

Supporting Information

A Porous Metal-Organic Framework with Dynamic Pyrimidine Groups Exhibiting Record High Methane Storage Working Capacity

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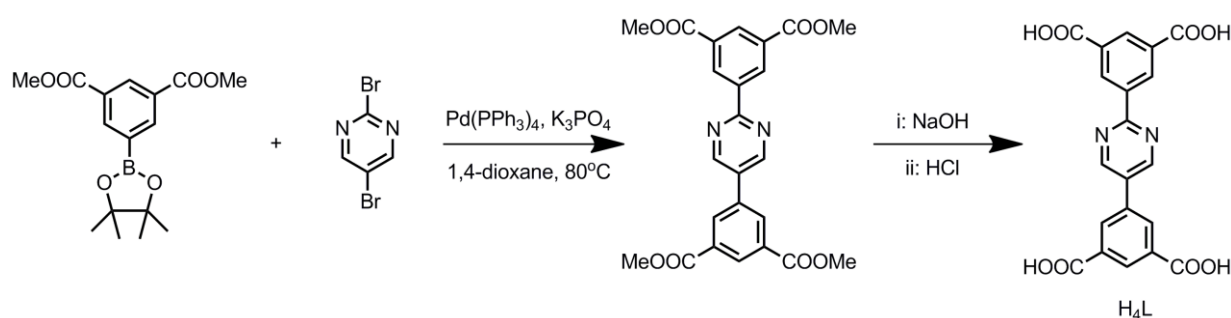
1. General Procedures and Materials. All reagents and solvents were commercially available and used without further purification. Dimethyl 5-(4, 4, 5, 5-tetramethyl-1, 3, 2-dioxaborolan-2-yl) isophthalate was prepared according to the literature procedure.¹ ¹H NMR spectra were recorded on a Varian Mercury 500 MHz spectrometer using tetramethylsilane (TMS) as internal standards. The coupling constants reported in Hertz. FTIR spectra were performed on a Bruker Vector 22 spectrometer at room temperature. The elemental analyses were performed with Perkin–Elmer 240 CHN analyzers from Galbraith Laboratories, Knoxville. Thermogravimetric analyses (TGA) were carried out using a Shimadzu TGA-50 analyzer under a nitrogen atmosphere with a heating rate of 5 °C min⁻¹. Powder X-ray diffraction (PXRD) patterns were measured by a Rigaku Ultima IV diffractometer operated at 40 kV and 44 mA with a scan rate of 1.0 deg min⁻¹. The neutron scattering experiment was performed on the High Flux Backscattering Spectrometer at the NIST Center for Neutron Research, which has an incident neutron wavelength of 6.27 Å (2.08 meV) and a resolution of 0.8 meV eV full width at half maximum (FWHM).² Elastic neutron scattering intensities were scanned in the T range of 10 K – 320 K, with a ramping rate of 1 K/min.

2. Gas sorption Measurements. A Micromeritics ASAP 2020 surface area analyzer was used to measure gas adsorption isotherms. To remove all the guest solvents in the framework, the fresh sample of UTSA-76 was guest-exchanged with dry acetone at least 10 times, filtered and degassed at room temperature (296 K) for one day, and then at 373K for another 20 hours until the outgas rate was 5 µmHg min⁻¹ prior to measurements. The activated sample of UTSA-76a was maintained at 77 K with liquid nitrogen. High-pressure CH₄ sorption isotherms were measured using a Sieverts-type apparatus. A detailed description of the experimental setup, calibration, and the isotherm can be found in a previous publication.³

3. Single-crystal X-ray crystallography. The crystal data were collected on an Agilent Supernova CCD diffractometer equipped with a graphite-monochromatic enhanced Cu Kα radiation (λ = 1.54184 Å) at 100 K. The datasets were corrected by empirical absorption correction using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm. The structure was solved by direct methods and refined by full matrix least-squares methods with the SHELX-97 program package.⁴ The central pyrimidine ring of organic ligand is disordered, which was refined as disordered model with occupancies of 0.25 for C7, 0.25 for N1, 0.25 for C7', and 0.25 for N1'. The

solvent molecules in the compound are highly disordered. The SQUEEZE subroutine of the PLATON software suit was used to remove the scattering from the highly disordered guest molecules.⁵ The resulting new files were used to further refine the structures. The H atoms on C atoms were generated geometrically.

Scheme S1. Synthetic routes to the organic linker H₄L.



Tetramethyl 5, 5'-(pyrimidine-2, 5-diyl)diisophthalate. 2, 5-Dibromopyrimidine (1.18 g, 5 mmol), 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) isophthalate (3.52 g, 11 mmol), K₃PO₄ (2.55g, 12 mmol) and tetrakis(triphenylphosphine) palladium(0) (0.3 g, 0.26 mmol) were dissolved in dry 1,4-dioxane (80 mL) under N₂ atmosphere. The mixture was stirred at 80 °C for two days. After that, the precipitate was collected by filtration, washed with 1, 4-dioxane for several times, and then recrystallized in toluene to obtain the pure product. Yield: 56% (1.3 g). ¹H NMR (500 MHz, CDCl₃, ppm): δ 9.38 (s, 2H), 9.15 (s, 2H), 8.86 (s, 1H), 8.80 (s, 1H), 8.53 (s, 2H), 4.03 (s, 12H).

5, 5'-(pyrimidine-2, 5-diyl)diisophthalic acid (H₄L). Tetramethyl 5, 5'-(pyrimidine-2, 5-diyl)diisophthalate (1.3g, 2.8 mmol) was suspended in 50 mL THF, and then a 2M KOH aqueous solution (75 mL) was added. The mixture was stirred under reflux overnight until it became clear. After that THF was removed under reduced pressure and dilute HCl was then added to the remaining aqueous solution to acidify PH = 2. The precipitate was collected by filtration, washed with water for several times, and dried to afford white powder. Yield: 1.08 g (95%). ¹H NMR (500 MHz, d₆-DMSO, ppm): δ = 13.11 (s, 4H), 9.31 (s, 2H), 9.13 (s, 2H), 8.54 (s, 1H), 8.50 (s, 2H),

8.50 (s, 1H). ^{13}C NMR ($\text{d}^6\text{-DMSO}$, ppm): δ = 166.69, 166.65, 161.42, 156.24, 137.96, 135.20, 132.79, 132.57, 132.36, 131.95, 130.80, 130.45.

Synthesis of UTSA-76. A mixture of the organic linker H_4L (15.0 mg, 0.037 mmol) and $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (30.0 mg, 0.129 mmol) was dissolved into a 8mL mixed solvent ($\text{DMF}/\text{MeCN}/\text{H}_2\text{O}$, 6/1/1, v/v) in a screw-capped vial (20 mL). 50 μL of 37% HCl were added. The vial was capped and heated in an oven at 80 $^\circ\text{C}$ for 24 h. Blue block crystals were obtained by filtration and washed with DMF several times to afford UTSA-76 in 65% yield. UTSA-76 has a best formula as $[\text{Cu}_2\text{L}(\text{H}_2\text{O})_2] \cdot 5\text{DMF} \cdot 3\text{H}_2\text{O}$, which was obtained based on the basis of single-crystal X-ray structure determination, elemental analysis and TGA. Anal. Calcd for $\text{C}_{35}\text{H}_{53}\text{N}_7\text{O}_{18}\text{Cu}_2$: C, 42.59; H, 5.41; N, 9.93; found: C, 42.28; H, 5.34; N, 9.98. TGA data for loss of 5DMF and 5 H_2O : calcd: 46.22%, found: 46.75%. IR (neat, cm^{-1}): 1652, 1625, 1591, 1442, 1381, 1362, 1247, 1091, 770, 755, 728, 659.

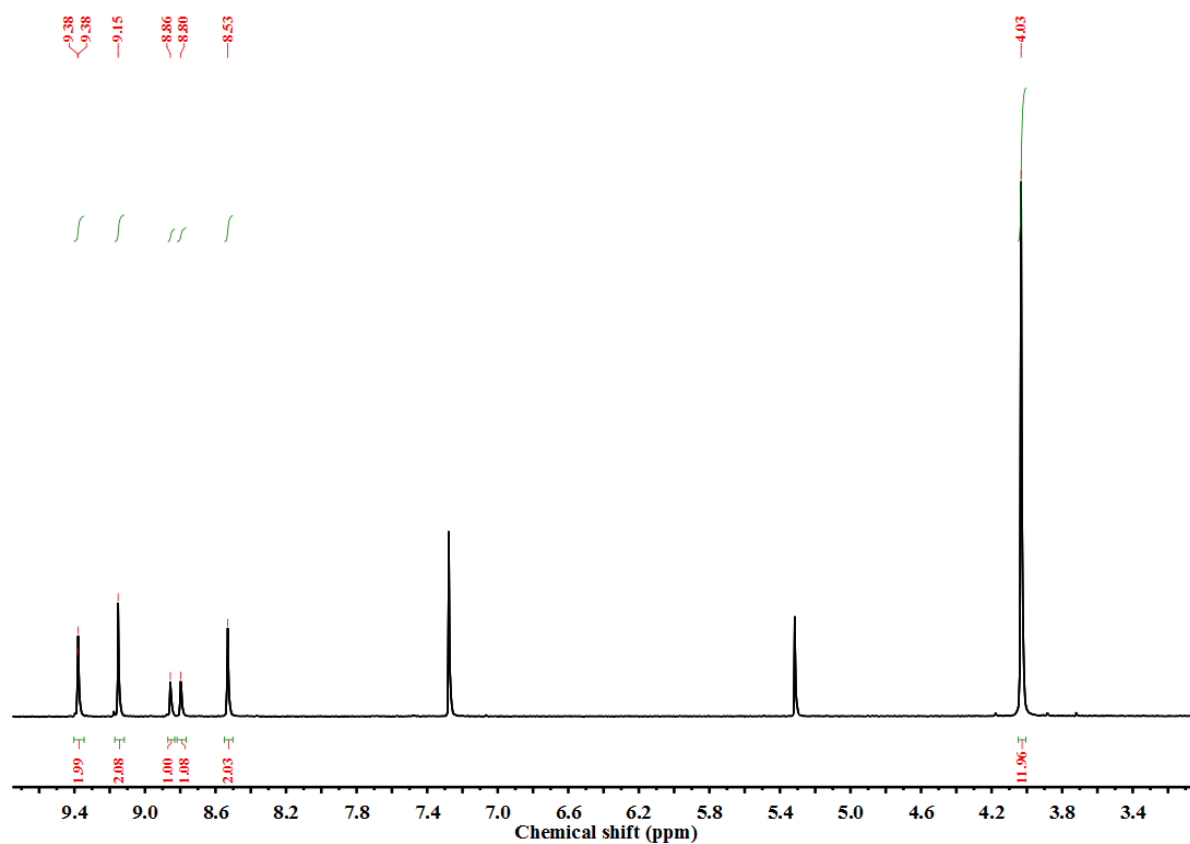


Figure S1. ^1H (CDCl_3 , 500MHz) spectra of tetramethyl 5, 5'-(pyrimidine-2, 5-diyl)diisophthalate.

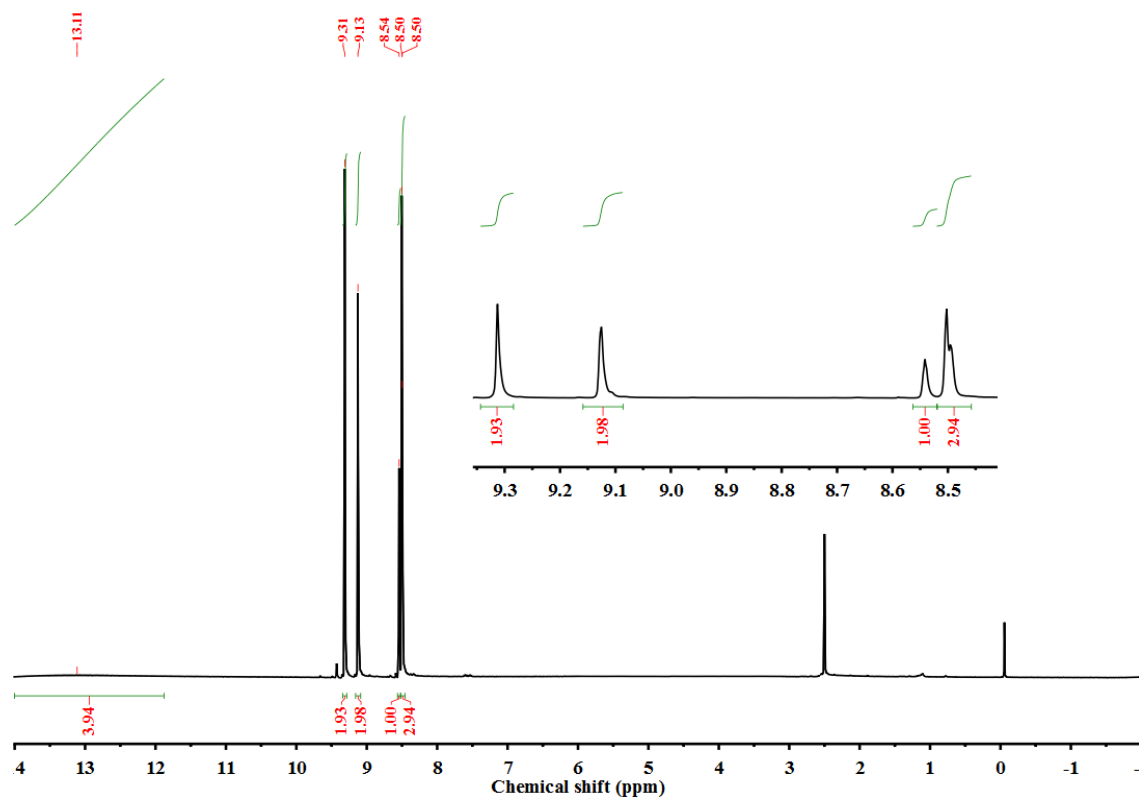


Figure S2. ¹H (DMSO-d₆, 500MHz) spectra of the ligand H₄L.

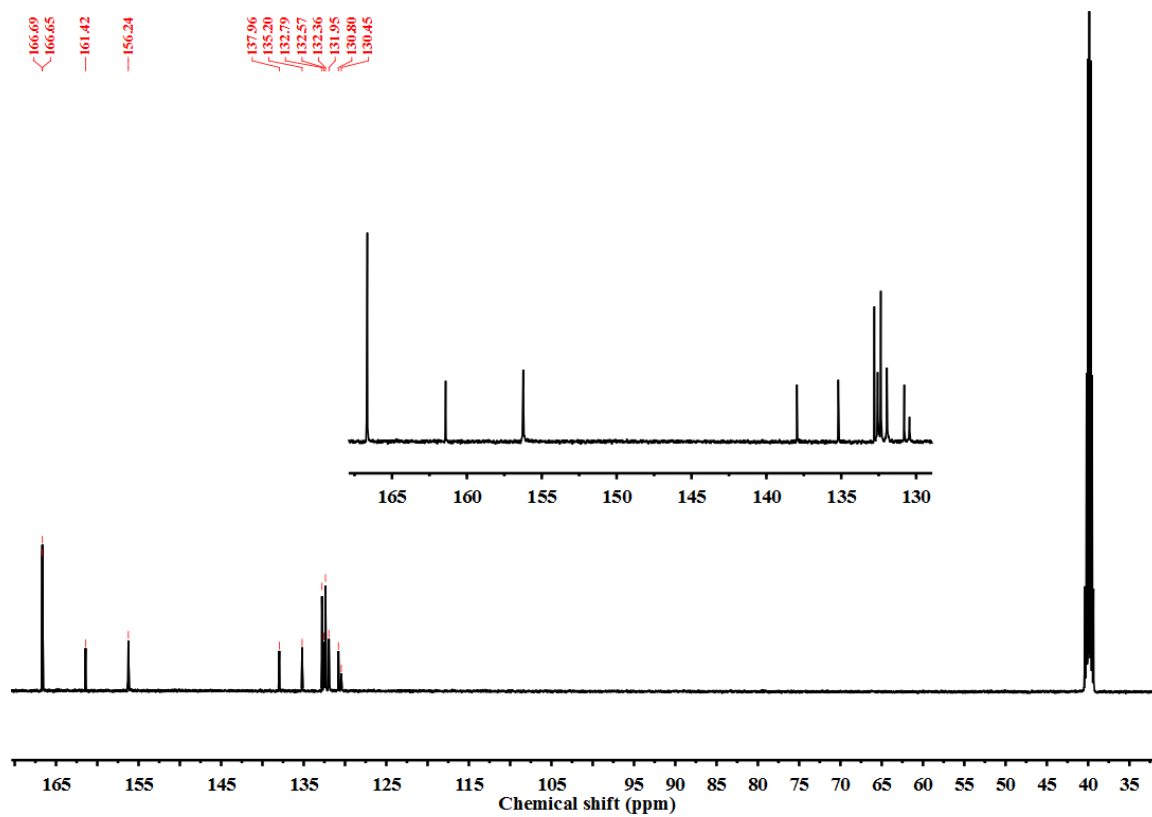


Figure S3. ¹³C (DMSO-d₆, 500MHz) spectra of the ligand H₄L.

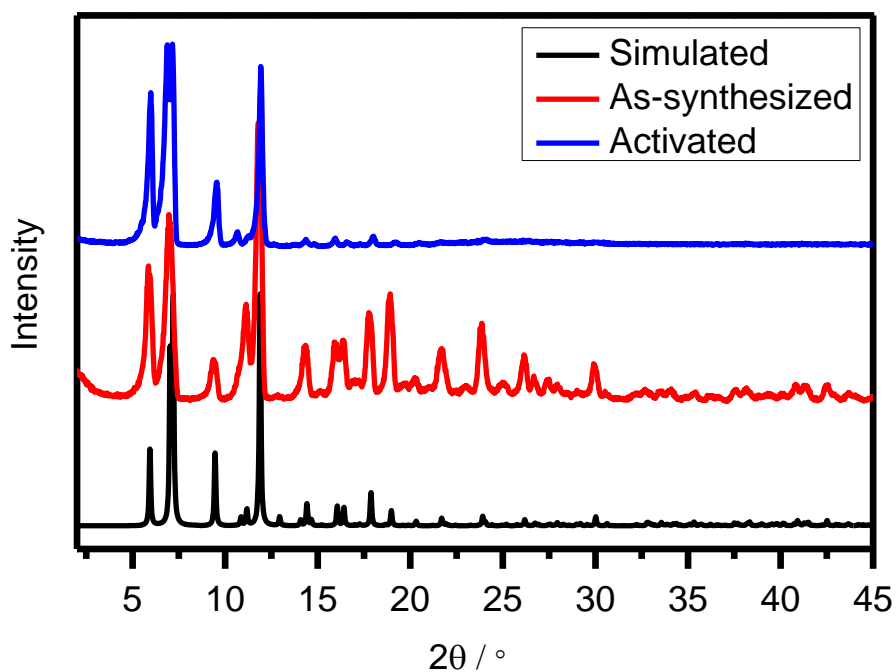


Figure S4. PXRD patterns of as-synthesized UTSA-76 (red) and activated UTSA-76a (blue) along with the simulated XRD pattern from the single-crystal X-ray structure (black).

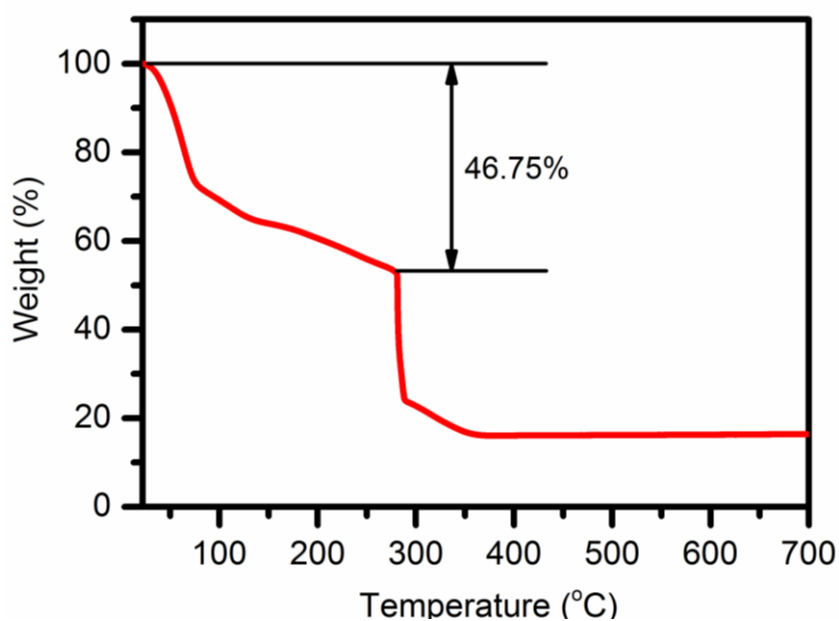


Figure S5. TGA curves of as-synthesized UTSA-76.

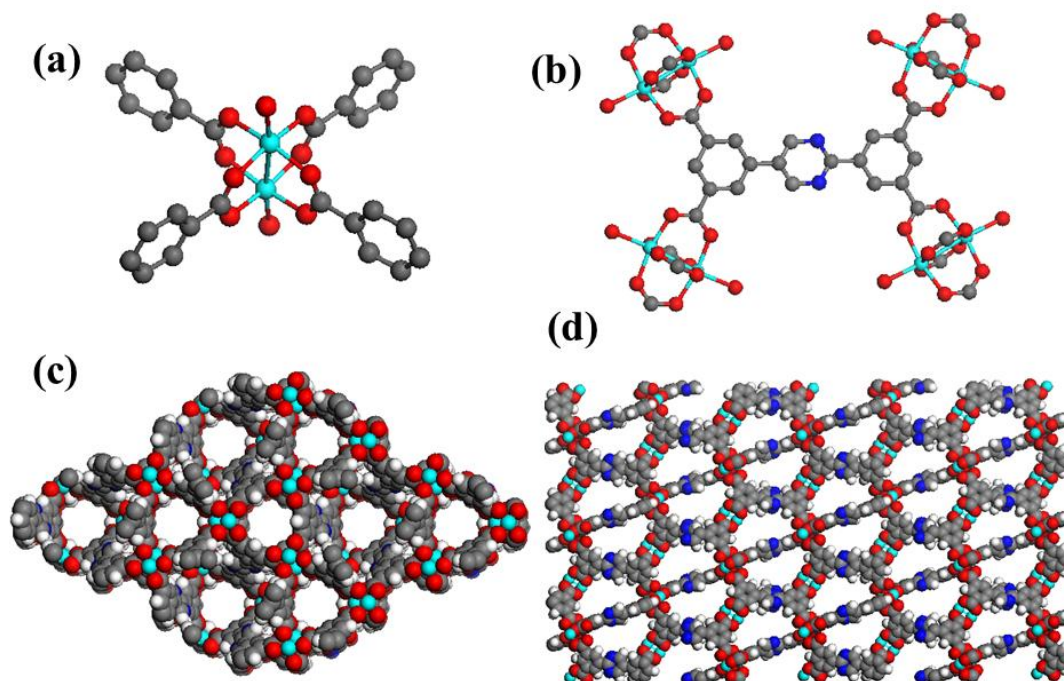


Figure S6. X-ray single crystal structure of UTSA-76: (a) the 4-connected $\text{Cu}_2(\text{O}_2\text{CR})_4$ paddle-wheel unit; (b) one tetracarboxylate ligand connects with four $\text{Cu}_2(\text{O}_2\text{CR})_4$ clusters; (c) the hexagonal channels viewed along the c axes; (d) triangular windows viewed along the a axes. Turquoise, red, blue, and gray spheres represent Cu, O, N, and C atoms, respectively.

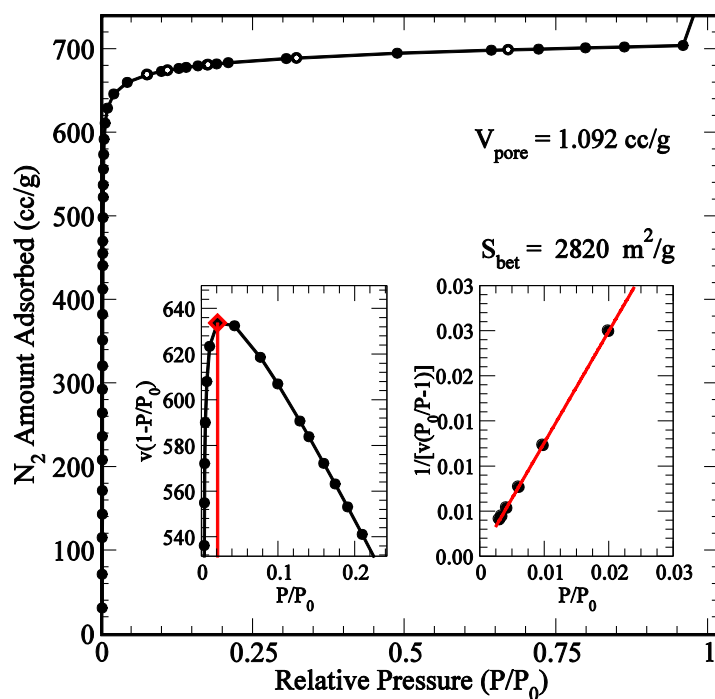


Figure S7. Nitrogen isotherm at 77 K with consistency and BET plots for the activated UTSA-76a sample.

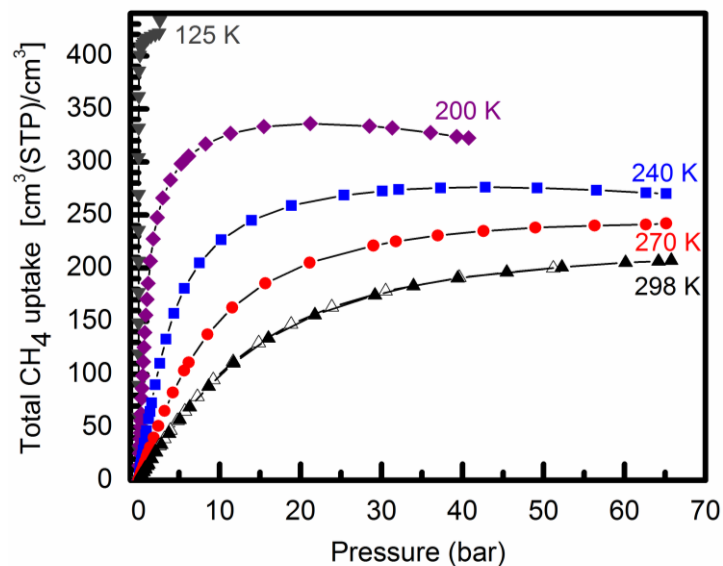


Figure S8. Excess volumetric high-pressure methane sorption isotherms of UTSA-76a at different temperatures. Filled and open symbols represent adsorption and desorption data, respectively.

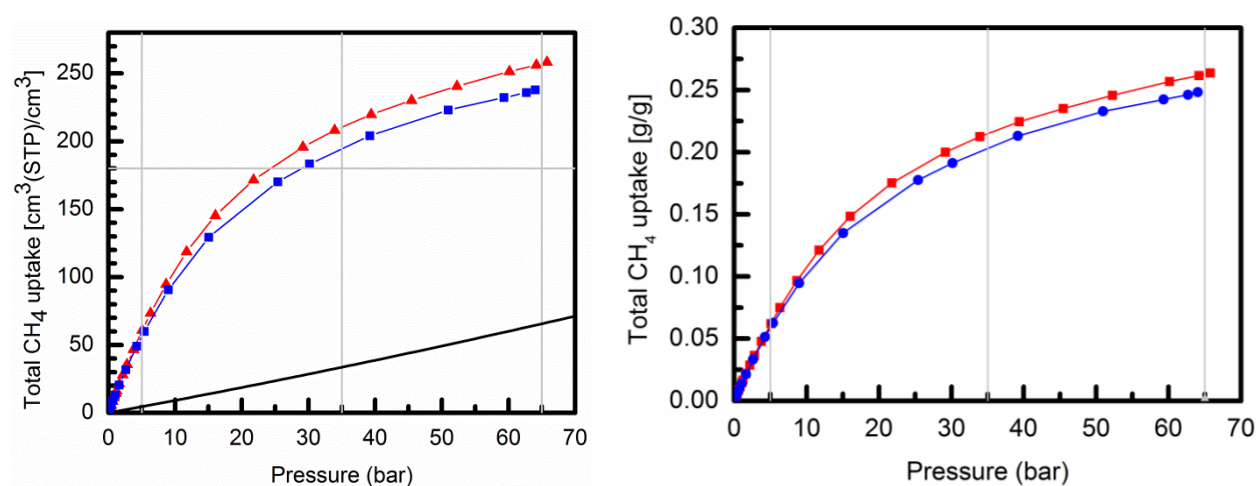


Figure S9. The comparison of the total volumetric (left) and gravimetric (right) methane uptake at 298 K of UTSA-76a (red) and NOTT-101a (blue). For comparison, data of pure methane gas stored in a high pressure gas tank is represented as black line in left graph.

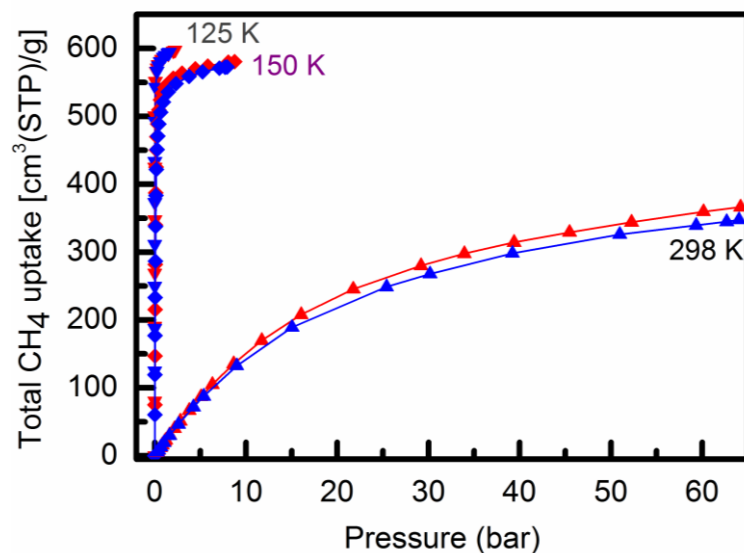


Figure S10. A comparison of the total methane uptake at different temperature of UTSA-76a (red) and NOTT-101a (blue).

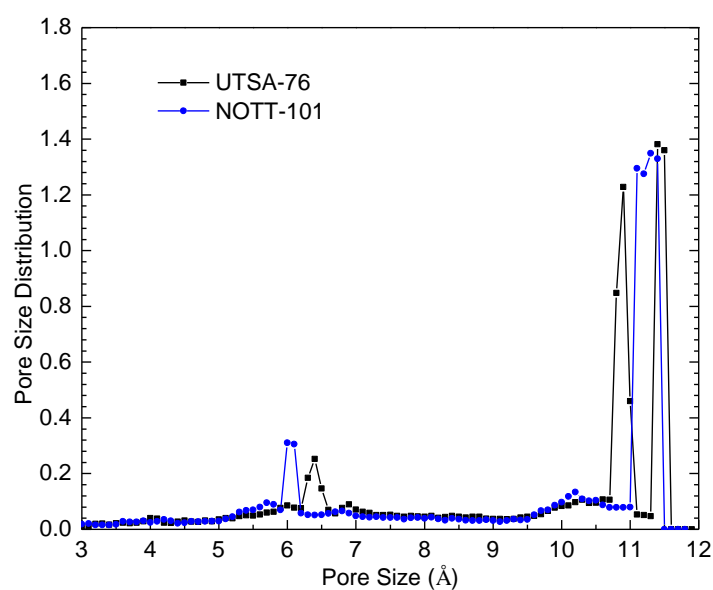


Figure S11. Pore size distributions (PSDs) of UTSA-76a and NOTT-101a. PSDs were calculated using the well-known method by Gubbins *et al.*⁶ The van der Waals diameters of the framework atoms were adopted from the Cambridge Crystallographic Centre.

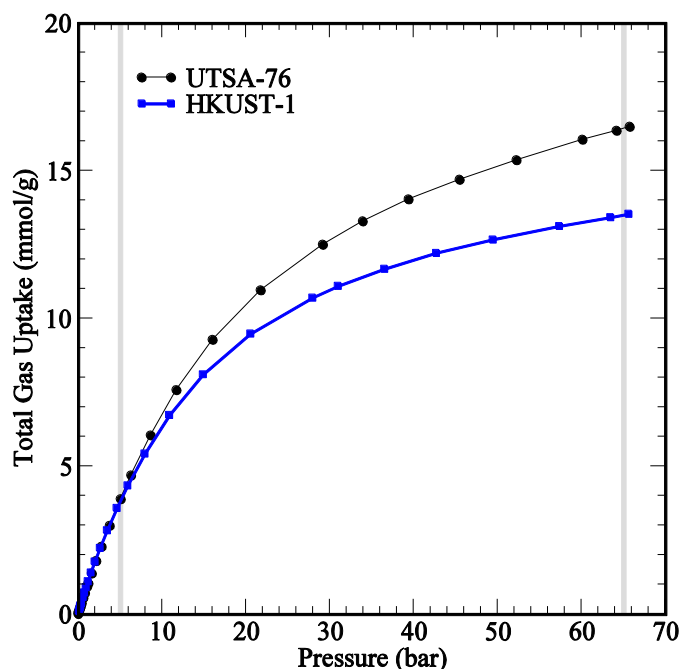


Figure S12. A comparison of the total gravimetric methane uptake at 298 K of UTSA-76a and HKUST-1.

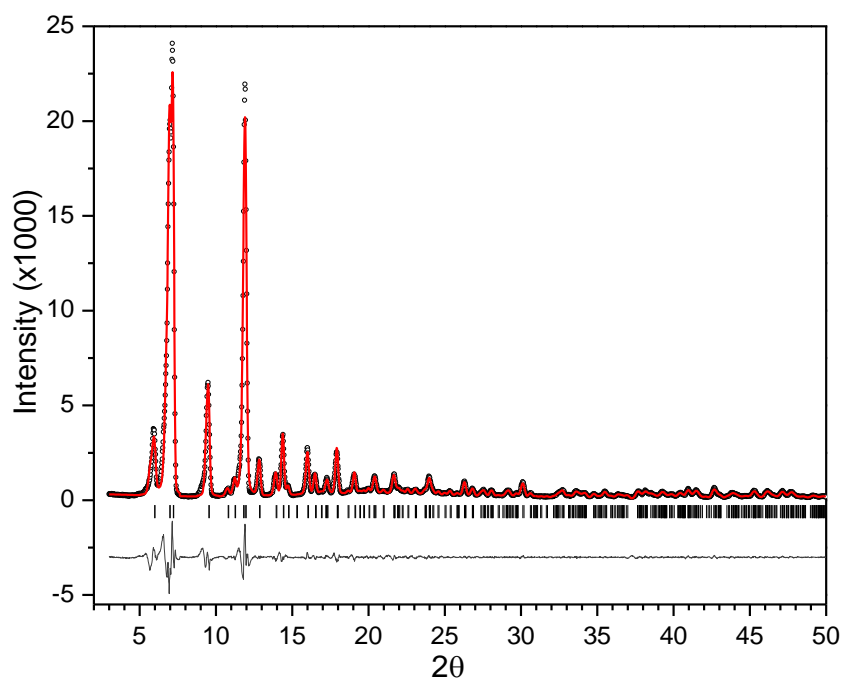


Figure S13. Experimental (circles), Le Bail fitted (line), and difference (line below observed and calculated patterns) PXRD profile for activated UTSA-76a at 298 K (Cu K α radiation). Vertical bars indicate the calculated positions of Bragg peaks. Refined lattice parameters: $a=18.574(2)$ Å and $c=38.022(8)$ Å. $R_p=0.071$, $R_{wp}=0.090$. Corresponding crystal density: 0.699 g/cc.

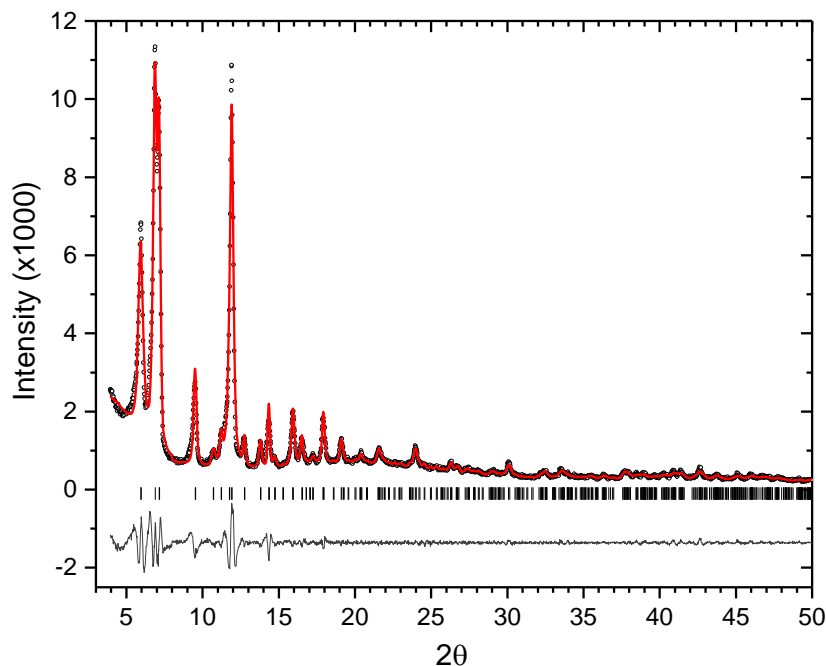


Figure S14. Experimental (circles), Le Bail fitted (line), and difference (line below observed and calculated patterns) PXRD profile for activated NOTT-101a at 298 K (Cu K α radiation). Vertical bars indicate the calculated positions of Bragg peaks. Refined lattice parameters: $a=18.578(2)$ Å and $c=38.469(8)$ Å. $R_p=0.071$, $R_{wp}=0.090$. Corresponding crystal density: 0.688 g/cc.

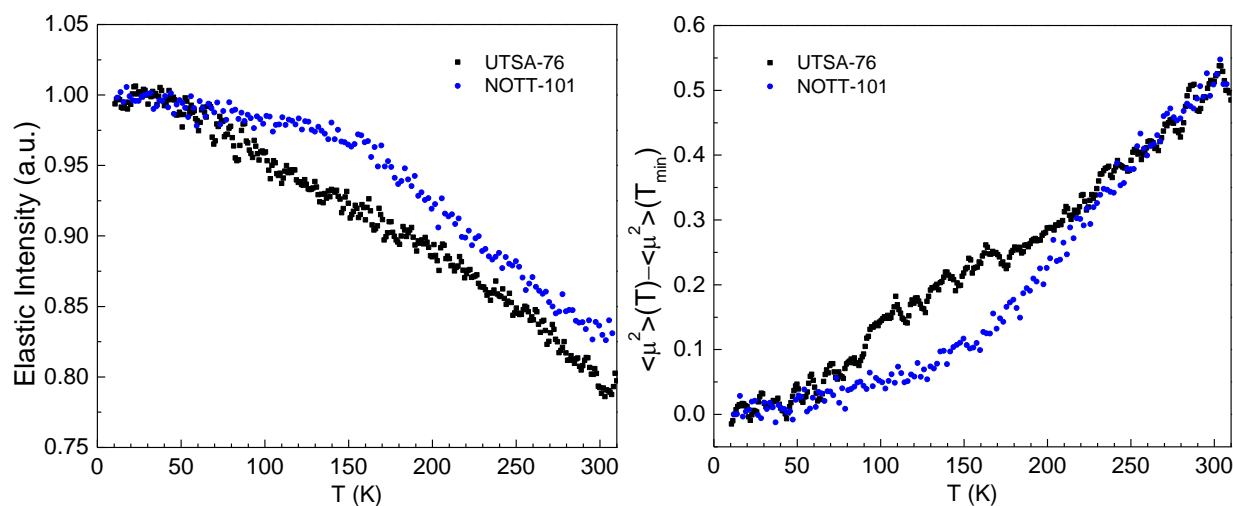


Figure S15. Left: A comparison of the normalized elastic neutron scattering intensity vs. temperature for UTSA-76a and NOTT-101a. Right: Temperature-dependent atomic mean-square-displacements (MSD), derived from data in the left panel. The MSD were deduced

using classic Debye Waller approximation.⁷ Note the increased MSD of UTSA-76 over NOTT-101 above $\sim 70\text{K}$.

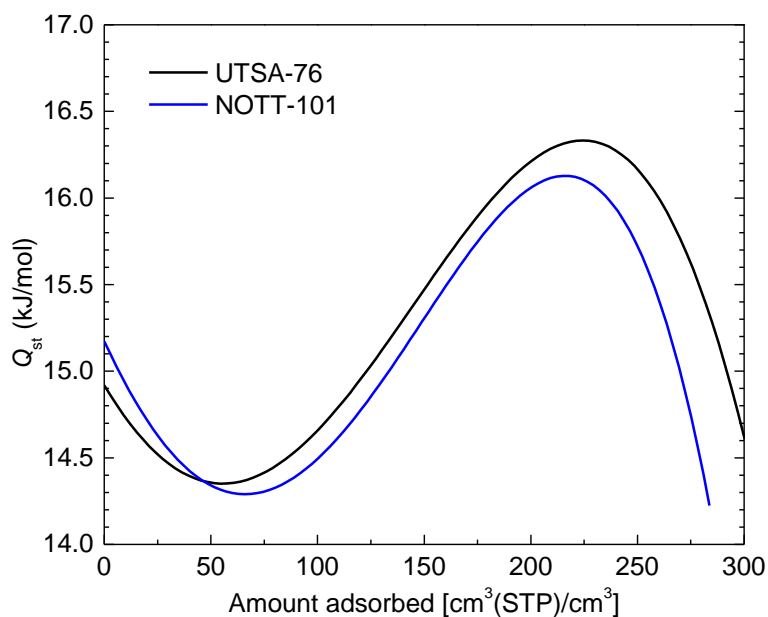


Figure S16. A comparison of Q_{st} for CH_4 adsorption for UTSA-76a and NOTT-101a.

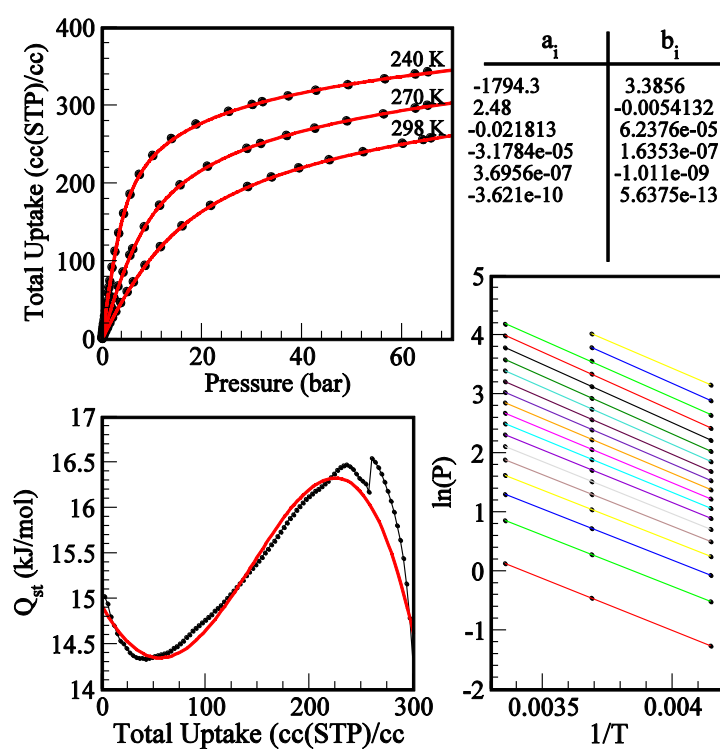


Figure S17. Derivation of Q_{st} for CH_4 adsorption for UTSA-76a. The red line in the Q_{st} plot is obtained from virial fitting of the absolute adsorption isotherm data. The fit and the virial

coefficients are also shown. The black line in the Q_{st} plot is obtained from the raw isotherm data using cubic spline method without any fitting.

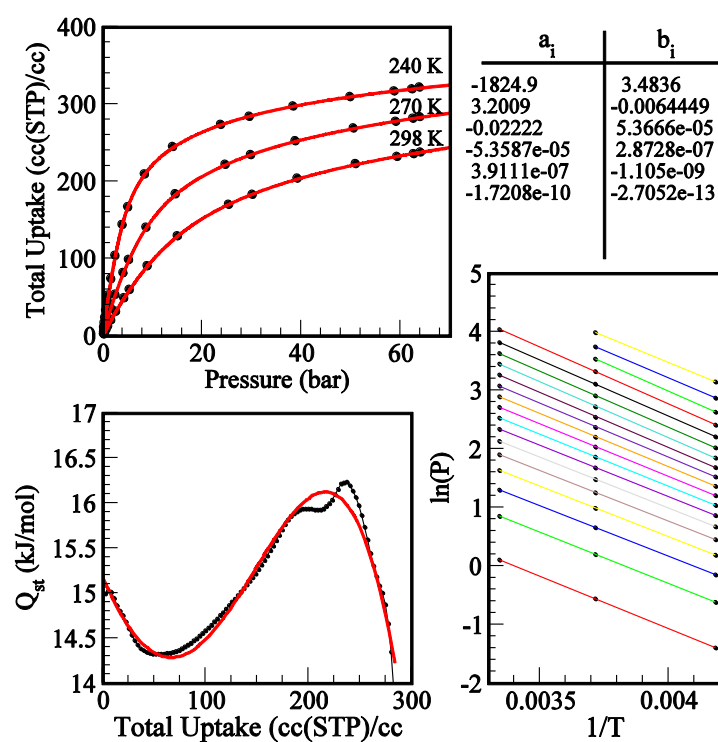


Figure S18. Derivation of Q_{st} for CH_4 adsorption for NOTT-101a. The red line in the Q_{st} plot is obtained from virial fitting of the absolute adsorption isotherm data. The fit and the virial coefficients are also shown. The black line in the Q_{st} plot is obtained from the raw isotherm data using cubic spline method without any fitting.

Table S1. Crystallographic data and structure refinement results for UTSA-76 (from single-crystal X-ray diffraction analysis on the as-synthesized sample).

	UTSA-76
Formula	C ₂₀ H ₈ Cu ₂ N ₂ O ₁₁
Formula weight	579.36
Temperature/K	100.00(19)
Crystal system	Trigonal
Space group	R-3m
<i>a</i> , <i>b</i> (Å)	18.6895(5)
<i>c</i> (Å)	37.6886(9)
α (°)	90.00
β (°)	90.00
γ (°)	120.00
<i>V</i> (Å ³)	11400.8(5)
<i>Z</i>	9
<i>D</i> _{calcd} (g cm ⁻³)	0.759
μ (mm ⁻¹)	0.868
<i>F</i> (000)	2592.0
Crystal size/mm ³	0.42 × 0.35 × 0.20
GOF	1.108
<i>R</i> _{int}	0.0338
<i>R</i> _I , <i>wR</i> ₂ [<i>I</i> ≥ 2σ (<i>I</i>)]	0.0808, 0.2558
<i>R</i> _I , <i>wR</i> ₂ [all data]	0.0896, 0.2627
Largest diff. peak and hole (e Å ⁻³)	1.12, -0.44

Disclaimer: Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

References

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