Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supporting Information (ESI)

Formation of a Metal-Organic Framework with High Gases Uptakes Based upon Amino-Decorated Polyhedral Cages

1. Low-Pressure Gas Sorption Measurements

In the gas sorption measurements, all of the gases used are of 99.999% purity. Low-pressure (up to 1 bar) nitrogen (N_2, at 77 K; Ar, at 87 K), hydrogen (H_2, at 77 and 87 K), carbon dioxide (CO_2, at 273 and 298 K), methane (CH_4, at 273 and 298 K), and N_2 (at 273 and 298 K) sorption experiments were carried out on a Micromeritics ASAP 2020 M+C surface area analyzer. For all low-pressure isotherms, warm and cold free space correction measurements were performed using ultra-high purity He gas (UHP grade 5.0, 99.999% purity). A part of the N_2 sorption isotherm at 77 K in the P/P_0 range 0.0003-0.003 was fitted to the BET equation to estimate the BET surface area and the Langmuir surface area calculation was performed using all data points (Figure S1). The pore size distribution (PSD) was obtained from the DFT model in the Micromeritics ASAP2020 software package (assuming split pore geometry) based on the N_2 sorption isotherm.

Isotherm data were analysed using the virial equation:

$Ln(P) = Ln(N)+(a_0+a_1N+a_2N^2+\cdots)/T+(b_0+b_1N+b_2N^2+\cdots);$

Where P is the pressure, N is the amount adsorbed, and a_0, a_1, b_1, etc. are virial coefficients.

2. Estimation of the Enthalpy of Gas Adsorption

A Virial-type function contains the temperature-independent parameters a_i and b_i was employed to calculate the enthalpy of adsorption for CO_2 (at 273 and 298 K) on NJU-Bai6. In each case, the data were fitted using the equation:

$$\ln P = \ln N + 1/T\sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i \qquad (1)$$

Here, P is the pressure in torr, N is the adsorbed amount in mmol/g, T is the temperature in K, a_i and b_i are Virial coefficients. The values of the virial coefficients a_0 through a_m were then used to calculate the isosteric enthalpy of adsorption using the following equation.

$$Q_{st} = -R\sum_{i=0}^{m} a_i N^i \qquad (2)$$

Q_{st} is the coverage-dependent isosteric enthalpy of adsorption and R is the universal gas constant. The enthalpy of sorption of CO_2 in this manuscript is determined by using the data measured in the pressure range from 0-1 bar (at 273 and 298 K).

2. CO_2 Selctivity Calculations

Here, the adsorption capacities of component n (q_n) are defined to be molar absolute adsorption capacities determined experimentally, and p_n is defined to be the pressure of component n as experimentally measured. Selectivity (S) is defined according to equation:[3]

$$S = \frac{q_{CO_2} / q_{N_2}}{p_{CO_2} / p_{N_2}} \quad (3)$$

1. G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **64**, 112.
2. Spek, A. L. *Acta Crystallogr., Sect. A*, 1990, **46**, C34.
3. K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T. H. Bae and J. R. Long, *Chem. Rev.*, 2012, **112**, 724.

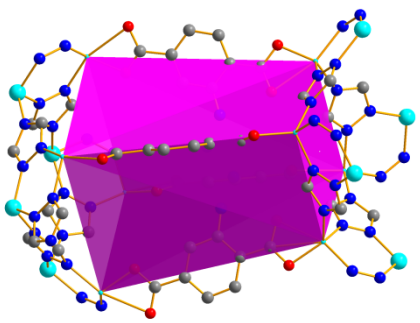

Figure S1. The polyhedron constructed by four ATPA and eight Zn atoms.

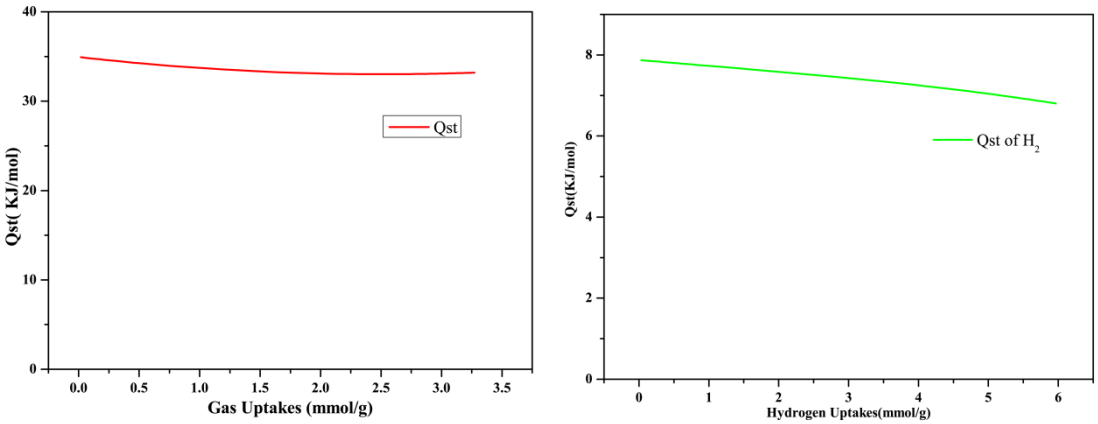

Figure S2. The isosteric adsorption enthalpies of CO_2 (left) and H_2 (right).

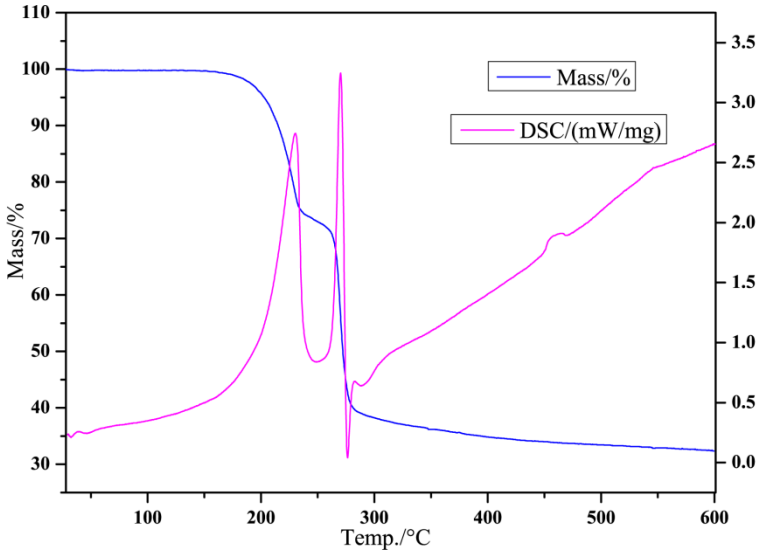

Figure S3. TG-DSC curves of 1.

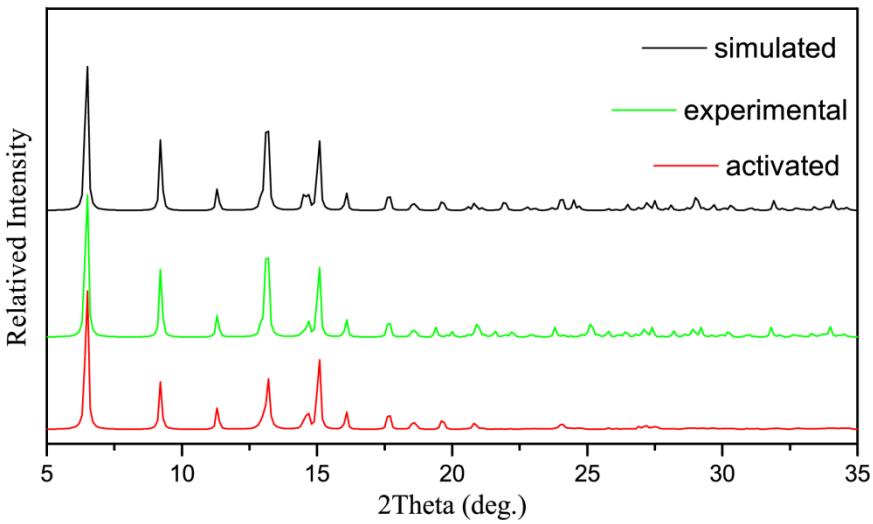

Figure S4. PXRD patterns of 1.

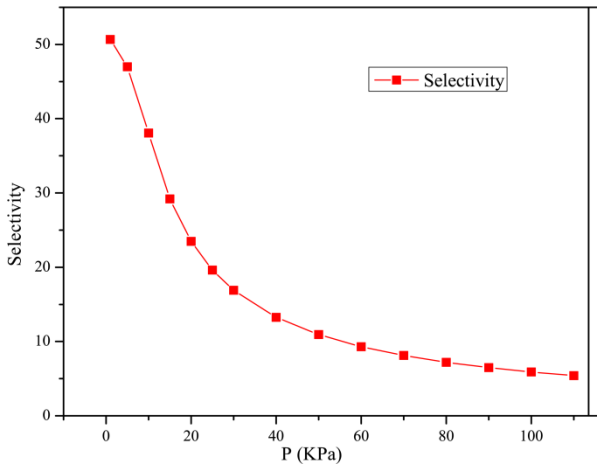

Figure S5 The selectivity of CO_2/N_2 calculated by IAST.

Figure S5

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

compound	**1**
Empirical formula	C12 H9 N7 O4 Zn2
Formula weight	446.00
Crystal system	Tetragonal
Space group	P4/ncc
Unit cell dimensions.	a = 13.4537(9) Å
	b = 13.4537(9) Å
	c = 27.329(4) Å
Volume	4946.6(8) Å^3
Z	8
Density (calculated)	1.192 g/ cm^3
F(000)	1776
Final R indices [I>2sigma(I)]	R1 = 0.0258, wR2 = 0.0537
R indices (all data)	R1 = 0.0437, wR2 = 0.0551