Supporting Information

Highly Rigid and Stable Porous Cu(I) Metal-Organic Framework with Reversible Single-Crystal-to-Single-Crystal Structural Transformation

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Experimental

Materials: All the reagents and solvents employed were commercially available and used as supplied without further purification. $Cu(NO_3)_2{\cdot}2.5H_2O$, 2,3-dihyroxyfumaric acid, 2,3-pyrazinedicarboxylic acid, were obtained from Aldrich Chemical Company.

Physical measurements:

The elemental analyses were carried out by a Perkin Elmer 2400 CHN analyzer. IR spectra were recorded on a Bruker IFS 66v/S spectrophotometer with sample prepared in KBr pellet in the region 4000-400 cm^{-1}. X-ray powder diffraction (PXRD) pattern were recorded on a Bruker D8 Discover instrument using Cu-Kα radiation.

Adsorption measurements

Gas Adsorption: N_2 at 77 K and CO_2 at 195 K adsorption studies with the dehydrated sample of **1** were carried out using QUANTACHROME QUADRASORB-*SI* analyzer. In the sample tube about 100 -120 mg sample was placed which had been prepared at 413 K under a dynamic vacuum (10^{-1} pa) for about 12 h prior to the measurement of the isotherms. Helium gas (99.999% purity) at a certain pressure was introduced in the gas chamber and allowed to diffuse into the sample chamber by opening the valve. The amount of gas was adsorbed was readily calculated from the pressure difference (P_{cal}-P_e), where P_{calc} is the calculated pressure

with no gas adsorption and P_e is the observed equilibrium pressure. All operations were computer controlled and automatic.

Vapour Adsorption: The adsorption isotherms of different solvents (H_2O, CH_3CN, EtOH, at 298 K and MeOH at 293 K) were measured in the vapor state by using BELSORP-aqua-3 volumetric adsorption instrument from BEL, Japan. In the sample chamber (~12 mL) maintained at $T \pm 0.03$ K was placed the adsorbent sample (~100 mg), which had been pre-treated at 413 K with vacuum level of 10^{-1} Pa for about 12 hours prior to measurement of the isotherms. The adsorbate was charged into the sample tube, and then the change in pressure was monitored and the degree of adsorption was determined by the decrease in pressure at the equilibrium state. All operations were computer-controlled and automatic.

X-ray crystallography:

Suitable single crystals of compound **1** and **1″,** were mounted on a thin glass fiber and X-ray single crystal structural data were collected on a Bruker Smart–CCD diffractometer using graphite monochromated Mo-*Kα* radiation (λ = 0.71073 Å). The programme SAINT was used for integration of diffraction profiles and absorption correction were made with SADABS programme. X-ray single crystal structural data for **1′** (455 K) was collected on Rigaku/MSc Saturn CCD diffractometer with confocal monochromated Mo-*Kα* radiation (λ = 0.71073 Å) and processed using CrystalClear programme (Rigaku). All the structures were solved by direct methods using SIR-92 and followed by successive Fourier and difference Fourier Syntheses. For all the compounds the non-hydrogen atoms were refined anisotropically except o1w of **1**. All hydrogen atoms were located by Fourier analysis. All calculations were carried out using SHELXL 97,[1] SHELXS 97,[2] PLATON 99[3]and WinGX system, ver. 1.70.01.[4] Crystal data and structure refinement parameters for **1**, **1′** and **1″** are summarized in Table 1. Selected bond distances and angles for **1**, **1′** and **1″** are given in Table S1-S3. Crystallographic refinement and cell parameters are given Table S4. X-ray

(1) G. M. Sheldrick, SHELXL 97, *Program for the Solution of Crystal Structure*, University of Gottingen, Germany, 1997.

(2) G. M. Sheldrick, SHELXS 97*, Program for the Solution of Crystal Structure*, University of Gottingen, Germany, 1997.

(3) A. L. Spek, PLATON, *Molecular Geometry Program*, University of Utrecht, The Netherlands, 1999.

(4) L. J. Farrugia, *WinGX - A Windows Program for Crystal Structure Analysis*. *J. Appl.* Crystallogr. 1999, **32**, 837

Table S1: Selected bond length and bond angles of **1.**

	Bond length(Å)		**Bond Angle (˚)**
Cu1-O1	2.194(6)	O1 -Cu1-N1	80.7(2)
Cu1-N1	1.956(5)	O2 -Cu3-O2_a	88.20(17)
Cu1-O3_d	2.096(6)	O1-Cu1-O3_d	95.4(2)
Cu1-N2_g	1.956(5)	O2 -Cu3 -O3_a	138.92(17)
Cu2-O1	2.789(5)	O1 -Cu1-N2_g	115.4(2)
Cu2 -O2	2.880(5)	O1W_a-Cu3 -O3	84.6(4)
Cu2 -O1_a	2.789(5)	O3_d-Cu1-N1	120.7(2)
Cu2-O2_a	2.880(5)	O2_a -Cu3-O3	138.92(17)
Cu2-O4_b	2.729(6)	N1 -Cu1-N2_g	140.7(3)
Cu2-O4_c	2.728(6)	O3 -Cu3-O3_a	151.02(16)
Cu3-O1W	2.95(2)	O3_d-Cu1 -N2_g	94.5(2)
Cu3-O2	2.663(5)	O1W_a-Cu3 -O2_a	111.2(4)
Cu3-O3	2.943(6)	O1W_a -Cu3-O3_a	70.4(4)
Cu3-O1W_a	2.95(2)	O1 -Cu2-O1_a	172.20(17)
Cu3-O2_a	2.663(5)	O2_a -Cu3-O3_a	66.77(16)
Cu3-O3_a	2.943(6)	O1-Cu2-O4_b	104.32(18)
		O1-Cu2 -O4_c	80.44(17)
		O1_a-Cu2 -O2	126.14(16)
		O1_a-Cu2-O4_b	80.44(18)
		O1_a -Cu2-O4_c	104.32(18)
		O4_b-Cu2-O4_c	106.6(2)
		O1W-Cu3-O2	111.2(4)
		O1W -Cu3 -O3	70.4(4)
		O1W -Cu3 -O2_a	150.6(5)
		O1W-Cu3-O3_a	84.6(4)
		O2 -Cu3-O3	66.77(16)
		O1W_a -Cu3 -O2	150.6(5)

Translation of Symmetry code to equiv. Points

a = x,y,-1/2-z, b = x,1-y,-z, c = x,1-y,-1/2+z, d =x,1-y,1/2+z, g =1/2-x,1/2+y,1/2-z

Table S2: Selected bond length and bond angles of **1′.**

	Bond length(Å)		**Bond Angle (˚)**
Cu1-O1	2.211(4)	O1 -Cu1-N1	80.67(16)
Cu1-N1	1.951(4)	O2 -Cu3-O2_a	84.46(17)
Cu1-O3_d	2.074(4)	O1-Cu1-O3_d	96.07(16)
Cu1-N2_g	1.980(5)	O2 -Cu3 -O3_a	138.08(15)
Cu2-O1	2.777(4)	O1 -Cu1-N2_g	111.27(17)
Cu2 -O1_a	2.777(4)	O3_d-Cu1-N1	124.17(17)
Cu2-O2_a	2.834(5)	O2_a -Cu3-O3	138.08(17)
Cu2-O4_b	2.692(6)	N1 -Cu1-N2_g	138.33(18)
Cu2-O4_c	2.692(6)	O3 -Cu3-O3_a	150.41(13)
Cu3-O2	2.643(5)	O2_a -Cu3-O3_a	68.54(14)
Cu3-O3	2.933(4)	O1-Cu2-O4_b	99.12(15)
Cu3-O2_a	2.643(5)	O1-Cu2 -O4_c	86.10(15)
Cu3-O3_a	2.933(4)	O1_a-Cu2 -O2	124.42(14)
		O1_a-Cu2-O4_b	86.10(15)
		O1_a -Cu2-O4_c	99.12(15)
		O4_b-Cu2-O4_c	107.80(17)
		O2 -Cu3-O3	68.54(14)

Translation of Symmetry code to equiv. Points

a = x,y,-1/2-z, b = x,1-y,-z, c = x,1-y,-1/2+z, d =x,1-y,1/2+z, g =1/2-x,1/2+y,1/2-z

Table S3: Selected bond length and bond angles of **1″.**

	Bond length(Å)		**Bond Angle (˚)**
Cu1-O1	2.195(4)	O1 -Cu1-N1	80.92(16)
Cu1-N1	1.950(5)	O2 -Cu3-O2_a	87.96(16)
Cu1-O3_d	2.081(4)	O1-Cu1-O3_d	95.39(16)
Cu1-N2_g	1.965(5)	O2 -Cu3 -O3_a	139.06(13)
Cu2-O1	2.788(4)	O1 -Cu1-N2_g	114.91(18)
Cu2 -O2	2.870(5)	O1W_a-Cu3 -O3	83.8(3)
Cu2 -O1_a	2.788(4)	O3_d-Cu1-N1	120.99(17)
Cu2-O2_a	2.870(5)	O2_a -Cu3-O3	139.06(13)
Cu2-O4_b	2.721(6)	N1 -Cu1-N2_g	140.2(2)
Cu2-O4_c	2.721(6)	O3 -Cu3-O3_a	150.91(12)
Cu3-O1W	2.930(12)	O3_d-Cu1 -N2_g	94.77(19)
Cu3-O2	2.645(5)	O1W_a-Cu3 -O2_a	111.6(3)
Cu3-O3	2.943(4)	O1W_a -Cu3-O3_a	71.2(3)
Cu3-O1W_a	2.930(12)	O1 -Cu2-O1_a	172.42(13)
Cu3-O2_a	2.645(5)	O2_a -Cu3-O3_a	66.80(12)
Cu3-O3_a	2.943(4)	O1-Cu2-O4_b	104.62(14)
		O1-Cu2 -O4_c	80.01(14)
		O1_a-Cu2 -O2	126.00(14)
		O1_a-Cu2-O4_b	80.04(14)
		O1_a -Cu2-O4_c	104.62(14)
		O4_b-Cu2-O4_c	106.20(17)
		O1W-Cu3-O2	111.6(3)
		O1W -Cu3 -O3	71.2(3)
		O1W -Cu3 -O2_a	149.7(3)
		O1W-Cu3-O3_a	83.8(3)
		O2 -Cu3-O3	66.80(12)
		O1W_a -Cu3 -O2	149.7(3)

Translation of Symmetry code to equiv. Points

a = x,y,-1/2-z, b = x,1-y,-z, c = x,1-y,-1/2+z, d =x,1-y,1/2+z, g =1/2-x,1/2+y,1/2-z

Table S4: Crystallographic cell and structure refinement parameters for as-synthesized(**1**), dehydrated (**1′**) and rehydrated (**1″**) crystals.

Parameters	**As-synthesized(1)**	**Dehydrated (1′)**	**Rehydrated (1″)**
Empirical formula	$C_6H_2Cu_2N_2O_{4.83}$	$C_6H_2Cu_2N_2O_4$	$C_6H_4Cu_2N_2O_5$
M_r	308.48	293.2	311.2
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*	*C*2/*c*
a (Å)	19.4082(4)	19.3848(4)	19.3929(10)
b (Å)	12.5929(2)	12.5209(3)	12.5914(6)
c (Å)	7.5885(2)	7.7134(2)	7.5890(3)
α (°)	90	90	90
β (°)	107.034(1)	107.822(1)	107.013(2)
γ (°)	90	90	90
V (Å ^{3})	1773.31(7)	1782.32(7)	1772.02(14)
Z	8	8	8
T (K)	293	455	293
λ (Mo K_α)	0.71073	0.71073	0.71073
D_c (g / cm^3)	2.296	2.185	2.318
μ (mm$^{-1)}$	4.794	4.758	4.800
θ_{max} (°)	26.3	31.1	26.6
F(000)	1189	1136	1200
Total data	7091	7189	7089
Data [$I>2\sigma(I)$]	1517	1785	1391
R^a	0.0695	0.0764	0.0697
$R_w{}^b$	0.1714	0.1834	0.1991
GOF	1.09	1.58	1.00

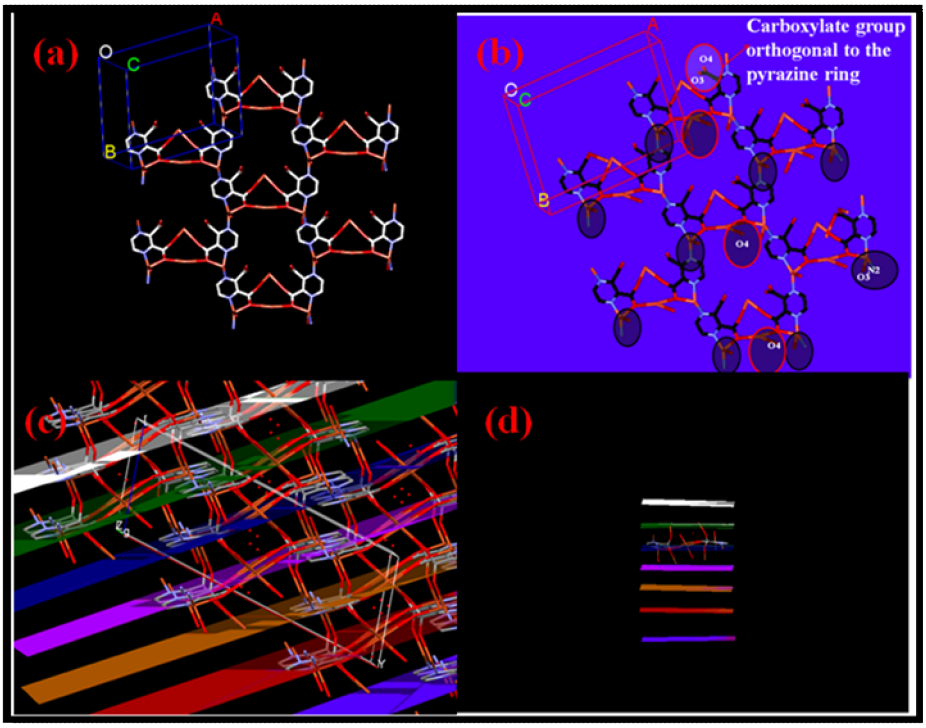

Fig S1: Formation of 3D framework structure: (a) structure of 2D sheet, (b) red and black circles are the connecting sites of two adjacent 2D sheets, (c) and (d) showing the parallel equally spaced 2D sheets.

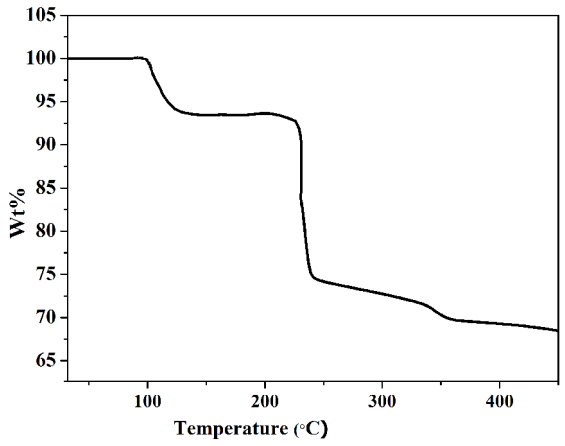

Fig. S2: TGA profile of the compound **1** in the temperature range of 30- 450 °C under N_2 atmosphere.

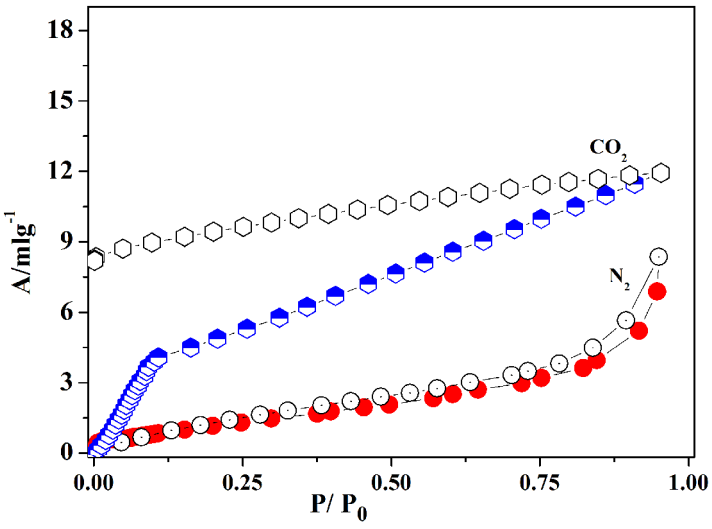

Fig. S3: N_2 (at 77K) and CO_2 (at 195K) gas sorption isotherms of the dehydrated compound **1′.**

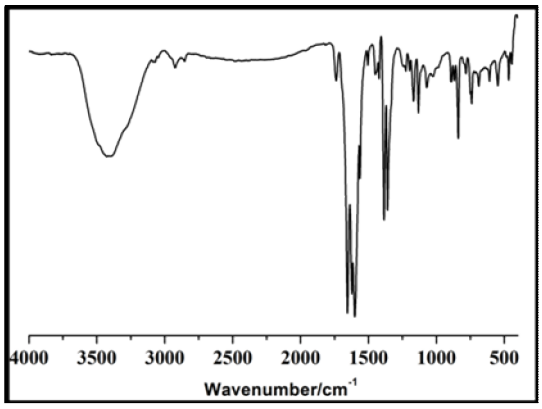

Fig. S4: IR spectrum of the as-synthesized compound **1**.