Supporting Information for

A three-dimensional microporous metal-organic framework with large hydrogen sorption hysteresis

Di-Chang Zhong, Wei-Xiong Zhang, Feng-Lei Cao, Long Jiang, and Tong-Bu Lu*

Experimental Section

General Remarks. All of the chemicals are commercially available and used without further purification. Elemental analyses were determined using Elementar Vario EL elemental analyser. The IR spectra were recorded in the 4000 to 400 cm⁻¹ region using KBr pellets and a Bruker EQUINOX 55 spectrometer. The thermogravimetric analyses (TGA) was carried out on Netzsch TG-209 Thermogravimetry Analyzer in air atmosphere. The Powder X-ray diffraction patterns were recorded on D8 ADVANCE X-Ray Diffractometer. The single crystal data were collected on a Bruker Smart 1000 CCD diffractometer.

 $[Cd_2(Tzc)_2:(H_2O)_2]_n$ (1). $Cd(OAc)_2:4H_2O$ (0.5 mmol, 0.133 g), ethyl tetrazolate-5-carboxylate (0.5 mmol, 0.071 g), and KOH (0.5 mmol, 0.028 g) were mixed and dissolved in 8 mL of DMF and water (v:v/1:1). After stirred for about ten minutes, the solution was transferred to Teflon-lined autoclave and heated at 110 °C for 72 h. Colorless octahedron-shaped crystals of **1** were produced when the autoclave was cooled to room temperature. The crystals were collected by filtration, washed with water, and dried in air. Anal. Calcd for C₄H₄Cd₂N₈O₆: C, 9.91; H, 0.83; N, 23.11. Found: C,

9.96; H, 0.72; N, 23.25. IR (KBr, cm⁻¹): 3270(s), 1618(vs), 1508(s), 1434(s), 1384(w), 1349(s), 1219(m), 1185(m), 1174(m), 1128(w), 1098(m), 1070(m), 809(w), 733(w), 683(w), 596(w), 494(w).

Single X-ray Diffraction. Single-crystal data for 1 were collected on a Bruker Smart 1000 CCD diffractometer, with Mo-K α radiation ($\lambda = 0.71073$ Å). All empirical absorption corrections were applied using the SADABS program.¹ The structure was solved using direct methods, which yielded the positions of all non-hydrogen atoms. These were refined first isotropically and then anisotropically. The hydrogen atoms attached two coordinated water molecules were not added. All calculations were performed using the SHELXTL system of computer programs.²

Powder X-ray Diffraction. The Powder X-ray diffraction data of **1d** were collected on Bruker D8 ADVANCE Diffractometer (Cu K α radiation, 40 kV, 40 mA). The sample of **1** was first loaded on the sample holder of high-temperature option, and then heated to 150 °C under N₂ gas flow. After about 1 hour, the step-scanned X-ray powder diffraction data was in-situ recorded in the range of 8-90° 2 θ with 0.017° 2 θ step size and 10 seconds/step scan speed.

Pattern indexing was then performed by means of the computer program TREOR90³ from the first 20 peaks, and an orthorhombic cell similar with **1** was found: a =11.782976 Å, b = 8.306503 Å, c = 11.877628 Å. As shown at Figure S2b, the sample of **1d** can be recovered to **1** easily by exposing to the air within several minutes, implying that the structure transition is not very drastic. Therefore, the origin space group *Pna*2₁ could be the first choice for 1d, and the asymmetric unit of 1d should also consist of two Tzc⁻ ligands and Cd²⁺ ions. Then, these structure fragments were imported into the new cell, assigned as four motion groups, and adjusted to model a similar structure of 1 as the approximate structure of 1d.

Then various parameters, including Pseudo-Voigt profile parameters, background parameters, the cell constants, the zero point of the diffraction pattern, the position and orientation of motion groups, the dihedral angels between carboxylate group and global isotropic tetrazolate group, the atom displacement parameter, the Berar-Baldinozzi asymmetry correction parameters and the March-Dollase preferred orientation correction parameters, were optimized step by step to improve the agreement between the calculated and the experimental powder diffraction pattern, which was carried on Reflex Powder Refinement module of Material Studio. Total 58 parameters were refined together in the final Rietveld refinement, giving the final R-factors $R_p =$ 3.78% and $R_{wp} = 6.37\%$, and the following unit cell parameters: $Pna2_1$, a = 11.818(1) Å, b = 8.324(1) Å, c = 11.915(1) Å, and V = 1159.4(3) Å³.

Gas Sorption Measurements. All the gas sorption experiments were measured with a BELSORP-max gas adsorption instrument. The N_2 , H_2 and CO_2 adsorption isotherms were collected in a relative pressure range from 10^{-4} to 1 atm. The cryogenic temperatures of 77 K required for N_2 and H_2 and 87 K for H_2 sorption measurements were controlled by liquid nitrogen and liquid argon, respectively, and the 195 K required for CO_2 sorption measurements was obtained using dry ice-acetone bath. The

initial outgassing process for the sample was carried out under a high vacuum (less than 10^{-6} mbar) at 150°C for 10 h. The desolvated sample and sample tube were weighed precisely and transferred to the analyzer.

Analysis of Gas Sorption Isotherms. All the methods employed here for dealing with the sorption data are according to the reference,⁴ including determining the surface area of 1d by fitting the CO₂ sorption isotherms using BET equation and Langmuir equation, fitting H_2 adsorption isotherms using the Langmuir-Freundlich equation to predict the H_2 adsorption capacity of the framework at saturation, and the calculation of the enthalpy of H_2 adsorption using Clausius-Clapeyron equation.

$$\ln\left(\frac{P_1}{P_2}\right) = \Delta H_{ads} \times \frac{T_2 \cdot T_1}{RT_1 T_2} \qquad (I)$$

where P_i = pressure for isotherm *i* T_i = temperature for isotherm *i* $R = 8.315 \text{ J} / (\text{K} \cdot \text{mol})$

Equation (I) can be used as a function of the quantity of adsorbed hydrogen to calculate the adsorption enthalpy of hydrogen. The pressure as a function of the amount of hydrogen adsorbed was determined by using Langmuir-Freundlich fit for the adsorption isotherms.

Supplementary Material (ESI) for Chemical Communications This journal is (c) The Royal Society of Chemistry 2011

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

where Q = moles adsorbed Q_m = moles adsorbed at saturation P = pressure B and t are constants

Rearranging (II) to obtained:

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

Replacing *P* in equation (**I**), therefore, the ΔH_{ads} can be calculated from the following formula:

$$\Delta H_{ads} = \frac{RT_1T_2}{T_2 \cdot T_1} \times \ln \frac{\left(\frac{Q/Q_{m1}}{B_1 \cdot B_1 Q/Q_{m1}}\right)^t}{\left(\frac{Q/Q_{m2}}{B_2 \cdot B_2 Q/Q_{m2}}\right)^t} \quad (IV)$$

References

- Sheldrick, G. M. SADABS, Program for Empirical Absorption Correction of Area Detector Data; University of Göttingen: Göttingen, 1996.
- (2) Sheldrick, G. M. SHELXS 97, Program for Crystal Structure Refinement; University of Göttingen, Göttingen, 1997.
- (3) Werner, P. E.; Eriksson, L.; Westdahl, M. J. Appl. Crystallogr. 1985, 18, 367-370.
- (4) Dincă, M.; Long, J. R. J. Am. Chem. Soc. 2005, 127, 9376-9377.



Scheme S1. Two coordination modes of Tzc anion in 1 and 1d.



Fig. S1. The TGA curve for 1.



Fig. S2. (a) The variable temperature XRD patterns for **1**. (b) The XRD patterns of **1** collected at 25, 90 and 150 °C, respectively. The XRD pattern of 150 °C is immediately

back to the original one when cooled to room temperature (26°C), indicating **1d** is readily to re-adsorb water molecules and transforms back to **1**.