Electronic supplementary information (ESI)

Temperature dependent selective gas sorption of unprecedented stable microporous metal-imidazolate framework

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Experimental

Materials and methods

All commercially available chemicals are of reagent grade and were used as received without further purification. The ligand H$_2$L was prepared according to the literature. Elemental analyses of C, H, and N were taken on a Perkin-Elmer 240C elemental analyzer at the analysis center of Nanjing University. Infrared spectra (IR) were recorded on a Bruker Vector22 FT-IR spectrophotometer by using KBr pellets. Thermogravimetric analyses (TGA) were performed on a simultaneous SDT 2960 thermal analyzer under nitrogen with a heating rate of 10 °C min$^{-1}$. Powder X-ray diffraction (PXRD) patterns were measured on a Shimadzu XRD-6000 X-ray diffractometer with Cu Kα ($λ = 1.5418$ Å) radiation at room temperature. Carbon dioxide (CO$_2$) and nitrogen (N$_2$) sorption experiments were carried out on a Belsorp-max volumetric gas sorption instrument and methane (CH$_4$) and hydrogen (H$_2$)
on Autosorb-1MP, Quantachrome. The sample was activated by using the “outgas” function of the surface area analyzer for 10 hours at 160 °C.

**X-ray crystallography**

The crystallographic data collections for 1 was carried out on a Bruker Smart Apex CCD area-detector diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293(2) K using ω-scan technique. The diffraction data were integrated by using the SAINT program, which was also used for the intensity corrections for the Lorentz and polarization effects. Semi-empirical absorption correction was applied using the SADABS program. The structures were solved by direct methods and all the non-hydrogen atoms were refined anisotropically on $F^2$ by the full-matrix least-squares technique using the SHELXL-97 crystallographic software package.

**Figure S1.** The coordination environments of Cu1 atoms in 1. Atoms with ‘A’, ‘B’, ‘C’ or ‘D’ in labels are symmetry-generated. Symmetry code: A 1+x-y, 2-y, 2.5-z; B 1-y, 1-x, 0.5+z; C 1+x-y, 1+x, 2-z; D 1-x, 2-y, 2-z.
Figure S2. (a) View of the 4-connected L$^2$ ligand. (b) 4-connected node of Cu(II). (c) Schematic representations of the (4, 4)-connected framework of 1 with (6$^5$.10) topology.

Figure S3. CO$_2$ adsorption enthalpy for 1 calculated from the CO$_2$ adsorption isotherms at 273 and 298 K.

Figure S4. H$_2$ adsorption enthalpy for 1 calculated from the H$_2$ adsorption isotherms at 77 and 87 K.

Analysis of Gas Sorption Isotherms:
The methods are applied to deal with the sorption data according to the literature 14 (*J. Am. Chem. Soc.* 2005, **127**, 9367). The Langmuir-Freundlich equation is used to fit CO$_2$ and H$_2$ adsorption isotherms and predict the adsorption capacity of the framework at saturation, and Clausius-Clapeyron equation is employed to calculation the enthalpies of CO$_2$ and H$_2$. 

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adsorption.

\[
\ln \left( \frac{P_1}{P_2} \right) = \Delta H_{ads} \times \frac{T_2 - T_1}{RT_2} \quad (I)
\]

Where \(P_i\) = pressure for isotherm \(i\)

\(T_i\) = temperature for isotherm \(i\)

\(R = 8.315 \text{ J} / (\text{K} \cdot \text{mol})\)

The equation (I) can be applied to calculate the enthalpy of adsorption of a gas as a function of the quantity of gas adsorbed. Pressure as a function of the amount of gas adsorbed was determined using the Langmuir-Freundlich fit for the isotherms.

\[
\frac{Q}{Q_m} = \frac{BP_i^{1/(l)}}{1 + BP_i^{1/(l)}} \quad (II)
\]

where \(Q\) = moles adsorbed

\(Q_m\) = moles adsorbed at saturation

\(P\) = pressure

\(B\) and \(l\) are constants

Rearrange (II) to get:

\[
P = \left( \frac{Q / Q_m}{B - BQ / Q_m} \right)^l \quad (III)
\]

Replace \(P\) in equation (I) to obtain:

\[
\Delta H_{ads} = \frac{RT_2}{T_2 - T_1} \times \ln \left( \frac{Q / Q_{m1}}{B - B_1Q / Q_{m1}} \right)^l \quad (IV)
\]

1. Dealing with the carbon dioxide adsorption data in details:

(1) Fitting \(CO_2\) adsorption isotherms using the Langmuir-Freundlich equation.
(2) Building the relationship between lnP and the quantity of CO$_2$ adsorbed for the two isotherms by calculating.
(3) Calculating the $H_{\text{ads}}$ using the equation IV.

2. Calculation of CO$_2$/N$_2$ selectivity

The methods are applied to estimate the CO$_2$/N$_2$ selectivity according to the literature 18a (J. Am. Chem. Soc., 2010, 132, 38). The ratios of these initial slopes of the CO$_2$ and N$_2$ adsorption isotherms were applied to estimate the adsorption selectivity for CO$_2$ over N$_2$. 
**Figure S6.** The fitting initial slope for CO$_2$ and N$_2$ isotherms collected at 273K (CO$_2$: red squares; N$_2$: green triangles).

**Figure S7.** The fitting initial slope for CO$_2$ and N$_2$ isotherms collected at 298K (CO$_2$: red squares; N$_2$: green triangles).

3. Dealing with the hydrogen adsorption data in details:

(1) Fitting H$_2$ adsorption isotherms using the Langmuir-Freundlich equation.
(2) Building the relationship between \( \ln P \) and the quantity of hydrogen adsorbed for the two isotherms by calculating.
(3) Calculating the $H_{\text{ads}}$ using the equation IV.

Reference:


S3 Sheldrick, G. M. *SADABS*, University of Göttingen, Göttingen, Germany.