

Supporting Information

for

A metal-organic framework constructed by a flexible tripodal ligand and tetranuclear copper cluster for sensing small molecules

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Experimental Section

All starting materials and solvents were purchased commercially and used without purification. IR spectra were recorded in the range of 400-4000 cm⁻¹ on a Nicolet Avatar-370 spectrometer. The elemental analyses (CHN) were performed with German elemental analyzer Vario ELIII. The thermogravimetric analysis was performed with a STA409PC instrument. The X-ray powder diffraction patterns were collected by a Rigku D/max-2200. The gas adsorption were performed with an ASAP 2020. The magnetic data are measured with a Quantum Design MPMSXL SQUID (Superconducting Quantum Interference Device). Crystallographic data were collected with Bruker diffractometer.

Synthesis of **1**: An acetone solution (6 mL) containing Cu(NO₃)₂·6H₂O (0.2 mmol) was layered upon an aqueous solution (4 mL) containing H₃tci (0.1 mmol), 4,4'-bipy (0.1 mL) and triethylamine (60 μL) in test tube, then the tube was sealed and left undisturbed at room temperature. Blue block crystals of **1** were collected in two weeks and the crystals are stable in air. Yield: 40% (based on the H₃tci).

Single-crystal X-ray crystallography:

Single-crystal X-ray data was collected with a Bruker SMART Apex-II CCD diffractometer at 296(2) K by using Mo-K α radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined

by full-matrix least-squares calculations (F^2) by using the SHELXTL-97 software.¹ All non-H atoms were refined in the anisotropic approximation against F^2 for all reflections. Some disordered guest water molecules were calculated by SQUEEZE program,² and the results were attached to the CIF file. The original hkl file was replaced by hkp file resulted from SQUEEZ results and the crystal data was further refined by new HKP file. The formula of compound **1** was elucidated by single-crystal X-ray diffraction, elemental analysis and thermogravimetric analysis (TGA). Calcd for $C_{44}H_{64}N_{10}O_{31}Cu_4$ (Found): C, 35.63 (34.01); H, 4.35(4.81); N, 9.44 (8.91). The calculation results and measurement results of elemental analysis are not in good agreement, which may be due to the crystals easily lose some guest water molecules in the air. Crystallographic data of **1** is summarized in **Table S1** (CCDC: 1042356).

Table S1. Crystallographic data for **1**.

Compound	1
Molecular formula	$C_{44}H_{64}N_{10}O_{31}Cu_4$
Fw	1483.21
Temperature, T / K	296(2)
crystal system	monoclinic
space group	$C2/c$
a (Å)	22.877(3)
b (Å)	23.111(3)
c (Å)	18.364(2)
β (°)	105.399(2)
V (Å ³)	9361(2)
Z	4
D (g/cm ³)	1.053
$F(000)$	3048
μ (mm ⁻¹)	0.960
Goodness-of-fit, GOF	0.948
R_1^a , wR_2 [$I > 2\sigma(I)$]	$R_1 = 0.0540$, $wR_2 = 0.1413$
R_1^a , wR_2 (all data)	$R_1 = 0.0878$, $wR_2 = 0.1540$
$^aR_1 = \sum F_o - F_c / \sum F_o $; $wR_2 = [\sum w(F_o ^2 - F_c ^2)^2 / \sum w F_o ^2]^2$	

References: 1. G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112.

2. A. L. Spek, *J. Appl. Crystallogr.* **2003**, 36, 7.

Figure S2. Three-dimensional MOF constructed by Cu^{2+} and tci ligand, 4,4'-bpy ligands were omitted for clarity(left) and 3D porous framework of **1**(right).

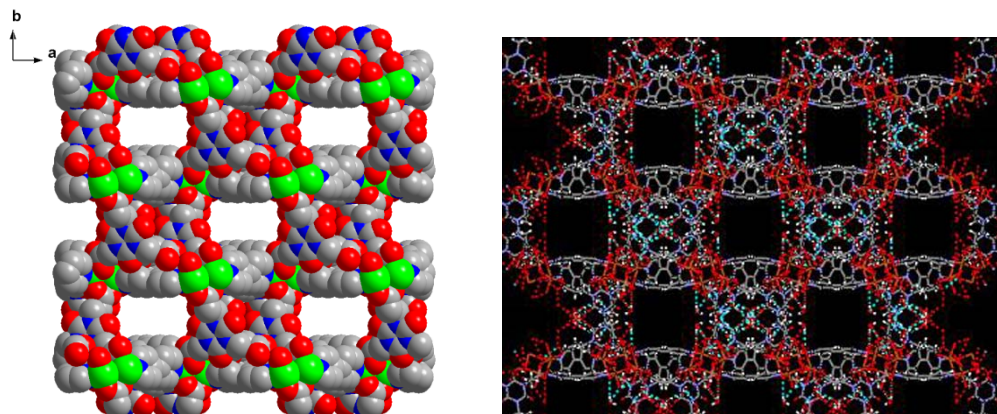


Figure S3. 3D spacefilling graph (left) and 3D hydrogen bonding network (right) of **1** along *c*-axis.

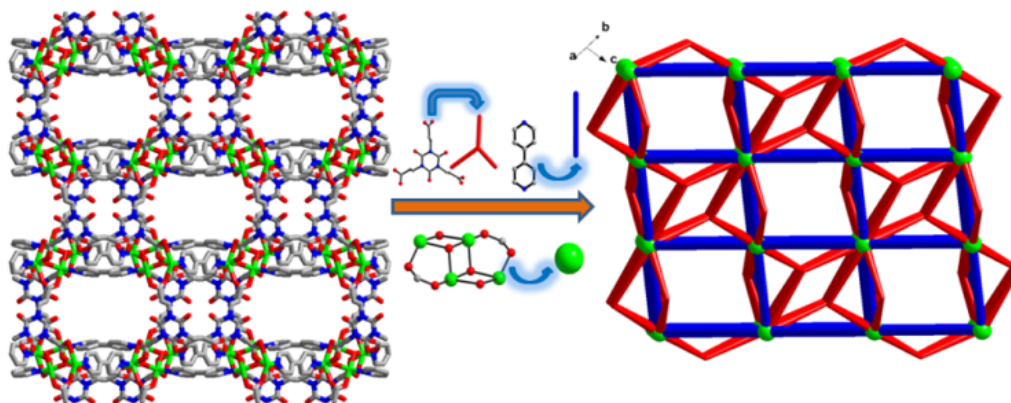


Figure S4. 3D framework (left) and 3D topological network (right) of **1**. Topological analysis exhibits **1** is a 2-nodal 3,10-connected new topology with the point symbol of $\{3\cdot4\cdot5\}_2\{3^4\cdot4^8\cdot5^{14}\cdot6^8\cdot7^9\cdot8\cdot9\}$.

$$\Delta f = \left(\frac{-2.3 \times 10^6 \times f_0^2}{A} \right) \Delta m$$

Sauerbrey's equation:

f_0 = Basic frequency (Hz)

Δf = Frequency change (Hz)

Δm = Mass change (g)

A = Surface area of the electrode (cm²)

AT cut Quartz

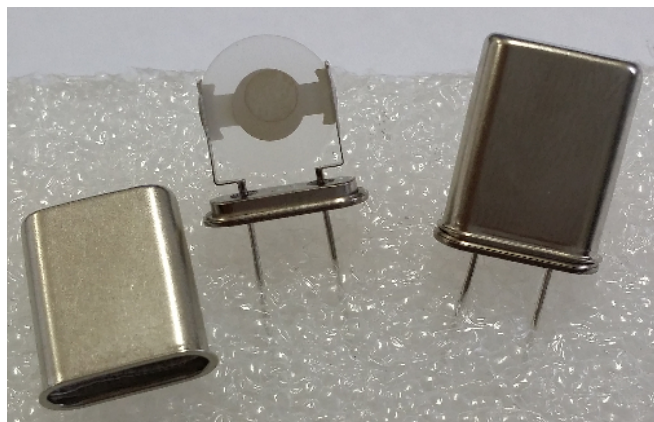
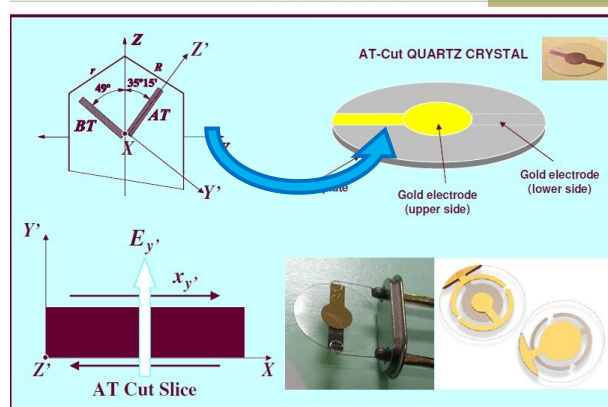


Figure S5. The complete electrode structure of QCM, the electrode in the figure is made of gold, ours is silver electrode. The up picture is coming from the internet and the below picture is our actual device.

Preparation of the QCM sensor:

1g compound **1** was placed in an acetone solution of 5ml, ultrasonic for 30min and the suspension was obtained. The suspension was dropped onto a silver electrode, dried in air, and then placed in a vacuum drying oven for 2 h at 60 °C, the as-made QCM sensor was yielded.

It should be noted that the sensing experiment was performed in air (298 K, 65 % RH), no deducting the effects of air humidity and environment. According to the response frequency values of QCM sensor to different solvent gases, the relative quantity of adsorbed molecules was got if the quantity of adsorbed water molecule was assumed to be 1, the calculation process and results were as follows:

$$\frac{\Delta f_{\text{water}}}{\Delta f_x} = \frac{\Delta m_{\text{water}}}{\Delta m_x} = \frac{n_{\text{water}} M_{\text{water}}}{n_x M_x}$$
$$\frac{n_{\text{methanol}}}{n_{\text{water}}} = \frac{\Delta f_{\text{methanol}} M_{\text{water}}}{\Delta f_{\text{water}} M_{\text{methanol}}} = 1.71$$
$$\frac{n_{\text{acetone}}}{n_{\text{water}}} = \frac{\Delta f_{\text{acetone}} M_{\text{water}}}{\Delta f_{\text{water}} M_{\text{acetone}}} = 0.98$$
$$\frac{n_{\text{benzene}}}{n_{\text{water}}} = \frac{\Delta f_{\text{benzene}} M_{\text{water}}}{\Delta f_{\text{water}} M_{\text{benzene}}} = 0.23;$$
$$\frac{n_{\text{chlorlbenzene}}}{n_{\text{water}}} = \frac{\Delta f_{\text{chlorlbenzene}} M_{\text{water}}}{\Delta f_{\text{water}} M_{\text{chlorlbenzene}}} = 0.08;$$
$$\frac{n_{\text{ethanol}}}{n_{\text{water}}} = \frac{\Delta f_{\text{ethanol}} M_{\text{water}}}{\Delta f_{\text{water}} M_{\text{ethanol}}} = 1.36$$
$$\frac{n_{\text{acetone}}}{n_{\text{water}}} = \frac{\Delta f_{\text{acetone}} M_{\text{water}}}{\Delta f_{\text{water}} M_{\text{acetone}}} = 0.79;$$
$$\frac{n_{\text{methylbenzene}}}{n_{\text{water}}} = \frac{\Delta f_{\text{methylbenzene}} M_{\text{water}}}{\Delta f_{\text{water}} M_{\text{methylbenzene}}} = 0.09;$$
$$\frac{n_{\text{ethylbenzene}}}{n_{\text{water}}} = \frac{\Delta f_{\text{ethylbenzene}} M_{\text{water}}}{\Delta f_{\text{water}} M_{\text{ethylbenzene}}} = 0.07$$

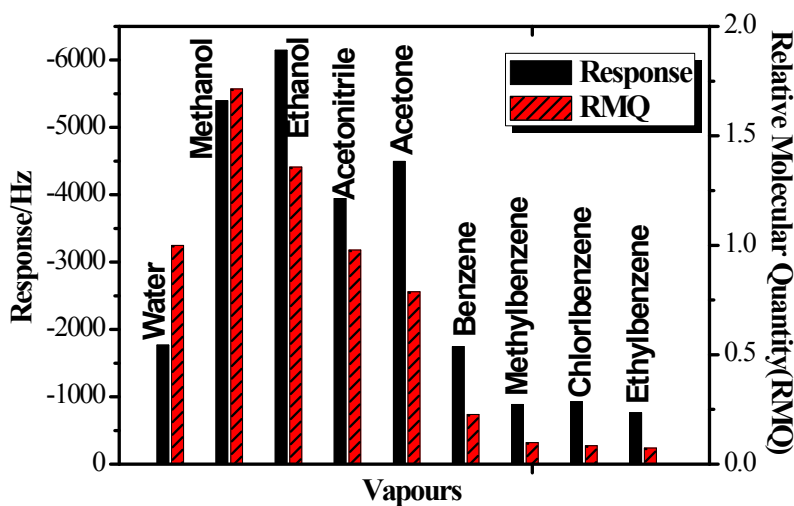


Figure S6. QCM results showing difference of various vapors.

Vapor sorption and QCM results indicate the significantly different sorption capacities between polar small molecules and benzene and its derivatives, which mainly caused by oxygen-rich pore surface characteristics and size effect. The strong H-bond interactions could generate between small polar molecules and pore surface, while benzene could not. In addition, although the compound has

large channels, the actual void space is much smaller due to 3D interweaving channels, which resulted in small polar molecules could easily enter into the pores, and benzene and its derivatives with larger size are less accessible.

N₂ sorption:

The pore characteristic of **1** was characterized by N₂ adsorption at 77K. The BET surface area of **1** is 87.31 m²/g, which is much lower. However, the porosity of **1** can be still confirmed.

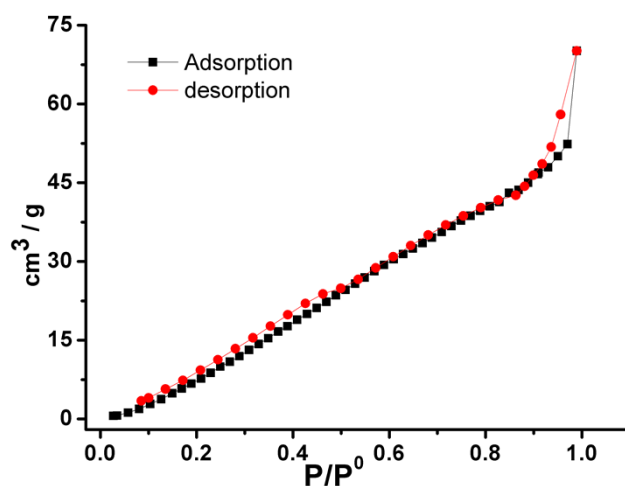


Figure S7. N₂ adsorption and desorption isotherms for **1** at 77 K.

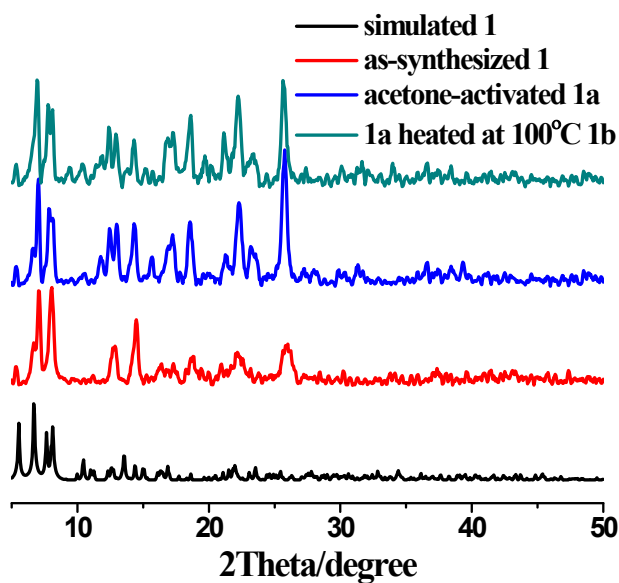


Figure S8. PXRD patterns of simulated **1**, as-synthesized **1**, acetone-activated sample **1a** and acetone-activated sample (**1a**) was heated under 100 °C for 10 hours **1b**.

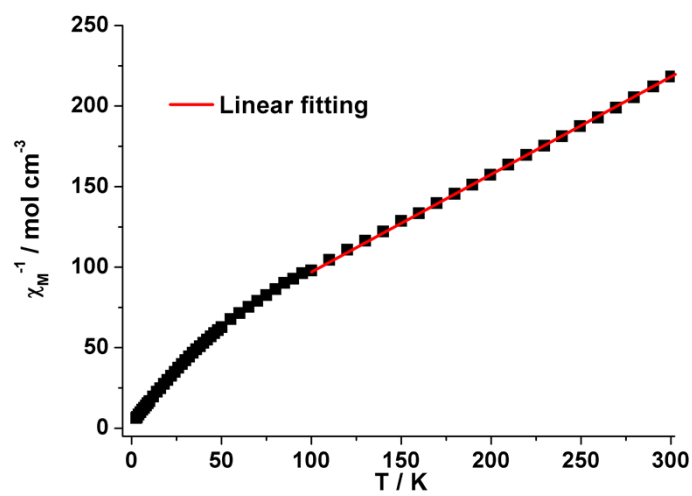


Figure S9. $\chi_M^{-1} - T$ curve of **1**. The solid line represents the best fit to Curie-Weiss law.

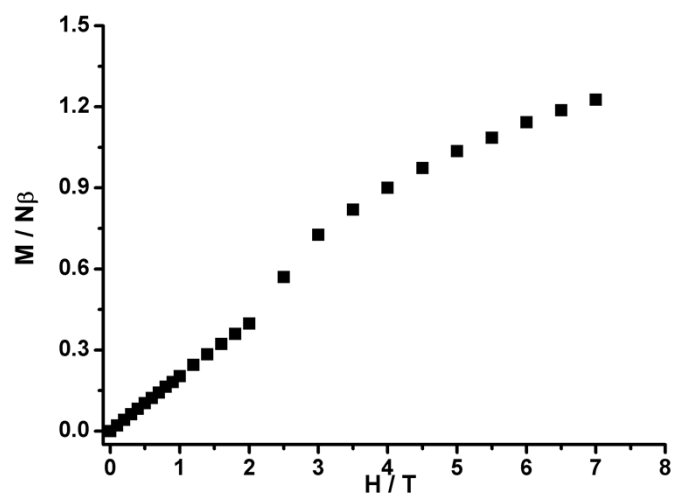


Figure S10. Field-dependent magnetizations of as-synthesized **1**.

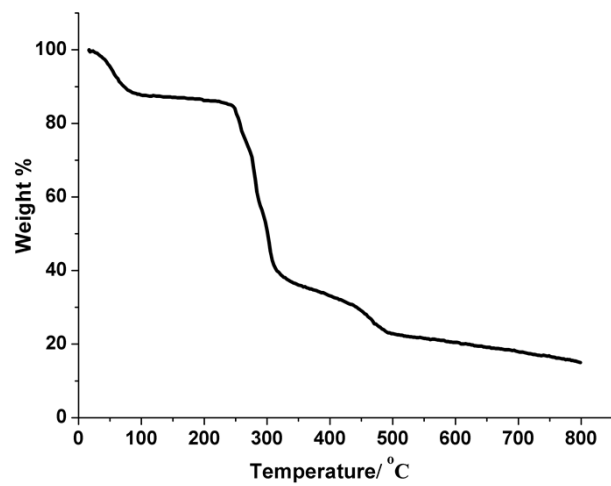


Figure S11. TG curve of as-synthesized **1**.

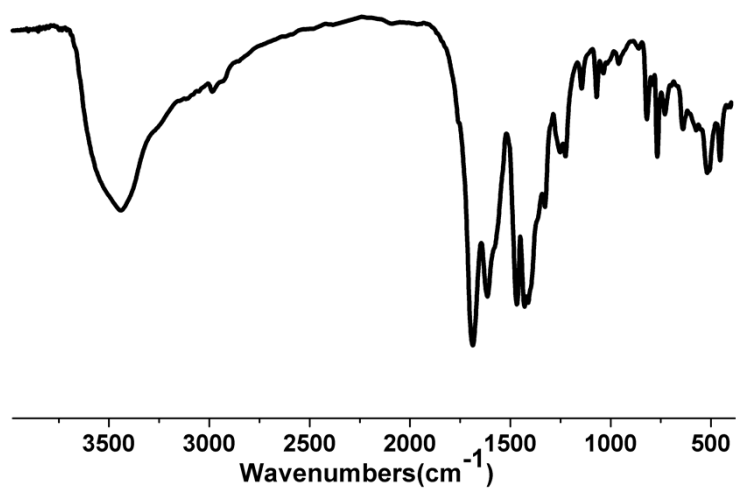


Figure S12. Infrared spectra curve of as-synthesized **1**.