

## **Designed assembly of heterometallic zeolite-like framework materials from two different supertetrahedral metal clusters**

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### **This file includes:**

<b>Section S1</b> Experimental Section	S2-S3
<b>Section S2</b> Additional Tables	S4-S4
<b>Section S3</b> Additional Figures	S5-S9
<b>Section S4</b> References	S10

## Section S1 Experimental Section

**Materials and Instruments:** All the reactants and solvents were obtained from commercial sources and used for reactions without further purification. The H<sub>3</sub>L ligand was synthesized according to literature procedure.<sup>[1]</sup> X-ray photoelectron spectroscopy (XPS) was carried out on an ESCALAB 250 spectrometer with an Al-K $\alpha$  (1486.6 eV) achromatic X-ray source. Powder XRD patterns were obtained using a RIGAKU-Miniflex II diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ). IR spectra were recorded on PerkinElmer Spectrum One FT-IR infrared spectrophotometer with pressed KBr pellets in the range of 4000-400 cm<sup>-1</sup>. The UV-Vis spectra were measured at room temperature using a Perkin-Elmer Lambda 900 Uv-vis spectrophotometer equipped with an integrating sphere attachment and BaSO<sub>4</sub> as reference.

**Gas adsorption measurement:** N<sub>2</sub> and CO<sub>2</sub> adsorption isotherm were recorded in the ASAP (Accelerated Surface Area and Porosimetry) 2020 System.

**Proton-conducting measurement:** Proton-conducting measurement: Ac impedance measurements were carried out with a SI 1260 IMPEDANCE/GAINPHASE analyzer over the frequency range from 0.1 Hz to 5 MHz with an applied voltage of 50 mV. The relative humidity was controlled by a STIKCorp CIHI-150BS3 incubator. The samples were pressed to form a cylindrical pellet of crystalline powder sample (~1 mm thickness  $\times$  5 mm  $\phi$ ) coated with C-pressed electrodes. Two silver electrodes were attached to both sides of pellet to form four end terminals (quasi-four-probe method). The bulk conductivity was estimated by semicircle fittings of Nyquist plots.

**Synthesis of Compound 1:** Co(Ac)<sub>2</sub>·2H<sub>2</sub>O (0.11 mmol, 27 mg), CuI (0.13 mmol, 25 mg), CH<sub>3</sub>COONa (0.10 mmol, 8 mg), H<sub>3</sub>L (0.10 mmol, 18 mg), N-Methylformamide (NMF, 5 mL) and ethyl alcohol (EtOH, 1 mL) were placed in a 25 mL Teflon-lined stainless steel container, which was sealed and heated to 100 °C for 72 h and then cooled to room temperature. Large pure green blocklike crystals were obtained after cooling to room temperature. Yield: about 30mg (38.85 % based on CuI). IR (KBr pellet,  $\nu/\text{cm}^{-1}$ , Fig. S12): 3283(w), 2929(w), 2864(w), 1655(vs), 1549(m), 1407(m), 1377(vs), 1238(w), 1145(w), 1084(vs), 930(m), 822(m), 788(s), 670(m), 564(m), 527(w).

**Synthesis of Compound 2:** Co(Ac)<sub>2</sub>·2H<sub>2</sub>O (0.10 mmol, 25 mg), CuI (0.26 mmol, 50 mg), CH<sub>3</sub>COONa (0.30 mmol, 24 mg), H<sub>3</sub>L (0.10 mmol, 18 mg), N,N-Dimethylformamide (DMF, 5 mL) and ethyl alcohol (EtOH, 1.5 mL) were placed in a 25 mL Teflon-lined stainless steel container, which was sealed and heated to 100 °C for 72 h and then cooled to room temperature. Large pure green blocklike crystals were obtained after cooling to room temperature. Yield: about 35mg (23.14 % based on CuI). IR (KBr pellet,  $\nu/\text{cm}^{-1}$ , Fig. S12): 3321(W), 2919(w), 2859(w), 1551(vs), 1403(vs), 1334(w), 1234(w), 1077(vs), 931(vs), 812(m), 6787(m), 585(m), 552(w).

**Single-crystal structure analysis:** Single-crystal X-ray diffraction data of **1** and **2** was collected on a Bruker Apex Duo CCD diffractometer with a graphite-monochromatized Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) operating at 150 K. The structures of **1** and **2** were solved through a direct method and refined by full-matrix least-squares refinements based on  $F^2$  adopting the SHELX-2018 program package. All non-H atoms were located with successive difference Fourier syntheses and refined anisotropically. The H atoms of the free water molecules and coordinated water molecules were not included in the final refinement. The residual electron density that could not sensibly be modeled as solvents were removed via application of the SQUEEZE function in PLATON. Due to the porous characteristic of the two framework, the charge balancing anions and guest solvent molecules in **1** and **2** cannot be mapped by single crystal X-ray diffraction structural analysis, which is common in porous crystalline materials.<sup>[2]</sup> Crystallographic data and structure refinements for **1** and **2** are summarized in Table S1. CCDC 2063858 and 2063859 contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

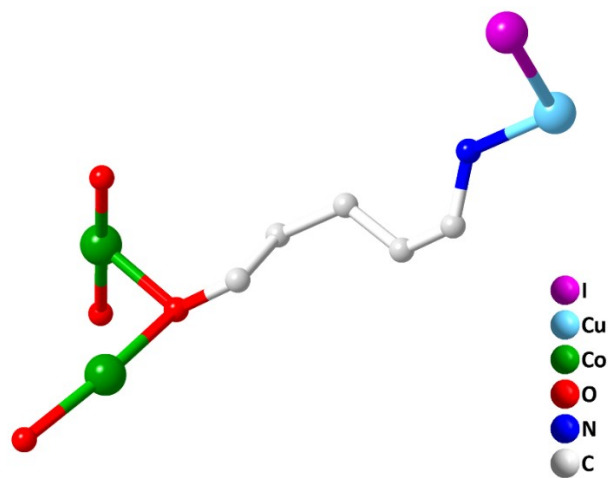
## Section S2 Additional Tables

**Table S1** Crystal Data and Structure Refinements for **1** and **2**

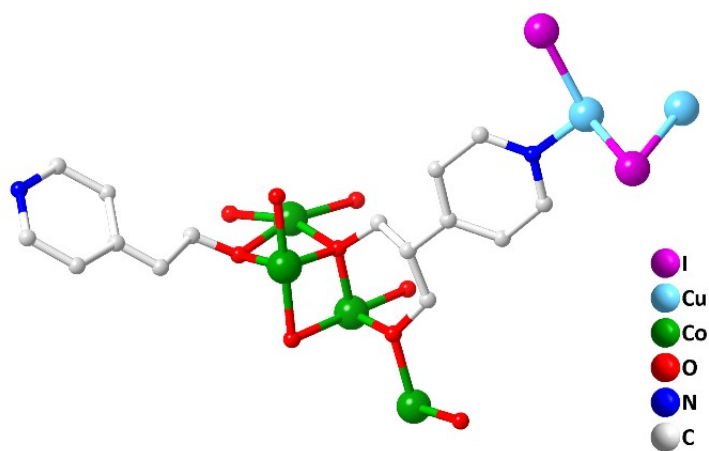
	<b>1</b>	<b>2</b>
Empirical formula	C <sub>36</sub> H <sub>40</sub> Co <sub>10</sub> Cu <sub>4</sub> N <sub>4</sub> I <sub>4</sub> O <sub>31</sub>	C <sub>36</sub> H <sub>40</sub> Co <sub>10</sub> Cu <sub>4</sub> N <sub>4</sub> I <sub>4</sub> O <sub>31</sub>
Formula weight	2375.78	2327.65
Crystal system	Cubic	Hexagonal
Space group	<i>F3m</i>	<i>P6<sub>3</sub>mc</i>
<i>a</i> (Å)	27.880(14)	19.6109(12)
<i>b</i> (Å)	27.880(14)	19.6109(12)
<i>c</i> (Å)	27.880(14)	31.970(4)
<i>V</i> (Å <sup>3</sup> )	21672(33)	10647.9(18)
<i>Z</i>	4	2
<i>F</i> (000)	4520	2260
crystal size / mm	0.18 x 0.15 x 0.1	0.15 × 0.16 × 0.18
$\vartheta$ range / °	1.461 to 23.197	2.482 to 25.058
	-30 ≤ <i>h</i> ≤ 25	-23 ≤ <i>h</i> ≤ 2 <sub>1</sub>
limiting indices	-22 ≤ <i>k</i> ≤ 20	-23 ≤ <i>k</i> ≤ 23
	-30 ≤ <i>l</i> ≤ 28	-38 ≤ <i>l</i> ≤ 36
$\rho_{calcd}$ (g cm <sup>-3</sup> )	0.728	0.741
Temperature (K)	150(2)	150(2)
$\mu$ (mm <sup>-1</sup> )	1.721	1.752
Refl. Collected	12626	48672
Independent refl.	1563	6867
Parameters	59	193
<i>R</i> <sub>int</sub>	0.0681	0.0475
GOF on <i>F</i> <sup>2</sup>	1.161	0.959
Final <i>R</i> indices ( <i>I</i> = 2σ( <i>I</i> ))	<i>R</i> <sub>1</sub> = 0.0825, <i>wR</i> <sub>2</sub> = 0.2468	<i>R</i> <sub>1</sub> = 0.0543, <i>wR</i> <sub>2</sub> = 0.1474
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.1038, <i>wR</i> <sub>2</sub> = 0.2726	<i>R</i> <sub>1</sub> = 0.0764, <i>wR</i> <sub>2</sub> = 0.1645

<sup>a</sup>*R*<sub>1</sub> = Σ ||*F*<sub>o</sub>| - |*F*<sub>c</sub>|| / Σ |*F*<sub>o</sub>|, <sup>b</sup>*wR*<sub>2</sub> = [Σ*w*(*F*<sub>o</sub><sup>2</sup> - *F*<sub>c</sub><sup>2</sup>)<sup>2</sup> / Σ*w*(*F*<sub>o</sub><sup>2</sup>)<sup>2</sup>]<sup>1/2</sup>, *w* = 1/[σ<sup>2</sup>(*F*<sub>o</sub><sup>2</sup>) + (*xP*)<sup>2</sup> + *yP*], *P* = (*F*<sub>o</sub><sup>2</sup> + 2*F*<sub>c</sub><sup>2</sup>)/3, where *x* = 0.189, *y* = 0 for **1**; *x* = 0.1144, *y* = 0 for **2**.

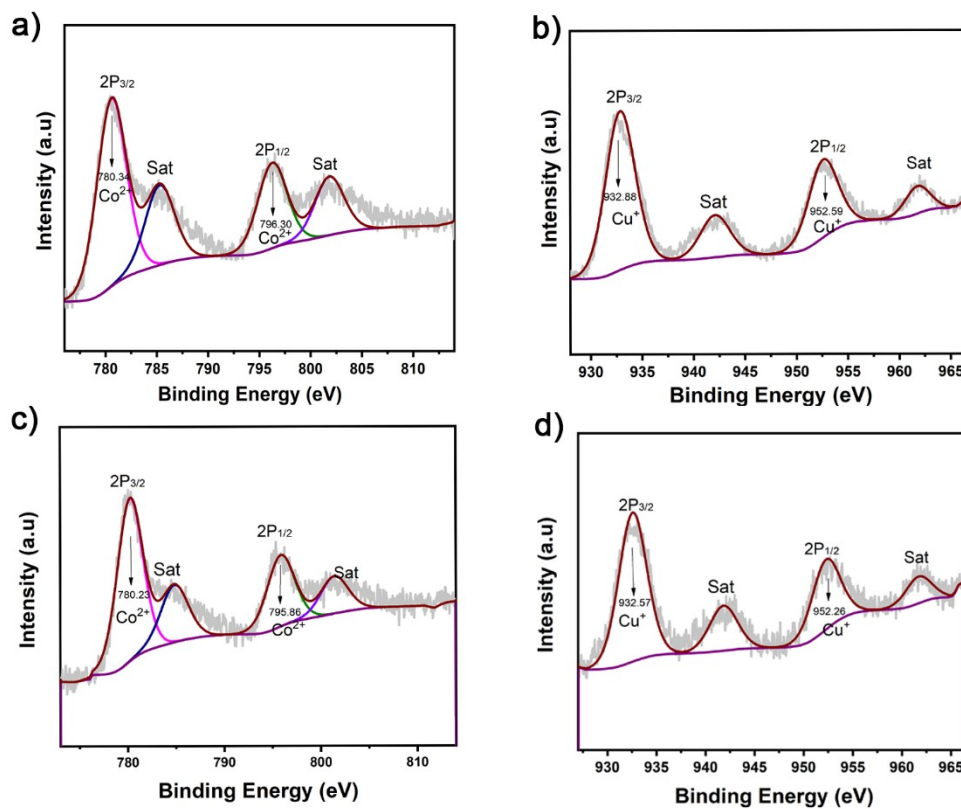
### Section S3 Additional Figures



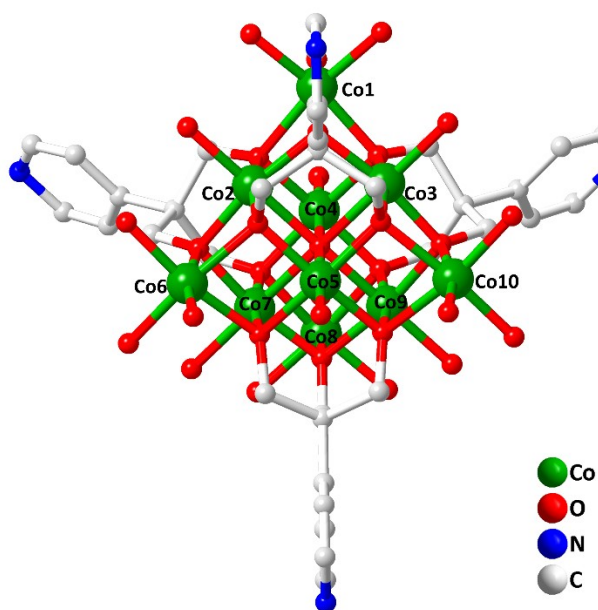
**Fig. S1.** The asymmetric unit of compound 1.



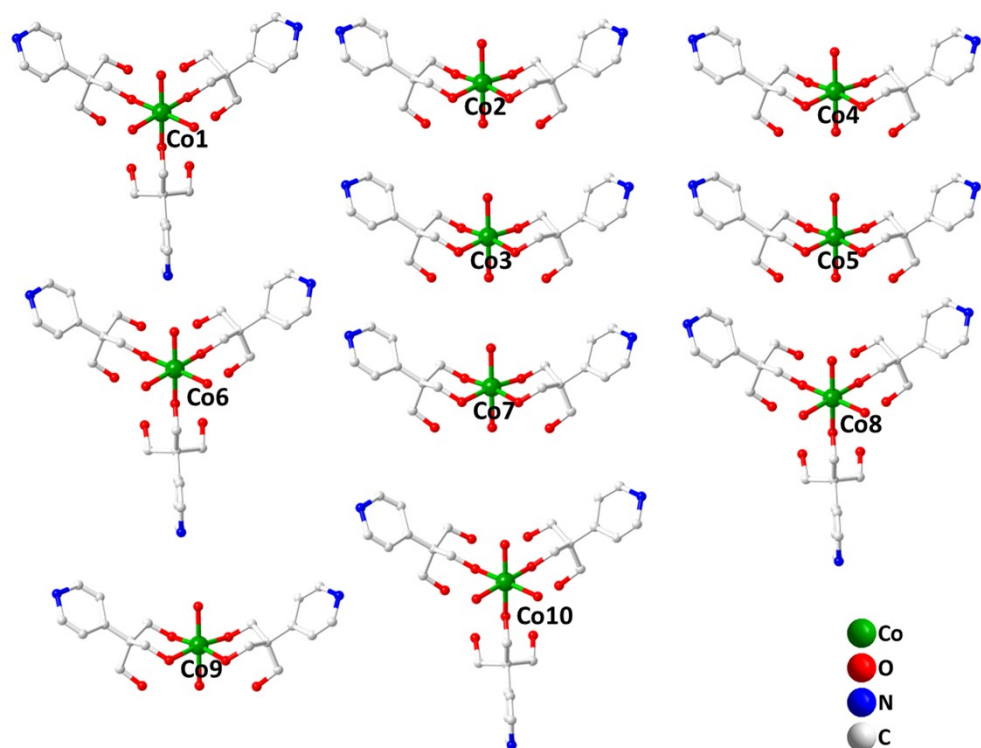
**Fig. S2.** The asymmetric unit of compound 2.



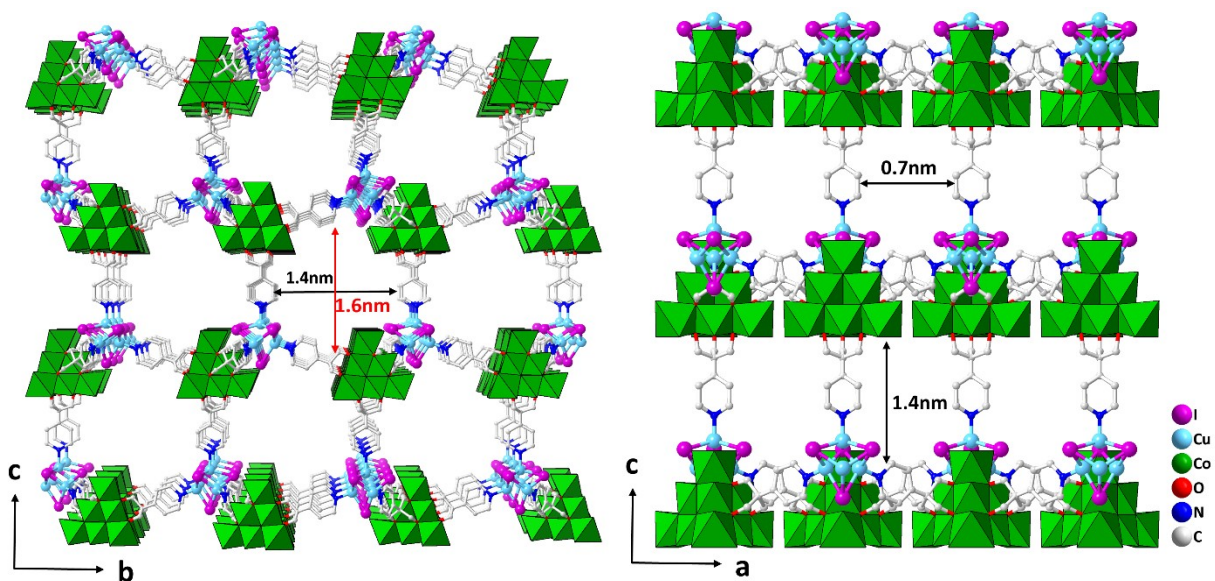
**Fig. S3.** a) Co XPS spectrum of **1**. b) Cu XPS spectrum of **1**. c) Co XPS spectrum of **2**. d) Cu XPS spectrum of **2**.



**Fig. S4.** Ball and stick mode of the  $Co_{10}$  cluster



**Fig. S5.** View of the coordination environments of  $\text{Co}^{2+}$  ions, all hydrogen atoms are omitted for clarity.



**Fig. S6.** View of the 3D framework structure of compound 2 along a axis and b axis.

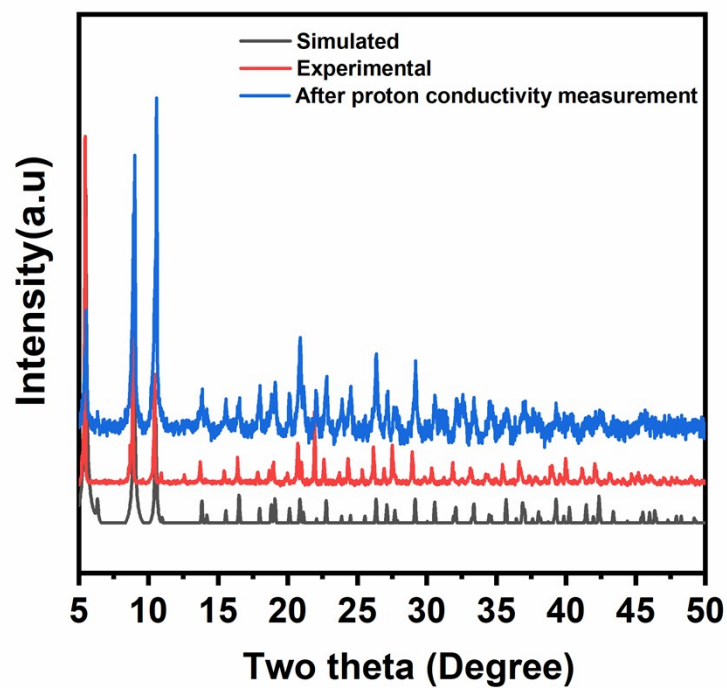
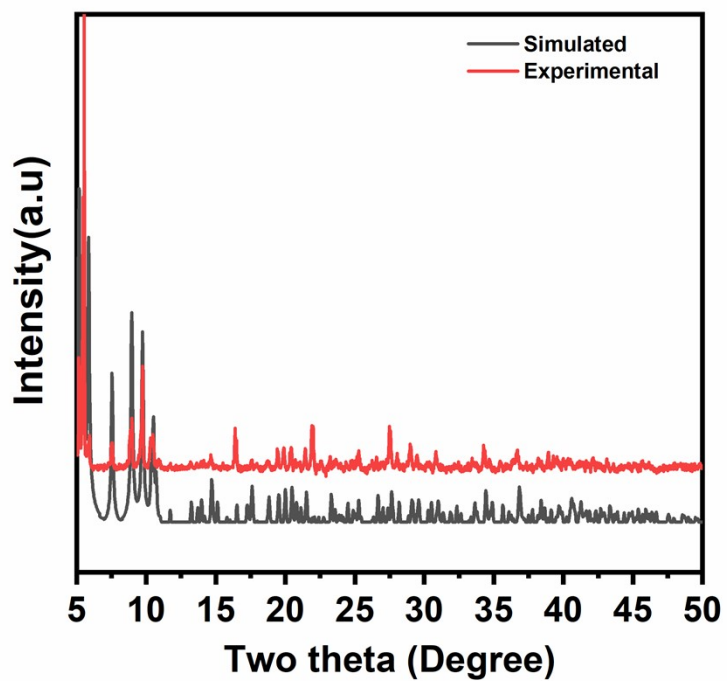
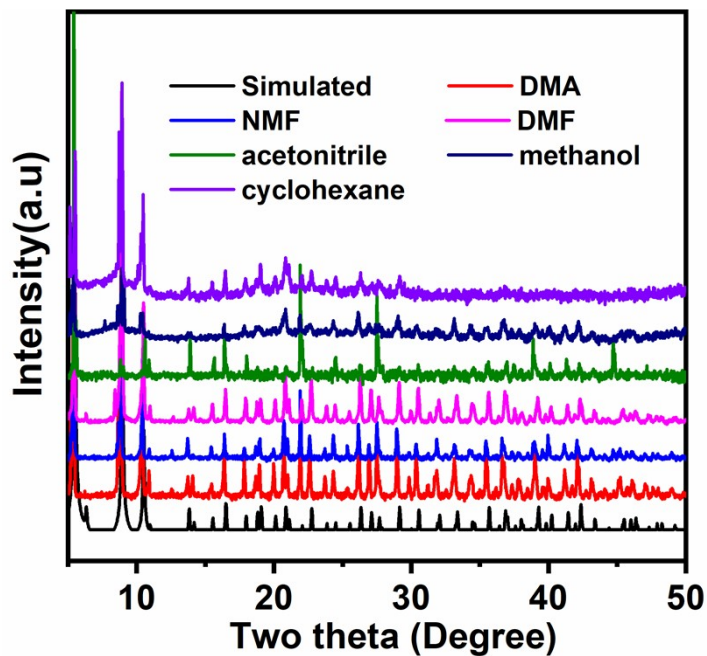


Fig. S7. The simulated and experimental PXRD patterns of 1.

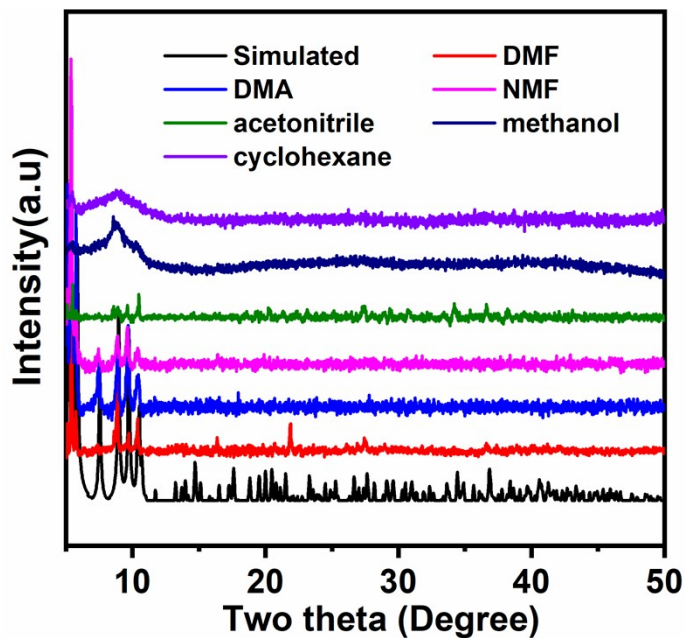




**Fig. S8.** The simulated and experimental PXRD patterns of **2**.



**Fig. S9.** PXRD patterns of crystals of **1** after soaking in various organic solvent for 24 hours.



**Fig. S10.** PXRD patterns of crystals of **2** after soaking in various organic solvent for 24 hours.

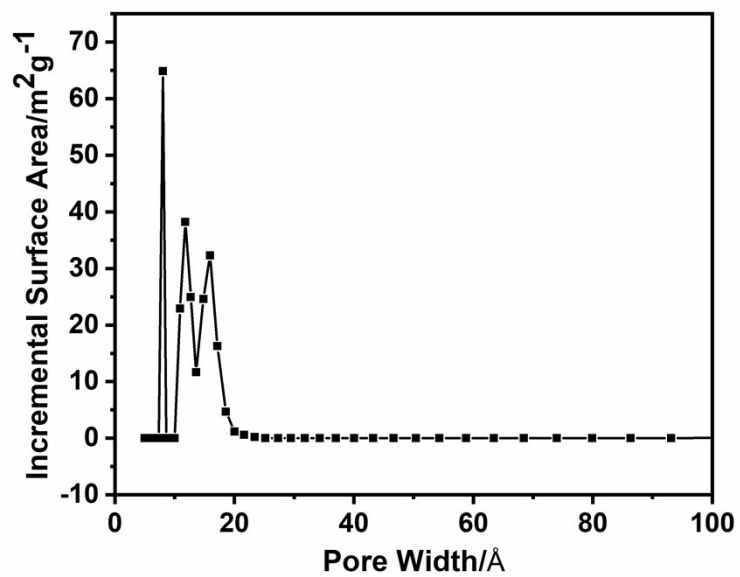


Fig. S11. The pore size distribution of 1

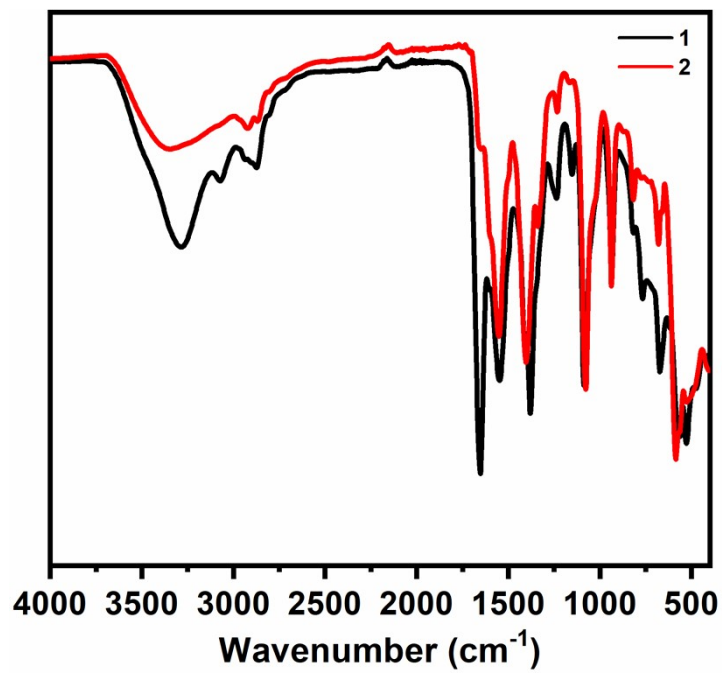
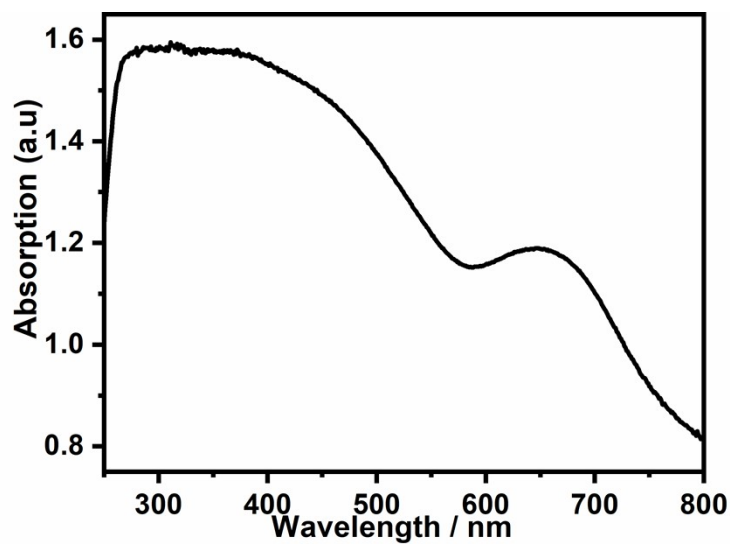
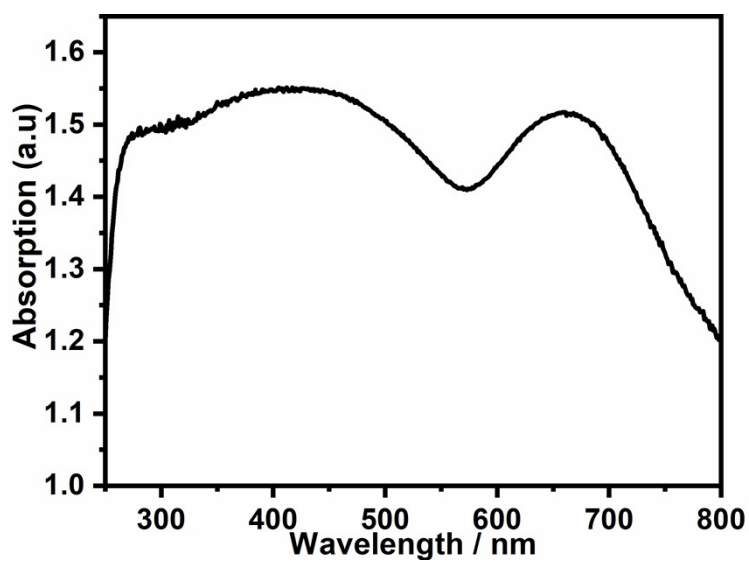


Fig. S12. The IR spectrum of 1 and 2.



**Fig. S13.** The UV spectrum of **1**.



**Fig. S14.** The UV spectrum of **2**.

The broad bands at 250-560 nm were assigned to the UV characteristic adsorption of Cu-I clusters in compound **1** and **2**.<sup>[3]</sup> The narrow bands around 650 nm were assigned to the d-d electronic transition of the octahedral-coordinated  $\text{Co}^{2+}$  ions in compound **1** and **2**.<sup>[4]</sup>



## Section S4 References

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- 2 (a) L. D. Lin, C. C. Deng, D. Zhao, X. X. Li, S. T. Zheng, *Chem. Eur. J.*, 2018, 24, 251-258; (b) H. Xue, X.-S. Huang, Q. Yin, X.-J. Hu, H.-Q. Zheng, G. Huang, T.-F. Liu, *Cryst. Growth Des.*, 2020, **20**, 4861-4866; (g) Z. Wang, C. Y. Zhu, P. Y. Fu, J. T. Mo, J. Ruan, M. Pan, C. Y. Su, *Chem. Eur. J.*, 2020, **26**, 7458-7462.
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- 4 H. Zhang, J. He, X. Lu, L. Yang, C. Wang, F. Yue, D. Zhou, Q. Xia, *New J. Chem.*, 2020, **44**, 17413-17421.