Supporting Information

A novel expanded metal-organic framework for balancing volumetric and gravimetric methane storage working capacities

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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. 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 2.0 deg min⁻¹.

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 samples of UTSA-111 were guest-exchanged with dry acetone at least 10 times, filtered and degassed at room temperature (296 K) for one day, and then at 373 K for another 24 hours until the outgas rate was 5 mmHg min⁻¹ prior to measurements. The activated sample was maintained at 77 K with liquid nitrogen. High-pressure methane sorption isotherms were measured using a Sieverts-type apparatus under computer control. A detailed description of the experimental setup, calibration, and the isotherm can be found in a previous publication.²

3. Single-crystal X-ray crystallography. The crystal data of UTSA-111 was collected on an Agilent Supernova CCD diffractometer equipped with a graphite-monochromatic enhanced Cu K α radiation ($\lambda = 1.54184$ Å) at 293 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.³ 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.⁴ The resulting new files were used to further refine the structures. The H atoms on C atoms were generated geometrically. The crystal data are summarized in Table S1.

Synthesis of 5-bromo-2-(4-bromophenyl)-pyrimidine: To a solution of toluene (60 mL), ethanol (20 mL) and CsCO₃ aqueous solution (2.0 M, 40 mL) in a three-necked round-bottom flask, 2,5-dibromopyridine (7.10 g, 0.03 mol) and 4-bromophenyl boronic acid (5.0 g, 0.025 mol) were added under N₂ atmosphere. After stirred at room temperature for 10 min under N₂ gas, tetrakis(triphenylphosphine) palladium(0) (0.03 mmol, 0.35 g) was added into the mixture and then heated slowly to 95 °C for 24 h. After cooling to room temperature, the reaction mixture was filtered and the filtrate was evaporated under reduced pressure to remove toluene and ethanol. The residue was then extracted with dichloromethane for three times. The combined organic layer was dried with MgSO₄, filtered and evaporated in vacuo. The residue was purified by silica gel chromatograph using petroleum ether/dichloromethane (8:1) as the eluent to afford a white power. Yield: 5.84 g (74.7%). ¹H NMR (500 MHz, CDCl₃, ppm): δ = 8.82 (s, 2H), 8.28 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 8.3 Hz, 2H).

Synthesis of H₄L: 5-bromo-2-(4-bromophenyl)-pyrimidine (1.5 g, 4.8 mmol), 5-(4,4,5,5tetramethyl-1,3,2-dioxaborolan-2-yl) isophthalate (3.2 g, 10 mmol) and Pd(PPh₃)₄ (0.3 g, 0.26 mmol) were dissolved in a solution of glyme (70 mL) under N₂ atmosphere. A NaHCO₃ solution (45 mL) was then added. The mixtures were stirred at 100 °C for 3 days. After that, the precipitate was collected by filtration, washed with glyme and 1, 4-dioxane for several times to obtain the pure product (Me₄L). The final product H₄L was obtained by hydrolysis of Me₄L with 2M aqueous KOH, followed by acidification with concentrated HCl. Yield: 1.4 g (60 %). ¹H NMR (500 MHz, d⁶-DMSO, ppm): δ = 13.48 (s, 4H), 9.33 (s, 2H), 8.58 (d, *J* = 7.0 Hz, 2H), 8.54 (s, 2H), 8.53 (s, 1H), 8.48 (s, 3H), 7.96 (d, *J* = 7.0 Hz, 2H). MS(ESI+): m/z (%) = 483.08 (100) [M–H]⁻. Anal. Calcd for C₂₆H₁₆N₂O₈: C, 64.47; H, 3.33; N, 5.78; found: C, 64.33; H, 3.18; N, 5.65.

Synthesis of UTSA-111. A mixture of the organic linker H_4L (10.0 mg, 0.02 mmol) and $Cu(NO_3)_2 \cdot 6H_2O$ (30.0 mg, 0.129 mmol) was dissolved into a DMF/dioxane/ H_2O (5/0.75/0.75 mL) mixed solvent in a screw-capped vial (20 mL). 40 mL of 37% HCl was added. The vial was capped and heated in an oven at 80 °C for 2 days. Blue block crystals were obtained by

filtration and washed with DMF several times to afford UTSA-111 in 69% yield (based on the ligand). UTSA-101 has a best formula as $[Cu_2L(H_2O)_2] \cdot 2DMF \cdot 4H_2O$, which was obtained based on single-crystal X-ray structure determination, elemental analysis and TGA. Anal. Calcd for $C_{32}H_{38}N_4O_{16}Cu_2$: C, 44.57; H, 4.41; N, 6.50; found: C, 44.61; H, 4.44; N, 6.56. TGA data for loss of 2DMF and 6H₂O: calcd: 29.48%, found: 31.64%.



Figure S1. ¹H (CDCl₃, 500MHz) spectra of 5-bromo-2-(4-bromophenyl)-pyrimidine.



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



Figure S3. PXRD patterns of as-synthesized UTSA-111 (red) and activated UTSA-111a (blue) along with the simulated XRD pattern from the single-crystal X-ray structure (black).



Figure S4. (a) TGA curves of as-synthesized UTSA-111 and (b) the activated UTSA-111a.



Figure S5. Nitrogen isotherm at 77 K with consistency and BET plots for the activated UTSA-111a sample.



Figure S6. Experimental (circles), Le Bail fitted (line), and difference (line below observed and calculated patterns) PXRD profile for activated UTSA-111a at 298 K (Cu K α radiation). Vertical bars indicate the calculated positions of Bragg peaks. Refined lattice parameters: a=18.569(4) Å and 51.63(2) Å. Goodness of fit: R_p =0.1498, R_{wp} =0.2257. Corresponding crystal density: 0.59 g/cm³.



Figure S7. Excess volumetric high-pressure methane sorption isotherms of UTSA-111a at 273 K and 298 K. Filled and open symbols represent adsorption and desorption data, respectively.



Figure S8. Excess and absolute gravimetric high-pressure CO₂ sorption isotherms of UTSA-111a at 273 K and 298 K. Filled and open symbols represent adsorption and desorption data, respectively.



Figure S9. Excess and absolute gravimetric high-pressure CO_2 sorption isotherms of NOTT-101a at 240 K, 273 K and 300 K. Filled and open symbols represent adsorption and desorption data, respectively.



Figure S10. Comparison of (a) the total gravimetric high-pressure CO_2 sorption isotherms of UTSA-111a (red) and NOTT-101a (black) at room temperature; (b) the total volumetric high-pressure CO_2 sorption isotherms of UTSA-111a (red) and NOTT-101a (black) at room temperature.



Figure S11. Total CH₄ gravimetric/volumetric uptakes at 65 bar and RT for UTSA-111a in comparison to the best-performing robust MOF materials reported, indicating a rare balance of both high gravimetric and volumetric storage capacities in UTSA-111a.



Figure S12. Comparison of Q_{st} for (a) CH₄ and (b) CO₂ adsorption for UTSA-111a and NOTT-101a.



Figure S13. The mass spectra data of the organic linker H_4L , which is consistent well with the calculated value.

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	UTSA-111			
Formula	$C_{24}H_{10}N_4Cu_2O_{10}$			
Formula weight	641.44			
Temperature/K	293.00(19)			
Crystal system	Trigonal			
Space group	R-3m			
<i>a</i> (Å)	18.3055(4)			
<i>b</i> (Å)	18.3055(4)			
<i>c</i> (Å)	52.0549(12)			
α (°)	90.00			
β (°)	90.00			
γ (°)	120.00			
$V(Å^3)$	15106.2(6)			
Ζ	9			
D_{calcd} (g cm ⁻³)	0.635			
μ (mm ⁻¹)	1.003			
F(000)	2880.0			
GOF	1.189			
R _{int}	0.0358			
$R_{I}, wR_{2}[I \ge 2\sigma(I)]$	0.0743, 0.2673			
R_1 , wR_2 [all data]	0.0829, 0.2797			
CCDC number	2021014			

Table S1. Crystallographic data and structure refinement results of UTSA-111 (from singlecrystal X-ray diffraction analysis).

 ${}^{a}R_{1} = \Sigma |F_{o} - F_{c}| / \Sigma F_{o}, {}^{b}wR_{2} = \Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}] / \Sigma [w(F_{o})^{2})]^{1/2}$

	$S_{\rm BET}{}^a$	$V_{\rm p}{}^b$	$D_{\rm c}{}^{\rm c}$	Total uptake ^d at 65 bar		Working capacity ^e		Initial $Q_{\rm st}$	
MOFs	(m ² g ⁻¹)	(cm ³ g ⁻¹)	(g cm ⁻³)					kJ mol ⁻¹	Ref.
				cm ³ g ⁻¹	cm ³ cm ⁻³	cm ³ g ⁻¹	cm ³ cm ⁻³	-	
UTSA-111a	3252	1.229	0.590	396	234	309	183	14.5	This work
NOTT-101a	2805	1.08	0.688	347	237	250	172	15.5	5
UTSA-76a	2820	1.092	0.699	363	257	267	187	15.5	6
HKUST-1	1850	0.78	0.883	302	267	207	183	17.0	7
NU-1501-Al	7310	2.91	0.283	576	163	505	143	9.7	8
NU-1501-Fe	7140	2.90	0.299	562	168	492	147	9.7	9
LIFM-82	1624	0.71	0.922	267	245	199	182	17.5	9
MFM-115a	3394	1.38	0.611	389	238	296	181	16.3	10
AlMOF-soc-1	5585	2.30	0.34	579	197	497	169	11.0	11
MOF-905	3490	1.34	0.537	377	207	318	175	11.7	12
MAF-38	2022	0.808	0.761	346	263	231	176	21.6	13
FDM-8	3643	1.54	0.563	343	193	297	167	10.4	14
NU-125	3286	1.41	0.589	395	232	297	174	15.1	15
BUT-22	4380	2.01	0.381	478	182	398	152	12.0	16
NU-111	4930	2.09	0.409	503	206	422	173	14.2	7
PCN-14	2170	0.85	0.829	277	230	181	154	17.6	7

Table S2. Comparison of UTSA-111a with some of the indicated promising robust MOFs for high-pressure methane storage.

^{*a*} BET surface areas calculated from N₂ isotherms at 77 K. ^{*b*} Pore volumes calculated from the maximum amounts of N₂ adsorbed. ^{*c*} Framework densities of fully activated MOFs without guest molecules and terminal waters. ^{*d*} At 298 K. ^{*e*} Defined as the difference of the amount of methane adsorbed between 65 bar and 5.8 bar.

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.

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