Supporting Information

A tetranuclear copper cluster-based MOF with sulfonate-carboxylate

ligands exhibiting high proton conduction property

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Scheme 1. The structure of the ligand NaH₂L (5-sulfoisophthalic acid monosodium salt).



Fig. S1 The Cu^{II}_4 core of compound 1.



Fig. S2 The 3D framework of 1 viewing along *c*-axis.



Fig. S3 The (3,6)-connected 3D non-interpenetrating network of 1.



Fig. S4 Powder X-ray diffraction patterns of simulated from the X-ray single structure of **1**, and as-synthesized **1**.



Fig. S5 The TGA curve of the compound 1.

Donor – HAcceptor	D – H (Å)	HA (Å)	DA (Å)	D – HA (°)
C(6) - H(6)O(3)	0.93	2.54	2.921(13)	105
C(10) – H(10)O(18)	0.93	2.47	3.057(16)	122
C(13) – H(13)O(4)	0.93	2.32	2.955(16)	125
C(14) – H(14A)O(12)	0.96	2.46	3.380(17)	160
C(15) – H(15A)O(12)	0.96	2.56	3.465(17)	158
C(17) – H(17)O(15)	0.93	2.35	2.700(15)	102

 Table S1 Hydrogen bond details in compound 1

Table S2 The crystal data of compound 1

Compound	1			
formular	$C_{22}H_{22}N_2S_2O_{18}Cu_4\\$			
weight	920.70			
space group	Fdd2			
a [Å]	24.748(5)			
<i>b</i> [Å]	32.354(5)			
c [Å]	21.712(5)			
α [deg]	90.000(5)			
β [deg]	90.000(5)			
γ [deg]	90.000(5)			
$ ho_{ m cald}[m gcm^{-3}]$	1.407			
V[Å ³]	17385(6)			
Ζ	16			
$R_{\rm int}$	0.0813			
F (000)	7360			
Reflns collcd/unique	24833 / 7630			
GOF on F^2	1.050			
${}^{a}R_{1}[I > 2\sigma(I)]$	0.0658			
${}^{b}wR_{2}(all data)$	0.1902			

 ${}^{a}\overline{R_{1}} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|; {}^{b}wR_{2} = \Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}] / \Sigma [w(F_{o}^{2})^{2}]^{1/2}$

Experimental Section

Materials and Measurements

All starting materials and solvents were reagent grade, commercially available and used without further purification. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. TG analyses were performed on a Perkin–Elmer Thermal Analysis Pyris Diamond heated from room temperature to 900 °C under a N₂ atmosphere at a rate of 10 °C min⁻¹. The experimental powder X-ray diffraction data (PXRD) were collected on a Bruker D8-FOCUS diffractometer equipped with Cu K α 1 (λ = 1.5406 Å; 1600 W, 40 kV, 40 mA) at a scan speed of 8° min⁻¹. The simulated PXRD patterns were calculated by using single-crystal X-ray diffraction data and processed by the free Mercury v1.4 program provided by the Cambridge Crystallographic Data Center.

Synthesis of 1: Cu(NO₃)₂·3H₂O (0.1 mmol), NaH₂L (0.1 mmol) and DMF (1.5 mL) was sealed in a 15 mL Teflon-lined stainless-steel autoclave under autogenous pressure and heated at constant 85 °C for 3 days and then was cooled to room temperature slowly. The resulting blue crystals were collected with a yield of 42% (based on Cu(NO₃)₂·3H₂O). Elemental analysis for C₂₂H₂₂N₂S₂O₁₈Cu₄ (1) (920.70) (%): calcd. C 28.70, H 2.41, N 3.04; found C 28.76, H 2.34, N 3.09.

Crystal data for 1: $C_{22}H_{22}N_2S_2O_{18}Cu_4$, $M_r = 920.70$, Orthorhombic, space group *Fdd2*, a = 24.748(5) Å, b = 32.354(5) Å, c = 21.712(5) Å, alpha = 90, beta = 90, gamma = 90, V = 17385(6) Å³, Z = 16, $\rho_{calcd} = 1.407$ g cm⁻³, final $R_1 = 0.0658$ and w $R_2 = 0.1902$ ($R_{int} = 0.0813$) for 7630 independent reflections [$I > 2\sigma(I)$]. CCDC 1037879.

X-ray crystallography

The X-ray intensity data for the compound was collected on a Bruker SMART APEX-II CCD diffractometer with graphite monochromatized Mo-K α radiation (λ = 0.71073 Å) operating at 1.575 kW (45 kV, 35 mA) at room temperature. Data integration and reduction were processed with SAINT software.¹ Multiscan absorption corrections were applied with the SADABS program.² All structures were

solved by direct methods and refined employing full-matrix least squares techniques based on F^2 using the SHELXTL-97 crystallographic software package.³ All non-hydrogen atoms were refined with anisotropic temperature parameters.

Proton conductivity measurements

The powders were prepared by grinding the sample into a homogeneous powder with a mortar and pestle. The powders were then added to a standard 8 mm die, sandwiched between two stainless steel electrodes and pressed at 10 MPa for 5 min. the pellet was 8 mm in diameter and 0.8 mm in thickness. The impedances were measured with a frequency response analyzer/potentiostat (PARSTAT 4000, Ametek, USA) over a frequency range from 0.1 Hz to 1 MHz, with a quasi-four probe electrochemical cell and an applied ac voltage of 100 mV. Measurements were taken in the temperature range of 35–95 °C with 95% relative humidity (controlled by using an HDHWHS-50 incubator). ZSimpWin software was used to extrapolate impedance data results by means of an equivalent circuit simulation to complete the Niquist plots and obtain the resistance values. Conductivity was calculated using the following equation:

 $\sigma = L / RS$

where σ is the conductivity (S cm⁻¹), *L* is the measured sample thickness (cm), *S* is the electrode area (cm²) and *R* is the impedance (Ω).



Fig. S6 Nyquist plots at the indicated temperatures of compound 1 at 95% RH.



Fig. S7 $Log(\sigma/S \text{ cm}^{-1})$ versus temperature plot of compound 1 at 35-95 °C under 95% RH.

Table S2 Impedance and proton conductivity in 35–95 °C with 95% relative humidity

<i>T</i> / °C	35	45	55	65	75	85	95
R/Ω	866000	123000	53900	16000	5725	565.6	214
σ/ S cm ⁻¹	1.84×10 ⁻⁷	1.29×10 ⁻⁶	2.95×10 ⁻⁶	9.95×10 ⁻⁶	2.78×10-5	2.81×10-4	7.44×10-4

- 1 SAINT, Program for Data Extraction and Reduction; Bruker AXS, Inc.: Madison, WI, 2001.
- 2 G. M. Sheldrick, SADABS; University of Göttingen: Göttingen, Germany, 1996.
- 3 (a) G. M. Sheldrick, SHELXS 97, Program for the Solution of Crystal Structure;
 University of Göttingen: Göttingen, Germany, 1997; (b) G. M. Sheldrick, SHELXS
 97, Program for the Crystal Structure Refinement; University of Göttingen:
 Göttingen, Germany, 1997.