Supplementary Information

An Indium-based microporous metal-organic framework with unique

three-way rod-shaped secondary building units for efficient methane

and hydrogen storage

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Instruments

Fourier transform infrared (FT-IR) data were recorded on an IRAffinity-1 instrument. The powder X-ray diffraction patterns (PXRDs) were recorded on a Rigaku Smartlab3 X-ray Powder Diffractometer equipped with a Cu sealed tube ($\lambda = 1.54178$ Å) at room temperature (RT). Simulation of the PXRD patterns was carried out by the single-crystal data and diffraction-crystal module of the Mercury program available free of charge via internet at http://www.ccdc.cam.ac.uk/mercury/. Thermogravimetric analysis (TGA) data were obtained on a TGA-50 (SHIMADZU) thermogravimetric analyzer with a heating rate of 5 °C min⁻¹ under N₂ atmosphere.

Synthesis

Synthesis of H₃TTETA ligand

Synthesis following a recently published protocol.¹ ¹H NMR(400 MHz, DMSO- d_6): δ 13.13 (s, 3H), 7.92 (d, 6H, J = 8 Hz), 7.62 (d, 6H, J = 8 Hz), 2.66 (s, 9H) ppm (Figure S4); in accordance with the literature.

Synthesis of $[In_5(TTETA)_{11/3}(OH)_4(H_2O) \cdot 30H_2O \cdot 19DMF]$ (UTSA-22)

In(NO₃)₃·6H₂O (0.04 mmol, 12 mg), H₃TTETA (0.03 mmol, 20.42 mg) were mixed together before dissolved in water (0.3 ml), DMF (1.2 ml) and nitric acid (10 μ L ,16 M) in a 20 ml glass vial and capped. The mixture was heated at 120 °C in an oven for 48 hours. After cooling to room temperature, the colorless crystals were obtained and washed with DMF (yield 65% based on the ligand).

Single-Crystal X-ray Crystallography

The crystal data of **UTSA-22** were collected by Advanced Light Source on beamline 12.2.1 at Lawrence Berkeley National Laboratory, and its structure was solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement using the *SHELXTL* software package. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms of the ligands were calculated in ideal positions with isotropic displacement parameters. There is large solvent accessible pore volume in the crystals of **UTSA-22**, which are occupied by highly disordered solvent molecules. No satisfactory disorder model for these solvent molecules could be assigned, and therefore the *SQUEEZE* program implemented in *PLATON* was used to remove the electron densities of these disordered species. Thus, all of electron densities from free solvent molecules have been "squeezed" out. The details of structural refinement can be found in Tables S1 and cif file.

Sample activation and gas adsorption measurements

As-synthesized sample of **UTSA-22** was firstly soaked in fresh DMF for 2 h and then the extract was discarded. This procedure was repeated five times over 2 hours. Fresh methanol was subsequently added, and the sample was allowed to stay in it for 1 hour. This procedure was again repeated eight times over 8 hours. After decanting the methanol extract, the sample was dried under a dynamic vacuum (< 10^{-3} Torr) at RT for 3 hours.

 N_2 sorption isotherm was recorded at 77 K in a Micromeritics ASAP 2020 surface area analyzer. Before adsorption measurement, the sample was further activated using the "outgas" function at 120 °C for 10 hours.

High-pressure adsorption isotherms

High-pressure adsorption isotherms of CH_4 and H_2 were measured on a HPVA-II from Particulate Systems, a Micromeritics company. In a typical measurement, about 0.2 g of activated sample was loaded into a tared 2 mL stainless steel sample holder inside a glove box under a N_2 atmosphere. Prior to connecting the sample holder to the vacuum coupling radiation (VCR) fittings of the complete high-pressure assembly inside the glove box, the sample holder was weighed to determine the sample mass. The sample holder was then transferred to the HPVA-II, connected to the analysis port via an VCR fitting, and evacuated at 353 K for at least 10 h.

Derivation of the isosteric heat of adsorption (Q_{st})

A virial type expression of the following form was used to fit the CH_4 (or H_2) total adsorption isotherm data at 273 K and 298 K.

$$\ln P = \ln N + \frac{1}{T} \sum_{i=0}^{m} a_i N_i + \sum_{i=0}^{n} b_i N_i$$

Here, *P* is the pressure expressed in bar, N is the amount adsorbed in mmol/g, *T* is the temperature in K, a_i and b_i are virial coefficients, and *m*, *n* represents the number of coefficients required to adequately describe the isotherms. *m* and *n* were gradually increased until the contribution of extra added *a* and *b* coefficients was deemed to be statistically insignificant towards the overall fit, as determined using the average value of the squared deviations from the experimental values was minimized. The values of the virial coefficients a_0 through a_m were then used to calculate the isosteric heat of adsorption using the following expression.

$$Q_{\rm st} = -R\sum_{i=0}^m a_i N_i$$

Here, Q_{st} is the coverage-dependent isosteric heat of adsorption and R is the universal gas constant of 8.3147 J K⁻¹ mol⁻¹.

Structure refinement of UTSA-22

Table S1. Crystal data and	d structure refinement	for UTSA-22
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UTSA-22 (CCDC: 2204487)	
Empirical formula	$C_{132}H_{71}In_5O_{27}$
Formula weight	2662.98
Measurement temperature	273.15 K
Crystal system	Trigonal
Space group	<i>R</i> -3 <i>c</i>
<i>a</i> (Å)	51.504(3)
b (Å)	51.504(3)
<i>c</i> (Å)	50.096(4)
α (°)	90
в (°)	90

γ (°)	120
Volume(ų)	115083(17)
Z	18
Calculated density(g/cm ³)	0.692
Absorption coefficient (mm ⁻¹)	0.507
Independent reflections ($l > 2\sigma(l)$)	14236 [<i>R</i> (int) = 0.1000]
F(000)	23832
Reflections collected	133123
Completeness to theta = 133°	100%
2ϑ range for data collection	2.98-43.656°
Data/restraints/parameters	14236/133/727
Goodness-of-fit on F ²	1.061
$R_1^{a}, wR_2^{b} [l > 2\sigma(l)]$	$R_1 = 0.0828, wR_2 = 0.2553$
R_1^{a} , wR_2^{b} (all data)	$R_1 = 0.1051, wR_2 = 0.2875$
Largest diff. peak and hole (e/ų)	1.68 and -0.80

 $^{a}R_{1} = \Sigma(||F_{0}| - |F_{C}||) / \Sigma |F_{0}|.$

^b $wR_2 = [\Sigma w(|F_0|^2 - |F_C|^2)^2 / \Sigma w(F_0^2)]^{1/2}.$

In1-01	2.050(4)	In2-08	2.026(6)
In1-02	2.034(5)	In2-010	2.142(8)
In1-03	2.149(7)	In2-0135	2.204(7)
In1-051	2.209(6)	In3- 08	2.094(6)
In1-06	2.201(8)	In3- 086	2.094(6)
In1-0112	2.132(6)	In3-09	2.164(7)
In2-024	2.071(6)	In3-096	2.164(7)
In2-04	2.163(7)	In3-0147	2.142(9)
In2-07	2.169(7)	In3-0145	2.142(9)

 Table S2. Selected bond lengths (Å) for UTSA-22

Symmetry code: 11/3+Y-X,-1/3+Y,1/6+Z; 2-2/3+Y,-1/3+X,7/6-Z; 42/3+Y-X,1/3+Y,-1/6+Z; 54/3-Y,2/3+X-Y,-1/3+Z; 61-X,1-Y,1-Z; 7-1/3+Y,1/3-X+Y,4/3-Z; 81+Y-X,1-X,+Z



Figure S1. Coordination environment of In³⁺ atoms and connection models of the ligands in **UTSA-22** (color code: In, turquiose; C, black; O, red; octahedral geometry constituted by In and O; hydrogen atoms are not shown for clarity)



Figure S2. Crystal structure of **UTSA-22** highlighting the disordered octahedral cage. (color code: In, turquiose; C, black; O, red; octahedral geometry constituted by In and O; hydrogen atoms are not shown for clarity).



Figure S3. Crystal structure of **UTSA-22** highlighting the thickness of the pore-walls (color code: In, turquiose; C, black; O, red; octahedral geometry constituted by In and O; hydrogen atoms are not shown for clarity).



Figure S4. Liquid ¹HNMR of H₃TTETA.







Figure S6 TGA curve of UTSA-22.



Figure S7 FT-IR spectrum of UTSA-22 and the ligand H₃TTETA



Figure S8. Plot of $n(1-P/P_0)$ vs. P/P_0 to determine the maximum P/P_0 used in the BET linear fit according to the first BET consistency criterion



Figure S9. Plot of P/P0/(n(1-P/P0)) vs. P/P0 to determine the BET surface area. The slope of the best fit line for P/P0< 0.068 is 0.002, and the y-intercept is 4.23×10^{-6} , which satisfies the second BET consistency criterion. This results in a BET surface area of 2173 m²/g.



Figure S10. Excess high-pressure CH₄ adsorption isotherms of UTSA-22 at 298 K.



Figure S11. Excess high-pressure CH₄ adsorption isotherms of UTSA-22 at 273 K.



Figure S12. Isosteric heat of adsorption (Q_{st}) of H₂ in **UTSA-22**, derived using the virial method.

MOF	D_c^a	V_c^b	BET ^c	total uptake ^d at 80 (65) bar		working capacity ^e at 80(65)-		Q _{st}
	g/cm ³	cm³ /g	m² /g				5 bar	
				cm³/cm³	g/g	cm³/cm³	g/g	- 1
HKUST-1 ²	0.883	0.78	1850	272 (267)	0.220 (0.229)	200 (190)	0.162 (0.154)	17.0
NU-111 ²	0.409	2.09	4930	(205)	(0.358)	(177)	(0.309)	14.2
LIMF-82 ³	0.922	0.71	1624	271 (245)	0.210 (0.19)	218 (182)	0.169 (0.141)	17.5
PCN-14 ³	0.829	0.85	2170	250 (230)	0.215 (0.198)	178 (157)	0.153 (0.135)	17.6
UTSA-76 ⁴	0.699	1.09	2820	(257)	(0.263)	(197)	(0.201)	15.44
VNU-21 ⁵	1.04	0.58	1440	194 (182)	0.133 (0.125)	(140)	(0.096)	15.7
VNU-22 ⁵	1.17	0.41	1030	164 (155)	0.100 (0.095)	(101)	(0.062)	16.5
Fe-NDC ⁵	1.03	0.54	1240	167 (160)	0.116 (0.111)	(108)	(0.075)	16.6
BUT-22 ⁶	0.381	2.11	4488	202 (182)	0.379 (0.340)	178 (158)	0.334 (0.295)	12.05
MFM-132 ⁷	0.65	1.06	2466	213 (201)	0.237 (0.221)	162 (150)	0.178 (0.165)	15.7
FJI-H23 ⁸	0.540	1.426	3740	(179)	(0.237)	(129)	(0.171)	-
MOF-519 ⁹	0.953	0.938	2400	279 (260)	0.209 (0.195)	230 (211)	0.172 (0.157)	14.6
MOF-520 ⁹	0.586	1.227	3290	230	0.281	194	0.234	13.6
Ni-MOF-74 ⁹	1.195	0.51	1438	267 (251)	0.195 (0.150)	152 (129)	0.091 (0.077)	21.4
MOF-210 ⁹	0.25	3.60	6240	166 (143)	0.474 (0.409)	154 (131)	0.440 (0.374)	-
DUT-4 ¹⁰	0.77	0.68	1308	(164)	(0.152)	(124)	(0.115)	-
DUT-5 ¹⁰	0.634	0.81	1613	(134)	(0.151)	(114)	(0.128)	-
Cu-tbo-MOF- 5 ¹¹	0.959	1.120	3971	216 (199)	0.217 (0.148)	175 (158)	0.217	20.4
FJU-101 ¹²	0.846	0.762	1909	(212)	(0.179)	(144)	(0.122)	17.3
MAF-38 ¹³	0.761	0808	2022	273 (263)	0.256 (0.247)	197 (187)	0.185 (0.176)	21.6
pbz-MOF- 1 ¹⁴	0.99	0.664	2415	192/210	0.207 (0.227)	162/180	0.174 (0.195)	-
NOTT-101- IPA ¹⁵	0.660	1.12	2880	240 (227)	0.260 (0.245)	190 (177)	0.206 (0.192)	14.5
NOTT-101 ¹⁵	0.684	1.08	2843	240 (228)	0.250 (0.238)	184 (172)	0.192 (0.180)	15
Spe-MOF ¹⁶	0.71	0.98	2678	212 (186)	0.213 (0.187)	183 (157)	0.184 (0.158)	12.3
Fe-8T18- ABDC ¹⁷	0.729	0.95	2337	225 (212)	0.221 (0.208)	172 (159)	0.169 (0.156)	16.5
UTSA-22	0.7	0.9	2185	188 (174)	0.192 (0.178)	160 (146)	0.163 (0.149)	9.8

Table S3. comparison of some microporous MOFs for the high pressure CH_4 storage at room temperature and 80 and 65 bar

^a Framework density without guest molecules and terminal waters. ^b Pore volumes calculated from the maximum amounts of N₂ adsorbed. ^c BET surface areas calculated from N₂ isotherms at 77 K. ^d At 298 K and 80 (65) bar. ^e Defined as the difference of the amount of methane adsorbed between 80 (65) bar and 5 bar.

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total uptake [®] at 65 bar		working capacity ⁶ (65-5 bar)	reference
cm³/cm³	g/g	cm ³ /cm ³	
277 ^c	0.162 ^c	106 ^c	2
238	0.197	134	18
288	0.227	189	19
250 ^c	0.193 ^c	112 ^c	20
301 ^c	0.243 ^c	168 ^c	2
269 ^c	0.244 ^c	157 ^c	20
270 ^c	0.233 ^c	153 ^c	2
293	0.3	203	21
289	0.3	201	21
292	0.301	202	21
291	0.301	201	21
281	0.296	196	21
267 ^c	0.319 ^c	197 ^c	22
242 ^c	0.51 ^c	215 ^c	23
257 ^c	0.429 ^c	230 ^c	24
192	0.197	157	this work
	total uptake cm ³ /cm ³ 277 ^c 238 288 250 ^c 301 ^c 269 ^c 270 ^c 293 289 292 291 281 281 267 ^c 242 ^c 257 ^c 192	total uptake³ at 65 barcm³/cm³g/g 277^{c} 0.162^{c} 238 0.197 288 0.227 250^{c} 0.193^{c} 301^{c} 0.243^{c} 269^{c} 0.244^{c} 270^{c} 0.233^{c} 293 0.3 292 0.301 291 0.301 281 0.296 267^{c} 0.319^{c} 242^{c} 0.51^{c} 257^{c} 0.429^{c} 192 0.197	total uptake³ at 65 barworking capacity b (65-5 bar) cm^3/cm^3 g/g cm^3/cm^3 277°0.162°106°2380.1971342880.227189250°0.193°112°301°0.243°168°269°0.244°157°270°0.233°153°2930.32032890.32012910.3012022910.3012012810.296196267°0.319°197°242°0.51°215°257°0.429°230°1920.197157

Table S4. comparison of some microporous MOFs for the high pressure CH₄ storage at 273 K and 65 bar

^a At 298 K and 65 bar.

^b Defined as the difference of the amount of methane adsorbed between 65 bar and 5 bar.

^c at 270 K.

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