Electronic Supplementary Information for

A robust porous PtS-type Cu(II) metal-organic framework: single-crystal-to-single-crystal transformation with reversible guest intercalation accompanied by color change

Yun Ling,[a] Lei Zhang,*[a] Jing Li,[a] and Miao Du[b]

1. Materials and Physical Measurements

All chemicals were commercially available and used as received without further purification. 3,5-dimethyl-1H,1,2,4-triazole was synthesized according to previous reports. Elemental analyses for C, H, and N were carried out by using a Vario EL III Elemental Analyzer. Infrared spectra were recorded on a Bruker Equinox 55 FT-IR spectrophotometer with KBr pellets in the range 4000 – 400cm^{-1}. Differential scanning calorimeter-thermogravimetry analyses (DSC-TG) were performed on STA449C (Netzsch) under a flow of N_2 at a temperature range of 30 – 800°C (10 °C/min). The powder X-ray diffraction (PXRD) patterns were collected on a Rigaku D/max-IIIA powder diffractometer and Bruker D8 with Cu Kα radiation (λ = 1.5406 Å) over the range 5° < 2θ < 50° with a step size of 0.02° at room temperature. Magnetic susceptibility measurements were performed in the temperature range of 2–300 K with an applied field of 1000 Oe on a Quantum Design MPMS

[a] School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China.

[b] College of Chemistry and Life Science, Tianjin Normal University, Ttianjin, 300074, China

* Corresponding author: Dr. Prof. L. Zhang, Fax. and Tel.: +86 20 8711 0234,
E-mail: lzhangce@scut.edu.cn

XL-5 SQUID system. The N_2 sorption analysis was performed on a ASAP 2010 at 77 K. The samples were dried at 393 K under high vacuum for 2 h. Low-pressure hydrogen adsorption measurements were performed at 77 K and 87 K on a Belsorp-miniII.

2. X-ray Crystallography

Suitable single crystals of **1**, **1'** and **1''** (**1'** and **1''** are the crystals after the dehydration and rehydration) were mounted on a glass capillary and data collection were carried out on a Bruker Apex II CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K. Cell parameters were retrieved using SMART software and refined with SAINT on all observed reflections. Data reduction was performed with the SAINT program and corrected for Lorentz and polarization effects. Semi-empirical absorption corrections were applied by SADABS program. The structures were solved by direct methods using SHELXS program of the SHELXL package and refined with SHELXL program [1]. The heavy atoms and other non-hydrogen atoms are directly obtained from difference Fourier map. The final refinements were performed by full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms on F^2. The hydrogen atoms on the ligand and guest water were located from differential Fourier map and then refined as rigid modes. The SQUEEZE method was used for **1'** for highly disordered water molecules.

1. G. M. Sheldrick, SHELXS 97, Program for the Solution of Crystal Structures: University of Göttingen, Germany, 1997. (b) G. M. Sheldrick, SHELXL 97, Program for the Solution of Crystal Structures: University of Göttingen, Germany, 1997. (c) G. M. Sheldrick, Acta Cryst. 2008, A64, 112-122.

Table S1. Crystal data and refinement of **1**

	1
Formula	$C_{12}H_{35}Cu_3N_6O_{19.50}$
F.W.	766.08
Crystal System	Tetragonal
Space group	$P4_32_12$ (No. 96)
a (Å)	14.043(3)
b (Å)	14.043(3)
c (Å)	29.214(6)
α (°)	90
β (°)	90
γ (°)	90
V(Å^3)	5761(2)
Z	8
D_c (g·cm^{-3})	1.718
μ (mm^{-1})	2.283
Date collected/Unique	44954/5179
R_1, wR_2 (>2σ)	0.0332, 0.0766
GOF	0.92
Residues (e·Å^{-3})	-0.34, 0.50
Flack	0.31(2)

$w = 1/[\sigma^2(Fo^2)+(0.0076P)^2]$ where $P=(Fo^2+2Fc^2)/3$

Table S2. The comparing data of the single crystal structures after reversible experiments

	1	**1'**	**1"**
Formula	$C_{12}H_{35}Cu_3N_6O_{19.50}$	$C_8H_{10}Cu_2N_4O_6$	$C_8H_{10}Cu_2N_4O_6$
Crystal System	Tetragonal	Tetragonal	Tetragonal
Space group	$P4_32_12$ (No. 96)	$P4_2/ncm$ (No.138)	$P4_2/ncm$ (No.138)
a	14.043(3)	14.0722(3)	14.0455(1)
b	14.043(3)	14.0722(3)	14.0455(1)
c	29.214(6)	14.5000(8)	14.6075(2)
V	5761(2)	2871.39(18)	2881.71(5)
Flack	0.31(2)		

Table S3. Selected bond length (Å) around metal ions

1			
Cu(1)—N(6)	2.013(4)	Cu(1)—N(3)	2.017(4)
Cu(1)—O(5)	2.037(4)	Cu(1)—O(4)	2.045(4)
Cu(1)—O(6)	2.351(4)	Cu(1)—O(3)	2.358(4)
Cu(2)—O(8)	1.971(4)	Cu(2)—O(7)	1.968(4)
Cu(2)—N(4)^{i}	1.968(4)	Cu(2)—N(1)^{ii}	1.994(4)
Cu(2)—O(9)	2.342(3)	Cu(3)—O(1)	1.950(4)
Cu(3)—N(2)^{iii}	1.976(4)	Cu(3)—O(2)	1.984(4)
Cu(3)—N(5)^{iv}	1.997(4)	Cu(3)—O(9)^{v}	2.424(4)
Symmetry codes: (i) $-y+1/2$, $x-1/2$, $z-1/4$; (ii) $-x+3/2$, $y-1/2$, $-z+7/4$; (iii) $y+1/2$, $-x+3/2$, $z+1/4$; (iv) $x+1/2$, $-y+1/2$, $-z+9/4$; (v) $y+1$, x, $-z+2$			
1’			
Cu(1)—N(2)	2.011(6)	Cu(2)—N(1)	1.965(4)
Cu(1)—O(2)	2.187(5)	Cu(2)—O(1)	1.971(4)
Cu(2)—O(3)	2.426(7)		
1’’			
Cu(1)—N(2)	2.017(5)	Cu(2)—N(1)	1.973(4)
Cu(1)—O(2)	2.189(3)	Cu(2)—O(1)	1.976(3)
Cu(2)—O(3)	2.386(5)		

Figure S1. Single molecular structure of **1** (Symmetry codes: A: 3/2-x, 1/2+y, 7/4-z; B: 3/2-y, -1/2+x, -1/4+z; C: 1/2+y, 1/2-x, 1/4+z ; D: -1/2+x, 1/2-y, 5/4-z; E: 3/2-x, -1/2+y, 7/4-z; F: 1/2-y, -1/2+x, -1/4+z; G: 1+y, x, 2-z; H: 1/2+y, 3/2-x, 1/4+z; I: 1/2+x, 1/2-y, 5/4-z)

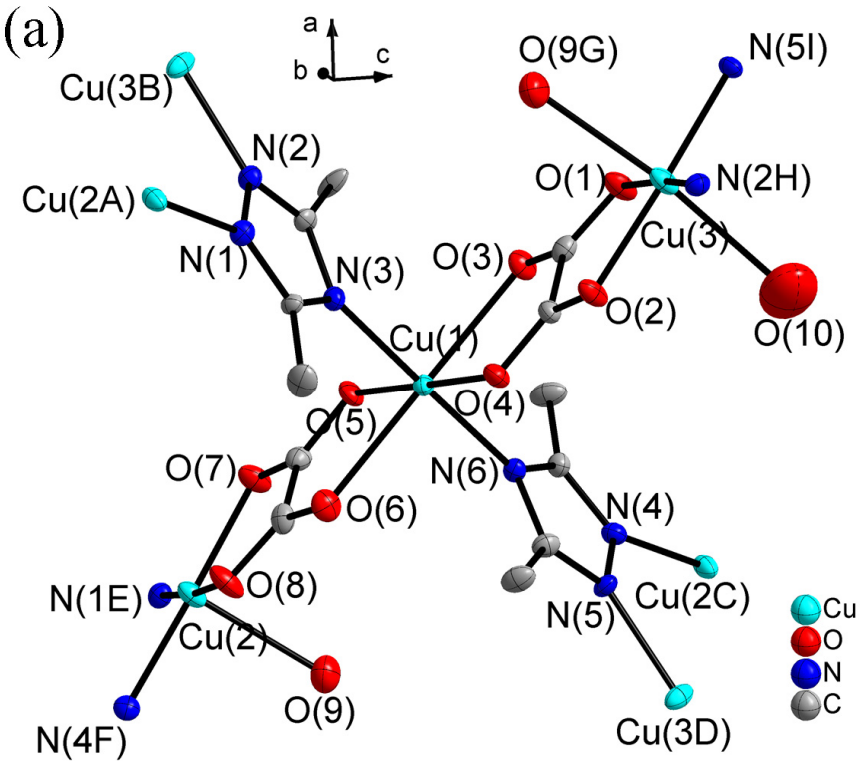


Figure S2. (a) Molecular structure of **1'** showing with 30% ellipticity (Symmetry codes: A: y, x, z; B:1/2-x, 1/2-y, z; C:1/2-y, 1/2-x, z; D: 1-x, 1-y, 1-z; E: 1-y, 1-x, 1-z)

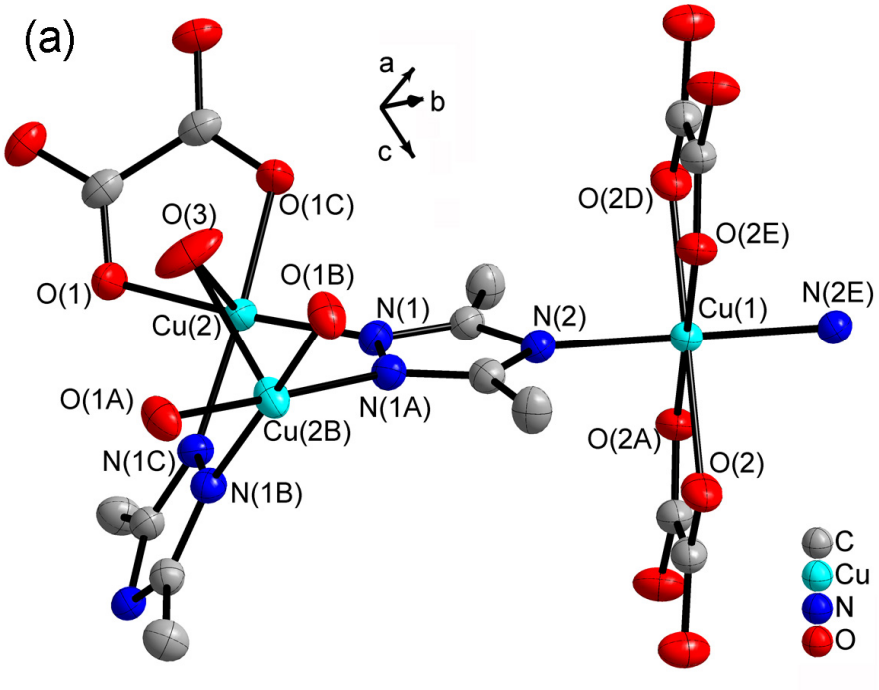


Figure S3. Optical pictures of color change from **1** to **1'** (*a*, crystal samples, *b* the powder samples)

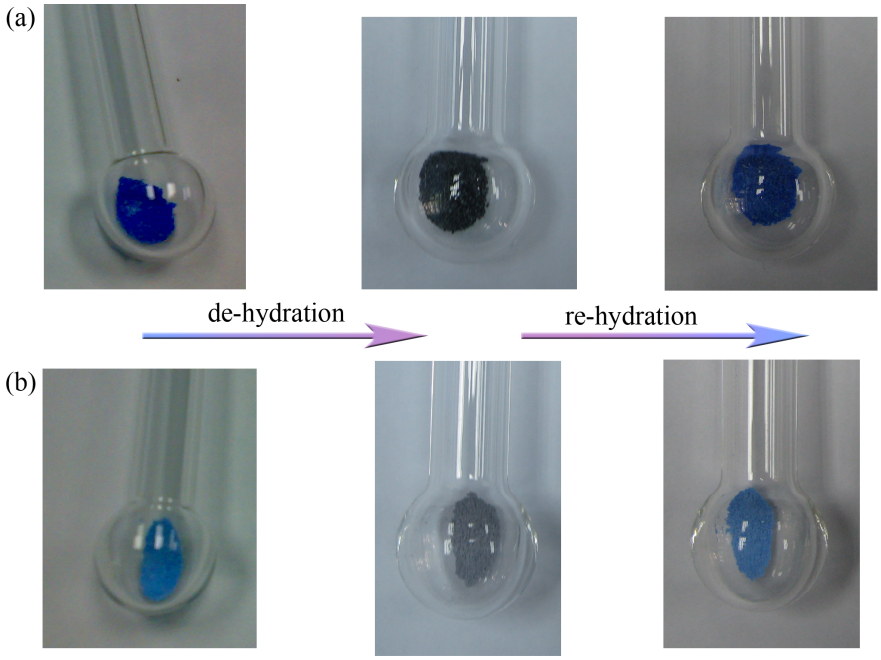


Figure S4. The N_2 sorption isortherm at 77 K

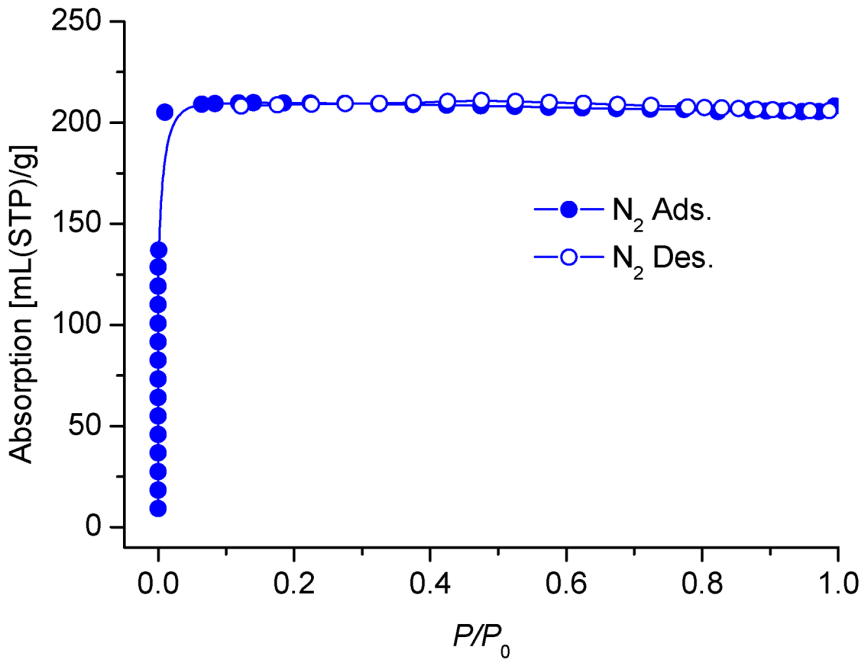
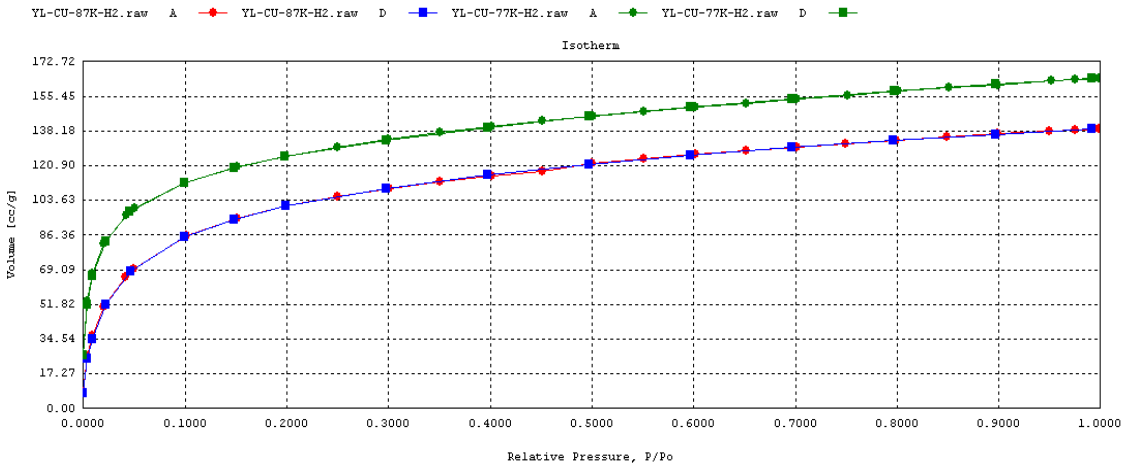


Figure S5. The H_2 sorption isortherm at 77K and 87 K



H_2 uptakes				
Gravimetric (mg/g)		Volumetric (g/L)		Qst
77K	87K	77K	87K	(kJ/mol@wt%)
14.8 (1.48%)	12.6 (1.26%)	19.2	16.3	8.25-6.06 @0.22-1.2

Figure S6. The PXRD data of as-made **1** and de-hydrated sample **1a** comparing with that of simulated data.

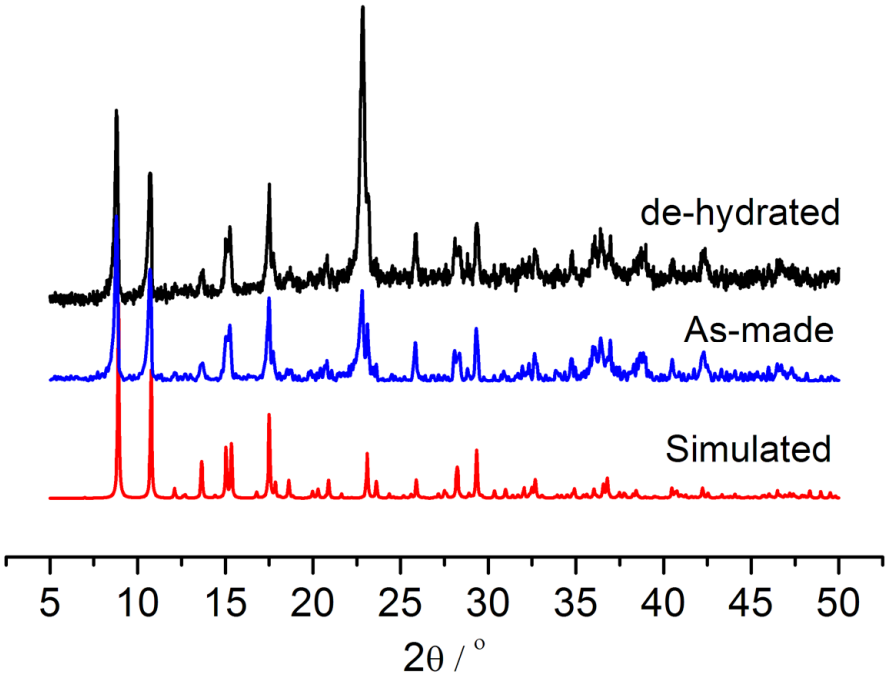


Figure S7. The PXRD data before sorption (blue) and after sorption (green) comparing with the simulated data (pink)

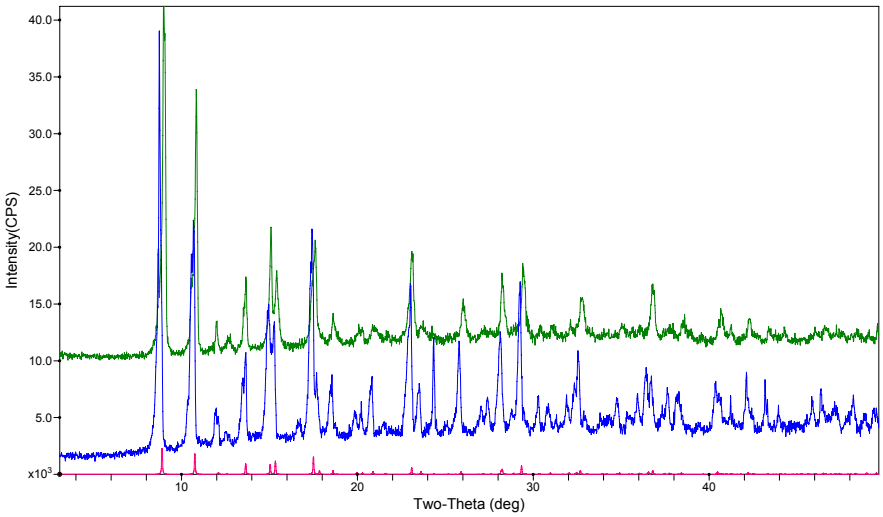


Figure S8. The TGA data of **1.**

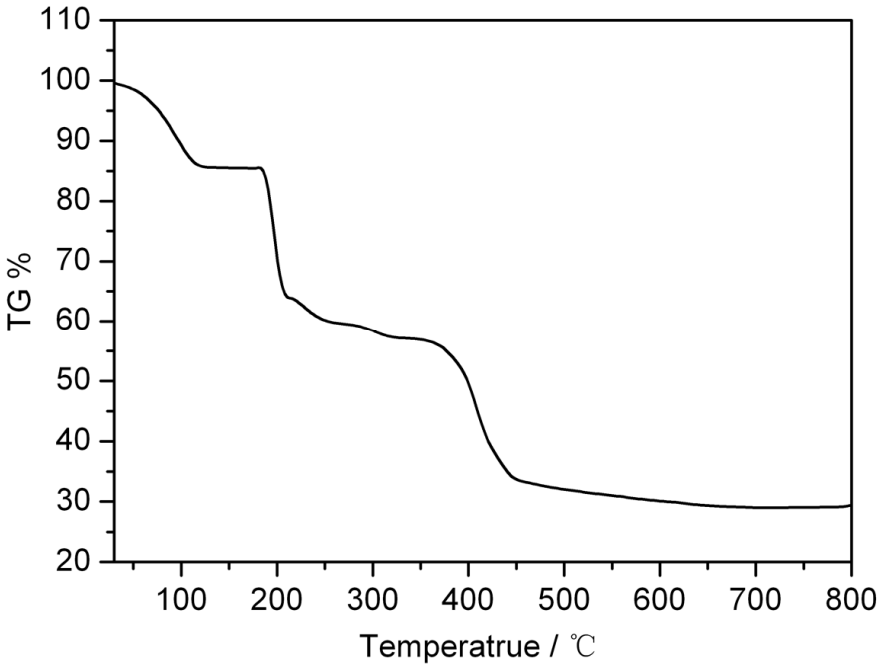


Figure S9. Plot of $\chi_M T$ *vs.* T for **1**