Electronic supplementary information (ESI)

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

Shui-Sheng Chen,[a,c] **Min Chen,**[a] **Satoshi Takamizawa,**[b] **Man-Sheng Chen,**[a] **Zhi Su**[a] **and Wei-Yin Sun***[a]

[a] *Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing National Laboratory of Microstructures, Nanjing University, Nanjing 210093, China E-mail: sunwy@nju.edu.cn; Fax: +86 25 83314502*

[b] *Graduate School of Nanobioscience, Yokohama City University, Kanazawa-ku, Yokohama, Kanagawa 236-0027, Japan*

[c] *School of Chemistry and Chemical Engineering, Fuyang Teachers College, Fuyang 236041, China*

Experimental

Materials and methods

All commercially available chemicals are of reagent grade and were used as received without further purification. The ligand H_2L was prepared according to the literature.[S1] 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 ºC 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 ℃.

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,[S2] which was also used for the intensity corrections for the Lorentz and polarization effects. Semi-empirical absorption correction was applied using the *SADABS* program.[S3] 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.[S4]
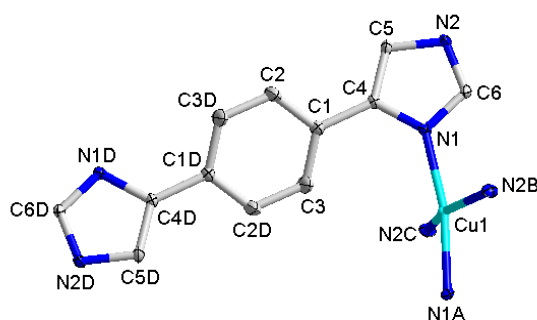

Figure S1. The coordination environments of Cu1 atoms in 1. Atoms with 'A', 'B', 'C' or 'D' in labels are symmetry-generated. Symmetry code: A 1+x-y, 2-y, 2.5-z; B 1-y, 1-x, 0.5+z; C 1+x-y, 1+x, 2-z; D 1-x, 2-y, 2-z.
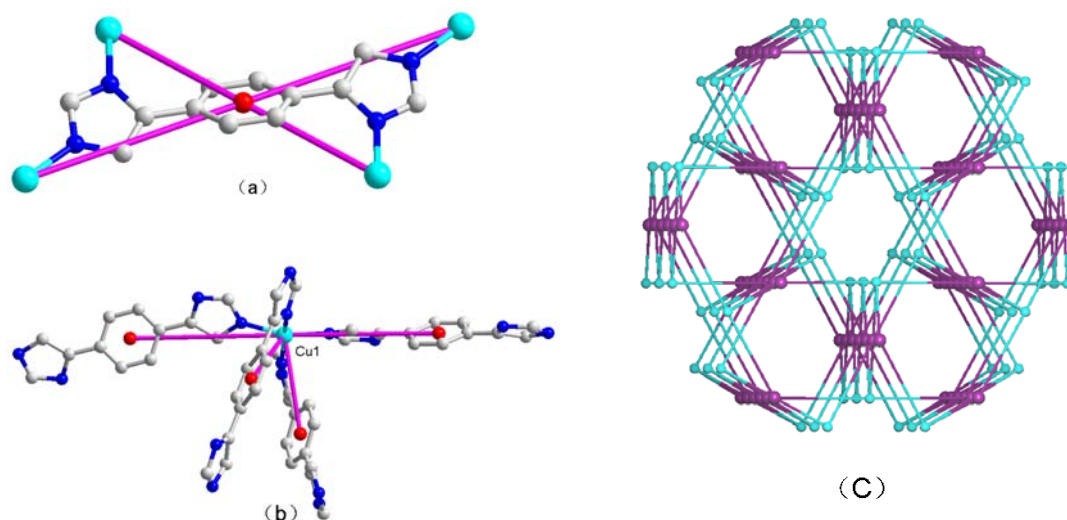
Figure S2. (a) View of the 4-connected L^{2-} ligand. (b) 4-connected node of Cu(II). (c)

Schematic representations of the (4, 4)-connected framework of **1** with ($6^5 \cdot 10$) topology.
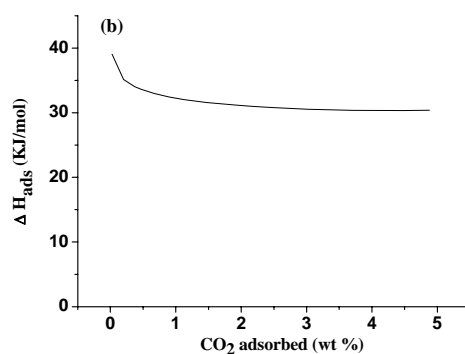
Figure S3. CO_2 adsorption enthalpy for **1** calculated from the CO_2 adsorption isotherms at 273 and 298 K.
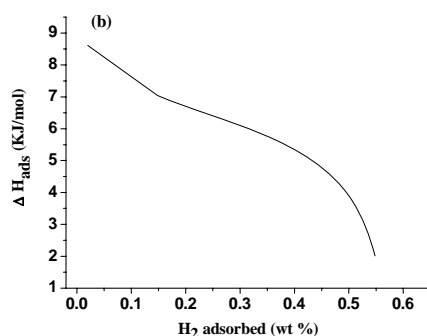
Figure S4. H_2 adsorption enthalpy for **1** calculated from the H_2 adsorption isotherms at 77

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

adsorption.

$$In\left(\frac{P_1}{P_2}\right) = \Delta H_{ads} \times \frac{T_2 - T_1}{RT_1T_2} \qquad (\text{I})$$

Where P_i = pressure for isotherm i

T_i = temperature for isotherm i

$R = 8.315$ J / (K·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.

$$\frac{Q}{Qm} = \frac{BP^{(1/t)}}{1 + BP^{(1/t)}} \qquad (\text{II})$$

where Q = moles adsorbed

Q_m = moles adsorbed at saturation

P = pressure

B and t are constants
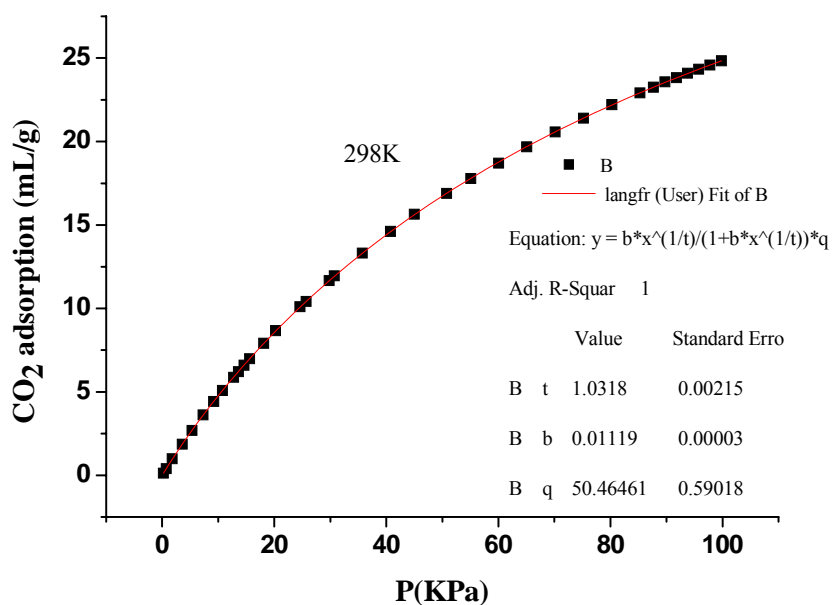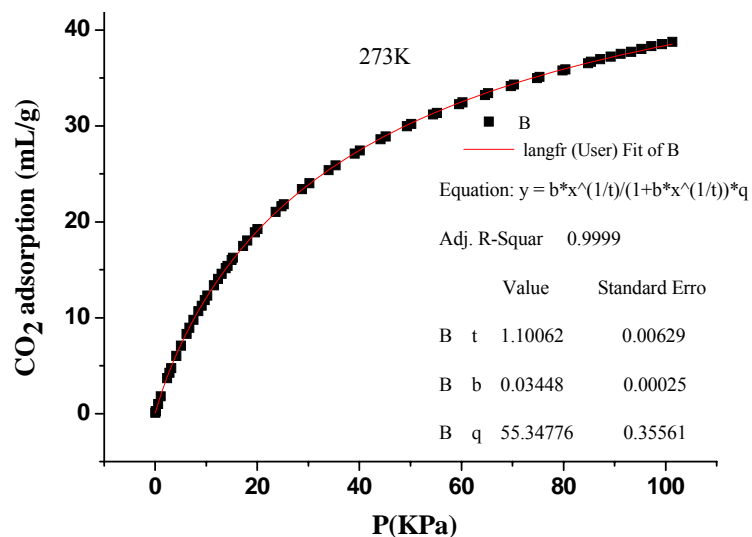
Rearrange (II) to get:

$$P = \left(\frac{Q/Q_m}{B - BQ/Q_m}\right)^t \qquad (\text{III})$$

Replace P in equation (I) to obtain:

$$\Delta H_{ads} = \frac{RT_1T_2}{T_2 - T_1} \times In \frac{\left(\frac{Q/Q_{m1}}{B_1 - B_1Q/Q_{m1}}\right)^t}{\left(\frac{Q/Q_{m2}}{B_2 - B_2Q/Q_{m2}}\right)^t} \qquad (\text{IV})$$

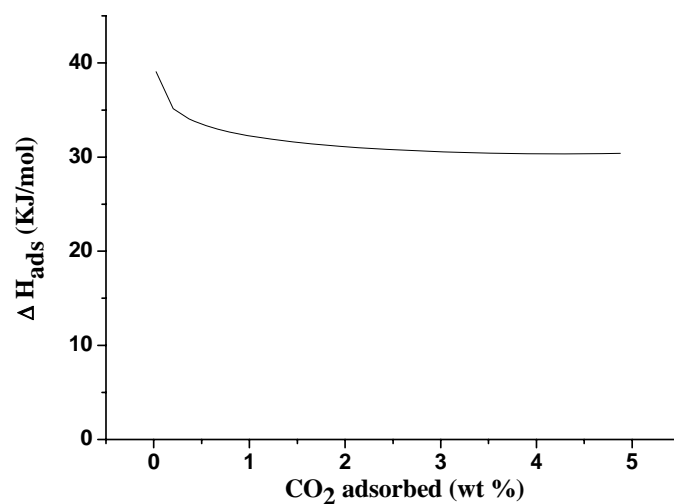## 1. Dealing with the carbon dioxide adsorption data in details:

(1) Fitting CO_2 adsorption isotherms using the Langmuir-Freundlich equation.

273K

B

langfr (User) Fit of B

Equation: y = b*x^(1/t)/(1+b*x^(1/t))*q

Adj. R-Squar   0.9999

		Value	Standard Erro
B	t	1.10062	0.00629
B	b	0.03448	0.00025
B	q	55.34776	0.35561

298K

B

langfr (User) Fit of B

Equation: y = b*x^(1/t)/(1+b*x^(1/t))*q

Adj. R-Squar   1

		Value	Standard Erro
B	t	1.0318	0.00215
B	b	0.01119	0.00003
B	q	50.46461	0.59018

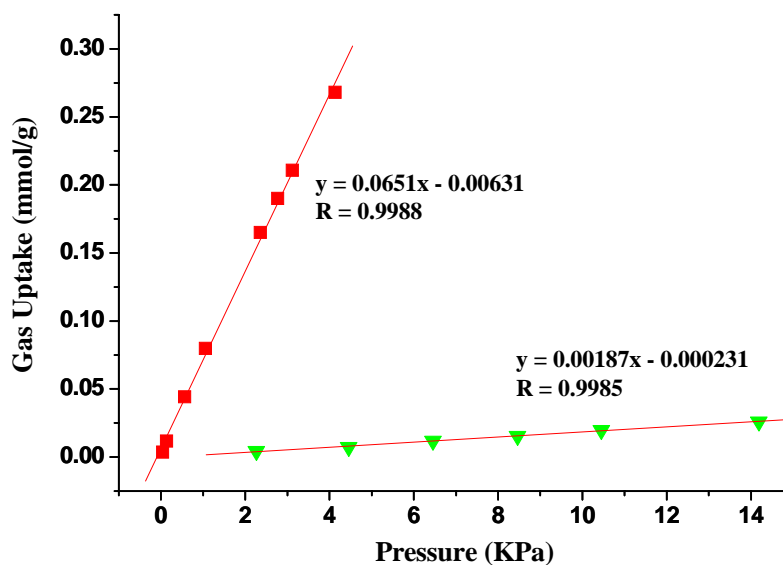(2) Building the relationship between $\ln P$ and the quantity of CO_2 adsorbed for the two isotherms by calculating.

5
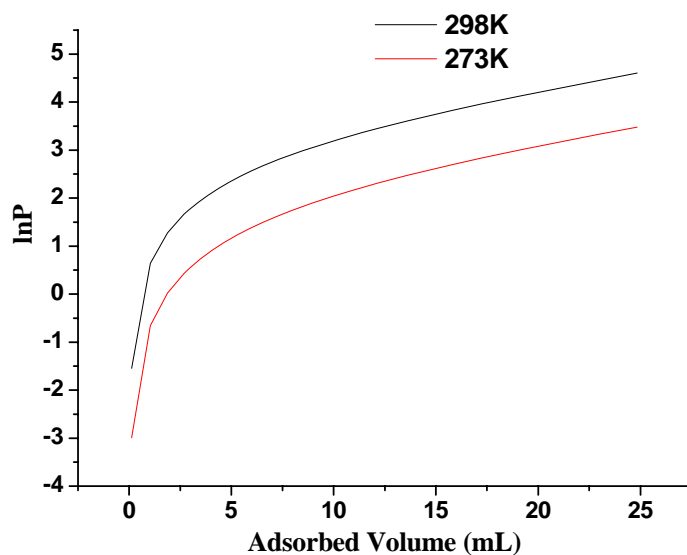
(3) Calculating the H_{ads} using the equation **IV**.

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.
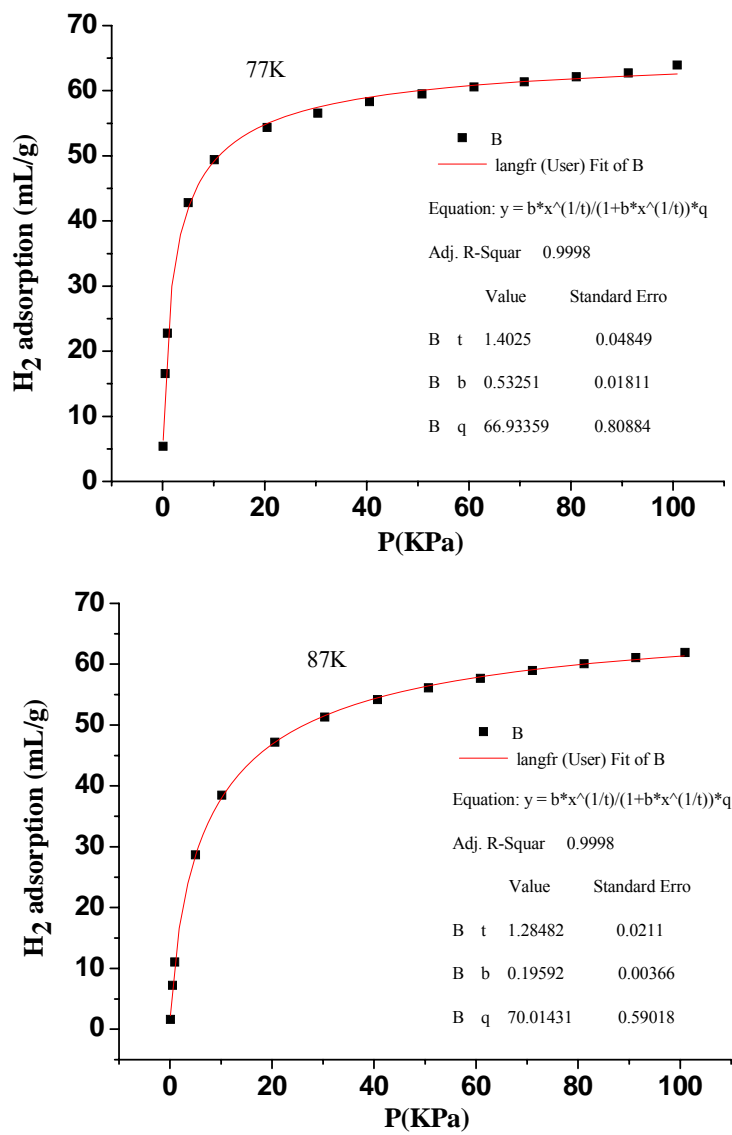
Figure S6. The fitting initial slope for CO_2 and N_2 isotherms collected at 273K (CO_2: red squares; N_2: green triangles).
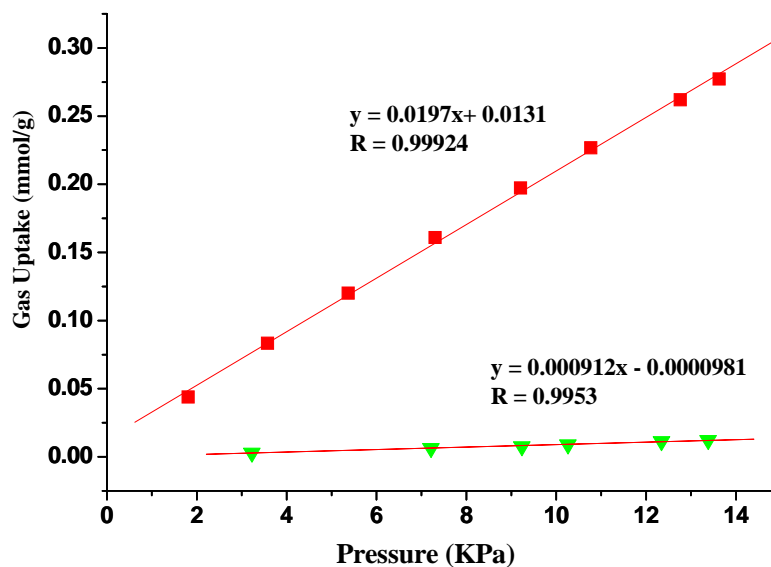
Figure S7. The fitting initial slope for CO_2 and N_2 isotherms collected at 298K (CO_2: red squares; N_2: green triangles).
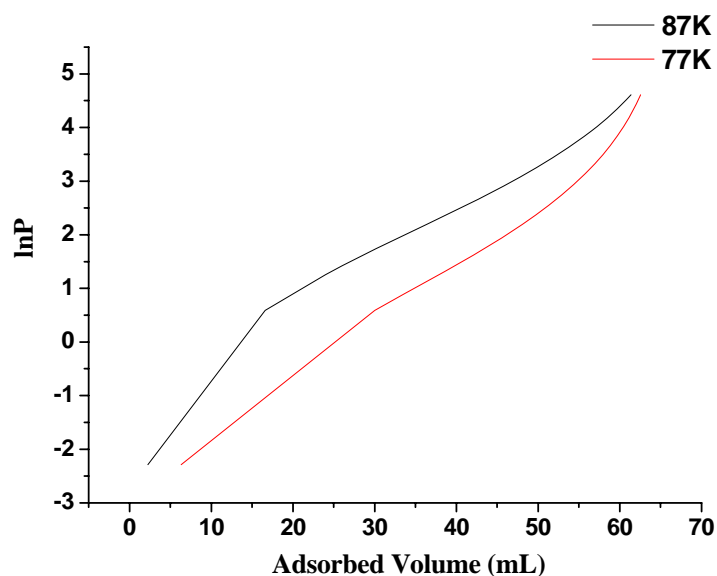
3. Dealing with the hydrogen adsorption data in details:

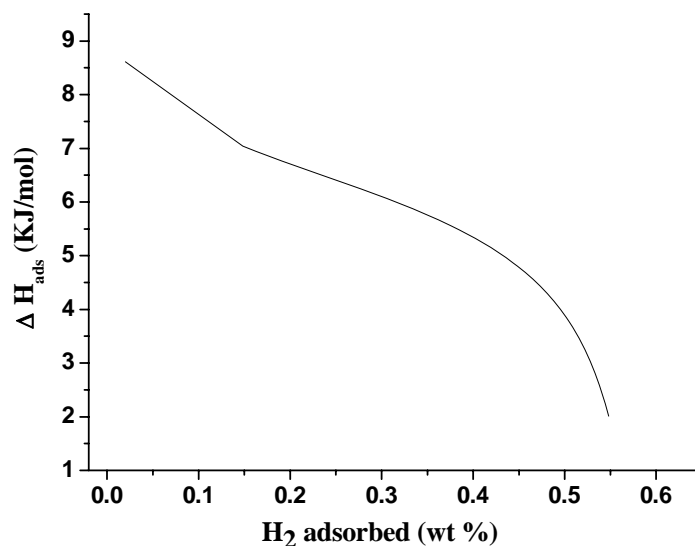(1) Fitting H_2 adsorption isotherms using the Langmuir-Freundlich equation.

(2) Building the relationship between ln$P$ and the quantity of hydrogen adsorbed for the two isotherms by calculating.

(3) Calculating the H_{ads} using the equation **IV**.

Reference:

S1 (a) R. ten Have, M. Huisman, A. Meetsma and A. M. van Leusen, *Tetrahedron*, 1997, **53**, 11355. (b) S. S. Chen, J. Fan, T.-a. Okamura, M. S. Chen, Z. Su, W. Y. Sun and N. Ueyama, *Cryst. Growth Des*. 2010, **10**, 812.

S2 S*AINT*, version 6.2; Bruker AXS, Inc., Madison, WI, 2001.

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

S4 Sheldrick, G. M. *SHELXTL*, version 6.10; Bruker Analytical X-ray Systems, Madison, WI, 2001.