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High-Stable Y(III)-Based Metal Organic Framework with Two Molecular Building Block for Selective Adsorption of C_2H_2 and CO_2 over CH_4

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Derivation of the isosteric heats of adsorption

A virial-type expression of the following form was employed to calculate the enthalpies of adsorption of C_2H_2, CO_2 and CH_4. The data were fitted using the equation:

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

where the p is pressure expressed in mmHg, N is the amount adsorbed in mmol g^{-1}, T is the temperature in K, a_i and b_i are virial coefficients, m, n represents the number of coefficients required to adequately describe the isotherms. The isosteric heat of adsorption, Q_{st}, defined as

$$Q_{st} = RT^2\left(\partial \ln P / \partial T\right) \qquad (2)$$

Here, Q_{st} is the coverage-dependent isosteric heat of adsorption and R is the universal gas constant of 8.3147 J K^{-1} mol^{-1}.

Fitting of pure component isotherms

The adsorption isotherms for C_2H_2, CO_2 and CH_4 in **ZJU-16a** were measured at 273 and 298 K and fitted on the basis of the dual site Langmuir-Freundlich equation:

$$N = N_1^{max} \times \frac{b_1 p^{1/n_1}}{1 + b_1 p^{1/n_1}} + N_2^{max} \times \frac{b_2 p^{1/n_2}}{1 + b_2 p^{1/n_2}} \qquad (3)$$

where p is the pressure of the bulk gas at equilibrium with the adsorbed phase in kPa, N is the adsorbed amount per mass of adsorbent in mol/kg, N_1^{max} and N_2^{max} are the saturation capacities of sites 1 and 2 in mol/kg, b_1 and b_2 are the affinity coefficients of sites 1 and 2 in 1/kPa, and n_1 and n_2 represent the deviations from an ideal homogeneous surface. The fitting parameters of DSLF equation are presented in Table S1.

Adsorption isotherms and gas selectivities calculated by Ideal Adsorbed Solution Theory (IAST) for mixed C_2H_2/CH_4 (C_2H_2/CH_4 = 50:50) and CO_2/CH_4 (CO_2/CH_4 = 50:50) in the **ZJU-16a.** The adsorption selectivities, S_{ads}, are defined by the following equation:

$$S_{ads} = \frac{q_1/q_2}{p_1/p_2} \qquad (4)$$

in which p_i the bulk gas pressure of species i, and q_i the component molar loading of species i.

Table1 S1. Crystallographic Data Collection and Refinement Results for **ZJU-16.**

	ZJU-16
Chemical formula	$C_{24}H_{12}Y_2N_3O_{10.5}$
Formula weight	688.19
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Hexagonal
Space group	P 6_3/mmc
a (Å)	22.3597(3)
b (Å)	22.3597(3)

c (Å)	28.2591(12)
V (Å^3)	12235.5(6)
Z	12
Density (calculated g/cm^3)	1.121
Absorbance coefficient (mm^{-1})	2.872
F(000)	4068
Crystal size(mm^3)	0.23×0.23×0.1
Goodness of fit on F^2	1.106
R_1, wR_2 [$I>2\sigma(I)$]	0.0893,0.2938
R_1, wR_2 (all data)	0.1378,0.3202
Largestdifference peak and hole(e/Å^3)	4.466,-1.331

Table S2. Equation parameters for the DSLF isotherm model.

Adsorbates	N_1^{max} (mmol/g)	b_1 (kPa-1)	n_1	N_2^{max} (mmol/g)	b_2 (kPa-1)	n_2
C_2H_2 (273 K)	2.77852	0.0002931	1.092885	3.03734	0.062	0.84566
CO_2 (273 K)	5.9613	0.00091124	1.1126	25.45111	0.00296	0.78477
CH_4 (273 K)	3.32223	0.00058575	1.019	1.79403	0.00251	0.9968
C_2H_2 (298 K)	25.5115	0.00114	0.91943	1.40662	0.02751	0.82859
CO_2 (298 K)	9.79892	0.00184	0.95983	9.73881	0.00171	0.71355
CH_4 (298 K)	10.36924	0.00017505	1.18464	0.28741	0.01241	1.10857

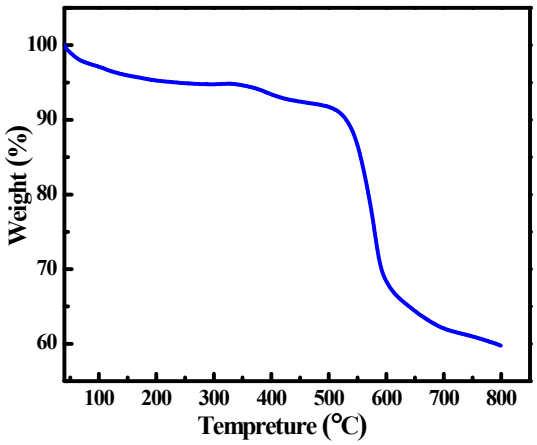
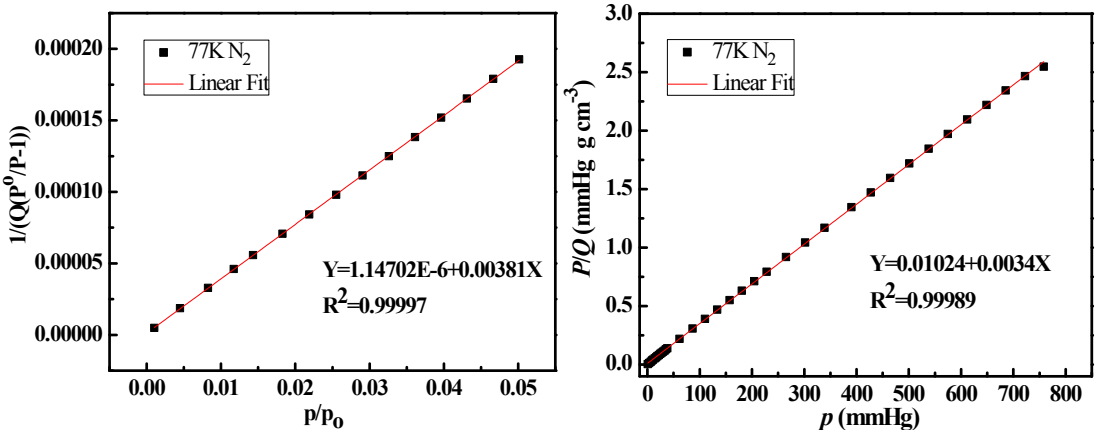


Fig. S1. TGA curves of as-synthesized **ZJU-16**.



S_{BET}=1/(Slope+Intercept)/22414×6.023×10^{23}×0.162×10^{-18} = 1125 m^2/g

$S_{Langmuir}$ = (1/Slope)/22414×6.023×10^{23}×0.162×10^{-18} = 1280 m^2/g

Fig. S2. N_2 sorption isotherm at 77 K and BET plot of **ZJU-16a**. Only the range below P/P_0 = 0.05 satisfies the first consistency criterion for applying the BET theory. Solid symbols: adsorption, open symbols: desorption

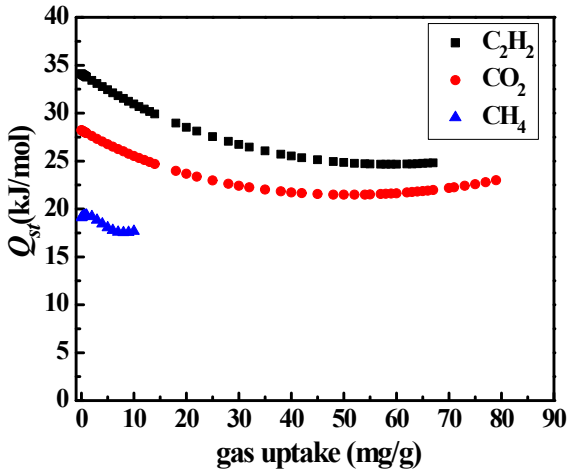


Fig. S3 the isosteric heats of adsorption of C_2H_2, CH_4 and CO_2 calculated using the virial method.