

(Supplementary information)

Gas Storage and Separation in Water-Stable [Cu^I₅BTT₃]⁴⁻ Anion Framework Comprising Giant Multi-prismatic Nanoscale Cage

B. X. Dong,^{*a} S. Y. Zhang,^a W. L. Liu,^a L. Chen,^a J. Ge,^a L. Song^a and Y. L. Teng^{*a}

College of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou, 225002, P. R.

China. Fax: +86 51487975590-9201; Tel: +86 51487975590-9201; E-mail: bxdong@yzu.edu.cn

(B-X. Dong); ylteng@yzu.edu.cn (Y-L. Teng).

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General Procedures.

All chemicals purchased were of reagent grade and were used as received. H₃BTT was synthesized according to a documented procedure.¹ FT-IR spectrum (KBr pellets) was recorded in range of 4000–400 cm⁻¹ on a BRUKER TENSOR 27 Fourier-transform infrared spectrometer. TGA/DSC measurement (TGA, Thermal gravimetric analyses; DSC, Differential Scanning Calorimetry) were performed on a TG/DSC Model STA 449 F3 Netzsch instrument at a ramp rate of 5 °C min⁻¹, by heating the sample under argon. Powder XRD data were collected with CuK α (λ =1.5406 Å) radiation on a Bruker-AXS D8 Advance X-ray diffractometer in the angular range 2θ =5°–50° at 296 K. Each pattern is recorded with a 2 s per step scan.

Synthesis of [NC₂H₈]₄Cu₅(BTT)₃·xG (G=guest molecule) (1)

16.0 mL DMA (*N, N'*-Dimethylacetamide) solution was added to a beaker, which contains CuCl₂·2H₂O (0.068 g, 0.4 mmol) and H₃BTT·2HCl (0.071 g, 0.2 mmol) with stirring for 30 min. Then the mixture was transferred and sealed in a 23 mL Teflonlined stainless steel container, and heated at 140 °C for 3 days. After slow cooling to room temperature with the rate of 5 °C h⁻¹, brown crystals **1** were collected and washed with DMA. Finally, the resulting crystals were dried in a vacuum oven at 80 °C for further treatment and characterization (yield: ca.40.6 mg, 42.2% based on Cu). Prominent FT-IR peaks for **1** (KBr Pellet, cm⁻¹): 3379(w), 3059(w), 2781(m), 2472(m), 1663(s), 1610(s), 1465(m), 1414(s), 1259(w), 1099(m), 1020(m), 899(m), 794(s).

I. X-ray Crystallographic Study

Single-crystal X-ray diffraction analysis data was collected on a Bruker Smart Apex II CCD diffractometer with Mo K α monochromated radiation (λ =0.71073 Å) at 296 K. All absorption corrections were performed by using the SADABS program. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using the SHELXTL package.² Anisotropic thermal parameters were used to refine all Cu, C and N atoms. After locating and refining the framework and the counter ions, the difference Fourier map showed many peaks of very low

electronic density, suggesting an extensive disorder of the solvent molecules. Thus, the solvent molecules reside in those regions of diffuse electron density were treated by the PLATON/SQUEEZE procedure,³ which suggested a unit cell accessible volume of 12836.4 Å³ (about 40.5%). The hydrogen atoms attached to carbon positions were placed in geometrically calculated positions. The crystal data and structure refinement results of squeezed compound **1** are summarized in Table S1. Selected bond lengths and angles are listed in Tables S2. Atomic coordinates and equivalent isotropic displacement parameters are listed in Table S3. Valence bond calculations for the three independent Cu centers in each asymmetric unit are listed in Table S4. Crystallographic data for the structure reported in this paper has been deposited in the Cambridge Crystallographic Data Center with CCDC number 1034129 for **1**.

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:: Resd 1 - Infinite (Type1) 3D-Framework: Det = 1
:: Base Vectors: 1 : 1 1 0 , 2 : 0 1 -1 , 3 : 2 1 0 ,
:: Resd 1, SOF 1.000, Z 16, C27 H9 Cu5 N36
:: Resd 2, SOF 1.000, Z 32, C2 H8 N
:: Resd 3, SOF 1.000, Z 32, C2 H8 N
:: Moiety_Formula = C27 H9 Cu5 N36, 4(C2 H8 N)
:: Sum_Formula = C35 H41 Cu5 N40
:: Formula_Weight = 1339.83 [Note: Based on SHELXL2014 Atomic Weights]
:: Formula_Z = 16
:: SpaceGroup_Z = 32
:: Formula_Z' = 0.500
:: mu(MoKa) = 13.68 cm-1 = 1.368 mm-1
:: Predicted Vol = 20803.7[ 20799.7] Ang**3, 298[296]K
:: ADP N1 0.024 0.030 0.215 - RATIO(MAX/MIN) = 9.0 prolate
:: ADP N11 0.018 0.046 0.203 - RATIO(MAX/MIN) = 11.1 prolate
:: ADP N12 0.021 0.036 0.209 - RATIO(MAX/MIN) = 10.0 prolate
:: ADP C20 0.123 0.385 1.267 - RATIO(MAX/MIN) = 10.3 prolate
:: ADP N21 0.099 0.202 1.061 - RATIO(MAX/MIN) = 10.7 prolate

:: VOID/SOLU Gridstep (Angstrom) (re)set to 0.20, Percent Memory = 4.1

van der Waals (or ion) Radii used in the Analysis
-----
C H Cu N O
-----
1.70 1.20 1.40 1.55 1.52
:: Note: VOID/SOLU/SQUEEZE is relatively compute intense and experimental

:: Total Potential Solvent Area Vol 12836.4 Ang^3
per Unit Cell Vol 31702.0 Ang^3 [40.5%]

Note: Expected volumes for solvent molecules are:
A hydrogen bonded H2O-molecule 40 Ang^3
Small molecules (e.g. Toluene) 100-300 Ang^3

Values below for gridpoints and volumes in []
refer to areas where atom centers may reside.

:: Use the CALC SQUEEZE instruction to calculate and optionally correct for
:: Density identified in solvent accessible areas (Reflection data required)

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Calculation result of PLATON/SQUEEZE.

II. Gas Sorption Measurements

In the gas sorption measurement, Ultra-high-purity grade N₂, He, H₂, CO₂ (>99.999% purity) and CH₄ (>99.995% purity) gases were used throughout the adsorption experiments. All of the measured sorption isotherms have been repeated several times to confirm the reproducibility within experimental error.

Low-Pressure Gas Sorption Measurements

Low-pressure N₂ adsorption measurements (up to 1 bar) were performed on a Micromeritics ASAP 2020 HD88 surface area and pore size analyzer. About 200 mg of acetone solvent-exchanged sample was degassed at 40 °C at the “degassing station” of ASAP 2020 surface area and porosity analyzer under dynamic high vacuum (oil pump) for 24 h and then at “analyzing station” under turbine molecular pump for 12 h. High vacuum was maintained at a pressure < 1 μm Hg after 8 hours degassing at “degassing station” and was maintained at a pressure < 0.05 μm Hg for the final 8 hours activation at the “analyzing station”. Helium was used for the estimation of the dead volume, assuming that it is not adsorbed at any of the studied temperatures. A part of the N₂ sorption isotherm in the P/P₀ range 0.005–0.05 was fitted to the BET equation to estimate the BET surface area⁴ and the Langmuir surface area calculation was performed using all data points.⁵

High-Pressure Gravimetric Gas Sorption Measurements

High-pressure excess adsorption isotherms of CO₂, H₂ and N₂ were measured on a Rubotherm MSB (magnetic suspension balance) apparatus by the gravimetric method. About 120 mg fully desolvated samples were used for high-pressure sorption measurements. The significance of the balance is ≤0.1 mg. Thus, a stainless steel sample holder was filled with the fully desolvated sample and the balance was evacuated for 24 h until constant mass was achieved. Afterwards, the gas was dosed into the balance chamber to elevated pressure. Equilibrium was achieved within 30 min and identified by constant weight and pressure. The temperature was kept constant with an accuracy of ±0.5 K for each measurement. The total gas uptake was calculated using the following equation,⁶

$$N_{\text{total}} = N_{\text{excess}} + \frac{100 \times V_{\text{pore}} \times \rho_{\text{gas}}}{(1 + V_{\text{pore}} \times \rho_{\text{gas}})} \quad (1)$$

where N_{total} is the total uptake amount of gas (wt%), N_{excess} is the surface excess uptake amount of gas (wt%), V_{pore} is the crystallographic pore volume ($0.302 \text{ cm}^3 \text{ g}^{-1}$ in this work) which is determined from the nitrogen isotherm, and ρ_{gas} (g cm^{-3}) is the density of the compressed gas as a function of pressure at certain temperature.⁷

III. Isotheric Heat of Adsorption (Q_{st}) Calculations

A virial-type⁸ expression comprising the temperature-independent parameters a_i and b_i was employed to calculate the enthalpies of adsorption for CO_2 (at 273 and 298 K) on **1a**. In each case, the data were fitted using the equation:

$$\ln P = \ln N + 1/T \sum_{i=0}^m a_i N^i + \sum_{j=0}^n b_j N^j \quad (2)$$

Here, P is the pressure expressed in Torr, N is the amount adsorbed in mmol g^{-1} , T is the temperature in K, a_i and b_i are virial coefficients, and m , n represent 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, and 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 isotheric heat of adsorption using the following expression:

$$Q_{\text{st}} = -R \sum_{i=0}^m a_i N^i \quad (3)$$

Q_{st} is the coverage-dependent isotheric heat of adsorption and R is the universal gas constant. The heat of CO_2 sorption for **1a** in this manuscript is determined by using the excess sorption data measured in the pressure range from 0–800 mmHg (273 and 298 K), which is fitted by the virial-equation very well ($R^2 > 0.999$).

IV. Prediction of the Gases Adsorption Selectivity by IAST

IAST (ideal adsorption solution theory)⁹ was used to predict binary mixture

adsorption from the experimental pure-gas isotherms. In order to perform the integrations required by IAST, the single-component isotherms should be fitted by a proper model. In practice, several methods to do this are available. For N₂/1a in the low pressure, the single-site Langmuir model (SSL),¹⁰

$$q = \frac{q_{\text{sat}} b P}{1 + b P} \quad (4)$$

was used for isotherm fitting. Where, b is the parameter in the pure component Langmuir isotherm (Pa⁻¹), P is the pressure of the bulk gas at equilibrium with the adsorbed phase P (Pa), q is the adsorbed amount of adsorbent (mol kg⁻¹), q_{sat} is saturation capacity of species (mol kg⁻¹).

The situations with CO₂/1a and H₂/1a in low pressure are different and a similar approach to the above using single-site Langmuir model fits is inadequate. We found for these sets of data that the dual-site Langmuir-Freundlich equation (DSLFF)¹⁰⁻¹² was successful in fitting the data:

$$q = \frac{q_{m,1} b_1 P^{1/n_1}}{1 + b_1 P^{1/n_1}} + \frac{q_{m,2} b_2 P^{1/n_2}}{1 + b_2 P^{1/n_2}} \quad (5)$$

Here, p is the pressure of the bulk gas at equilibrium with the adsorbed phase (Pa), q is the adsorbed amount of adsorbent (mol kg⁻¹), $q_{m,1}$ and $q_{m,2}$ are the saturation capacities of sites 1 and 2 (mol kg⁻¹). b_1 and b_2 are the affinity coefficients of sites 1 and 2 (Pa⁻¹), and n_1 and n_2 represent the deviations from an ideal homogeneous surface.

Pure-component isotherm fitting parameters were then used for calculating IAST binary-gas adsorption selectivities, $S_{A/B}$, defined as:

$$S_{A/B} = \frac{q_A / q_B}{P_A / P_B} \quad (6)$$

V. Gas Cycling Measurements.

CO₂ cycling experiments were performed on a TG/DSC Model STA 449 F3 Netzsch instrument. A flow of 15% (v/v) CO₂ mixture in N₂ was applied followed by

a stream of pure N₂ (>99.999%). The flow rates for pure N₂ gas and CO₂-N₂ (15:85 v/v) mixture gas are 60 mL min⁻¹ and 40 mL min⁻¹, respectively.

Table S1. Crystal data and structure refinement for compound **1**.

Compound	[NC ₂ H ₈] ₄ C ₂₇ H ₉ Cu ₅ N ₃₆
Empirical formula	C ₃₅ H ₄₁ Cu ₅ N ₄₀
Formula weight	1339.78
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	<i>Fddd</i>
a/Å	16.180(2)
b/Å	43.077(5)
c/Å	45.485(6)
V/Å ³	31702(7)
Z	16
D _{calc} (Mg/m ³)	1.123
Absorption coefficient (mm ⁻¹)	1.368
F(000)	10816
θ range for data collection	1.417 to 24.999 deg
Reflections collected / unique	68507 / 7000 [R(int) = 0.0840]
Limiting indices	-19<=h<=19, -49<=k<=51, -54<=l<=54
Completeness to θ= 25.242	97.4 %
Goodness-of-fit on F ²	0.993
Final R indices [I>2σ(I)]	<i>R</i> 1 = 0.0489, <i>wR</i> 2 = 0.1360
R indices (all data)	<i>R</i> 1 = 0.0853, <i>wR</i> 2 = 0.1474
Largest diff. peak and hole (e. Å ⁻³)	0.588 and -0.409
Total potential solvent area Vol Å ³	12836.4 (40.5%)
per Unit Cell Vol 31702.0 Å ³	

Table S2. Selected bond distances (Å) and angles (°) for **1**.

Cu(1)-N(18)	2.069(2)	N(18)-Cu(1)-N(4)#1	104.2(3)
Cu(1)-N(18)#1	2.070(7)	N(18)#1-Cu(1)-N(4)#1	119.3 (3)
Cu(1)-N(4)	2.068(2)	N(4)-Cu(1)-N(4)#1	99.9 (3)
Cu(1)-N(4)#1	2.068(7)	N(3)-Cu(2)-N(14)	113.91(13)
Cu(2)-N(3)	1.978(2)	N(3)-Cu(2)-N(5)	114.92(11)
Cu(2)-N(14)	2.010(3)	N(14)-Cu(2)-N(5)	114.57(10)
Cu(2)-N(5)	2.064(2)	N(3)-Cu(2)-N(17)	113.78(10)
Cu(2)-N(17)	2.097(2)	N(14)-Cu(2)-N(17)	99.74(12)
Cu(3)-N(6)	1.963(2)	N(5)-Cu(2)-N(17)	97.70(11)
Cu(3)-N(13)	2.063(3)	N(6)-Cu(3)-N(13)	107.84(10)
Cu(3)-N(9)#2	2.071(4)	N(6)-Cu(3)-N(9)#2	129.71(12)
Cu(3)-N(10)	2.071(4)	N(13)-Cu(3)-N(9)#2	99.84(13)
N(18)-Cu(1)-N(18)#1	110.3(3)	N(6)-Cu(3)-N(10)	120.02(15)
N(18)-Cu(1)-N(4)	119.26(9)	N(13)-Cu(3)-N(10)	97.75(13)
N(18)#1-Cu(1)-N(4)	104.3(3)	N(9)#2-Cu(3)-N(10)	95.98(17)
Symmetry transformations used to generate equivalent atoms: #1 $-x+5/4, y, -z+1/4$ #2 $-x+3/4, -y+3/4, z$			

Table S3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for compound **1**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Cu(1)	6250	4278(1)	1250	32(1)
Cu(2)	5013(1)	4288(1)	624(1)	34(1)
Cu(3)	4315(1)	4080(1)	-105(1)	42(1)
C(1)	4987(3)	4823(1)	1360(1)	46(1)
C(2)	5334(3)	4957(1)	1636(1)	44(1)
C(3)	5824(3)	4786(1)	1826(1)	39(1)
C(4)	6114(2)	4918(1)	2086(1)	35(1)
C(5)	5887(3)	4741(1)	197(1)	35(1)
C(6)	5914(3)	5222(1)	2151(1)	45(1)
C(7)	5426(3)	5394(1)	1959(1)	50(1)
C(9)	5127(3)	5256(1)	1703(1)	50(1)
C(10)	3750	3750	1057(1)	27(1)
C(11)	3024(3)	3688(1)	1211(1)	35(1)
C(12)	3021(3)	3688(1)	1519(1)	38(1)
C(13)	3750	3750	1666(1)	45(2)
C(14)	7251(3)	3864(1)	809(1)	38(1)
C(15)	3750	3750	733(1)	26(1)
N(1)	4336(3)	4946(1)	1223(1)	89(2)
N(2)	4237(3)	4776(1)	976(1)	72(1)
N(3)	4806(2)	4564(1)	967(1)	37(1)
N(4)	5287(2)	4585(1)	1206(1)	30(1)
N(5)	5349(2)	4516(1)	249(1)	29(1)
N(6)	5082(2)	4423(1)	-19(1)	33(1)
N(7)	5444(2)	4591(1)	-220(1)	49(1)
N(8)	5963(2)	4794(1)	-94(1)	50(1)
N(10)	4746(3)	3686(1)	-316(1)	59(1)
N(11)	5430(3)	3651(1)	-471(1)	88(2)
N(12)	5479(3)	3360(1)	-573(1)	90(2)
N(13)	3990(2)	3874(1)	286(1)	29(1)
N(14)	4149(2)	3958(1)	567(1)	28(1)
N(15)	7189(3)	3772(1)	530(1)	82(2)
N(16)	6434(3)	3868(1)	448(1)	71(1)
N(17)	6069(2)	4008(1)	665(1)	35(1)
N(18)	6576(2)	4004(1)	900(1)	26(1)
N(9)	4320(2)	3413(1)	-312(1)	47(1)
C(8)	4785(3)	3220(1)	-472(1)	58(2)
C(20)	8123(18)	5690(5)	-850(6)	590(40)

C(21)	8044(14)	5664(4)	-280(4)	319(12)
C(22)	11066(19)	4392(11)	-1538(11)	700(40)
C(23)	12749(19)	4241(8)	-1529(6)	550(30)
N(20)	8261(13)	5497(4)	-568(5)	398(14)
N(21)	11970(20)	4377(4)	-1662(3)	450(20)

Table S4. Valence bond calculations of three crystallographically independent Cu centers in compound **1**.

	Distance	BVS
Cu(1)-N(4) ^{#1}	2.068(7)	$\Sigma(\text{Cu1})=1.21$
Cu(1)-N(4)	2.068(2)	
Cu(1)-N(18) ^{#1}	2.070(7)	
Cu(1)-N(18)	2.069(2)	
Cu(2)-N(3)	1.978(2)	$\Sigma(\text{Cu2})=1.28$
Cu(2)-N(14)	2.010(3)	
Cu(2)-N(5)	2.064(2)	
Cu(2)-N(17)	2.097(2)	
Cu(3)-N(6)	1.963(2)	$\Sigma(\text{Cu3})=1.26$
Cu(3)-N(10)	2.071(4)	
Cu(3)-N(13)	2.057(3)	
Cu(3)-N(9)	2.071(4)	

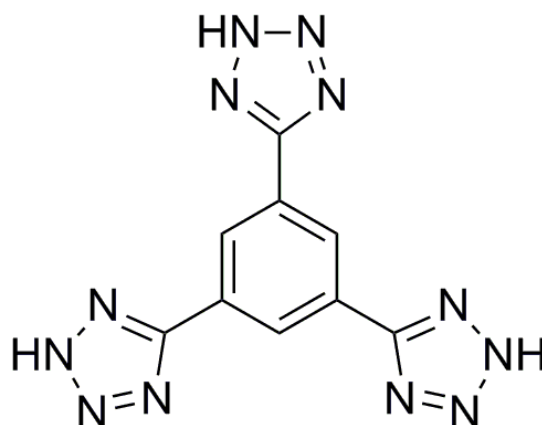


Figure S1. The structure of the H₃BTT ligand.

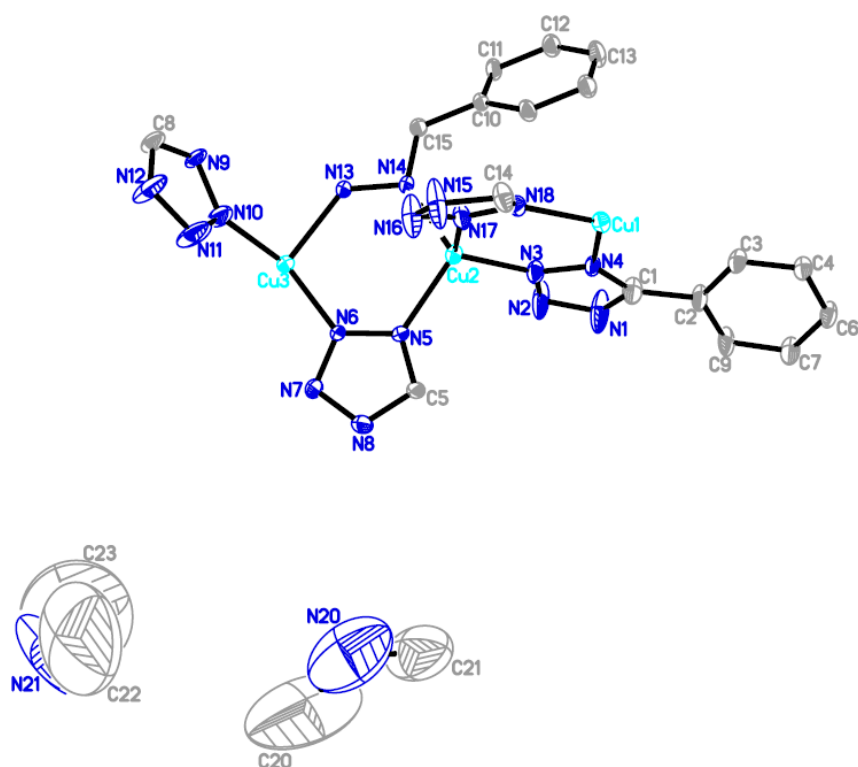


Figure S2. Ortep drawing of the asymmetric unit of the compound **1** after PLATON/SQUEEZE treatment.

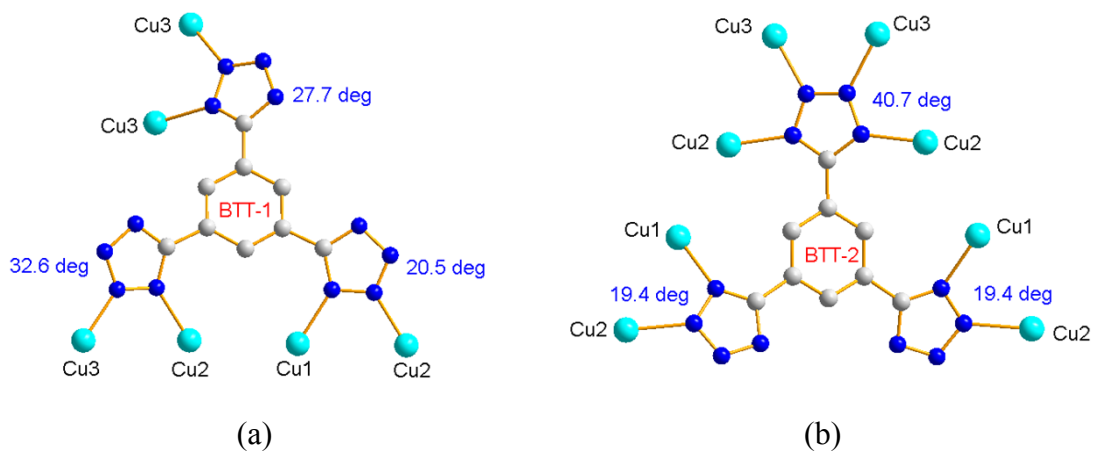


Figure S3. Representations of the (a) μ_6 -btt³⁻ and (b) μ_8 -btt³⁻ ligand, as well as the angles between planes in these two BTT ligands.

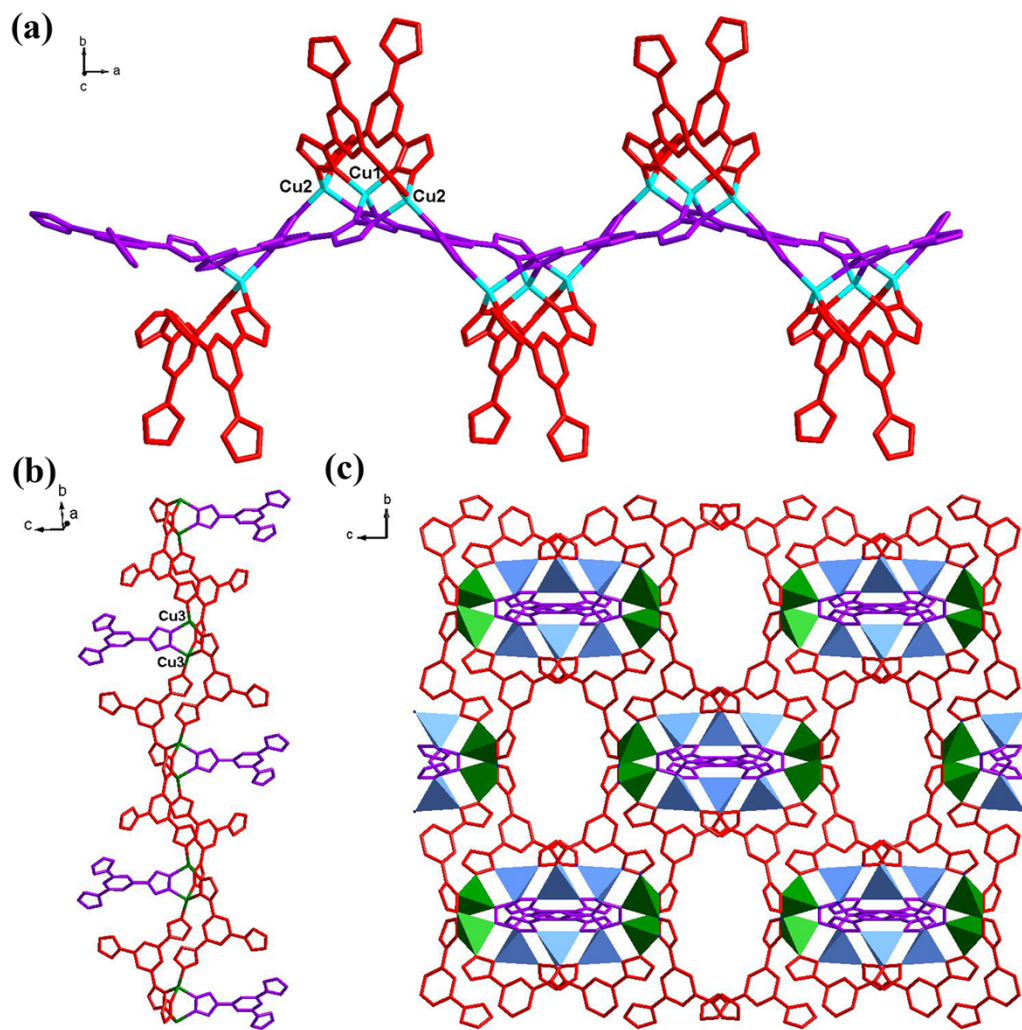


Figure S4. View of the 1D chain constructed by the tri-nuclear Cu₃ clusters (a) and bi-nuclear Cu₂ clusters (b); (c) View of the 3D open anion framework of **1** embedded with meso-helical chains.

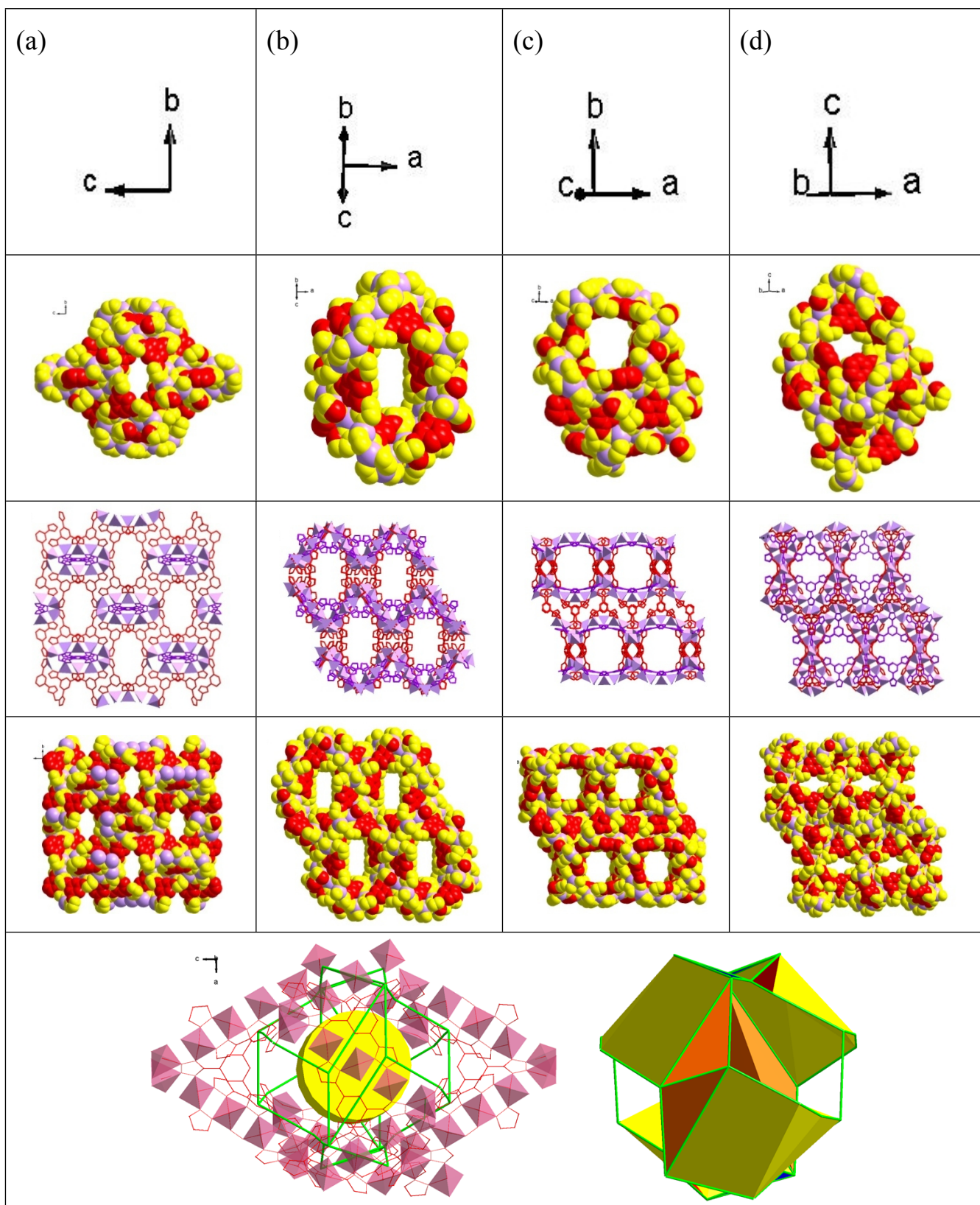


Figure S5. Representations of the four types of channels (a-d) and the giant cavity (e) in compound 1.

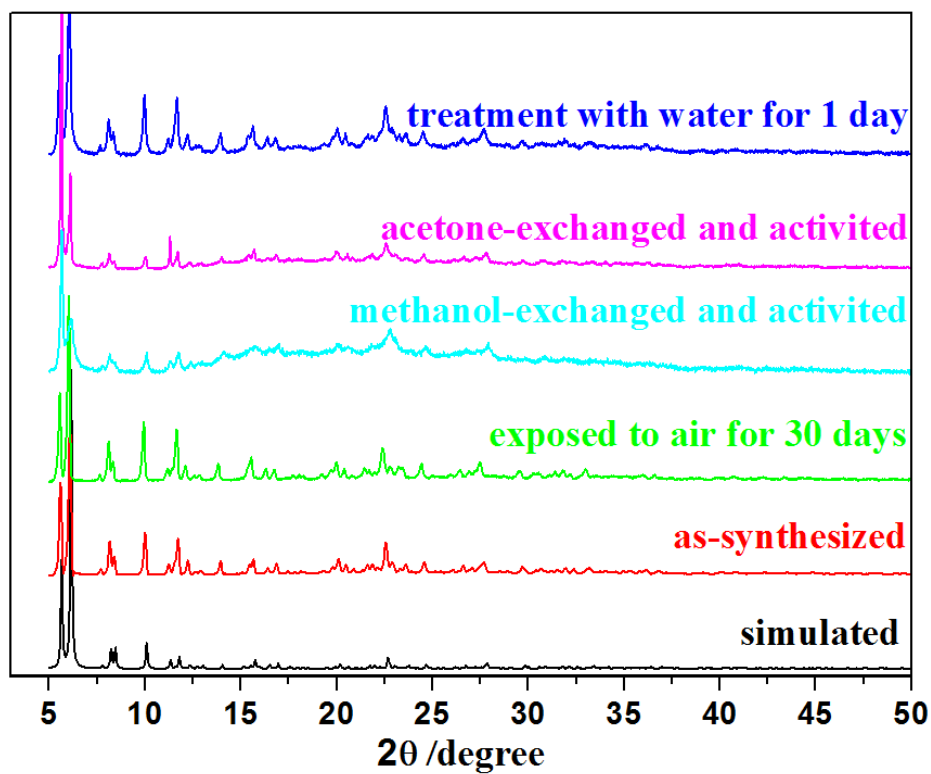


Figure S6. The PXRD patterns for compound **1** after different test.

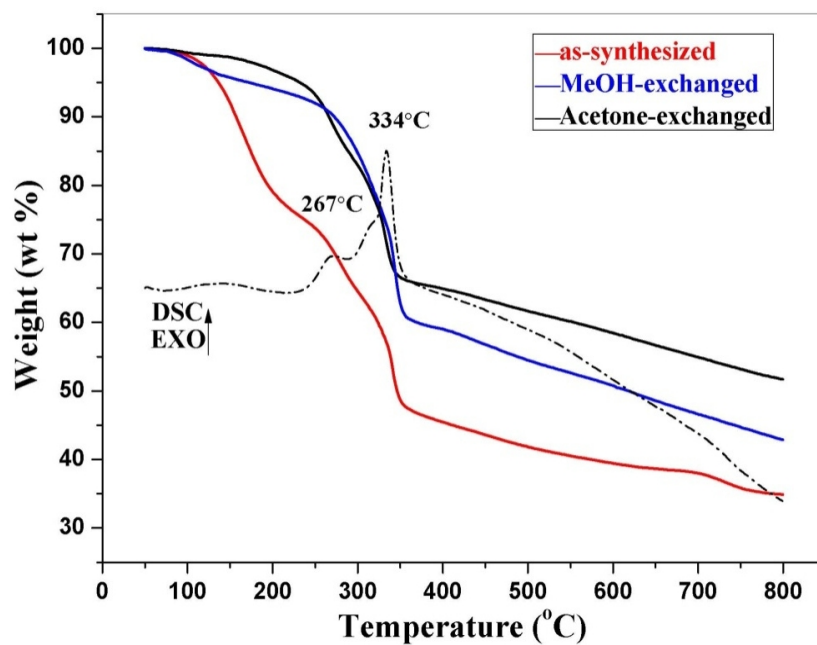


Figure S7. TG-DSC curves for the as-synthesized sample of **1** and samples after exchanged with methanol and acetone solvents.

Thermogravimetric analysis of as-synthesized sample of **1** showed a weight loss of 6.5 % up to 145 °C, suggesting that the absorbed solvents (DMA and water) both in the surface and in the voids are evacuated at this temperature. To attain a more complete evacuation, DMA was exchanged with methanol or acetone by soaking crystals of **1** in methanol or acetone for 4 days, respectively. TGA results indicate that the acetone, as compared with methanol, is a better solvent for exchanging the higher boiling point solvents of DMA and water remained in the void of **1**. The TGA curve for the acetone-exchanged sample shows a weight loss of 0.8% between 50 and 150 °C, corresponding to the evolution of guest solvent of acetone. A gradual further weight loss of 13.3% between 150 °C and 280 °C is corresponding to loss of 4 [NC₂H₈]⁺ ions (ca. 13.7%). This process is in agreement with the small exothermic peak at 267 °C. Further drastic weight loss from 280 °C is corresponding to the loss of the BTT molecules and the collapse of the framework.

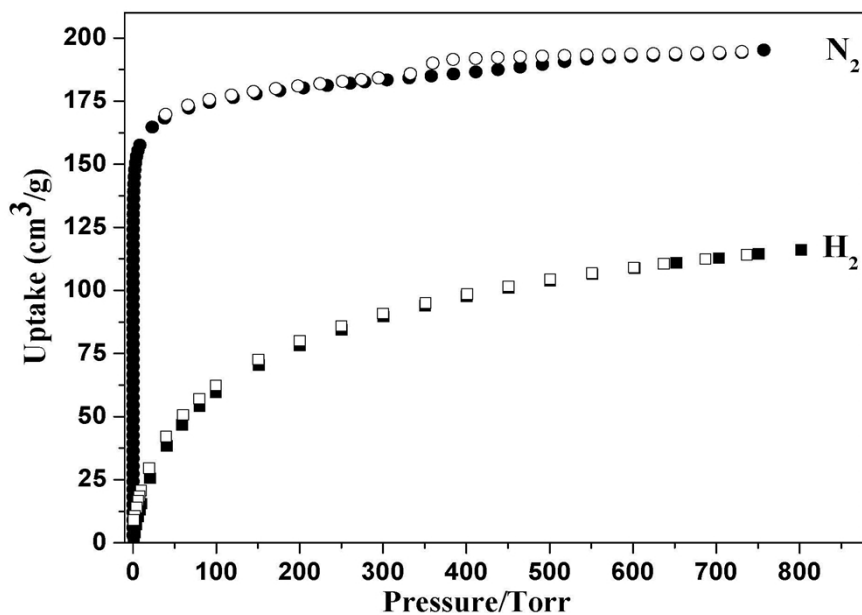


Figure S8. N₂ and H₂ sorption isotherms of **1a** at 77K, solid, adsorption; hollow, desorption.

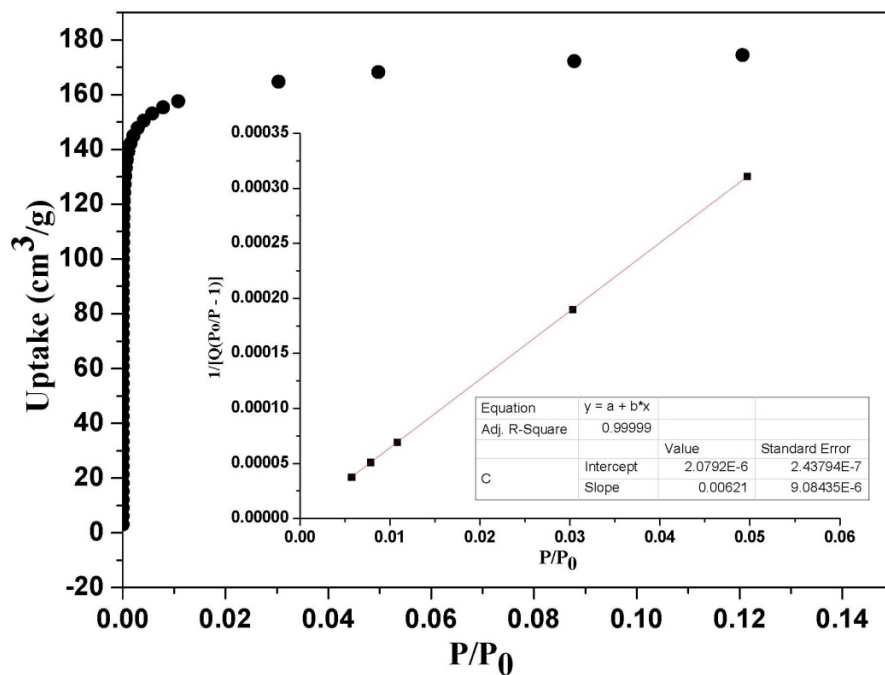


Figure S9. The plot of the linear region for the BET equation of **1a** ($P_0/P=0.005-0.05$).

Table S5. Low-pressure CO₂ (273–298 K) or H₂ (77 K) adsorption capacities in selected metal-organic frameworks.

MOFs	Pore Volume (cm ³ g ⁻¹)	Surface Area (m ² /g)		Capacity ^b /CO ₂		Capacity ^b /H ₂	
		Langmuir	BET	1 bar	Ref	77 K	Ref
1a	0.302	801	701	9.61 wt%, ^a 298 K 14.0 wt%, ^a 273 K	This work	1.03 wt%, ^a 1 bar	This work
Mg ₂ (dobdc)	0.573	2060	1800	26.7 wt%, 298 K	13	-	-
NTU-105	1.33	-	3543	26.8 wt%, 273 K	14	-	-
HKUST-1	-	-	1400	19.8 wt%, 293 K	15	-	-
SIFSIX-2-Cu-i	-	821	735	19.2 wt%, 298 K	16	-	-
SIFSIX-1-Cu	0.683	-	1468	18.5 wt%, 298 K	17	-	-
TIFSIX-1-Cu	0.696	-	1690	17.3 wt%, 298 K	17	-	-
SNIFSIX-1-Cu	0.636	-	1523	15.6 wt%, 298 K	17	-	-
mmen-Cu-BTTri	-	-	870	15.4 wt%, 298 K	18	-	-
MPM-1-TIFSIX	-	-	840	15.0 wt%, 298 K	19	-	-
Cu-BTTri	0.713	1900	1770	14.3 wt%, 298 K	20	1.7 wt%, 1.2 bar	20
Fe-BTT	-	-	2010	13.5 wt%, 298 K	21	2.3 wt%	22
CPF-6	-	883	599	16.1 wt%, 273 K	23	1.85 wt%	23
SIFSIX-2-Cu	-	3370	3140	7.5 wt%, 298 K	16		
en-Cu-BTTri	-	376	345	5.5 wt%, 298 K	20	-	-
MOF-177	1.89	5400	4690	3.6 wt%, 298 K	13	-	-
Mn-BTT	-	2100	1100	-	-	2.1 wt%	24
Cu-BTT	-	-	1710	-	-	2.3 wt%	25

^a Reported capacity was calculated from the excess adsorption.

^b It was not clear from the reference whether the reported isotherms were in absolute or excess adsorption.

Table S6. Low-pressure (LP) and high-pressure (HP) gas sorption capacities of **1a** towards CO₂, H₂, N₂ and CH₄ at different temperatures.

Gas	Pressure	77 K			273 K			298 K		
		cm ³ /g	mol/Kg	wt%	cm ³ /g	mol/Kg	wt%	cm ³ /g	mol/Kg	wt% ^a
CH ₄	LP	-			18.54 _a	0.83 ^a	1.31 ^a	10.62 _a	0.47 ^a	0.75 ^a
CO ₂	LP	-			82.80 _a	3.69 ^a	14.0 ^a	54.17 _a	2.42 ^a	9.61 ^a
	HP	-			-	5.76 ^a	20.2 ^a	-	5.30 ^a	18.9 ^a
					-	6.59 ^b	22.5 ^b	-	6.45 ^b	22.1 ^b
					30 bar			45 bar		
N ₂	LP	195.3 _a	8.71 ^a	19.6 _a	4.35 ^a	0.19 ^a	0.53 ^a	2.60 ^a	0.12 ^a	0.33 ^a
	HP (65 bar)	-			-	1.89 ^a	5.03 ^a	-	1.83 ^a	4.87 ^a
					-	2.87 ^b	7.44 ^b	-	2.72 ^b	7.07 ^b
H ₂	LP	116.1 _a	5.18 ^a	1.03 _a	0.45 ^a	0.02 ^a	0.004 _a	0.228 _a	0.01 ^a	0.002 ^a
	HP (65 bar)	-			-	1.48 ^a	0.30 ^a	-	1.00 ^a	0.2 ^a
					-	2.32 ^b	0.46 ^b	-	1.77 ^b	0.35 ^b
<p>In this work, wt% is defined as:</p> $\text{wt \%} = \frac{\text{mass gas absorbed}}{(\text{mass adsorbent} + \text{mass gas absorbed})} \times 100 \%$ <p>^a excess adsorption ^b total adsorption</p>										

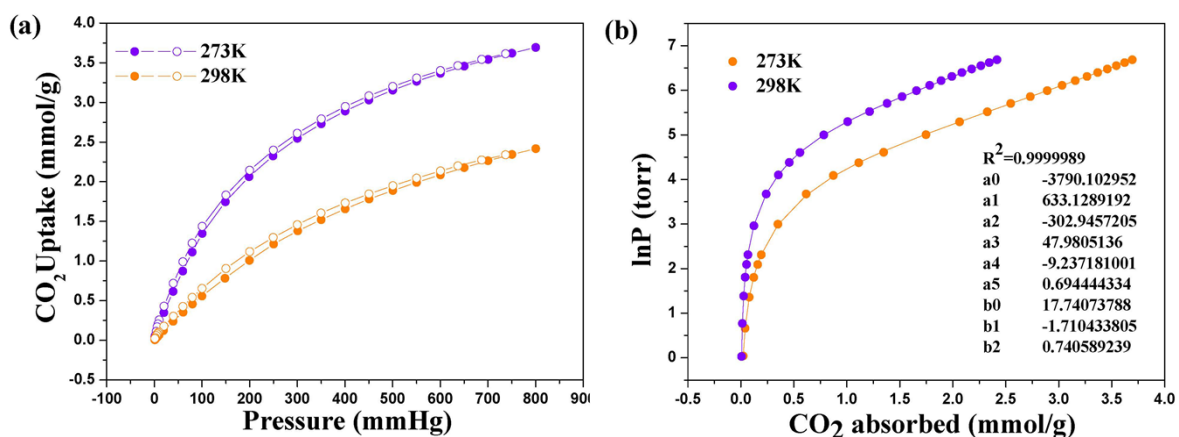


Figure S10. Virial fitting for CO₂ isotherms of **1a**: (a) The CO₂ adsorption isotherms for **1a** (solid circle, adsorption; hollow circle, desorption); (b) The details of virial equation (solid lines) fitting to the experimental CO₂ adsorption data (symbols) for **1a**.

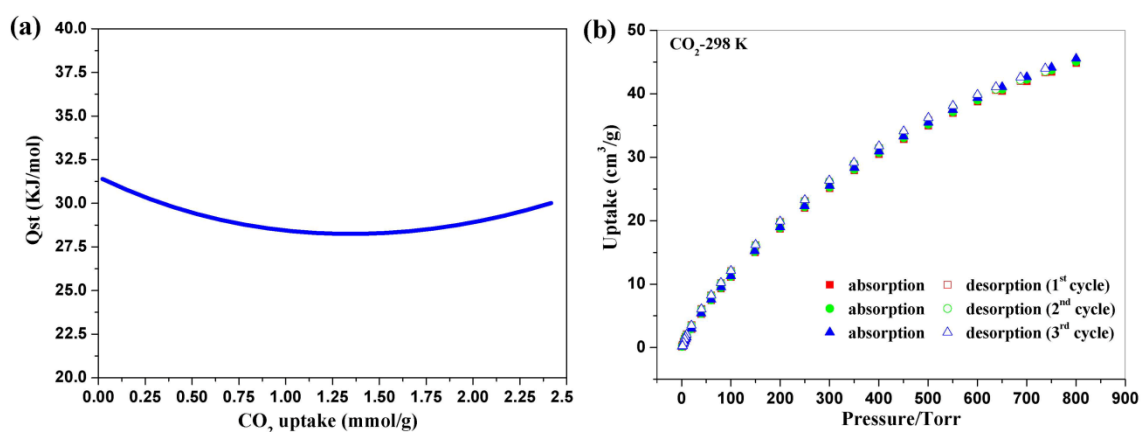


Figure S11. (a) The CO₂ adsorption enthalpy of **1a**; (b) CO₂ sorption isotherms of **1a** of three consecutive cycles.

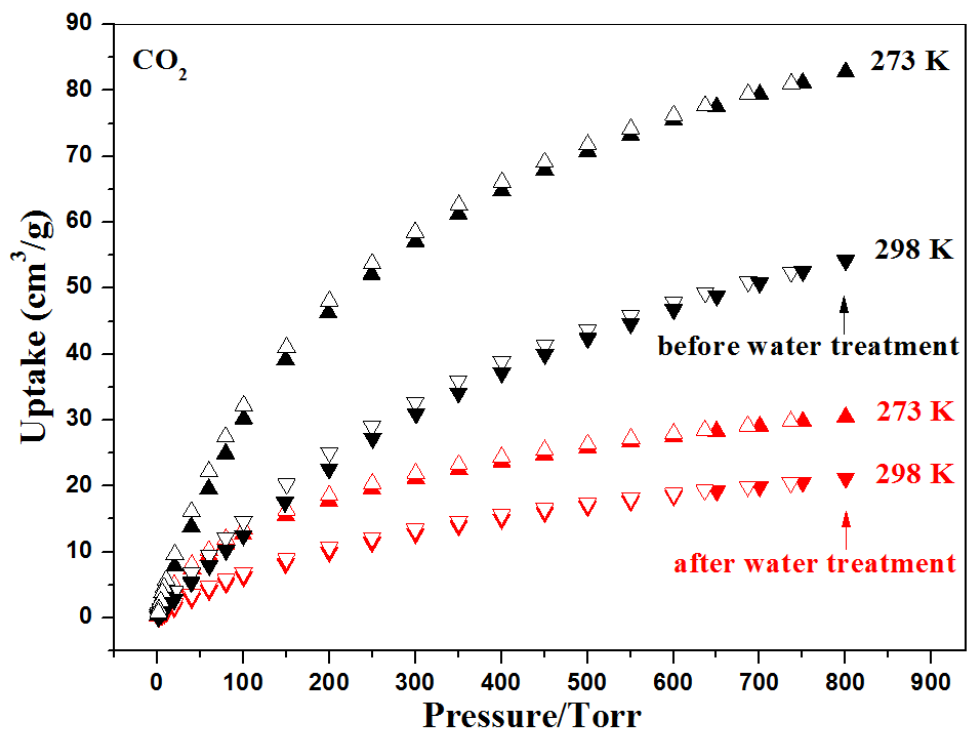


Figure S12. Comparisons of CO₂ uptakes before and after water treatment (immersion in liquid water for 1 day) at 273 and 298 K.

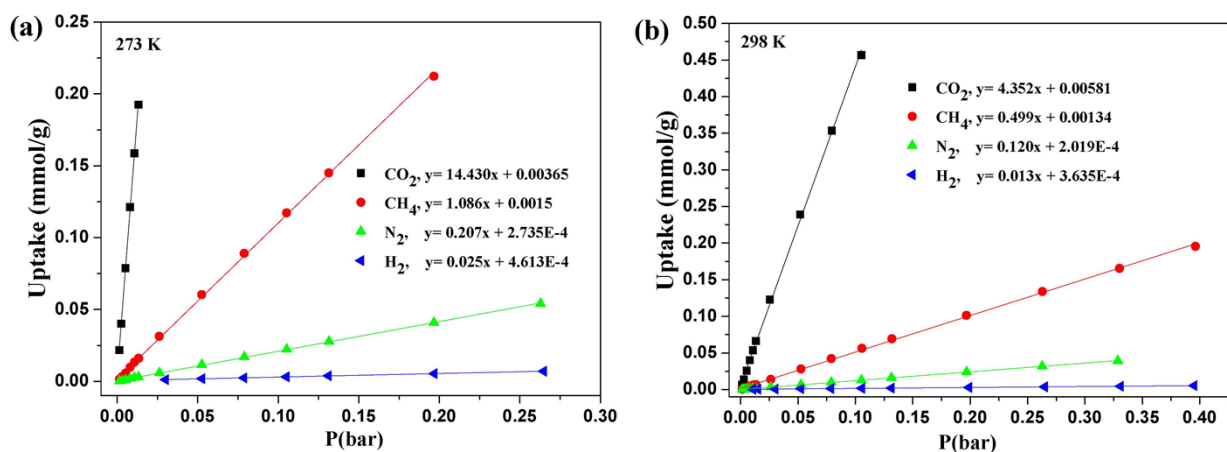


Figure S13. Low-pressure CO₂/N₂, CO₂/CH₄ and CO₂/H₂ initial slope selectivity studies for **1a** at 273 K (a) and 298 K (b).

Table S7. Low-pressure CO₂/N₂, CO₂/CH₄ and CO₂/H₂ selectivity results for **1a** analyzed by the initial slope ratio.

	CO ₂ /N ₂ selectivity		CO ₂ /H ₂ selectivity		CO ₂ /CH ₄ selectivity	
273 K	69.7	98.6%	577.2	99.8%	13.3	93.0%
298 K	36.3	97.3%	334.8	99.7%	8.7	89.7%

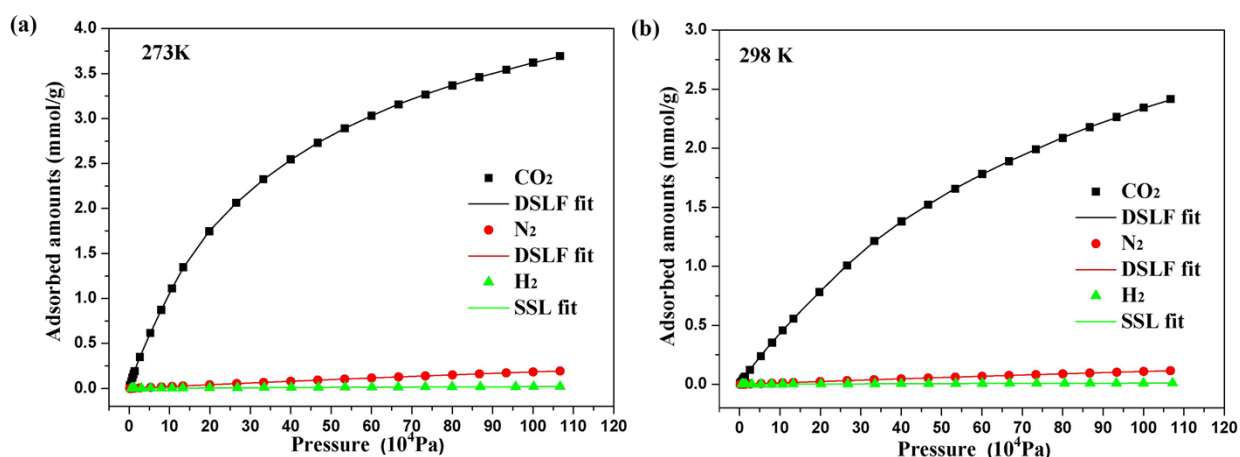


Figure S14. Low-pressure adsorption isotherms of CO₂, H₂ and N₂ at 273 K (a) and 298 K (b). Lines are fits to a dual-site Langmuir-Freundlich (DSLFL) or single-site Langmuir (SSL) equation.

Table S8. The refined parameters for the DSLFL and SSL equations fit for the pure isotherms of CO₂, N₂ and H₂ in **1a** at 273 K.

	CO ₂	H ₂		N ₂
R ²	0.999997	0.999709	R ²	0.999991
q _{m,1}	5.290562	0.047092	q _m	1.408277
q _{m,2}	0.140931	4.522968E-2	b	1.496390E-6
b ₁	5.292282E-5	2.876264E-6		
b ₂	7.554743E-21	9.558976E-9		
n ₁	1.096608	0.932293		
n ₂	0.200848	0.380865		

Table S9. The refined parameters for the DSLF and SSL equations fit for the pure isotherms of CO₂, N₂ and H₂ in **1a** at 298 K.

	CO ₂	H ₂		N ₂
R ²	0.999993	0.999537	R ²	0.999992
q _{m,1}	4.639673	0.007053	q _m	0.962695
q _{m,2}	0.061961	0.006664	b	1.282220E-6
b ₁	1309095E-5	8.654679E-12		
b ₂	3.200345E-32	1.671942E-4		
n ₁	1.027170	0.431704		
n ₂	0.139846	1.219561		

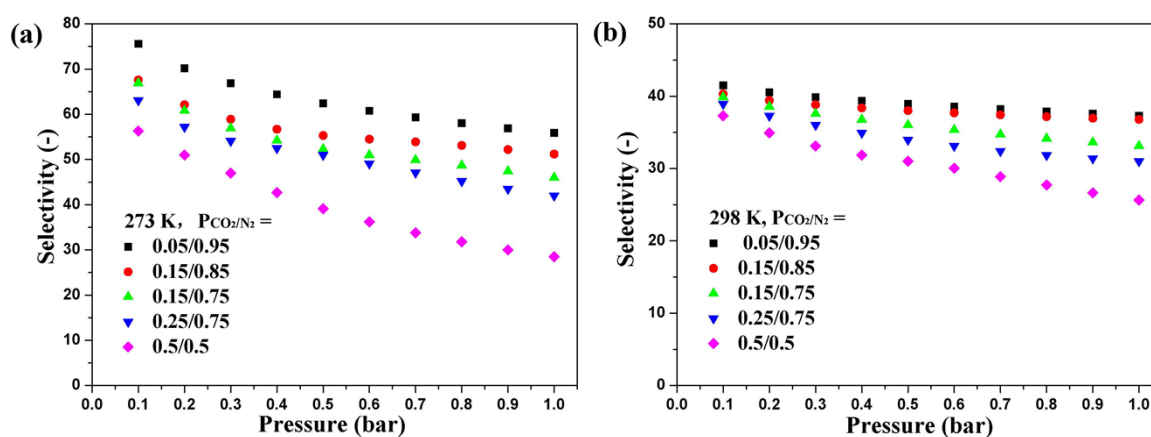


Figure S15. IAST selectivities of CO₂ over N₂ in **1a** at different mixture composition at 273 K (a) and 298 K (b).

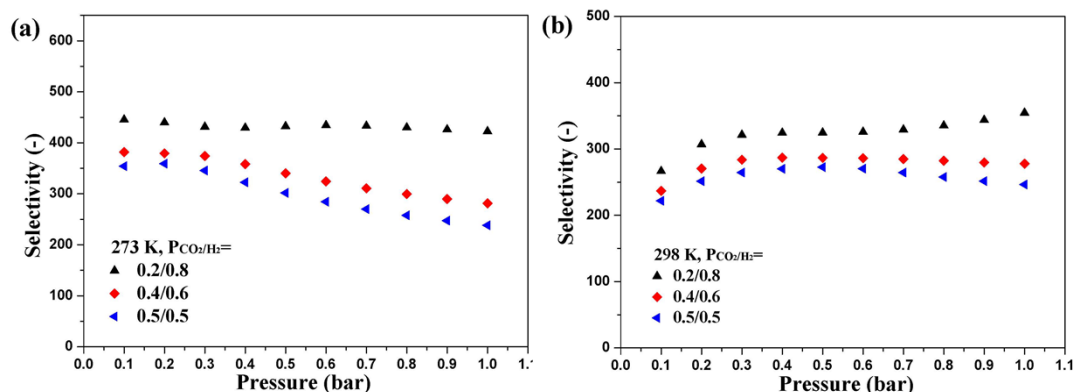


Figure S16. IAST selectivities of CO₂ over H₂ in **1a** at different mixture compositions as a function of total pressure at 273 K (a) and 298 K (b).

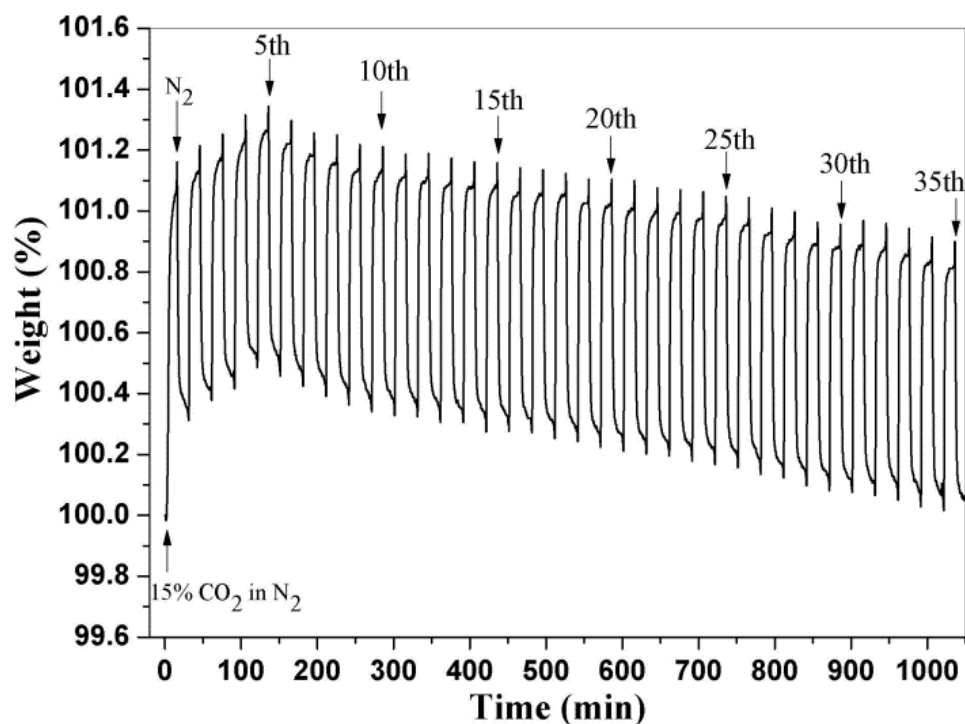


Figure S17. Gas cycling experiment for 1a under a mixed $\text{CO}_2\text{-N}_2$ (15:85 v/v) flow and a pure N_2 flow at a constant temperature of 303 K for 35 cycles.

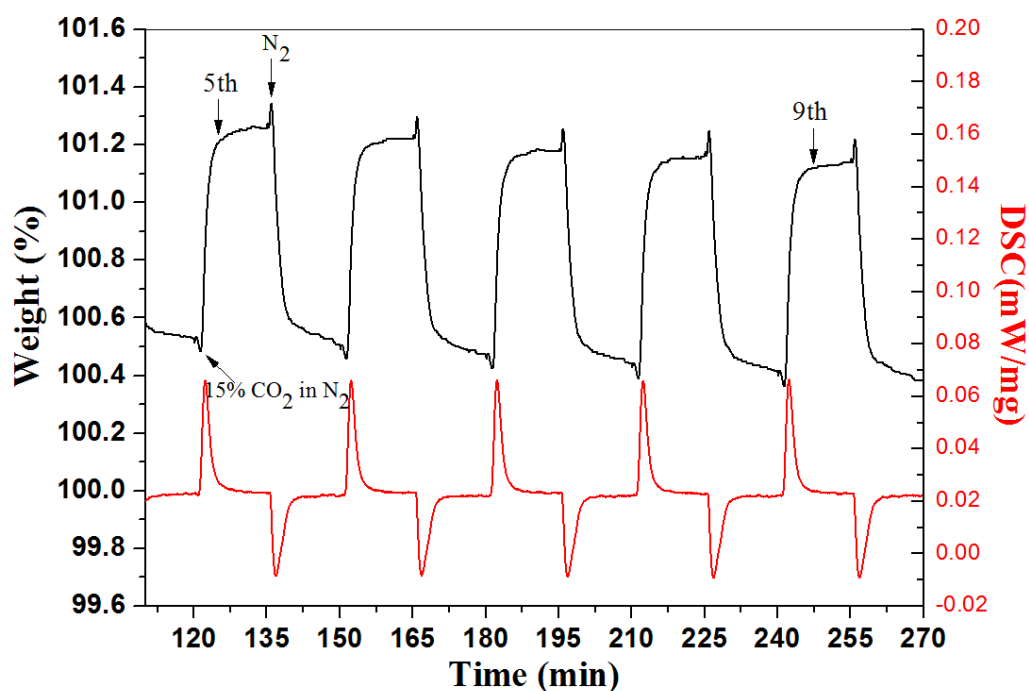


Figure S18. An enlargement of five cycles—TG-DSC curves from cycle 5th to cycle 9th.

The flow rates for pure N_2 gas and $\text{CO}_2\text{-N}_2$ (15:85 v/v) mixture gas are 60 mL min^{-1} and 40 mL min^{-1} , respectively.

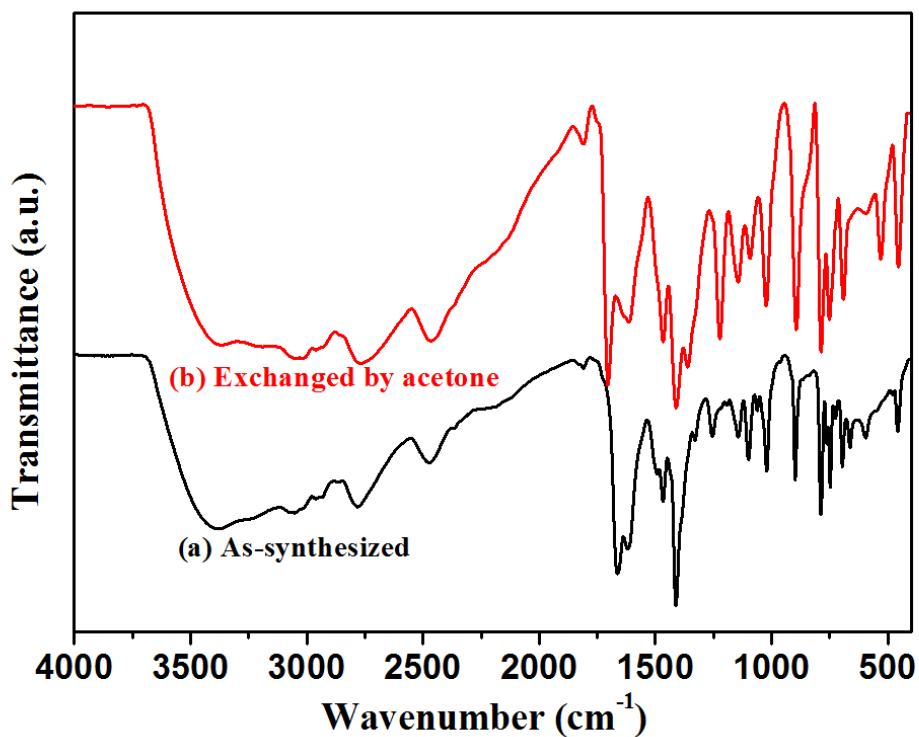


Figure S19. The IR spectra of the as-synthesized sample (a) and acetone-exchanged one (b).

Table S10. The weight change for the special cycle in the gas cycling experiment.

Cycle	2n d	5th	10t h	15t h	20t h	25t h	30t h	35t h
Weight change (wt%)	0.8	0.73	0.75	0.76	0.75	0.75	0.75	0.74

Table S11. High-pressure excess sorption and total sorption data of **1a**.

CO ₂ at 273K				
P (bar)	Excess Uptake (%)	Total Uptake (%)	Excess Uptake (mmol/g)	Total Uptake (mmol/g)
0.019	2.24709	2.248202	0.52244	0.522706

0.218	7.58666	7.59943	1.86579	1.869191
0.417	10.0336	10.05806	2.53468	2.541553
0.619	11.52851	11.56474	2.96154	2.97206
0.817	12.52434	12.57233	3.25398	3.268243
1.418	14.30794	14.39152	3.79476	3.820651
2.9179	16.23063	16.40458	4.40349	4.45995
5.9194	17.732	18.09159	4.89862	5.019907
9.9176	18.63566	19.25542	5.20545	5.419848
13.9188	19.19078	20.08776	5.39733	5.713016
17.9184	19.52486	20.71903	5.51408	5.939472
22.8337	19.8205	21.41577	5.61822	6.193637
27.8341	20.07605	22.13412	5.70885	6.460444
29.8341	20.21935	22.48383	5.75993	6.592122
26.0268	20.03147	21.9157	5.693	6.378801
22.0299	19.82394	21.35044	5.61943	6.169613
19.0329	19.66084	20.9422	5.56189	6.020395
15.0325	19.35676	20.33375	5.45522	5.800836
12.0318	19.02822	19.79184	5.34087	5.60809
9.0312	18.58693	19.1476	5.18873	5.382312
7.029	18.1587	18.589	5.04266	5.189438
5.0348	17.5034	17.80749	4.82207	4.923998
2.536	15.98438	16.13515	4.32397	4.372607
1.2374	13.97763	14.05066	3.69292	3.715365

CO ₂ at 298K				
P (bar)	Excess Uptake (%)	Total Uptake (%)	Excess Uptake (mmol/g)	Total Uptake (mmol/g)
0.018	0.68444	0.685405	0.15663	0.156849
0.22	3.55136	3.563171	0.83685	0.839733
0.617	6.84884	6.882049	1.671	1.6797
1.117	9.10571	9.165772	2.2768	2.293332
1.918	11.14969	11.25347	2.85201	2.881923
3.917	13.62753	13.84149	3.58583	3.65117
6.9215	15.29985	15.68312	4.10535	4.227322
9.9203	16.22361	16.7813	4.40122	4.583021
14.92	17.10881	17.96959	4.69093	4.978637
19.9215	17.68845	18.87083	4.88401	5.286414
24.8354	18.06204	19.58093	5.0099	5.533775
29.836	18.37208	20.25951	5.11525	5.774274
34.8338	18.60694	20.89449	5.19559	6.003056
39.8337	18.78761	21.51605	5.25771	6.230589
44.6492	18.91377	22.11849	5.30125	6.454588

38.0328	18.75359	21.31774	5.24599	6.157602
33.032	18.54064	20.67976	5.17287	5.925278
28.0309	18.31642	20.06761	5.09628	5.705848
23.032	17.9841	19.37688	4.98354	5.462251
18.0307	17.55996	18.61832	4.84097	5.199496
13.0324	16.89391	17.63819	4.62003	4.86716
9.0316	16.1128	16.6182	4.36539	4.529601
5.0336	14.58749	14.86366	3.88156	3.967876
3.036	13.06458	13.2298	3.41543	3.465214

H ₂ at 273K				
P (bar)	Excess Uptake (%)	Total Uptake (%)	Excess Uptake (mmol/g)	Total Uptake (mmol/g)
0.185	0.08061	8.11E-02	0.40337	4.06E-01
0.38	0.08267	0.083688	0.41367	0.418792
0.7298	0.08618	0.088135	0.43126	0.441066
0.981	0.09431	0.096939	0.47198	0.485165
4.02	0.11097	0.121723	0.55546	0.609355
6.9763	0.12513	0.143755	0.62643	0.719811
9.9868	0.14119	0.167792	0.70694	0.840371
11.944	0.15354	0.185316	0.76889	0.9283
14.9388	0.16743	0.207098	0.83854	1.037638
17.9513	0.18461	0.232203	0.92474	1.163717
19.9454	0.19314	0.245953	0.96755	1.232795
24.8406	0.21214	0.277685	1.06296	1.392292
29.8346	0.22719	0.30569	1.13852	1.533135
34.8627	0.23726	0.328694	1.18911	1.648891
39.8735	0.25441	0.35865	1.27527	1.799704
44.698	0.26228	0.37877	1.31483	1.901053
49.6993	0.28148	0.410588	1.41137	2.061405
54.6696	0.28227	0.423785	1.41536	2.127943
59.6921	0.29115	0.445221	1.45999	2.236063
64.6707	0.29532	0.461647	1.48098	2.318939
69.6691	0.30577	0.484438	1.53353	2.433983
63.0292	0.303	0.465277	1.51959	2.337259
58.0034	0.29489	0.444766	1.47881	2.233765
53.0227	0.28211	0.419508	1.41454	2.106375
48.0099	0.27089	0.395745	1.35815	1.986589
43.0021	0.25951	0.371663	1.30094	1.865245
38.0077	0.24144	0.340886	1.21011	1.710258
33.0271	0.22656	0.313251	1.13537	1.571175
28.0111	0.20659	0.280351	1.03507	1.405697

23.0134	0.1868	0.247639	0.93574	1.241269
19.0176	0.16712	0.217487	0.83702	1.089807
13.0284	0.14896	0.183597	0.74589	0.919674
8.0299	0.12528	0.146696	0.62718	0.734558
3.035	0.10365	0.11177	0.51878	0.559476
1.2352	0.08782	0.091129	0.4395	0.456058

H ₂ at 298K				
P (bar)	Excess Uptake (%)	Total Uptake (%)	Excess Uptake (mmol/g)	Total Uptake (mmol/g)
0.191	0.05727	0.057739	0.28649	0.288863
0.389	0.06787	0.068825	0.33959	0.344364
0.697	0.06582	0.067532	0.32934	0.337886
1.002	0.07034	0.0728	0.35196	0.364266
4.019	0.08168	0.09153	0.40872	0.458067
6.9517	0.09361	0.110617	0.4685	0.553696
9.944	0.10365	0.127933	0.51881	0.640485
11.9645	0.11405	0.143241	0.57088	0.717234
14.9398	0.12533	0.161859	0.62743	0.810605
17.9465	0.13014	0.173911	0.65155	0.871069
19.9516	0.13959	0.187887	0.69895	0.941202
24.858	0.15017	0.210232	0.752	1.053374
29.8578	0.15812	0.230246	0.79184	1.153886
34.8792	0.17058	0.254466	0.85437	1.275574
39.8694	0.17091	0.266552	0.85599	1.336324
44.6804	0.18471	0.291504	0.92526	1.46178
49.684	0.18655	0.305095	0.9345	1.530145
54.7093	0.19144	0.321433	0.95906	1.612347
59.6895	0.19381	0.335248	0.97094	1.681877
64.7093	0.19933	0.35221	0.99866	1.767274
69.6753	0.20551	0.369529	1.02967	1.854496
62.9699	0.19898	0.347946	0.99688	1.745803
58.0078	0.19337	0.330893	0.9687	1.659956
52.9969	0.17856	0.304637	0.8944	1.527839
47.9967	0.17033	0.284958	0.85309	1.428864
43.0217	0.15121	0.254086	0.7572	1.273666
38.0003	0.13698	0.228101	0.68585	1.143112
33.0108	0.1215	0.200863	0.60825	1.006336
28.0119	0.11042	0.178022	0.55272	0.891699
23.0204	0.09841	0.154249	0.49256	0.772435
19.0202	0.09378	0.139965	0.46935	0.700804
13.0288	0.07519	0.10689	0.37621	0.535022

8.0306	0.06701	0.086643	0.33528	0.433592
3.0355	0.05192	0.059366	0.25973	0.297007
1.2355	0.05634	0.059373	0.28186	0.297041

N ₂ at 273K				
P (bar)	Excess Uptake (%)	Total Uptake (%)	Excess Uptake (mmol/g)	Total Uptake (mmol/g)
0.22	0.0661	0.074301	0.02362	2.66E-02
0.6267	0.24688	0.270243	0.08839	9.68E-02
0.936	0.3735	0.40852	0.13389	1.46E-01
2.927	1.08293	1.192135	0.39099	4.31E-01
6.9261	2.07704	2.335486	0.75753	8.54E-01
9.9181	2.61324	2.98E+00	0.95834	1.10E+00
14.9282	3.24337	3.80016	1.19718	1.41E+00
19.9191	3.6513	4.394097	1.35346	1.64E+00
24.8392	4.01526	4.941887	1.49401	1.86E+00
29.838	4.24981	5.362246	1.58516	2.02E+00
34.8404	4.42817	5.725718	1.65477	2.17E+00
39.8415	4.61009	6.094111	1.72603	2.32E+00
49.6761	4.82807	6.674494	1.81179	2.55E+00
59.6663	5.00386	7.21725	1.88123	2.78E+00
65.0238	5.03202	7.439373	1.89237	2.87E+00
55.0196	4.92074	6.964033	1.84836	2.67E+00
45.0284	4.73839	6.412852	1.77646	2.45E+00
38.0288	4.51402	5.929701	1.68836	2.25E+00
33.0258	4.39183	5.621957	1.64056	2.13E+00
28.0247	4.1819	5.227253	1.55872	1.97E+00
23.0323	3.87654	4.735239	1.44031	1.78E+00
18.0314	3.52028	4.192512	1.30312	1.56E+00
13.033	3.03767	3.523631	1.11887	1.30E+00
8.0304	2.29223	2.59182	0.83786	9.50E-01
5.0337	1.68411	1.871903	0.61177	6.81E-01
2.536	0.96393	1.058367	0.34761	3.82E-01
1.2358	0.50087	0.547055	0.17978	1.96E-01

N ₂ at 298K				
P (bar)	Excess Uptake (%)	Total Uptake (%)	Excess Uptake (mmol/g)	Total Uptake (mmol/g)
0.223	0.03731	4.49E-02	0.01333	0.016052
0.624	0.18581	0.207125	0.06649	0.074127

0.926	0.28666	0.31836	0.10267	0.114063
2.936	0.93524	1.035404	0.33717	0.373656
6.9181	1.87834	2.114248	0.68368	0.771398
9.9208	2.35038	2.68868	0.85963	0.986774
14.9237	2.96945	3.477836	1.09297	1.286839
19.9236	3.37648	4.054671	1.24802	1.509294
24.8382	3.70286	4.547011	1.3733	1.701291
29.8436	4.01946	5.032569	1.49564	1.892592
34.8403	4.23522	5.415827	1.57947	2.044976
39.84	4.42671	5.775131	1.6542	2.188962
49.672	4.72126	6.396014	1.76972	2.440378
59.6682	4.91875	6.923486	1.84758	2.656603
65.0157	4.88615	7.065452	1.8347	2.715218
55.0238	4.66021	6.513034	1.74571	2.488137
45.0267	4.3059	5.827131	1.60702	2.209892
38.0246	4.07147	5.359308	1.51581	2.022427
33.0301	3.8126	4.933304	1.41561	1.853324
28.0302	3.54217	4.49458	1.31152	1.68075
23.0307	3.16898	3.952522	1.16882	1.469705
18.0277	2.8265	3.440598	1.03883	1.272569
13.0317	2.27244	2.716813	0.83046	0.997387
8.0304	1.63138	1.905447	0.5923	0.693735
5.032	1.13161	1.303454	0.40877	0.471667
2.536	0.59947	0.686069	0.21539	0.246717
1.2358	0.30692	0.349182	0.10995	0.125145

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