Electronic Supplementary Material (ESI) for CrystEngComm

Supporting Information for:

A Flexible Porous Metal-azolate Framework Constructed by $[Cu_3(\mu_3\text{-}OH)(\mu_2\text{-}O)(triazolate)_2]^+$ Building Blocks: Synthesis, Reversible Structural Transformation and Related Magnetic Properties

Bing Xia, Zhenxia Chen, Qingshu Zheng, Hua Zheng, Mingli Deng, Yun Ling,* Linhong Weng, Yaming Zhou*

Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Department of Chemistry,

Fudan University, Shanghai 200433, China

To whom corresponding: Dr. Y. Ling, Email: yunling@fudan.edu.cn;

Dr. Prof. Y.M. Zhou, Email: ymzhou@fudan.edu.cn

Table S1. Selected bond length (Å) and angles (°) of **1** and **2**.

1			
Cu(1)−O(1)	1.970(9)	Cu(1)−O(3)	1.961(11)
Cu(1)−O(5)	2.283(8)	Cu(1) –N(1)	1.998(8)
Cu(2)−O(1)	1.999(6)	Cu(2)−O(2)	1.948(8)
Cu(2)−O(7)	2.595(11)	Cu(2)–N(2)	1.948(8)
Cu(2)−O(6)$^{\#1}$	2.495(17)	Cu(2)−N(3)$^{\#3}$	1.980(12)
O(1)−Cu(1)−O(3)	163.2(3)	O(1)−Cu(1)−O(5)	99.1(3)
O(1)−Cu(1)−N(1)	86.8(3)	O(3)−Cu(1)−O(5)	97.8(4)
O(3)−Cu(1)−N(1)	92.9(3)	O(5)−Cu(1)−N(1)	91.1(3)
N(1)−Cu(1)−N(1)$^{\#2}$	173.4(3)	O(1)−Cu(2)−O(2)	81.6(3)
O(1)−Cu(2)−O(7)	74.5(3)	O(1)−Cu(2)−N(2)	86.5(3)
O(1)−Cu(2)−O(6)$^{\#1}$	90.0(5)	O(1)−Cu(2)−N(3)$^{\#3}$	169.4(4)
O(2)−Cu(2)−O(7)	80.9(4)	O(2)−Cu(2)−N(2)	168.1(3)
O(2)−Cu(2)−O(6)$^{\#1}$	92.5(4)	O(2)−Cu(2)−N(3)$^{\#3}$	95.8(4)
O(7)−Cu(2)−N(2)	96.4(4)	O(6)$^{\#1}$−Cu(2)−O(7)	163.9(5)
O(7)−Cu(2)−N(3)$^{\#3}$	94.9(4)	O(6)$^{\#1}$−Cu(2)−N(2)	87.0(4)
N(2)−Cu(2)−N(3)$^{\#3}$	96.0(4)	O(6)$^{\#1}$−Cu(2)−N(3)$^{\#3}$	100.4(5)
2			
Cu(1)−O(1)	1.953(7)	Cu(1)−O(3)	1.979(11)
Cu(1)−O(5)	2.266(14)	Cu(1)−N(1)	1.984(7)
Cu(2)−O(1)	1.974(7)	Cu(2)−O(2)	1.924(6)
Cu(2)−O(6)	2.438(13)	Cu(2)−N(2)	1.975(6)
Cu(2)−O(7)$^{\#1}$	2.602(12)	Cu(2)−N(3)$^{\#2}$	1.974(10)
O(1)−Cu(1)−O(3)	162.1(4)	O(1)−Cu(1)−O(5)	99.9(4)
O(1)−Cu(1)−N(1)	87.0(2)	O(3)−Cu(1)−O(5)	98.0(5)
O(3)−Cu(1)−N(1)	92.9(3)	O(3)−Cu(1)−N(1)$^{\#3}$	93.0(3)
O(5)−Cu(1)−N(1)	90.3(3)	N(1)−Cu(1)−N(1)$^{\#3}$	174.0(3)
O(1)−Cu(2)−O(2)	80.6(3)	O(1)−Cu(2)−O(6)	89.1(4)
O(1)−Cu(2)−N(2)	86.9(3)	O(1)−Cu(2)−O(7)$^{\#1}$	72.2(4)
O(1)−Cu(2)−N(3)$^{\#2}$	168.5(3)	O(2)−Cu(2)−O(6)	98.0(4)
O(2)−Cu(2)−N(2)	166.8(3)	O(2)−Cu(2)−O(7)$^{\#1}$	77.9(4)
O(2)−Cu(2)−N(3)$^{\#2}$	94.7(3)	O(6)−Cu(2)−N(2)	86.1(3)
O(6)−Cu(2)−O(7)$^{\#1}$	161.2(5)	O(6)−Cu(2)−N(3)$^{\#2}$	102.0(4)
O(7)$^{\#1}$−Cu(2)−N(2)	94.2(4)	N(2)−Cu(2)−N(3)$^{\#2}$	96.8(3)
O(7)$^{\#1}$−Cu(2)−N(3)$^{\#2}$	96.6(4)		

Symmetry codes used for **1**: #1: x,y,1+z; #2: 1-y,1-x,z; #3: 2/3-y,1/3+x-y,1/3+z

Symmetry codes used for **2**: #1: -1+x,y,z; #2: 2/3-x+y,2/3-x,-1/3+z; #3: x,1+x-y,z

Figure S1. The IR spectra of **1**, **2**, and the product obtained without DMF. (the clear peak at 1592 and 1638 cm^{-1} should be ascribed to the vibration of carboxylate group of $HCOO^-$ and CH_3COO^- respectively)

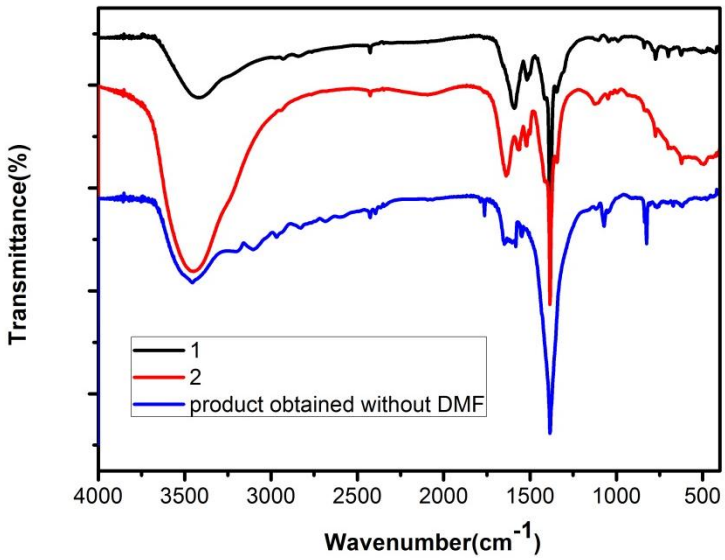


Figure S2. The PXRD patterns of as-made **1** and **2** compared with the simulated one

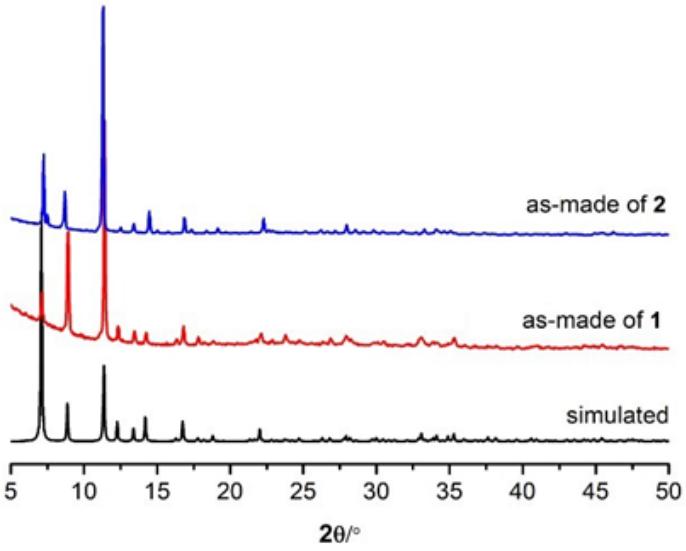


Figure S3. The PXRD patterns of the samples obtained using NaOAc or NaHCOO was used as the source of carboxylates without DMAC or DMF

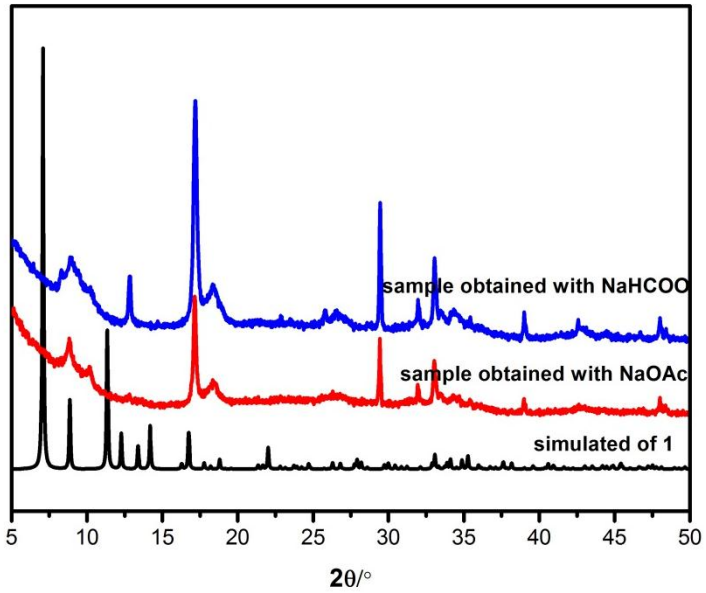


Figure S4. (a) the structural motif of **1** with atom number labeled (Symmetry code: A: 1-y,1-x, z; B: 2/3-y, 1/3+x-y, 1/3+z; C: x, y, 1+z, the hydrogen atoms and lattice water molecule are omitted for clarity)

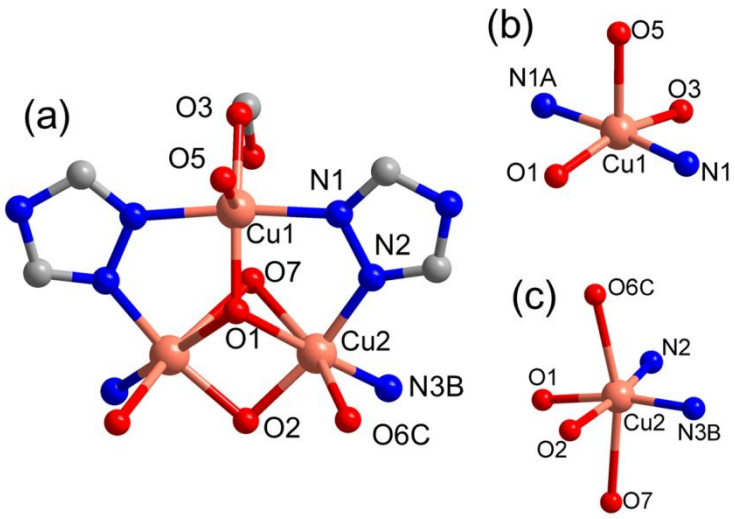


Figure S5. TGA data of **1** and **2**

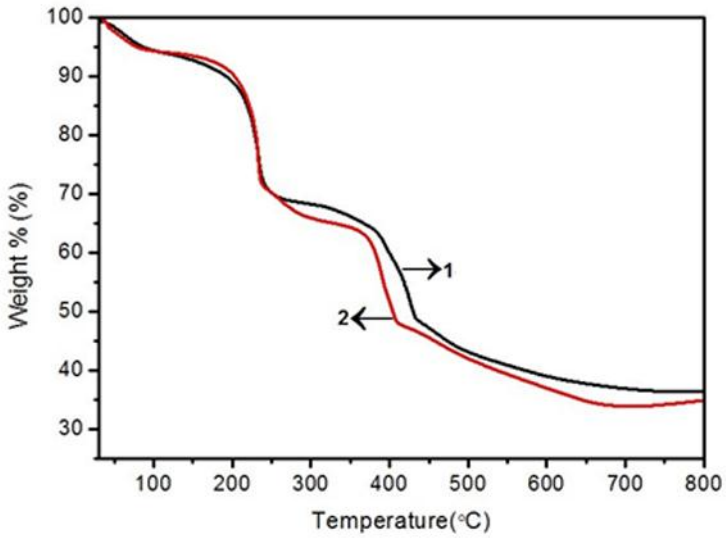


Figure S6. (a) The temperature-dependent PXRD patterns from room temperature to 200 ^{o}C; (b) the optic images of as-made sample and degased sample

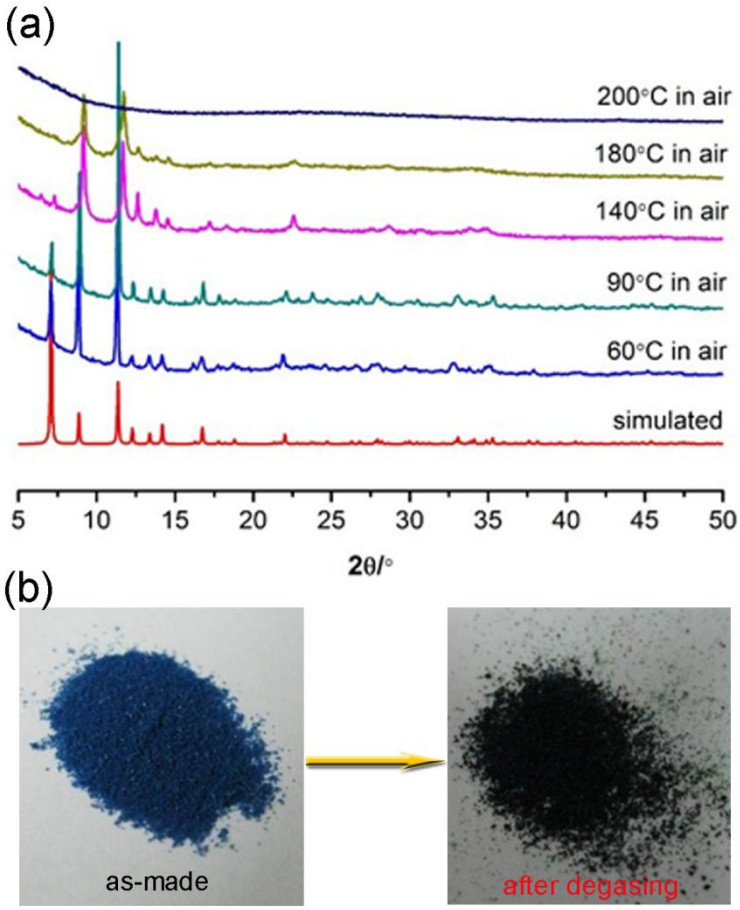


Figure S7. (a) the cleaved surface by (2, -1, 0) corresponding to the diffraction peak at 2θ = 7.08 ^{o}; (b) (2, 0, -1) corresponding to the diffraction peak at 2θ = 11.67^{o}, (c) (1, 0, 1) corresponding to the diffraction peak at 9.13 ^{o}

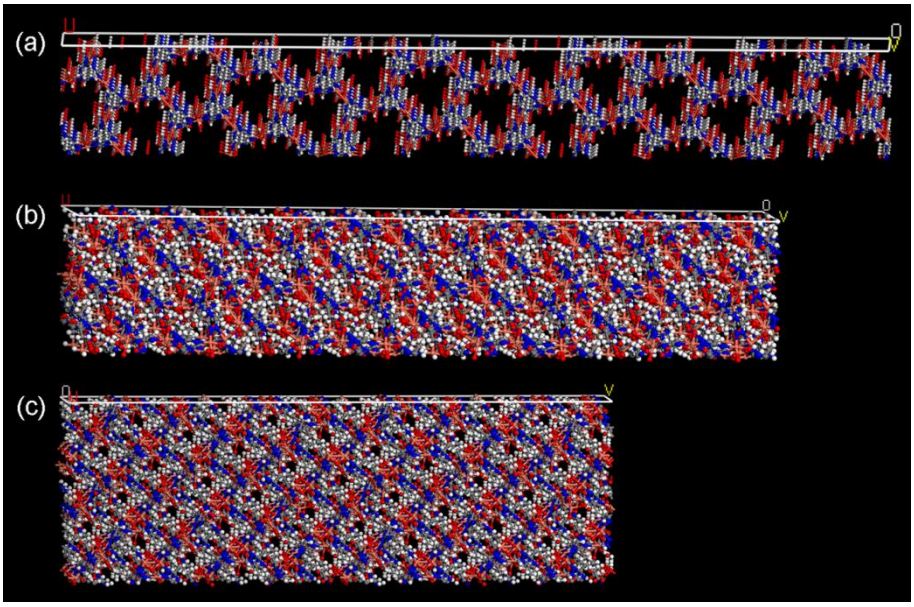
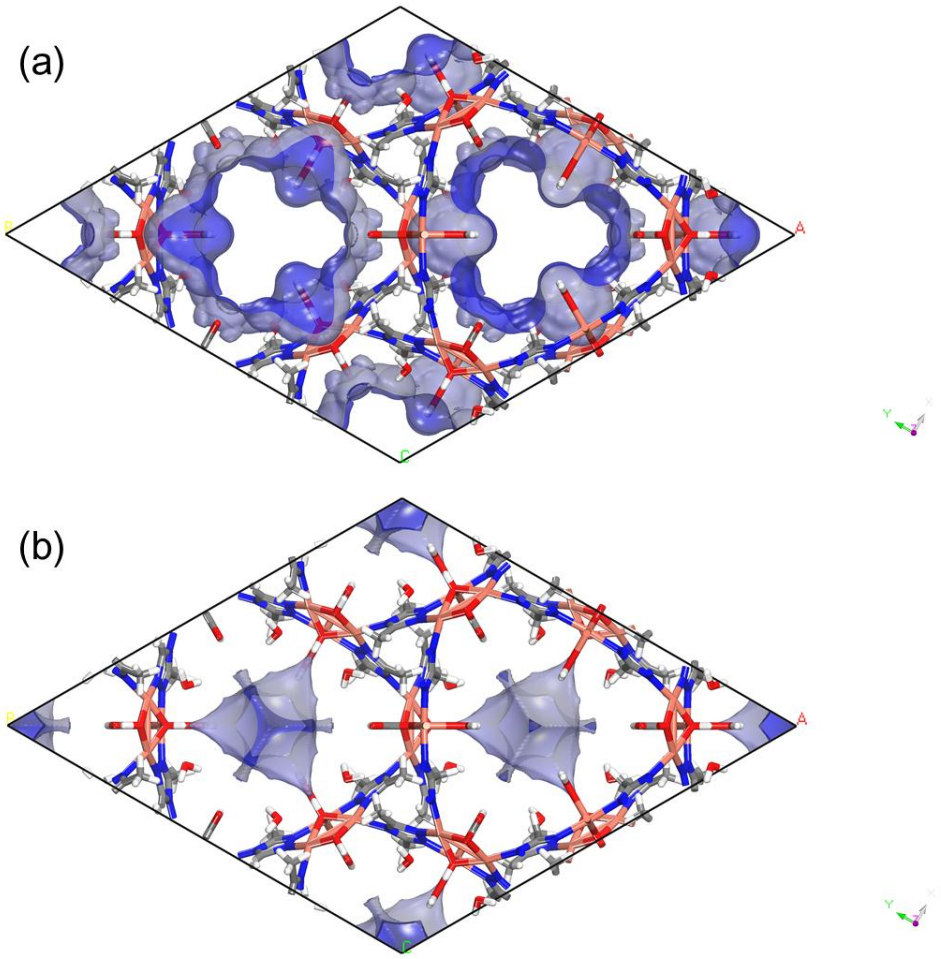


Figure S8. (a) the Connolly surface area calculated with probe atomic radii of 1.4 Å; (b) the theoretical accessible surface area calculated with the probe atomic radii of 1.84 Å.



Connolly Surface (Å^2)/cell	Accessible Solvent Surface (Å^2)/cell	Dc (g/cm^3)	Volume (Å^3)
1452.98	472.14	1.314	6059

Theoretical Surface area = A.S.S. / (Dc×Volume) × 10^4 m^2/g = 593 m^2/g

MOF-5 was calculated to be 3669.25 Å^2/cell, so theoretical surface area is 2739 m^2/g, which is similar to the experimental result.

Figure S9. (a) the high pressure CO_2 adsorption of **1** at 273 K; (b) the pore size distribution calculated wit NLDFT based on the adsorption data (For CO_2, the P_0 = 3.4851 MPa at 273 K. The six data points in the range of 0.03 ~ 0.25 were chosen for BET calculation).

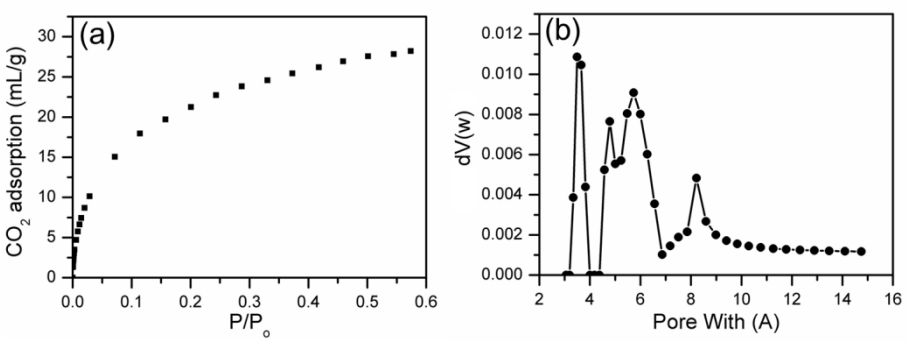


Figure S10. The χ_m^{-1} vs. T plot for as-made (a) and dehydrated (b) sample fitted by Curie–Weiss method above 120K