Supporting Information

Efficient gas and alcohols uptake and separation driven by two types of channels in a porous MOF: experimental and theoretical investigation

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^cSchool of Chemical Engineering, The University of Queensland, Brisbane 4072, Australia. [#]The two authors contribute equally to this work. **Synthesis of ligands**. To a stirred mixture of 2 mmol 1H-1,2,4-triazole and 1 mmol 2,5dimethylbromobenzene in 20 mL DMF was added 0.5 mmol CuO and 6 mmol K₂CO₃ and the solution was heated to reflux and stirred for 24 h at 100 °C. The mixture was filtered after cooling to room temperature. 100 mL of distilled water was added in filtrate and then the precipitate appeared immediately. The precipitate was isolated by filtration and washed extensively with water and diethyl ether, and dried under vacuum to afford a white powder (Yield ~60%). The obtained 0.5 mmol white powder and 20 mmol KMnO₄ were added to 50 mL water and heated to reflux and stirred for 24 h at 100 °C. The mixture was filtered after cooling to room temperature. The resulting filtrate was acidified to a pH of about 2 using concentrated HCl. The white precipitate was collected by filtration and washed with water and diethyl ether, and dried under vacuum to afford a white powder (Yield ~50%). ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) 8.90 (d, J = 17.2 Hz, 1H), 8.11 (d, J = 18.0 Hz, 1H), 7.97 (d, J = 17.2 Hz, 2H), 7.74 (d, J = 18.0 Hz, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ (ppm) 167.79, 166.67, 152.35, 145.24, 135.91, 134.83, 134.03, 130.27, 129.77, 126.38. HRMS (ESI/Q-TOF) m/z: [M–H]⁻ calcd for C₁₀H₆N₃O₄⁻ 232.0358, found 232.0326.

Synthesis of Cu-BTC, ZIF-8, MIL-101(Cr) and MIL-68(In). All classical MOFs were synthesized by reported methods^{S1-4} and degassed at 150 °C under high vacuum for 6 hours to get the activated samples.

References

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Fig. S1 (a) The 2-fold interpenerated 3D framework producing by terephthalate units of four tztp. (b) The topological net (a uninodal 4-connected *lvt* net with the point symbol of (4².8⁴)).
(c) A grid layer of Zn analog with *sql* network with the point symbol (4⁴.6²).



Fig. S2 PXRD patterns.



Fig. S3 TGA curves for as-synthesized, solvent exchanged and desolvated sample.



Fig. S4 The color of samples changed (a) before and (b) after degas.



Fig. S5 Gas sorption isotherms for CO₂, C₂H₆, C₂H₄, C₂H₂ and CH₄ at 313 K.



Fig. S6 Gas sorption isotherms for CO_2 , C_2H_6 , C_2H_4 , C_2H_2 and CH_4 at 333 K.



Fig. S7 The H₂O derived adsorption isotherm at 298 K.



Fig. S8 The EtOH derived adsorption isotherm at 298 K.



Fig. S9 The 2-propanol derived adsorption isotherm at 298 K.

Calculation of Sorption Heat Using Virial 2 Model

$$lnP = lnN + 1/T \sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i \qquad Q_{st} = -R \sum_{i=0}^{m} a_i N^i$$

The above virial expression was used to fit the combined isotherm data for **1a** at 298 and 313 K, where *P* is the pressure, *N* is the adsorbed amount, *T* is the temperature, a_i and b_i are virial coefficients, and *m* and *n* are the number of coefficients used to describe the isotherms. Q_{st} is the coverage-dependent enthalpy of adsorption and *R* is the universal gas constant.



Fig. S10 (a) CO₂, (b) C_2H_6 , (c) C_2H_4 , (d) C_2H_2 and (e) CH₄ adsorption isotherms of 1a with fitting by Virial 2 model.

Parameters obtained from the Virial 2 model fitting of the single-component adsorption isotherms at 298 and 313 K.

	CO_2	C_2H_6	C_2H_4	C_2H_2	CH ₄
a_0	-3156.07356	-3044.81083	-3902.11024	-4616.3514	-2266.84855
a_1	1.19227	-2.00096	1.77249	10.92003	-6.41224
a_2	0.01731	0.14039	0.03459	-0.15326	1.01803
a_3	-7.79083E-5	-6.43727E-4	-8.74023E-5	8.59038E-4	-0.03193
b_0	10.34187	9.06017	12.23216	13.7389	9.16871

Chi ²	5.84513E-5	0.00145	1.43622E-4	0.00291	0.00132
R^2	0.99998	0.99946	0.99995	0.99905	0.99946

Prediction of Adsorption Selectivity via IAST

The experimental isotherm data for pure CO₂, C₂H₆, C₂H₄, C₂H₂, CH₄, MeOH, 1-propanol, 2-propanol and 1-butanol were fitted using a dual Langmuir-Freundlich (L-F) model:

$$q = \frac{a_1 * b_1 * P^{C_1}}{1 + b_1 * P^{C_1}} + \frac{a_2 * b_2 * P^{C_2}}{1 + b_2 * P^{C_2}}$$

Where q and P are adsorbed amounts and the pressure of component i, respectively.

The adsorption selectivities for binary mixtures of CO_2/CH_4 , C_2H_6/CH_4 , C_2H_4/CH_4 , C_2H_2/CH_4 , C_2H_2/CO_2 , MeOH/1-propanol, MeOH/2-propanol and MeOH/1-butanol defined by

$$S_{i/j} = \frac{x_i * y_j}{x_j * y_i}$$

were respectively calculated using the Ideal Adsorption Solution Theory (IAST). Where x_i is the mole fraction of component *i* in the adsorbed phase and y_i is the mole fraction of component *i* in the bulk.



Fig. S11 (a) CO₂, (b) C₂H₆, (c) C₂H₄, (d) C₂H₂ and (e) CH₄ adsorption isotherms of **1a** at 298 K with fitting by dual L-F model.



Fig. S12 (a) MeOH, (b) 1-propanol, (c) 2-propanol and (d) 1-butanol adsorption isotherms of **1a** with fitting by dual L-F model.

Parameters	obtained	from	the	dual	Langmuir-Freundlich	fitting	of t	the	single-componen	ıt
adsorption i	sotherms	in 1a .								

	CO ₂	C ₂ H ₆	C ₂ H ₄	C_2H_2	CH ₄
a_1	7.76115	1.89772	1.07916	6.3986	2.81001
b_1	0.00738	0.02749	0.01832	0.0319	5.05417E-4
c_1	1.00514	1.39996	1.33663	0.80347	1.36274
a_2	0.04515	6.09836	5.92483	1.51582	0.35591
b_2	2.18783E-5	0.01397	0.01467	0.00246	0.02381
c_2	2.61231	0.73594	0.86746	1.80259	0.9824
Chi ²	1.28586E-7	7.31251E-6	1.90220E-6	3.52602E-	7 6.77174E-8
R^2	1	1	1	1	1
	MeOH	1-propano	ol 2-pro	panol	1-butanol
a_1	6.5322	2.05656	3.21691		0.09457
b_1	3.20668	0.48723	1.243	34	58.86865
c_1	1.31257	1.35717	2.181	44	1.7612
a_2	20914.34511	2.16329	0.648	84	3.20867
b_2	8.82498E-8	0.0866	4.936	71E-6	0.36503
C_2	2.44816	4.12507	7.461	77	2.03069

Chi ²	0.00562	1.74356E-4	0.00154	7.56108E-7
R^2	0.99945	0.99989	0.99900	0.99999

Calculation of Breakthrough Experiments

On the basis of the mass balance, the gas adsorption capacities can be determined as follows:

$$q_i = \frac{C_i V}{22.4 \times m} \times \int_0^t (1 - \frac{F}{F_0}) dt$$

Where q_i is the equilibrium adsorption capacity of gas *i* (mmol g⁻¹), C_i is the feed gas concentration, *V* is the volumetric feed flow rate (cm³ min⁻¹), *t* is the adsorption time (min), F_0 and *F* are the inlet and outlet gas molar flow rates, respectively, and *m* is the mass of the adsorbent (g).

The separation factor (α) of the breakthrough experiment is determined as:

$$\alpha = \frac{q_A y_B}{q_B y_A}$$

in which y_i is the molar fraction of gas i (i = A, B) in the gas mixture.

Empirical formula	$C_{10}H_5CuN_3O_4$					
Formula weight	294.71					
Temperature	150(2) K					
Wavelength	0.71073 Å					
Crystal system	Tetragonal					
Space group	P4 ₂ /nnm					
a	20.0928(3) Å					
b	20.0928(3) Å					
С	8.0460(3) Å					
Volume	3248.34(16) Å ³					
Ζ	8					
Density (calculated)	1.205 g/cm ³					
Absorption coefficient	1.351 mm ⁻¹					
Reflections collected/Independent/ <i>R</i> (int)	93955/1558/0.0648					
Completeness to theta = 25.242°	99.5 %					
Data/restraints /parameters	1558/12/124					
Goodness-of-fit on F^2	1.054					
Final R indices [I>2sigma(I)]	$R_1^a = 0.0387, wR_2^b =$					

Table S1. Crystal data and structure refinement for 1.

	0.0998				
R indices (all data)	$R_1^a = 0.0427, wR_2^b = 0.1027$				
Largest diff. peak and hole	0.494 and -0.494 e.Å ⁻³				
${}^{a}R_{1} = \sum (F_{o} - F_{c}) / \sum F_{o} . {}^{b}wR_{2} = [\sum w(F_{o}^{2} - F_{c}^{2})^{2} / \sum w(F_{o}^{2})^{2}]^{1/2}.$					

Cu(1)-O(1)	1.958(2)	O(1)-Cu(1)-O(2)#2	89.73(10)
Cu(1)-O(1)#1	1.958(2)	O(1)#1-Cu(1)-O(2)#2	167.21(10)
Cu(1)-O(2)#2	1.968(2)	O(1)-Cu(1)-O(2)#3	167.21(10)
Cu(1)-O(2)#3	1.968(2)	O(1)#1-Cu(1)-O(2)#3	89.73(10)
Cu(1)-N(3)#4	2.117(5)	O(2)#2-Cu(1)-O(2)#3	88.53(13)
Cu(1)-N(3)#5	2.117(5)	O(1)-Cu(1)-N(3)#4	92.01(17)
O(2)#2-Cu(1)-N(3)#4	90.07(17)	O(1)#1-Cu(1)-N(3)#4	102.70(17)
O(2)#3-Cu(1)-N(3)#4	100.66(17)	O(2)#2-Cu(1)-N(3)#5	100.66(16)
O(1)-Cu(1)-N(3)#5	102.69(17)	O(2)#3-Cu(1)-N(3)#5	90.07(17)
O(1)#1-Cu(1)-N(3)#5	92.01(17)	O(1)-Cu(1)-O(1)#1	89.16(13)

 Table S2. Bond lengths [Å] and angles [°] for 1.

Symmetry transformations used to generate equivalent atoms: #1 = y-1/2, x+1/2, z; #2 = -y+3/2, -x+3/2, -z; #3 = -x+1, -y+2, -z; #4 = -y+3/2, -x+3/2, -z+1; #5 = -x+1, -y+2, -z+1.

Table S3. The capture capacities (mmol g⁻¹) and selectivities from breakthrough curves for Cu-BTC, MIL-101(Cr), MIL-68(In) and ZIF-8.

	CO ₂ /CH ₄	C_2H_6/CH_4	C ₂ H ₄ /CH ₄	C ₂ H ₂ /CH ₄	C ₂ H ₂ -CO ₂
Cu-BTC	0.58/0.054(10.7)	0.69/0.050(13.8)	0.64/0.045(14.2)	0.75/0.039(19.2)	0.83/0.31(2.7)
MIL-101(Cr)	0.25/0.049(5.1)	0.39/0.042(9.3)	0.30/0.038(7.9)	0.40/0.035(11.4)	0.42/0.26(1.6)
MIL-68(In)	0.20/0.044(4.5)	0.25/0.037(6.7)	0.24/0.041(5.8)	0.21/0.043(4.9)	0.22/0.15(1.5)
ZIF-8	0.15/0.043(3.5)	0.20/0.041(4.8)	0.19/0.042(4.5)	0.16/0.040(4.0)	

GCMC Simulation

Grand canonical Monte Carlo (GCMC) simulations were performed for the gas adsorption in the framework by the Sorption module of Material Studio (Accelrys. Materials Studio Getting Started, release 5.0). The framework was considered to be rigid, and the optimized gas and epoxide molecules were used. The partial charges for atoms of the framework were derived from QEq method and QEq_neutral 1.0 parameter (Table S3). One unit cell was used during the simulations. The interaction energies between the gas molecules and framework were computed through the Coulomb and Lennard-Jones 12-6 (LJ) potentials. All parameters for the atoms were modeled with the universal force field (UFF) embedded in the MS modeling package. A cutoff distance of 12.5 Å was used for LJ interactions, and the Coulombic interactions were calculated by using Ewald summation. For each run, the 2×10^6 maximum loading steps, 2×10^6 production steps were employed.

Zn1	3.78328	02	-0.809613	C3	0.177390	C8	0.0301921	C2	0.0526992
N1	-0.348110	03	-0.465448	C4	-0.0921334	H4	0.102826	C7	0.169747
N2	-0.198616	04	-0.466373	C5	-0.218326	H5	0.0663657	H7	0.137432
N3	-0.416067	C1	0.232475	C6	-0.118395	H6	0.116880	H8	-0.0141496
01	-0.762236								

Table S4. The atomic partial charges (e) in the framework.