Supporting Information

A microporous zinc–organic framework with Lewis basic pyridyl sites for highly selective C_2H_2/CH_4 and C_2H_2/CO_2 gas separation

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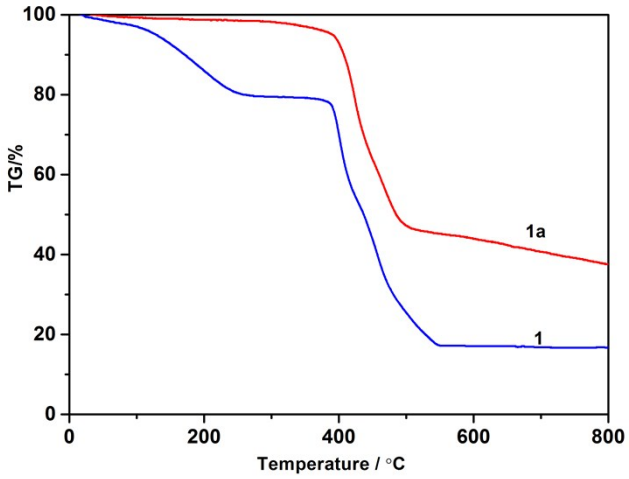

Figure S1. Themogravimetric curves for **1** and **1a**.

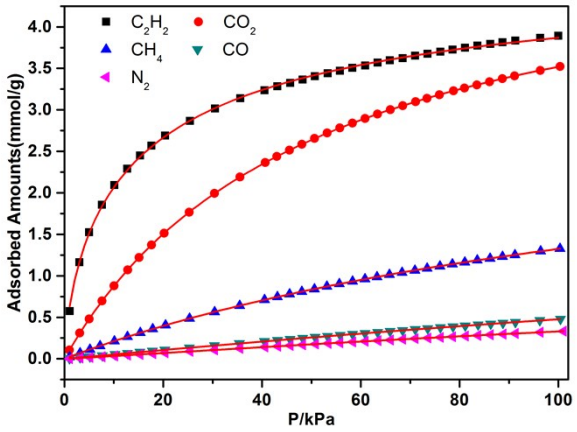

Figure S2. C_2H_2, CO_2, CH_4, CO and N_2 isotherms of **1a** fitted by LF model at 273 K.

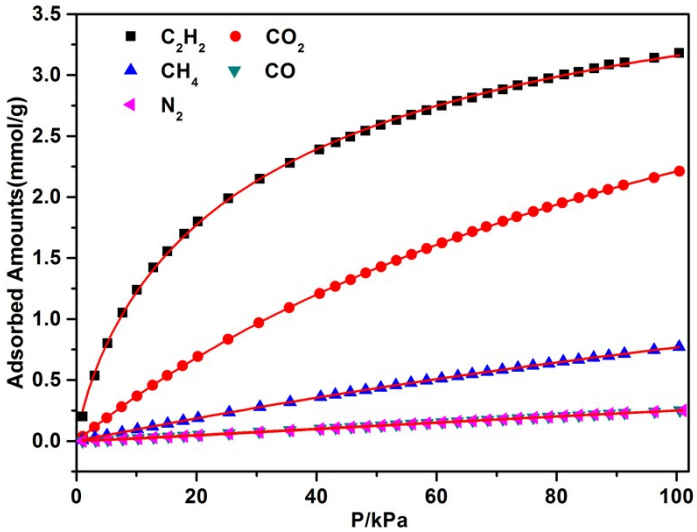

Figure S3. C_2H_2, CO_2, CH_4, CO and N_2 isotherms of **1a** fitted by LF model at 298 K.

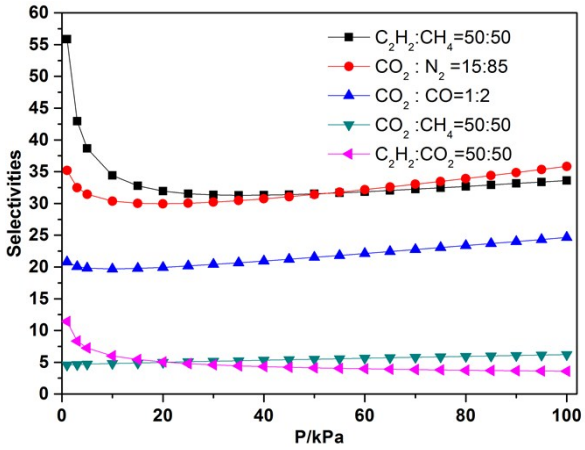

Fig. S4. IAST-predicted selectivities for C_2H_2/CH_4(50:50), C_2H_2/CO_2(50:50), CO_2/N_2 (15:85), CO_2/CO(1:2) and CO_2/CH_4 (50:50) mixtures on **1a** at 273 K.

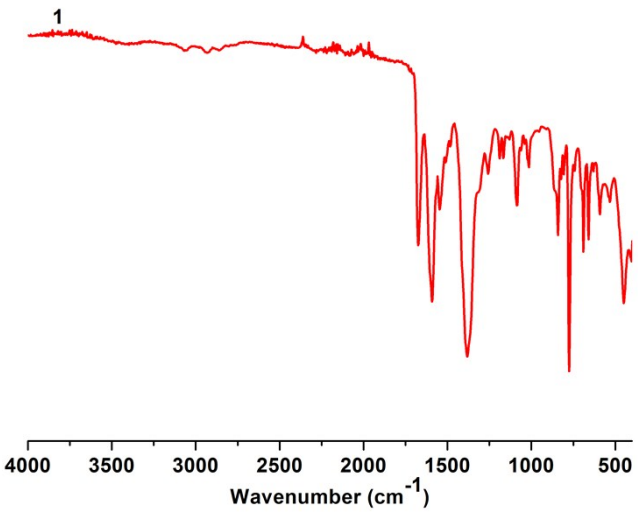

Figure S5. IR spectra of **1.**

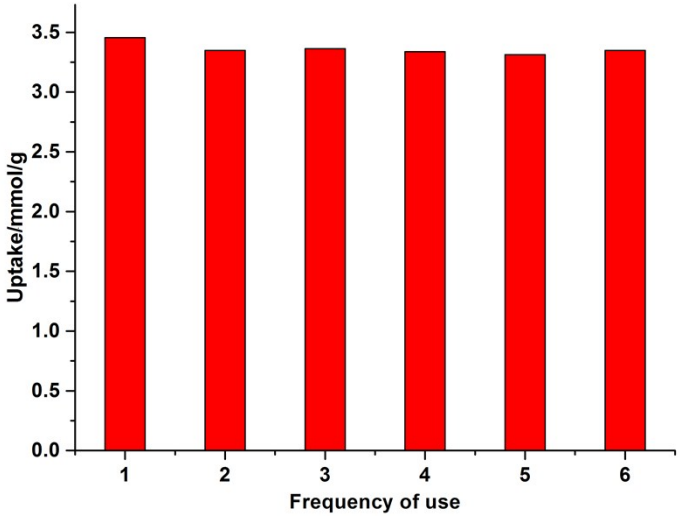

Figure S6. The reusability of **1a** for CO_2 adsorption.

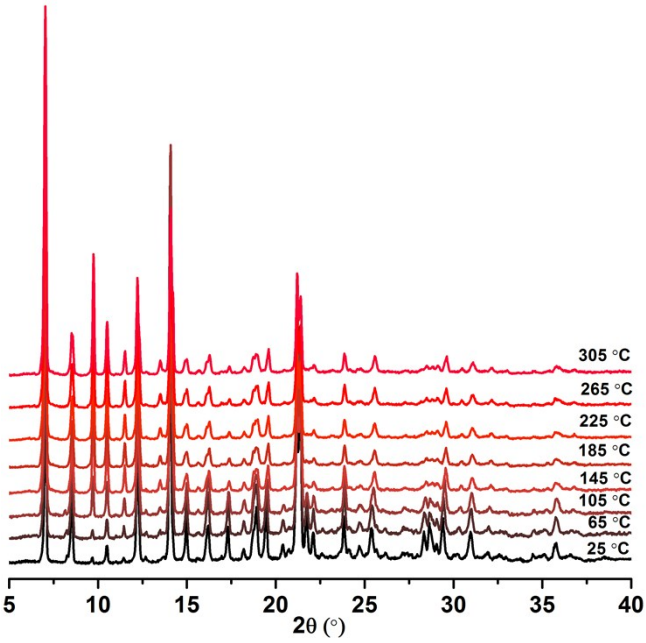

Figure S7. Variable-temperature PXRD patterns for **1**.

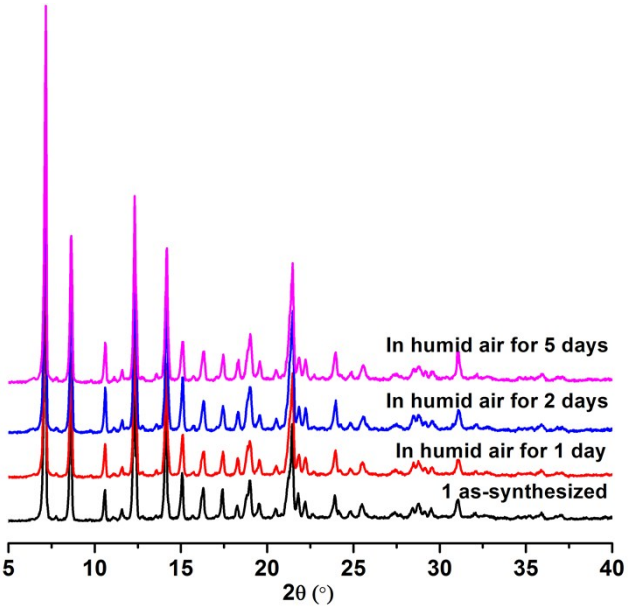

Figure S8. PXRD patterns for **1** exposed to humid air for 1, 2, and 5 days.

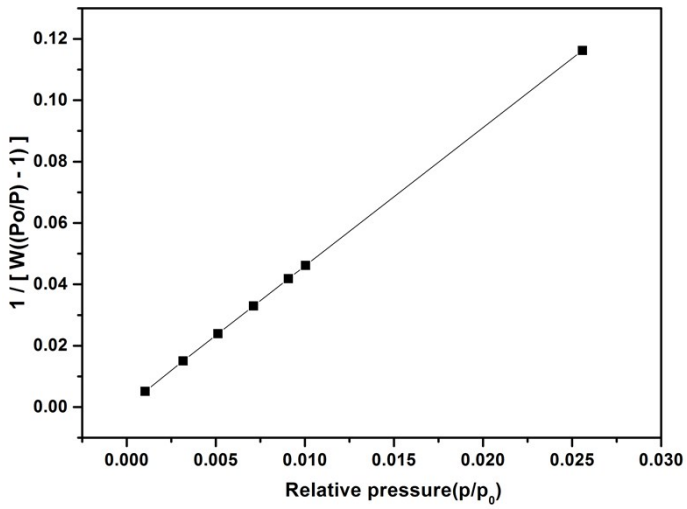

Figure S9. The BET surface area plot of **1a**.

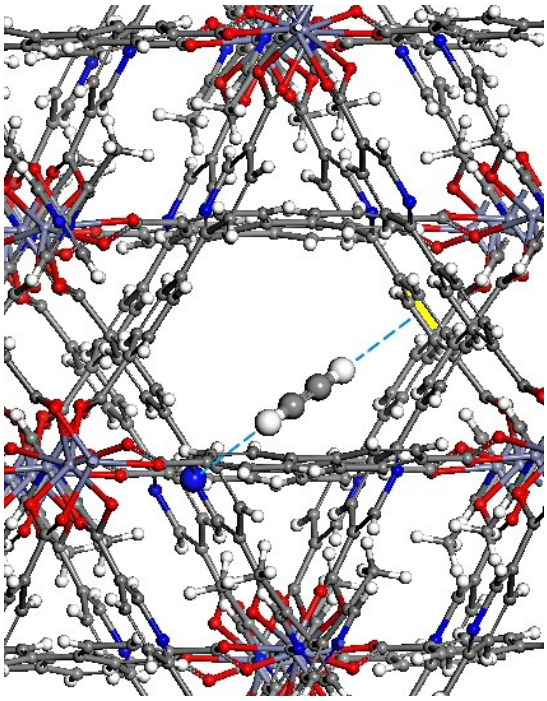

Figure S10. The DFT-calculated adsorption configurations of C_2H_2 in the channel. (Zinc, carbon, oxygen, nitrogen, and hydrogen atoms are in slateblue, gray, red, blue, and white, respectively.)

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

1			
Zn(1)-O(1)	1.939(3)	Zn(1)-N(1)	2.045(3)
Zn(1)-O(6)^{ii}	1.940(3)	Zn(1)-O(5)^{i}	1.982(3)
Zn(2)-O(2)^{i}	2.110(6)	Zn(2)-O(3)^{iii}	2.058(6
Zn(2)-O(4)^{iii}	2.134(6)	N(1)-Zn(1)-O(5)^{i}	104.37(13)

O(6)^{ii}-Zn(1)-O(5)^{i}	123.65(15)	O(1)-Zn(1)-N(1)	99.21(13)
O(1)-Zn(1)-O(5)^{i}	111.99(15)	O(1)-Zn(1)-O(6)^{ii}	115.15(12)
O(6)^{ii}-Zn(1)-N(1)	96.87(13)	O(3)^{iii}-Zn(2)-O(2)^{ii}	151.0(3)
O(2)^{ii}-Zn(2)-O(2)^{i}	112.8(4)	O(2)^{i}-Zn(2)-O(4)^{iii}	91.3(2)
O(3)^{iii}-Zn(2)-O(2)^{i}	93.3(3)	O(3)^{iii}-Zn(2)-O(3)	65.2(4)
O(3) -Zn(2)-O(4)	86.2(3)	O(4)^{iii}-Zn(2)-O(4)	150.9(4)

Symmetry codes: i = x, 1-y, 1.5+z; ii = 0.5-x, 0.5+y, z; iii = 1.5-x, 0.5-y, 1.5+z.

Table S2 Fitting parameters of the Langmuir-Freundlich modle at 273 K.

Parameters	**1**				
	C_2H_2	CO_2	CH_4	CO	N_2
q_m	4.9159	5.2880	3.2623	2.4980	1.6150
k	0.1423	0.0199	0.0071	0.0019	0.0017
n	0.7072	1.0001	0.9929	1.0419	1.0868
R^2	0.9995	0.9999	1	0.9999	0.9999

Table S3 Fitting parameters of the Langmuir-Freundlich modle at 298 K.

Parameters	**1**				
	C_2H_2	CO_2	CH_4	CO	N_2
q_m	4.4688	5.0619	3.0861	2.0099	1.2232
k	0.0585	0.0079	0.0030	0.0010	0.0011
n	0.8074	0.9967	1.0197	1.0792	1.1840
R^2	0.9996	0.9999	0.9999	0.9999	0.9999

The method for calculation of gas selectivity:

The ideal adsorbed solution theory (IAST) developed by Myers and Praunitz [1]. From the IAST, the spreading pressure π is expressed as follows:

$$\pi_i^0\left(p_i^0\right) = \frac{RT}{A}\int_0^{p_i^0}\frac{q_i}{p}dp \quad (1)$$

$$\pi^*_i = \frac{\pi_i^0 A}{RT} = \int_0^{p_i^0}\frac{q_i}{p}dp \quad (2)$$

where π and π^* are the spreading pressure and the reduced spreading pressure, separately. A is the specific surface area of the adsorbent. p_i^0 is the gas pressure of component *i* that corresponding to the spreading pressure π of the gas mixture.

At a constant temperature, the spreading pressure of single component is the same:

$$\pi_1^* = \pi_2^* = \cdots = \pi_n^* \quad (3)$$

For binary adsorption of component i, the IAST requires:

$$Py_i = p_i^0 x_i \quad (4)$$

where y_i and x_i are the molar fractions of component i in the gas phase and in the adsorbed phase, respectively. P is the total gas pressure, p_i^0 is the pressures of component i at the same spreading pressure as that of the mixture.

The adsorption isotherm of the pure component was fitted with a certain adsorption model to obtain the corresponding parameters. Then use formula (2) to get the specific spreading pressure expression. Finally, the x_i corresponding to a given total pressure P and the composition of y_i in the gas mixture is obtained according to formula (3) and (4).

Thus, adsorption selectivity S of a binary mixture is defined as:

$$S = \frac{x_1 / y_1}{x_2 / y_2} \quad (5)$$

The method for calculation of isosteric heat of adsorption:

The relationship between adsorption heat and temperature and pressure can be obtained by integrating the Clausius-Clapeyron equation as follows:

$$\ln p = -\frac{Q_{st}}{RT} + C$$

Using the adsorption isotherm data at different temperatures to draw a graph, the isosteric heat of adsorption can be obtained according to the slope of the straight line.

Density-Functional Theory Calculations:

To obtain the gas binding energies, we use the DMOL3 to calculate the energy for the system, framework and gas molecule. The static binding energy was then calculated by using: $EB = (E_{(MOF)}+Eg_{(gas)})-E_{(MOF+gas)}$.[2,3]

[1] A. Myers, J.M. Prausnitz, Thermodynamics of mixed-gas adsorption, *AIChE. J.*, 1965, **11**, 121-127.

[2] DMol3, v. Accelrys, Inc, San Diego, 2005.

[3] Babarao, R.; Jiang, J. *J. Phys. Chem. C,* 2009, **113**, 18287-18291.