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Single-Crystal-to-Single-Crystal Transformations and Selective Adsorption of Porous Copper(II) Frameworks

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Materials and methods. All commercially available chemicals are of reagent grade and used as received without further purification. The ligand H₂INAIP was prepared as reported previously.^[S1] C, H and N analyses were made on a Perkin-Elmer 240C elemental analyzer at the analysis center of Nanjing University. Infrared (IR) spectra were recorded on a Bruker model Vector22 FT-IR spectrophotometer using KBr disks. Solid state ¹³C NMR spectra were measured on a Bruker AVANCE III 400MHz NMR spectrometer at 295 K. 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 K α (λ = 1.5418 Å) radiation at room temperature. N₂, CO₂, H₂O, CH₃OH and CH₃CH₂OH sorption isotherms were measured on a volumetric adsorption apparatus (Bel-max), while H₂ and CH₄ sorption isotherms were measured on Quantachrome Autosorb-1-MP.

Syntheses. 1: A mixture of $CuCl_2 \cdot 2H_2O$ (17.1 mg, 0.1 mmol), H_2INAIP (28.6 mg, 0.1 mmol), bpy (16.0 mg, 0.1 mmol) and NaOH (8.0 mg, 0.2 mmol) in 10 mL H₂O was sealed in a 16 mL Teflon lined stainless steel container and heated at 160 °C for 5 days. Green block crystals of **1** were collected with a yield of 42%. Anal. Calcd for $C_{14}H_{12}CuN_2O_7$: C, 43.81; H, 3.15; N, 7.30%. Found: C, 43.78; H, 3.21; N, 7.33%.

1a and **1b**: **1a** was obtained by heating **1** at 180 °C. Methanol vapor absorption of **1a** was performed on a volumetric adsorption apparatus (Bel-max) at 298 K. The transformation from single crystals **1a** to **1b** was confirmed by X-ray crystallography. Anal. Calcd for **1a**, $C_{14}H_8CuN_2O_5$: C, 48.31; H, 2.30; N, 6.90%. Found: C, 48.26; H, 2.36; N, 6.85%. For **1b**, $C_{15}H_{12}CuN_2O_6$: C, 47.39; H, 3.16; N, 7.37%. Found: C, 47.36; H, 3.21; N, 7.34%.

1': Standing 1a in air $[T = 22(2) \degree C$, relative humidity = 36(5) %] for 48 h gave rise to the rehydrated sample 1'.

X-ray Crystallography. The crystallographic data collections for complexes 1 and 1a were carried out on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71075$ Å) at 200 and 453 K using the ω -scan technique, respectively. The structures of **1** and **1a** were solved by direct methods using SIR92 and expanded using Fourier techniques.^[S2,S3] All non-hydrogen atoms were refined anisotropically. All the hydrogen atoms except for those of water molecules were generated geometrically and refined isotropically using the riding model, while those ones of water molecules were not found. All calculations were performed using the CrystalStructure crystallographic software package.^[S4] Atoms O2 and O2B in **1** are disordered with the site occupancy factors of 0.467(13) and 0.533(13), respectively. Atoms O3, O3B and O3C in 1 are disordered with the site occupancy factors of 0.467(13), 0.244(10) and 0.289(15), respectively. The data collection for 1' and 1b were carried out on a Bruker Smart Apex CCD area-detector diffractometer using graphite-monochromated Mo K α radiation (λ = 0.71073 Å) at 293(2) K. The diffraction data were integrated by using the SAINT program.^[S5] Semi-empirical absorption correction were applied using the SADABS program.^[S6] The structures were solved by direct methods and all non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique using the SHELXL-97 crystallographic software package.^[S7] The hydrogen atoms were generated geometrically except for water and methanol molecules. Atoms O1WA, O2WA, O1WB and O2WB in 1' were disordered with the site occupancy factors of 0.78, 0.78, 0.22 and 0.22, respectively. And atoms O6, C15, O6A and C15A in **1b** were disordered with the site occupancy factors of 0.50(3), 0.50(3), 0.50(3) and 0.50(3), respectively.

References:

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	1	1'	1a	1b
molecular formula	$C_{14}H_{12}CuN_2O_7$	$C_{14}H_{12}CuN_2O_7$	$C_{14}H_8CuN_2O_5$	$C_{15}H_{12}CuN_2O_6$
fw	383.80	383.81	347.76	379.82
cryst syst	Monoclinic	Monoclinic	Monoclinic	Monoclinic
space group	$P2_{1}/c$	$P2_{1}/c$	$P2_{1}/c$	$P2_{1}/c$
a, Å	8.405(5)	8.4048(12)	8.497(5)	8.4283(11)
b, Å	10.293(4)	10.2379(15)	10.296(4)	10.2553(13)
c, Å	17.812(8)	17.7707(18)	17.749(7)	17.8159(18)
β , deg	104.582(19)	104.405(5)	104.624(18)	104.408(5)
temperature, K	293(1)	293(2)	453(1)	293(2)
volume, Å ³	1491.2(12)	1481.1(3)	1502.4(12)	1491.5(3)
Ζ	4	4	4	4
density (calcd),	1.709	1.721	1.537	1.691
g/cm ³				
abs coeff, mm ⁻¹	1.506	1.517	1.477	1.500
<i>F</i> (000)	780	780	700	772
reflns	13613/3410	7435/2752	13698/3435	7172/2694
collected/unique				
$R_{\rm int}$	0.0365	0.0474	0.0387	0.0491
restraint/param	4/222	0/235	0/199	106/216
GOF on F^2	1.090	1.062	1.032	1.314
$R_1 [I > 2\sigma(I)]$	0.0477	0.0501	0.0424	0.1262
wR_2 (all data) ^b	0.1381	0.1335	0.1145	0.2813

 Table S1.
 Crystal data and structure refinements for complexes 1, 1', 1a and 1b

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^{*a*} $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$. ^{*b*} $wR_2 = |\Sigma w(|F_0|^2 - |F_c|^2) | / \Sigma |w(F_0)^2|^{1/2}$, where $w = 1 / [\sigma^2 (F_0^2) + (aP)^2 + bP]$. $P = (F_0^2 + 2F_c^2) / 3$.

1					
Cu(1)-O(31)	1.882(3)	Cu(1)-O(51)#1	1.998(3)		
Cu(1)-O(52)#1	2.011(3)	Cu(1)-N(11)#2	1.974(3)		
O(31)-Cu(1)-O(52)#1	98.36(9)	O(51)#1-Cu(1)-O(52)#1	65.52(9)		
O(31)-Cu(1)-O(51)#1	162.69(10)	O(52)#1-Cu(1)-N(11)#2	161.24(9)		
O(51)-Cu(1)-N(11)#2	98.78(11)	O(31)#1-Cu(1)-N(11)#2	98.18(11)		
1'					
Cu(1)-O(1)	1.885(3)	Cu(1)-O(4)#1	1.993(3)		
Cu(1)-O(3)#1	2.002(3)	Cu(1)-N(1)#2	1.969(3)		
O(1)-Cu(1)-O(3)#1	98.71(13)	O(3)#1-Cu(1)-O(4)#1	65.32(12)		
O(1)-Cu(1)-O(4)#1	162.55(13)	O(3)#1-Cu(1)-N(1)#2	160.87(14)		
O(1)-Cu(1)-N(1)#2	98.24(14)	O(4)#1-Cu(1)-N(1)#2	98.71(13)		
1a					
Cu(1)-O(31)	1.883(2)	Cu(1)-O(52)#1	2.0067(19)		
Cu(1)-O(51)#1	1.998(2)	Cu(1)-N(11)#2	1.989(2)		
N(11)#2-Cu(1)-O(31)	97.37(9)	N(11)#2-Cu(1)-O(51)#1	98.68(9)		
O(31)-Cu(1)-O(51)#1	163.78(9)	N(11)#2-Cu(1)-O(52)#1	161.95(9)		
O(31)-Cu(1)-O(52)#1	99.19(8)	O(51)#1-Cu(1)-O(52)#1	65.22(7)		
1b					
Cu(1)-O(1)	1.998(7)	Cu(1)-O(4)#1	1.890(7)		
Cu(1)-O(2)	1.992(7)	Cu(1)-N(2)#2	1.969(8)		
N(2)#2-Cu(1)-O(2)	98.6(3)	N(2)#2-Cu(1)-O(1)	161.2(3)		
O(4)#1-Cu(1)-O(2)	162.6(3)	O(4)#1-Cu(1)-N(2)#2	98.3(3)		
O(4)#1-Cu(1)-O(1)	98.7(3)	O(2)-Cu(1)-O(1)	65.4(3)		

Table S2. Selected bond distances (Å) and angles (deg) for 1, 1', 1a and 1b^a

^aSymmetry transformation used to generate equivalent atoms: #1: x, -y + 3/2, z + 1/2, #2: x + 1, -y + 1/2, z + 1/2. for **1**; #1: x, -y + 5/2, z + 1/2, #2: x + 1, -y + 3/2, z + 1/2. for **1**'; #1: x, -y + 1/2, z + 1/2, #2: x + 1, -y + 3/2, z + 1/2. for **1**'; #1: x, -y + 1/2, z + 1/2, #2: x + 1, -y + 3/2, z + 1/2. for **1**a; #1: x, -y + 3/2, z - 1/2, #2: x + 1, y + 1, z. for **1**b.



Scheme S1 Schematic structure of H₂INAIP.



Figure S1. 1D chain structure linked by INAIP²⁻ ligands and Cu(II) centers in 1.



Figure S2. Schematic representation of the 4-fold interpenetrated (10,3)-b topology.



Figure S3. The TG curves of 1, 1a and 1b.



Figure S4. The variable temperature XPRD patterns for 1.

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 H_2 adsorption isotherms and predict the adsorption capacity of the framework at saturation, and Clausius-Clapeyron equation is employed to calculation the enthalpy of H_2 adsorption.

$$\operatorname{Ln}\left(\frac{P_1}{P_2}\right) = \Delta H_{ads} \times \frac{T_2 - T_1}{RT_1 T_2} \tag{I}$$

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 hydrogen adsorbed was determined using the Langmuir-Freundlich fit for the isotherms.

$$\frac{Q}{Qm} = \frac{BP^{(1/t)}}{1 + BP^{(1/t)}}$$
(II)
where Q = moles adsorbed
 Q_m = moles adsorbed at saturation
 P = pressure
 B and t are constants

Rearrange (II) to get:

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

Replace P in equation (I) to obtain:

$$\Delta H_{ads} = \frac{RT_{1}T_{2}}{T_{2} - T_{1}} \times In \frac{\left(\frac{Q/Q_{m1}}{B_{1} - B_{1}Q/Q_{m1}}\right)^{t}}{\left(\frac{Q/Q_{m2}}{B_{2} - B_{2}Q/Q_{m2}}\right)^{t}}$$
(IV)

Dealing with the hydrogen adsorption data in detail:



Figure S5. Fitting of the H_2 adsorption isotherm of 1 recorded at 77 K using Langmuir-Freundlich equation.



Figure S6. Fitting of the H_2 adsorption isotherm of 1 recorded at 87 K using Langmuir-Freundlich equation.



Figure S7. Isosteric heat of adsorption for H₂ uptake in 1.

Heat of Sorption Calculation for CO₂ Uptake

The isotherms were fit to the Langmuir-Freundlich model (Figs. S9 and S10).



Figure S8. CO₂ isotherm at 298K (black squares) and Langmuir-Freundlich fit to the experimental data (red solid line).



Figure S9. CO₂ isotherm at 273K (black squares) and Langmuir-Freundlich fit to the experimental data (red solid line).



Figure S10. Isosteric heat of adsorption for CO₂ at different CO₂ loadings in 1.