Tetranuclear $Cu_4(\mu_3$ -OH)_2-based metal-organic framework (MOF) with sulfonate-carboxylate ligand for proton conduction

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Supporting Information

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Section S1. Synthesis, photograph and SEM image

Materials: All chemicals were of reagent grade quality, and they were purchased from commercial sources and used as received. Na₂H₂DSOA was prepared following the method as described in the literature.^[1]

Preparation of ${[H_3O][Cu_2(DSOA)(OH)(H_2O)] \cdot 9.5H_2O}_n$ (Cu-DSOA):

Preparation was processed by reaction of Cu(ClO₄)₂.6H₂O/ Na₂H₂DSOA (0.1 : 0.1 mmol), in CH₃CN/H₂O solution (1:1, 4 mL) under hydrothermal conditions. The above mixture was stirred fully first and sealed in a 23-mL Teflon-lined stainless steel container, heated at 120°C for 3 days and then cooled to room temperature. Blue single crystals of {[H₃O][Cu₂(DSOA)(OH)(H₂O)]·9.5H₂O}_n were isolated. Yield, 92% (based on Cu). Anal. Calcd for {[H₃O][Cu₂(DSOA)(OH)(H₂O)]·9.5H₂O}_n (**Cu-DSOA**): H 4.07, C 21.93, S 8.37%. Found: H 4.01, C 21.78, S 8.29%.

References:

[1] J. Jouanneau, L. Gonon, G. Gebel, V. Martin and R. Mercier, J. Polym. Sci. Pol. Chem., 2010, **48**, 1732.



Fig. S1 Photograph of single crystals of Cu-DSOA.

SEM image of Cu-DSOA: The morphologies of as-prepared single crystals of Cu-DSOA were observed by field-emission scanning electron microscopy (FESEM, JSM 6700F) at an acceleration voltage of 15 kV.



Fig. S2 FESEM images of single crystals of Cu-DSOA at two different magnifications.

Section S2: Single Crystal XRD and Crystal Structure

X-ray Structural Studies.

X-ray single-crystal diffraction data were collected on a Bruker SMART1000 CCD diffractometer with Mo-K α radiation ($\lambda = 0.71073$ Å) at variable temperatures. The empirical absorption corrections were applied by using the SADABS program.^[2]

Refinement Procedures:

The structures were solved using direct method, which yielded the positions of all non-hydrogen atoms. The unit cell includes a large region of disordered solvent molecules, which could not be modeled as discrete atomic sites. We employed PLATON/SQUEEZE to calculate the diffraction contribution of solvent molecules and thereby to produce a set of solvent-free diffraction intensities. The structure was then refined again using the data generated. The lattice parameters and structural data are collected in Table S1. Crystallographic data for the structure reported in this paper have also been deposited with the CCDC as deposition no. CCDC 949514 (available free of charge, on application to the CCDC, 12 Union Rd., Cambridge CB2 1EZ, U.K.; e-mail deposit@ccdc.cam.ac.uk).

References:

[2] Sheldrick, G. M. *SADABS*, Empirical Absorption Correction Program; University of Göttingen: Göttingen, Germany, 1997.

Temperature	293 K
Formula	$C_{14}H_9Cu_2O_{13}S_2^{\ a}$
Formula weight	576.41
Crystal system	tetragonal
Space Group	P4/n
Z	8
<i>a</i> (Å)	24.1267(4)
<i>b</i> (Å)	24.1267(4)
<i>c</i> (Å)	11.3077(4)
$V(\text{\AA}^3)$	6582.2(3)
ρ_{calcd} (g cm ⁻³)	1.163
θ range (°)	2.99 to 24.99
F(000)	2296
$\mu (\mathrm{mm}^{-1})$	1.460
Refln.collected	12566
Independent reflections	5805
Completeness	99.8 %
Refinement Method	Full-matrix least-squares on F^2
Data / restraints / parameters	5805 / 0 / 281
R(int)	0.0365
GOF	1.005
$^{b} R_{1}[I > 2\sigma(I)], wR_{2}$	0.0509, 0.1369
R_1 [all data], w R_2	0.0684, 0.1449

Table S1. Crystal data and structure refinement for Cu-DSOA

^{*a*}The program SQUEEZE was used to model the electron density in the pores from the disordered hydronium ion and crystalline water molecules.

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

Bond lengths (Å)				
Cu(1)–O(2)	1.912(3)	Cu(2)–O(1)	1.943(3)	
Cu(1)-O(3)#1	1.925(3)	Cu(2)–O(11)	1.955(2)	
Cu(1)–O(11)	1.972(2)	Cu(2)-O(4)#4	1.965(3)	
Cu(1)-O(11)#2	1.9815(3)	Cu(2)–O(1W)	1.985(3)	
Cu(1)-O(10)#3	2.422(3)	Cu(2)–O(6)#3	2.396(3)	
Cu(1)–O(8)#6	2.482(3)			
	Bond A	angles (°)		
O(2)-Cu(1)-O(3)#1	86.74(12)	O(11)-Cu(1)-Cu(1)#2	41.79(8)	
O(2)–Cu(1)–O(11)	95.47(11)	O(11)#2-Cu(1)-Cu(1)#2	41.56(7)	
O(3)#1-Cu(1)-O(11)	177.77(12)	O(10)#3-Cu(1)-Cu(1)#2	84.31(4)	
O(2)-Cu(1)-O(11)#2	174.92(12)	O(8)#6-Cu(1)-Cu(1)#2	82.91(0)	
O(3)#1-Cu(1)-O(11)#2	94.45(11)	O(1)–Cu(2)–O(11)	93.99(11)	
O(11)-Cu(1)-O(11)#2	83.35(11)	O(1)-Cu(2)-O(4)#4	171.74(12)	
O(2)-Cu(1)-O(10)#3	98.20(14)	O(11)-Cu(2)-O(4)#4	94.12(11)	
O(3)#1-Cu(1)-O(10)#3	94.58(13)	O(1)-Cu(2)-O(1W)	84.89(14)	
O(11)-Cu(1)-O(10)#3	84.91(11)	O(11)-Cu(2)-O(1W)	178.69(14)	
O(11)#2-Cu(1)-O(10)#3	86.64(13)	O(4)#4-Cu(2)-O(1W)	86.99(13)	
O(10)#3-Cu(1)-O(8)#6	164.82(4)	O(1)-Cu(2)-O(6)#3	95.55(13)	
O(11)#2-Cu(1)-O(8)#6	78.08(3)	O(11)-Cu(2)-O(6)#3	84.34(11)	
O(3)#1-Cu(1)-O(8)#6	88.99(2)	O(13)#4-Cu(2)-O(6)#3	86.84(12)	
O(2)-Cu(1)-Cu(1)#2	137.05(8)	O(1W)-Cu(2)-O(6)#3	96.43(16)	
O(3)#1-Cu(1)-Cu(1)#2	136.02(9)			

Table S2. Selected bond lengths (Å) and bond angles (°) for Cu-DSOA

Symmetry transformations used to generate equivalent atoms: #1 = y - 1/2, -x + 1, -z + 1; #2 = -x + 1, -y + 1, -z; #3 = -x + 1, -y + 1, -z + 1, #4 = -y + 3/2, x, z - 1; #5 = y+1, x + 1/2, -z + 1; #6 = x, y, -1+z.

Crystal Structure of Cu-DSOA



Fig. S3 Perspective view of the asymmetric unit of complex **Cu-DSOA.** H atoms are omitted for clarity. Symmetry codes: a: 1 - x, 1 - y, 1 - z; b: x, y, 1 + z; c: y, 1.5 - x, 1 + z; d: 1 - y, 0.5 + x, 1 - z.



Fig. S4 Binodal (3,6)-connected topology network with Schäfli { $4^{2.6}$ 10.8³}. DSOA⁴⁻ ligand and the tetrameric copper act as 3- and 6-connected nodes, respectively.



Fig. S5 View showing channel **A** and **B** in the direction of the *c*-axis. The solvent water molecules and hydrogen atoms are omitted for clarity.

Section S3: FT-IR Spectroscopy

Fourier transform (FT) IR spectra (KBr pellet) were recorded at room temperature on a Perkin Elmer FT-IR spectrometer.



Fig. S6 IR spectra of **Cu-DSOA** at room temperature. The broad and strong peak at 3453 cm⁻¹ corresponds to a large number of water molecules forming H-bonds.

Section S4: PXRD of MOFs

Powder X-ray diffraction patterns were recorded on a Phillips XPERT PRO with Cu K α irradiation ($\lambda = 1.5418$ Å).



Fig. S7 PXRD patterns of **Cu-DSOA**, the corresponding simulation according to single crystal structural determinations (black line), the compressed pellet before and after the proton conduction experiment (red and blue, respectively).

Section S5: TGA/DTG and Elemental Analysis

TGA–DTG measurement was performed on a PE Diamond TG/DTA unit under air atmosphere at a rate of 10° C min⁻¹ in the temperature range of 25° C– 800° C.



Fig. S8 TG and DTG plots of as prepared Cu-DSOA.

Section S6: Impedance Measurements.

Proton conductivity was measured on the powdered crystalline samples with 1.0 mm in thickness and 13.0 mm in diameter under a pressure of 12–14 M Pa. Ac impedance spectroscopy measurement was performed on a chi660d (Shanghai Chenhua) electrochemical impedance analyzer with copper electrodes (the purity of Cu is more than 99.8 %) over the frequency range from $10^5 - 1$ Hz. The conductivity was calculated as $\sigma = (1/R)(h/S)$, where R is the resistance, h is the thickness, and S is the area of the tablet.

40

55



Fig. S9 Some of the Nyquist plots for at 98% relative humidity at different temperature (a) 40 °C (b) 55 °C (c) 70 °C (d) 100 °C

Temperature (°C)	RH (relative humidity)	σ [S cm ⁻¹]
25	RH = 35%	1.40867E-9
25	RH = 60%	6.0592E-9
25	RH = 75%	1.45023E-8
25	RH = 85%	5.36147E-8
25	RH = 98%	1.36561E-6

Table S3: Proton conductivities at 25°C and various relative humidity as well as at 98% relative humidity and various temperatures.

RH = 98%

RH = 98%

8.63066E-6

6.47615E-5

63	RH = 98%	8.50618E-5
70	RH = 98%	2.40392E-4
77	RH = 98%	4.42321E-4
85	RH = 98%	0.00192
90	RH = 98%	0.00164
95	RH = 98%	0.0017
100	RH = 98%	0.0014

Section S7: Cyclic voltammograms (CV).

Cyclic voltammograms (CV) measurements was performed on a pellet of powdered crystalline samples with 1.0 mm in thickness and 13.0 mm in diameter.



Fig. S10 Cyclic voltammograms (CVs) of **Cu-DSOA** at the scan rate: 50 mV/s. (a) 25°C, RH=98% (b) 50°C, RH=98%

Section S8: Dielectric Measurements and Data

Dielectric constant was measured using an automatic impedance HP4191A Analyzer with frequencies of 100 Hz to 1 MHz in the form of pellet. The process is as follows: the first step (1^{st}) : cooling from room temperature to -180 °C; the second step (2^{nd}) : heating from -180 °C to 75 °C; the third step (3^{rd}) : going on heating to 180 °C; the fourth step (4^{th}) : and then cooling to room temperature.



Fig. S11 The dielectric constant (ϵ') for **Cu-DSOA** measured as a function of temperature (25 °C \rightarrow -180 °C (1st step) \rightarrow 75°C (2nd step) \rightarrow 180 °C (3rd step) \rightarrow 25 °C (4th step) at various frequencies.

Table S4: Different dielectric constants of those reported MOFs incorporating guest small molecules, bulk water and **Cu-DSOA** at measured temperature and frequency.

Complex	Cu-DSOA	$\{(EMI)_2[Zn_3(1,2,4,5-$	[(CH ₂) ₃ NH ₂][Cu	Q[8] ^[3a]	
/guest cations	/ H_3O^+ and H_2O	$BTC)_2] \cdot 2H_2O\}_n^{[3b]}$	(HCOO) ₃] ^[3c]	/ Cu^{2+} and H_2O	bulk water
		/ $EMI^{\rm +}$ and H_2O	/(CH ₂) ₃ NH ₂ ⁺		
ε'	$\epsilon' = 5.1{\times}10^4$	$\epsilon' = 5.6 {\times} 10^4$	$\epsilon' > 10^4$	$\varepsilon' \approx 1.5 \times 10^3$	ε′≈ 80−60
(temp., freq.)	(75°C, 1 kHz)	(105.5°C, 1kHz)	(0–47°C,1kHz)	(0°C, 10 ⁴ Hz)	(25–80°C)

Complex	[{Co ₂ (L)(bpe)	$[Ln_2Cu_3(IDA)_6]_3$	[Cu ₂ (ADCOO) ₄	$[Dy(L_1)_2(acac)_2]$	[Mn ₃ (HCOO) ₆]·
/neutral guest	(H ₂ O)}	$\cdot nH_2O(Ln = La, Nd,$	(DMF) ₂]	NO ₃ ·CH ₃ OH	$(C_2H_5OH)^{[4e]}$
molecules	$\cdot 5H_2O]_n^{[4a]}$	Sm, Gd, Ho, Er) ^[4c]	·(DMF)2 ^[4d]	$\cdot H_2 O^{[4b]}$	/ C ₂ H ₅ OH
	/ H ₂ O	/ H ₂ O	/ DMF	/ CH ₃ OH·H ₂ O	
ε'	ε' = 11.2	${\epsilon_{\parallel}}'\approx 300\text{-}500$	ε′≈1000	ε′≈ 40	ε′≈20
(temp., freq.)	(25 °C, 1 kHz)	(80 °C, 10 kHz)	(85 °C, 1 kHz)	(57 °C, 10 Hz)	(150K,10 kHz)

References:

- [3] (a) H.-X. Zhao, J.-X. Liu, L.-S. Long, A. A. Bokov, Z.-G. Ye, R.-B. Huang and L.-S. Zheng, J. Phys. Chem. C, 2012, 116, 14199; (b) W.-J. Ji, Q.-G. Zhai, S.-N. Li, Y.-C. Jiang and M.-C. Hu, Chem. Commun., 2011, 47, 3834; (c) B. Zhou, Y. Imai, A. Kobayashi, Z.-M. Wang and H. Kobayashi, Angew. Chem. Int. Ed., 2011, 50, 11441.
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Section S9: Magnetic Measurements and Data

Magnetic measurements were carried out on crystalline samples of **Cu-DSOA** with a Quantum Design SQUID magnetometer in the temperature range 2-300 K in a field of 2 kOe. The susceptibility data were corrected for the diamagnetism of the constituent atoms and the sample holder.

$$\hat{H} = J_a(\hat{S}_1\hat{S}_2 + \hat{S}_3\hat{S}_4) + J_b(\hat{S}_1\hat{S}_4 + \hat{S}_2\hat{S}_3) + J_c(\hat{S}_1\hat{S}_3) + g\mu_B HS_{Tz}$$
(eq1)

$$Xm = \frac{Ng^2\beta^2}{3kT}\frac{A}{B}$$
 (eq 2)

$$A = 6\exp(\frac{3J_c}{4kT}) + 6\exp(-\frac{J_c - 4J_{ab}}{4kT}) + 6\exp(-\frac{J_c}{4kT}) + 30\exp(-\frac{J_c + 4J_{ab}}{4kT})$$

$$B = \exp(\frac{3J_c}{4kT}) + \exp(-\frac{J_c - 8J_{ab}}{4kT}) + 3\exp(\frac{3J_c}{4kT}) + 3\exp(-\frac{J_c - 4J_{ab}}{4kT})$$

$$+ 3\exp(-\frac{J_c}{4kT}) + 5\exp(-\frac{J_c + 4J_{ab}}{4kT})$$
(eq 3)

The room temperature (300 K) $\chi_{\rm M}T$ value (2.01 cm³ K mol⁻¹) is higher than the four uncoupled Cu(II) ions ($\chi_M T = 0.375 \text{ cm}^3 \text{ K mol}^{-1}$ for an S = 1/2 ion). Considering the structure of the tetranuclear Cu-DSOA, there are three different exchange-coupling parameters, viz. two different parameters between the peripheral Cu(2) and the two central Cu(1) and Cu(1#) (J_a and J_b) and one parameter between the two central Cu(1) $(J_{\rm c})$ inset). However, since the Cu(1)-O(11)-Cu(2)atoms (Fig.4, and Cu(1)-O(11#)-Cu(2#) angles are very close (119.41 and 122.38°, respectively), it is reasonable to assume that $J_a=J_b=J_{ab}$. The magnetic susceptibility in the whole temperature range was fitted by tetranuclear model^{5,6}, where all symbols have their normal meanings. The best fitting gave $J_{ab} = 29.2 \text{ cm}^{-1}$ and $J_{c} = 55.1 \text{ cm}^{-1}$ with a reasonable g-factor (2.24).

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