Electronic Supplementary Material (ESI) for Dalton Transactions.

A Microporous Zn(II)–MOF with Open Metal Sites: Structure and Selective Adsorption Properties

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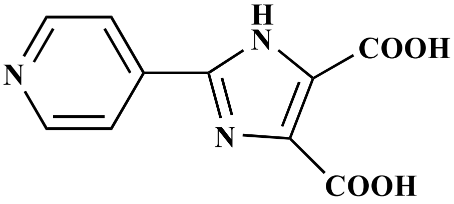
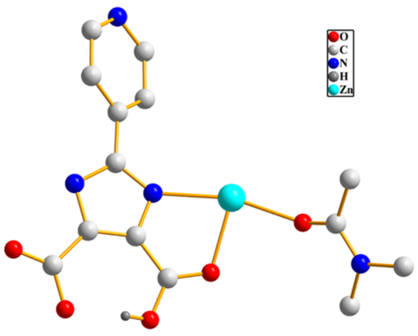
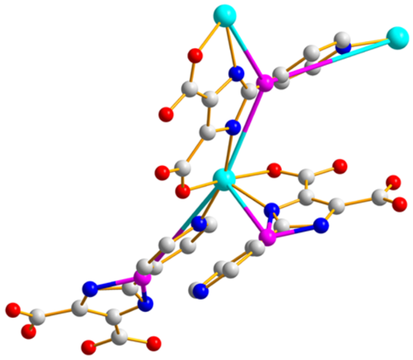


Scheme S1 2-(pyridine-4-yl)-1H-4,5-imidazoledicarboxylic acid



(a)



(b)

Figure S1. (a) The asymmetric unit of **1**, (b) coordination environment of the Zn center (blue) and HPyImDC⁻ fragment (violet), both viewed as 3-connected node.

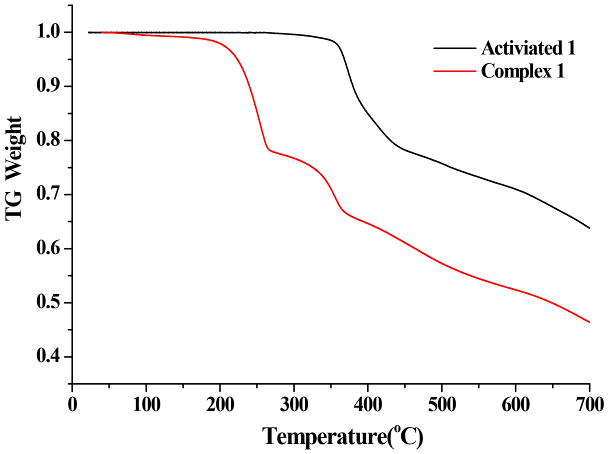


Figure S2. TG curves of complexes **1** and activated **1**.

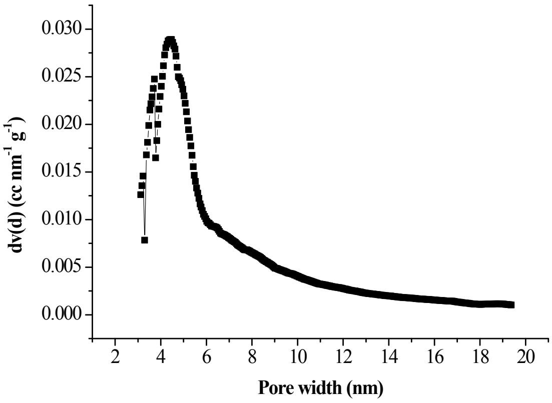


Figure S3. Calculated pore size distributions according to CO_2 isotherm (195 K).

CO_2 Selctivity Calculations

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.

$$S = \frac{q_{CO_2} / q_{N_2}}{p_{CO_2} / p_{N_2}} \qquad \text{(Equation S1)}$$

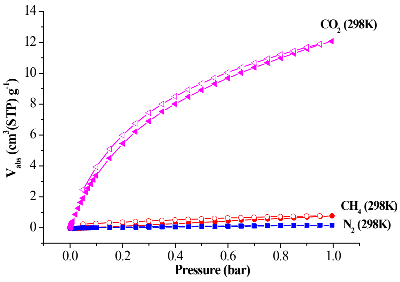


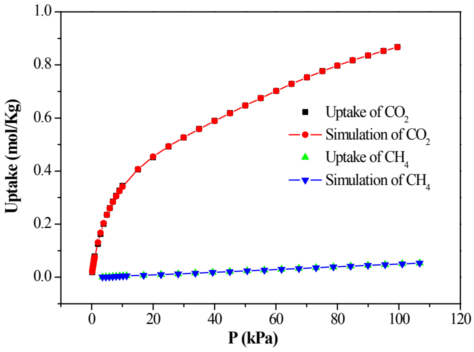
Figure S4. Sorption isotherms for CO_2, CH_4, and N_2 at 298K of desolvated **1** (adsorption and desorption branches are shown with filled and empty shape, respectively).

Selectivity Prediction for Binary Mixture Adsorption: Ideal adsorbed solution theory (IAST)

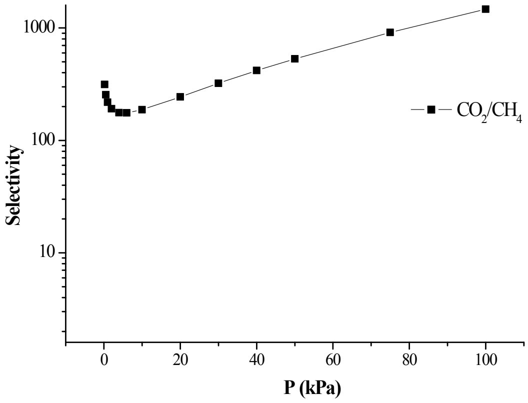
Ideal adsorbed solution theory (IAST) was used to predict binary mixture adsorption from the experimental pure-gas isotherms. To perform the integrations required by IAST, the single-component isotherms should be fitted by a proper model. There is no restriction on the choice of the model to fit the adsorption isotherm, however, data over the pressure range under study should be fitted very precisely. Several isotherm models were tested to fit the experimental pure isotherms for CH_4 and CO_2 of **1** at 273K, and the dual-site Langmuir-Freundlich equation were found to the best fit to the experimental data:

$$q = q_{m_1} \frac{b_1 p^{1/n_1}}{1 + b_1 p^{1/n_1}} + q_{m_2} \frac{b_2 p^{1/n_2}}{1 + b_2 p^{1/n_2}}$$

Here, P is the pressure of the bulk gas at equilibrium with the adsorbed phase (kPa), q is the adsorbed amount per mass of adsorbent (mol/kg), q_{m1} and q_{m2} are the saturation capacities of sites 1 and 2 (mol/kg), b_1 and b_2 are the affinity coefficients of the sites (1/kPa), and n_1 and n_2 are measures of the deviations from an ideal homogeneous surface. Figure S5 shows that the dual-site Langmuir-Freundlich equation fits the single-component isotherms extremely well. The R^2 values for all of the fitted isotherms were over 0.9998. Hence, the fitted isotherm parameters were applied to perform the necessary integrations in IAST.



(a)



(b)

Figure S5. Gas adsorption isotherms and the dual-site Langmuir–Freundlich fit curves for CH_4 and CO_2, (b) IAST predicted selectivity for CO_2/CH_4 in **1** at 273 K.

Estimation of the isosteric heats of gas adsorption

A virial-type expression comprising 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 **1**. In each case, the data were fitted using the equation:

$$\mathrm{In}P = \mathrm{In}N + 1/T\sum_{i=0}^{m} a_i N^i + \sum_{j=0}^{n} b_j N^i$$

Here, P is the pressure expressed in Pa, N is the amount adsorbed in mmol g^{-1}, T is the temperature in K, a_i and b_j are virial coefficients, and m, n represent the number of coefficients required to adequately describe the isotherms (m and n were gradually increased until the contribution of extra added a and b coefficients was deemed to be statistically insignificant towards the overall fit, and the average value of the squared deviations from the experimental values was minimized). The values of the virial coefficients a_0 through a_m were then used to calculate the isosteric heat of adsorption using the following expression.

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

Q_{st} is the coverage-dependent isosteric heat of adsorption and R is the universal gas constant.

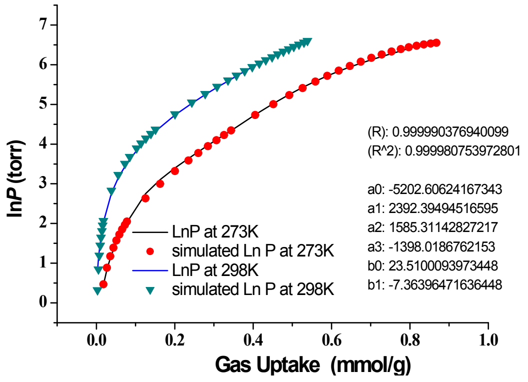


Figure S6. The details of virial equation (solid lines) fitting to the experimental for **1**.

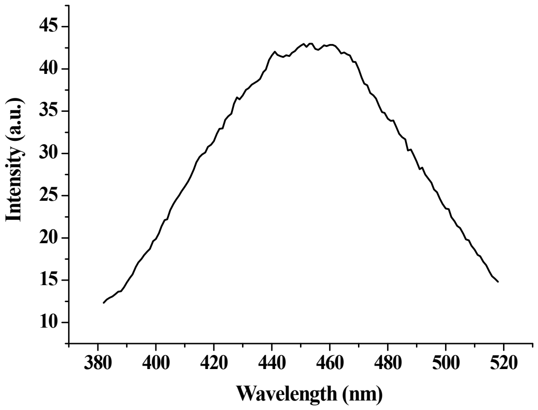


Figure S7. The solid-state fluorescent spectrum of H_3PyImDC at room temperature.