Electronic Supplementary Information

A novel trigonal bipyramidal cage-based Zn(II)-MOF featuring two types of trinuclear clusters with high gas sorption properties

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Table S1 Selected bond distances (Å) and angles (°) for **1**.

Zn(1)-O(5)	1.952(11)	Zn(1)-O(13)	1.70(3)
Zn(2)-O(2)	2.137(10)	Zn(2)-O(4)	2.148(11)
Zn(3)-O(8)	1.962(11)	Zn(3)-O(12)	1.999(12)
Zn(4)-O(3)#1	2.011(9)	Zn(4)-O(6)	1.937(12)
Zn(4)-O(9)#2	2.186(17)	Zn(4)-O(10)#2	2.167(18)
Zn(4)-O(11)	2.011(5)		

Symmetry transformations used to generate equivalent atoms: #1 -x+y,-x+1,z; #2 -y+1,x-y+1,z
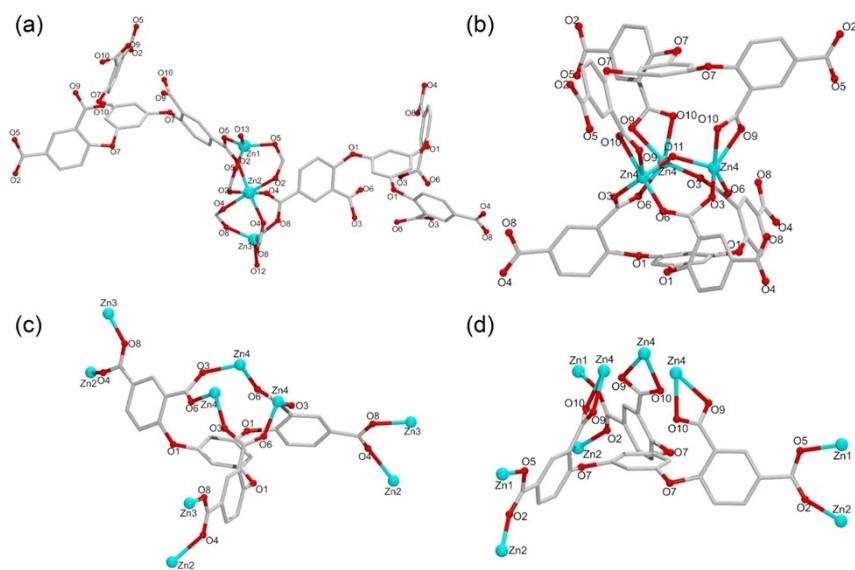
Fig. S1. (a), (b) Coordination environments of Zn^{2+} ions in **1**; (c), (d) Coordination modes of H_2tdpb in **1**.
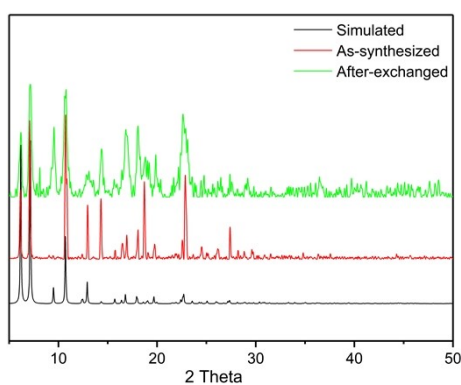

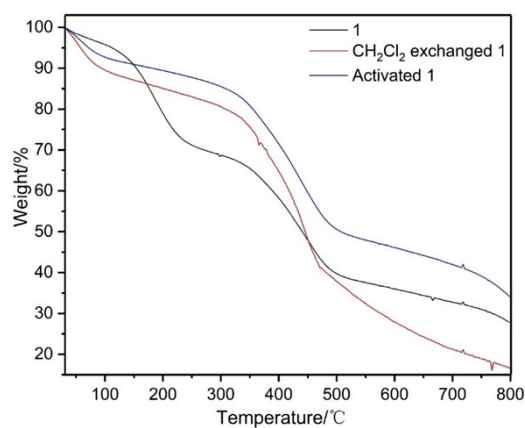**Fig. S2.** PXRD patterns for as-synthesized and after-exchanged of **1**

Fig. S3. TGA curves for as-synthesized, after CH_2Cl_2 exchanged and desolvated samples of **1**.

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 273.15 and 298 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.
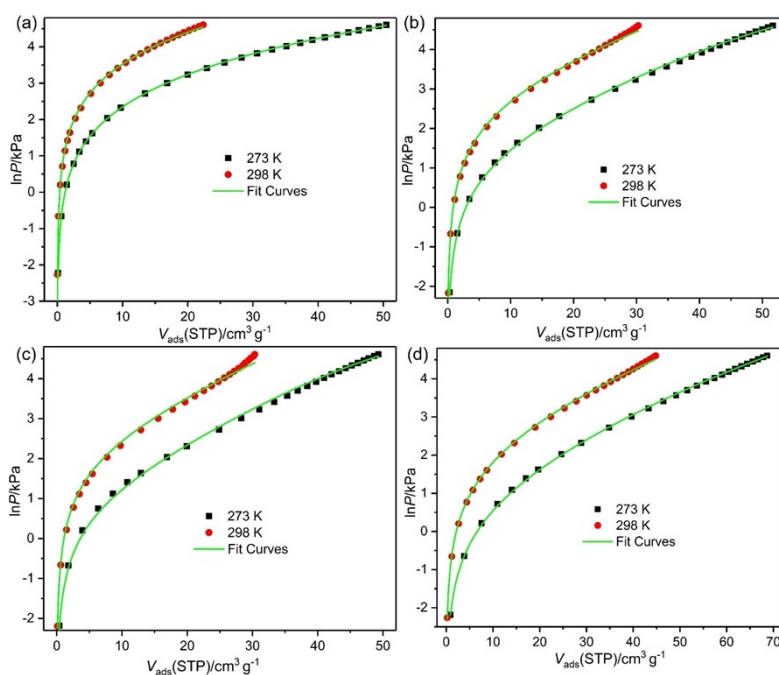

Fig. S4. (a) CO_2, (b) C_2H_4, (c) C_2H_6 and (d) C_2H_2 adsorption isotherms of **1a** with fitting by Virial 2 model.

Table S2 Parameters obtained from the Virial 2 model fitting of the single-component adsorption isotherms at 273.15 and 298 K.

	CO_2	C_2H_4	C_2H_6	C_2H_2
a0	-3926.41893	-4101.64865	-4050.16909	-4252.29504
a1	7.42318	6.45919	4.82542	10.15691
a2	-0.07727	0.15183	0.31531	0.01383
a3	4.62531E-4	-0.00186	-0.00376	-2.4707E-4

b0	14.17647	13.87906	13.46542	13.43283
Chi^2	0.1063	3.291E-03	6.984E-03	1.396E-03
R^2	0.969	0.999	0.998	1.000

Gas Selectivity Prediction via IAST

The experimental isotherm data for pure CO_2, C2-hydrocarbon and CH_4 were fitted using a dual Langmuir-Freundlich (L-F) model:

$$q = \frac{a_1 * b_1 * p^{c1}}{1 + b_1 * p^{c1}} + \frac{a_2 * b_2 * p^{c2}}{1 + b_2 * p^{c2}}$$

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

The adsorption selectivities for binary mixtures defined by

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

were respectively calculated using 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.
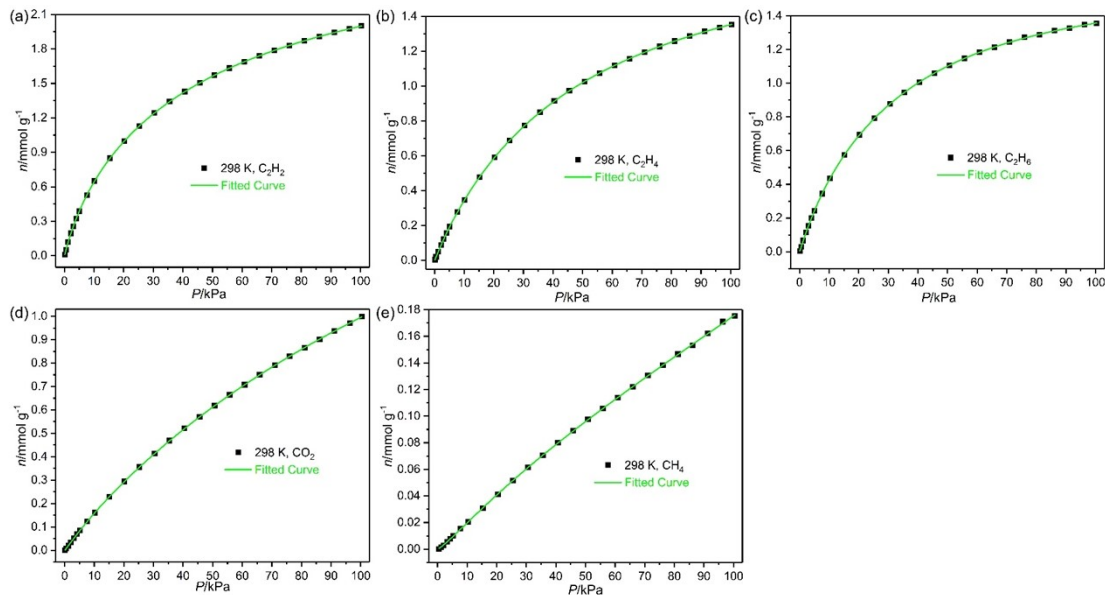

Fig. S5. Adsorption isotherms of **1a** fitting by dual L-F model.

Table S3 Parameters obtained from the dual Langmuir-Freundlich fitting of the single-

component adsorption isotherms.

298 K	C_2H_2	C_2H_4	C_2H_6	CO_2	CH_4
a1	2.53441	0.07133	1.42154	0.08772	0.10139
b1	0.02275	0.17963	0.0386	0.05646	0.01063
c1	0.93846	1.05235	1.02982	1.11408	1.1718
a2	0.4338	1.88344	0.23904	2.67742	9.75501
b2	0.10708	0.0163	4.61321E-4	0.00435	3.48725E-5
c2	1.00332	1.0594	2.00164	1.03871	1.24556
Chi^2	1.630E-6	7.417E-7	3.005E-6	5.351E-7	2.391E-7
R^2	1.000	1.000	1.000	1.000	1.000