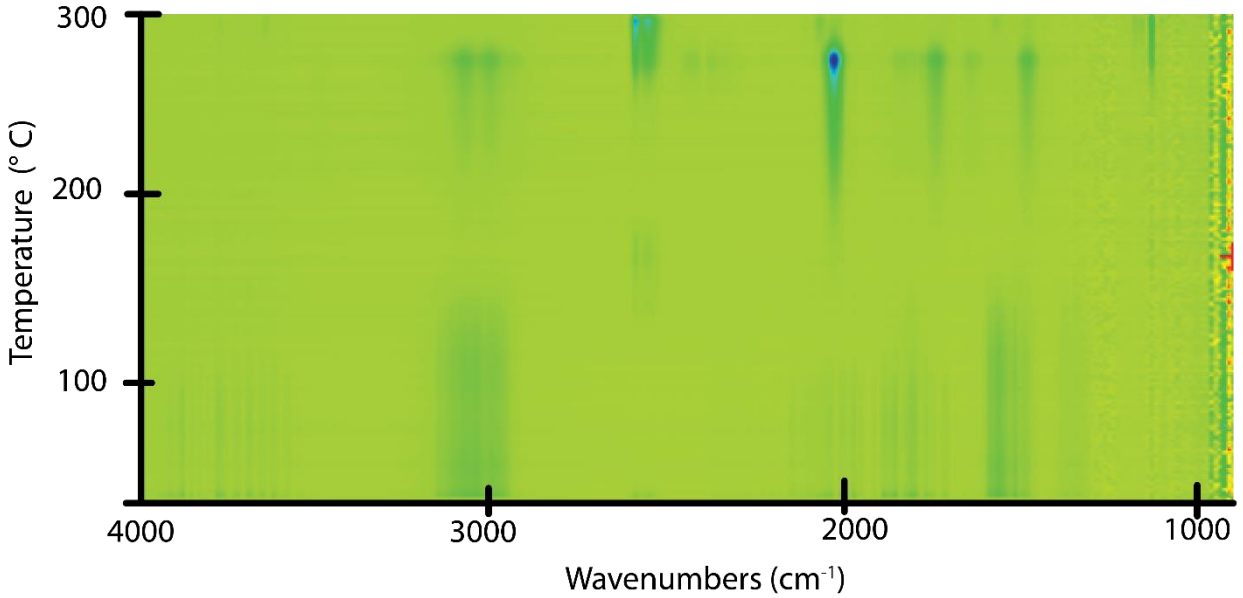


Figure S7. Two-dimensional contour plot of IR spectra of 1-hour DME exchanged HKUST-1. Experimental heating parameters set to 25 – 300 °C at a ramp rate of 5 °C/min.

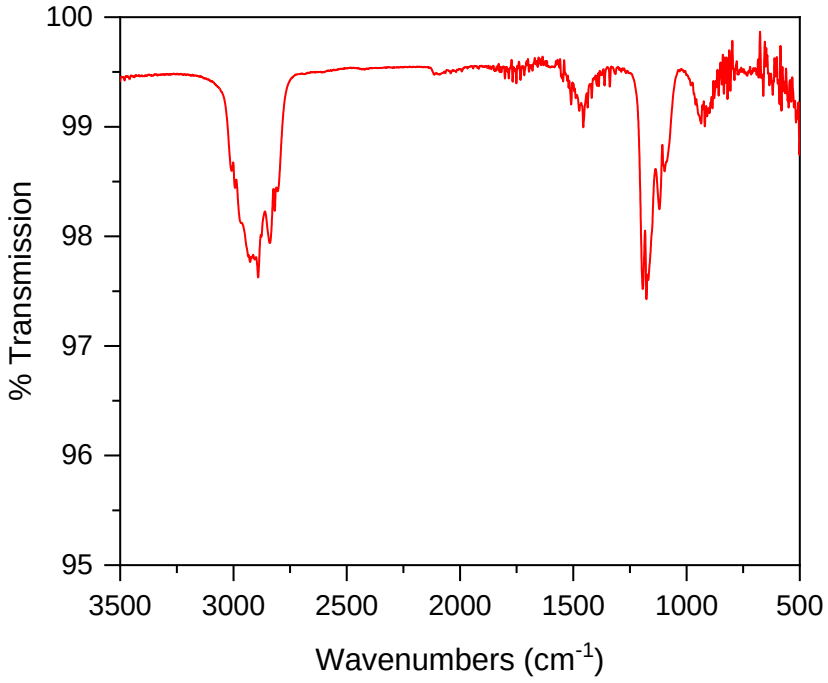


Figure S8. IR Spectrum of DME from 1-hour DME exchanged HKUST-1, at 87 °C the spectrum is consistent with DME and an absence of DMF.

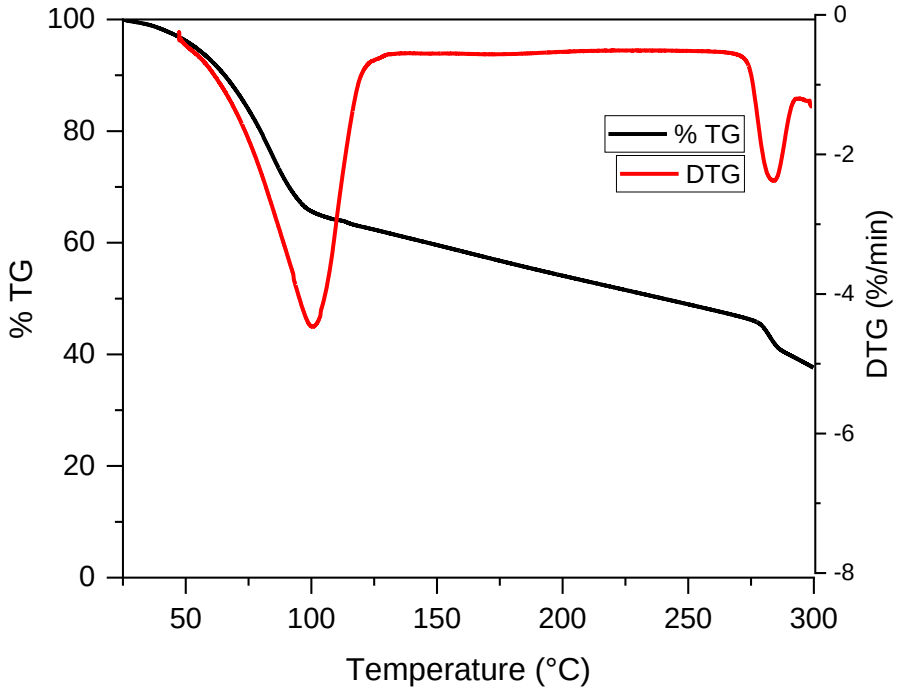


Figure S9. TGA thermogram of DMF exchanged HKUST-1 from room temperature to 300 °C with 1st derivative thermogram.

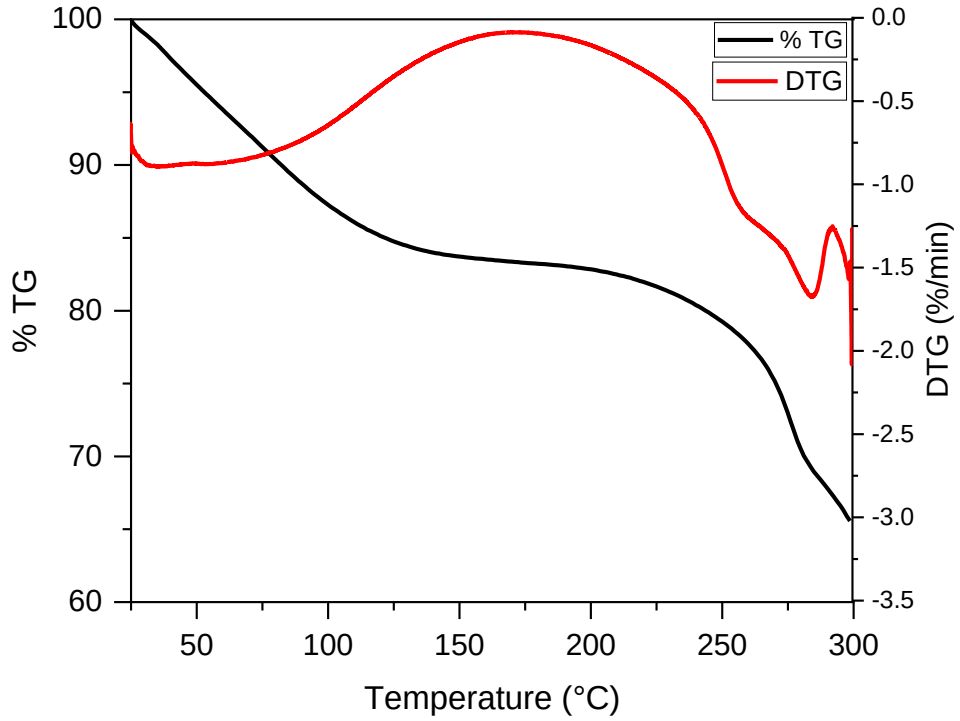


Figure S10. TGA thermogram of 1-hour DME exchanged HKUST-1 from room temperature to 300 °C with 1st derivative thermogram.

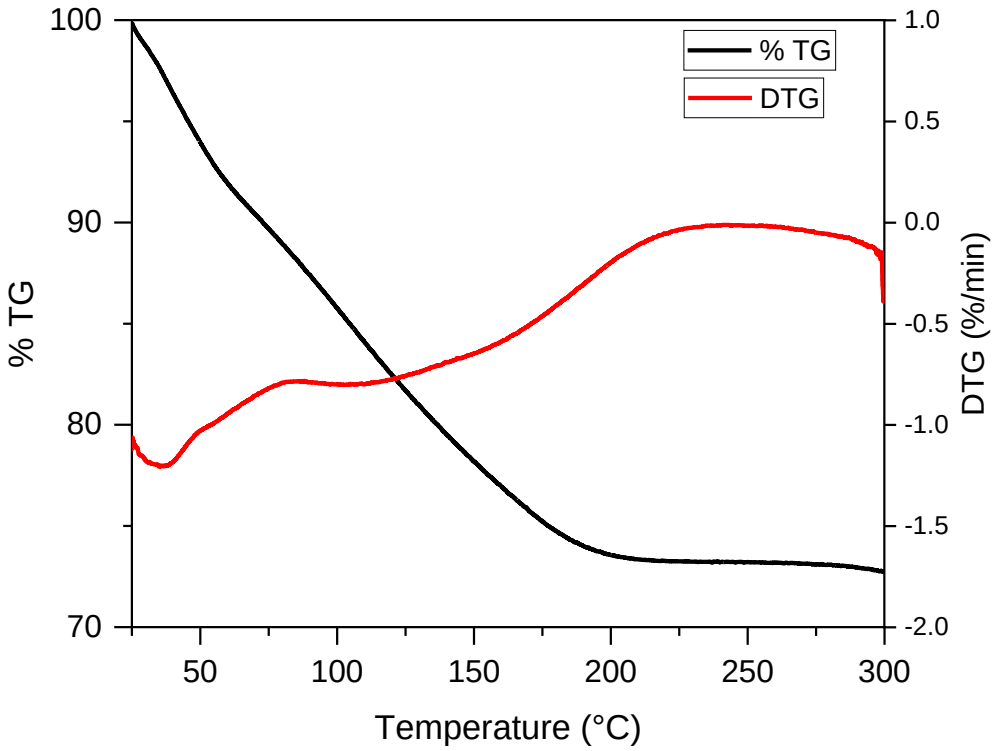


Figure S11. TGA thermogram of twice 4-hour DME exchanged HKUST-1 from room temperature to 300 °C with 1st derivative thermogram.

7. Measured nitrogen adsorption isotherms

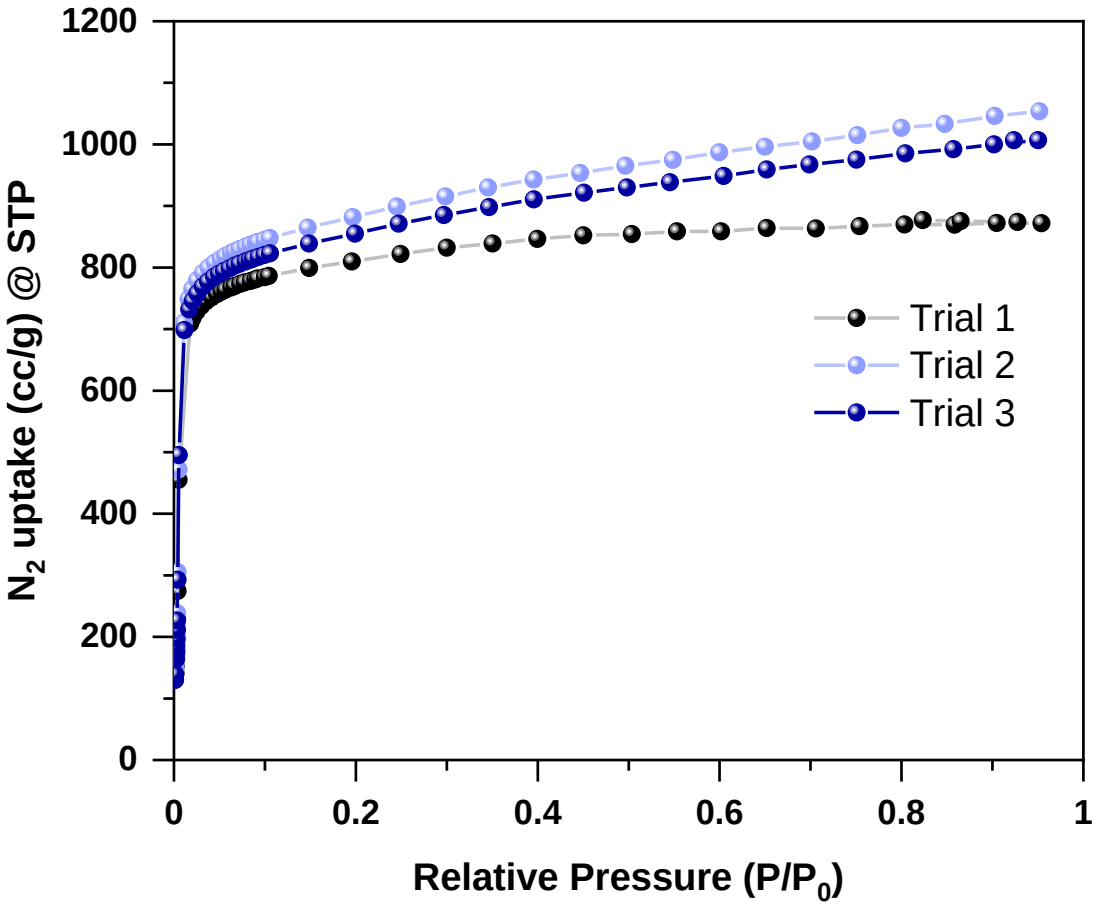


Figure S12. N_2 sorption isotherm at 77K of twice DME exchanged, and room temperature activated MOF-5. Experiments were performed in triplicate and yielded an average BET surface area = 3350 m^2/g.

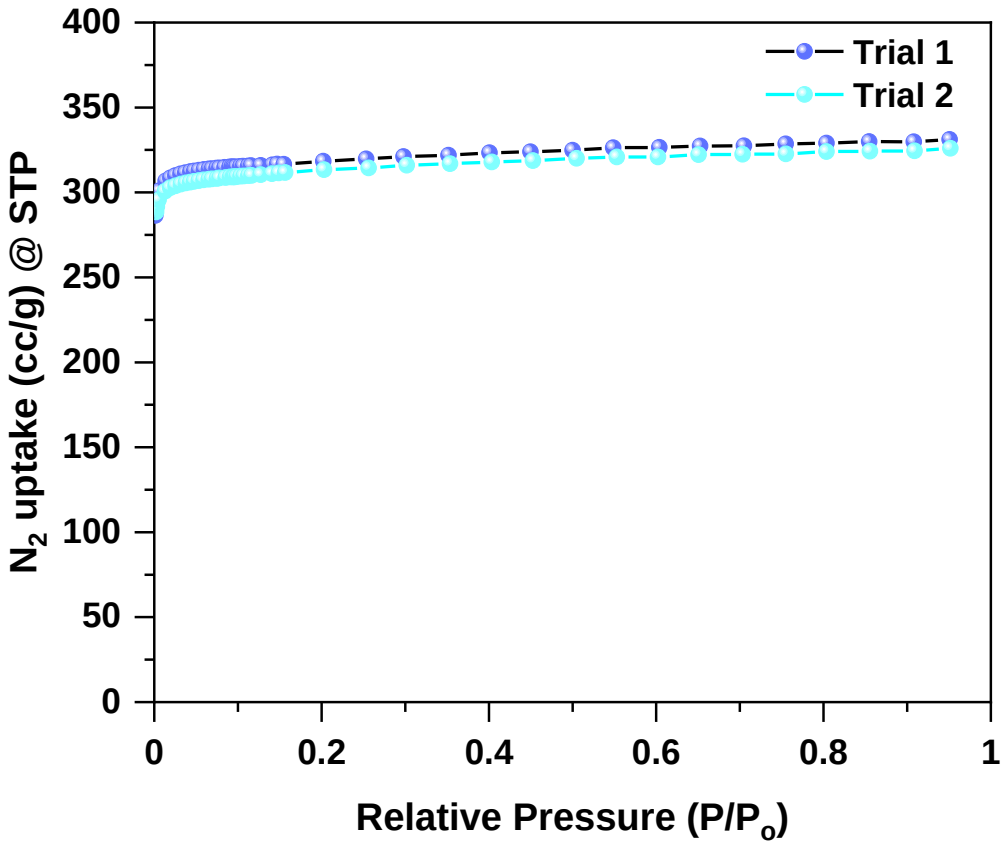


Figure S13. N_2 sorption isotherms at 77 K of twice exchanged DME activated Zn-MOF-74 at 120 °C. Experiments were performed in duplicate and yielded an average BET surface area ~1250 m^2/g.

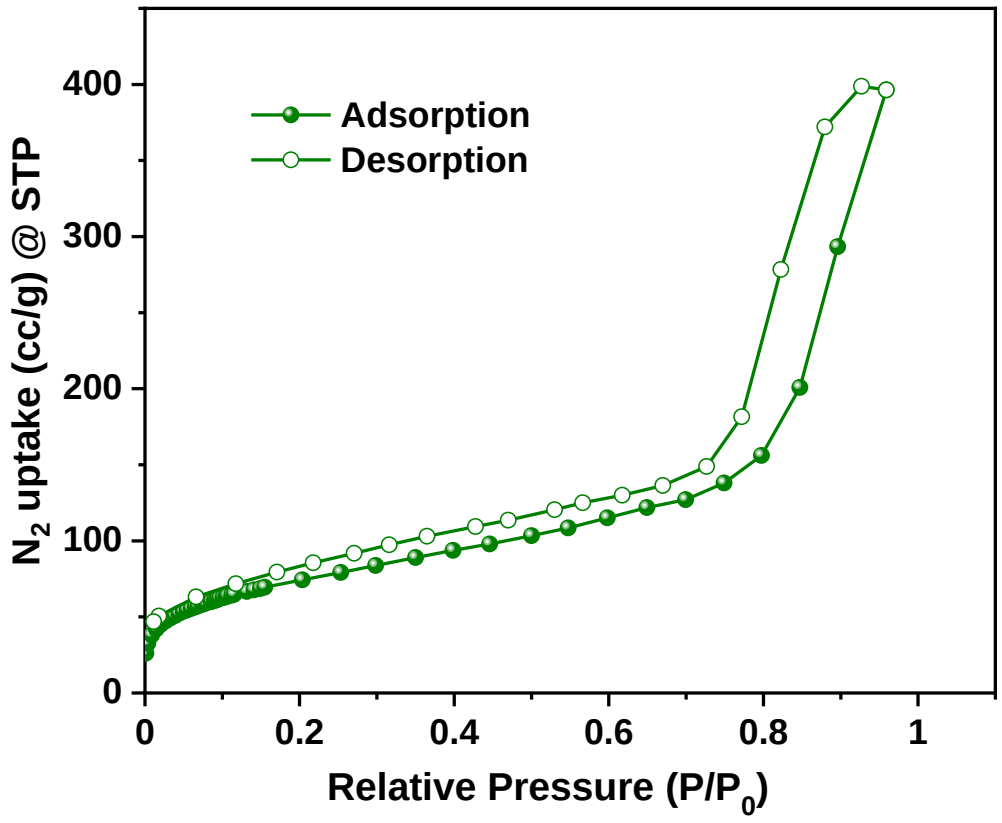


Figure S14. N_2 sorption isotherm at 77K for conventional heating activation at 60 °C from acetone of UMCM-151 with BET surface area of 263 m^2/g.

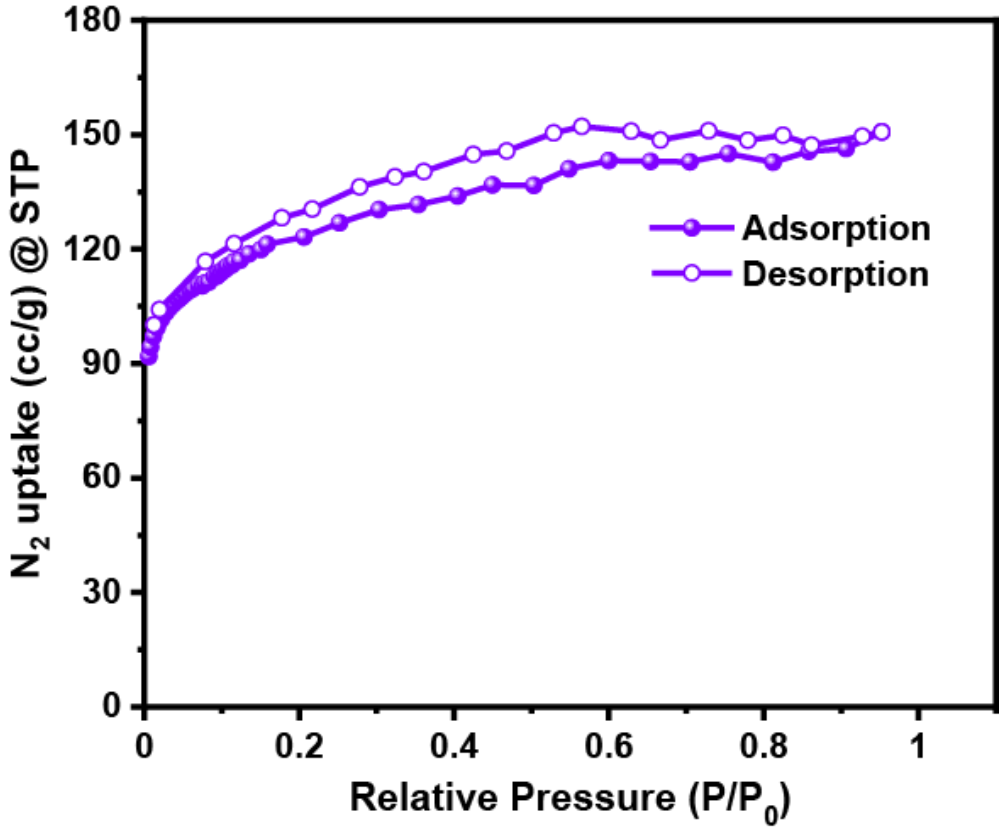


Figure S15. N_2 sorption isotherm at 77K for supercritical CO_2 activated UMCM-151 with BET surface area of 455 m^2/g.

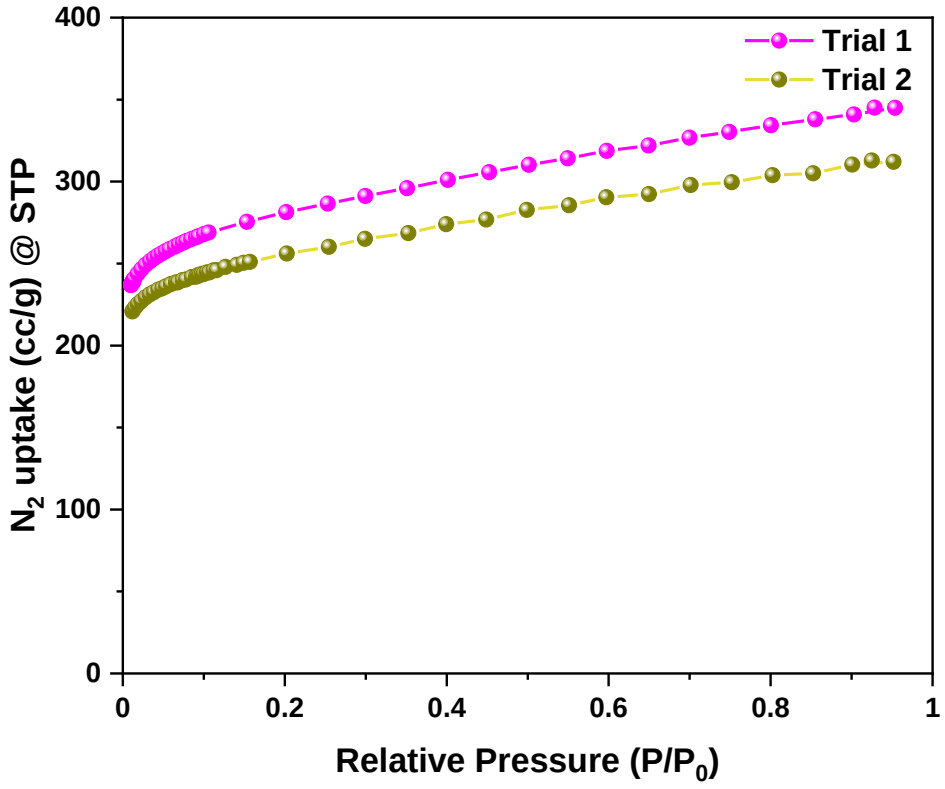


Figure S16. N_2 sorption isotherms at 77K for twice DME exchanged room temperature activated UMCM-151. Experiments were performed in duplicate and yielded an average BET surface area of ~960 m^2/g.

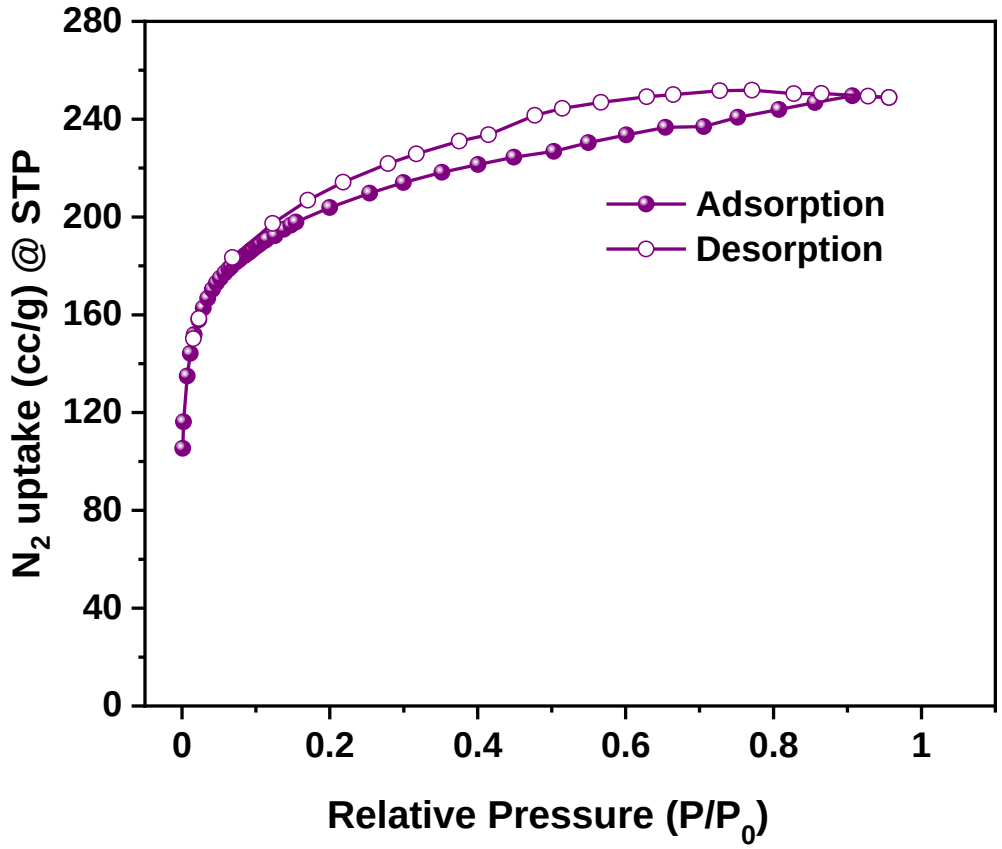


Figure S17. N_2 sorption isotherm at 77 K for supercritical CO_2 activated DUT-34, with BET surface area of 744 m^2/g.

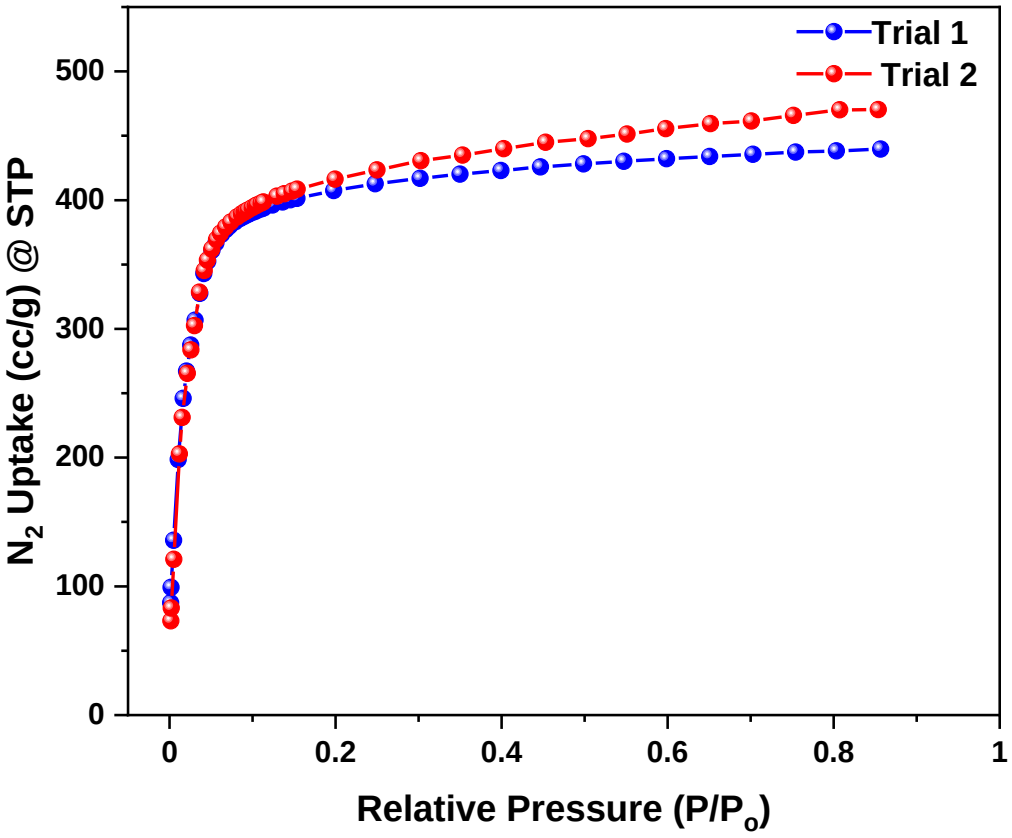


Figure S18. N_2 sorption isotherms at 77K for twice DME exchanged room temperature activated DUT-34. Experiments were run in duplicate and yielded an average BET surface area of ~1600 m^2/g.

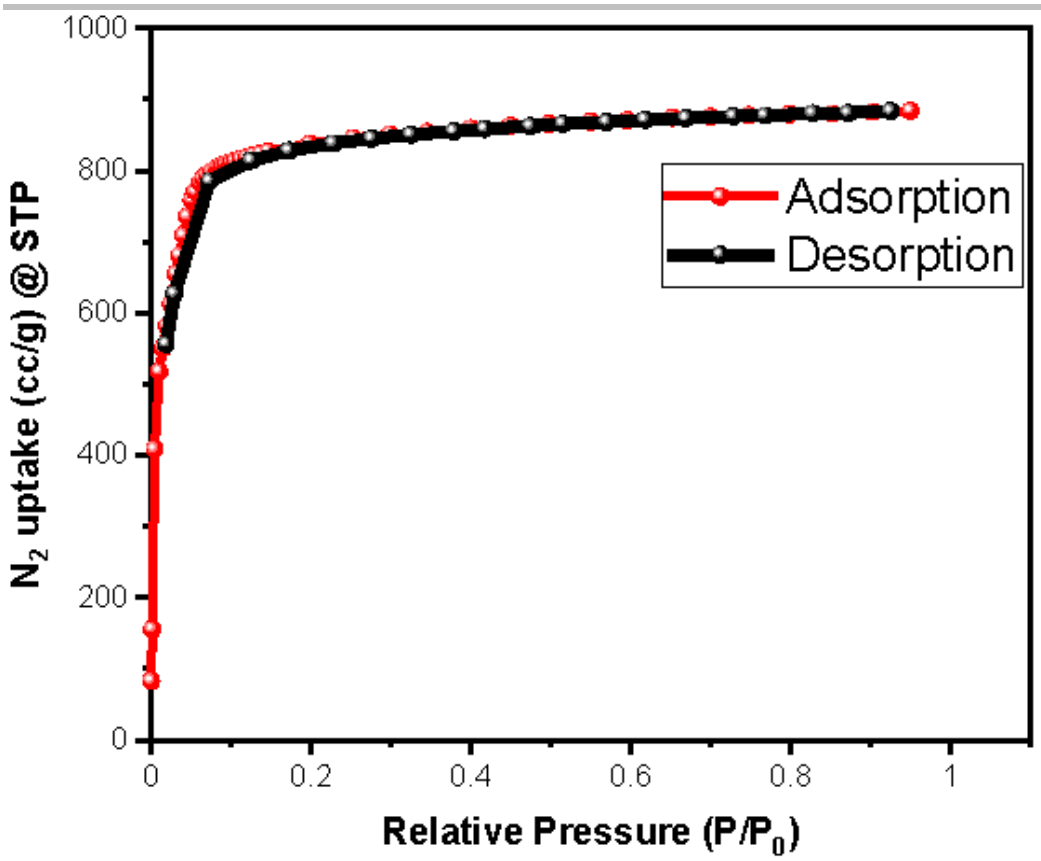


Figure S19. N_2 sorption isotherms at 77K for DME exchanged room temperature activated Cu-DUT-23. Experiments were run in triplicate and yielded an average BET surface area of 3047 m^2/g.

8. Table of pore volumes

Table S1. Table of pore volumes (calculated and experimental) for metal-organic frameworks.

MOF[a]	Calculated pore volume (cm^3/g)	Experimental pore volume at P/P_0 =0.95 (cm^3/g)	Reference
MOF-5	1.36	1.66	8
HKUST-1	0.88	0.88	10
UMCM-151	1.87	0.48	9
DUT-34	2.50	0.74	10
Mg-MOF-74	0.78	0.76	11,12
Zn-MOF-75	0.54	0.49	11,13
Cu-DUT-23	2.00	0.93	7,10

9. References

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