# Tetranuclear $\mathrm{Cu}_{4}\left(\mu_{3}-\mathrm{OH}\right)_{2}$-based metal-organic framework (MOF) with sulfonate-carboxylate ligand for proton conduction 

Xi-Yan Dong, ${ }^{a, b}$ Rui Wang, ${ }^{a}$ Jia-Bin Li, ${ }^{a}$ Shuang-Quan Zang, ${ }^{*}{ }^{a}$ Hong-Wei Hou ${ }^{a}$ and Thomas. C. W. Mak ${ }^{a, c}$<br>${ }^{a}$ College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450001, China<br>${ }^{b}$ School of Physics and Chemistry, Henan Polytechnic University, Jiaozuo 454000, China<br>${ }^{c}$ Department of Chemistry and Center of Novel Functional Molecules, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong SAR, China<br>Author for correspondence: Dr. S.-Q. Zang

## Supporting Information

Section S1: Synthesis, Photograph and SEM image, and Elemental Analysis ..... S2-S3
Section S2: Single Crystal XRD and Crystal Structure ..... S3-S6
Section S3: FT-IR Spectroscopy ..... S7
Section S4: PXRD ..... S7
Section S5: TGA/DTG ..... S8
Section S6: Impedance Analysis ..... S8-S10
Section S7: Cyclic voltammograms (CV) ..... S10
Section S8: Dielectric Data ..... S11-S12
Section S9: Magnetic Measurements and Data ..... S12-S13

## 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. $\mathrm{Na}_{2} \mathrm{H}_{2} \mathrm{DSOA}$ was prepared following the method as described in the literature. ${ }^{[1]}$

Preparation of $\left\{\left[\mathrm{H}_{3} \mathrm{O}\right]\left[\mathrm{Cu}_{2}(\mathrm{DSOA})(\mathbf{O H})\left(\mathrm{H}_{2} \mathrm{O}\right)\right] \cdot 9.5 \mathrm{H}_{2} \mathrm{O}\right\}_{n} \quad$ (Cu-DSOA): Preparation was processed by reaction of $\mathrm{Cu}\left(\mathrm{ClO}_{4}\right)_{2} \cdot 6 \mathrm{H}_{2} \mathrm{O} / \mathrm{Na}_{2} \mathrm{H}_{2} \mathrm{DSOA}(0.1: 0.1$ mmol ), in $\mathrm{CH}_{3} \mathrm{CN} / \mathrm{H}_{2} \mathrm{O}$ solution (1:1, 4 mL ) under hydrothermal conditions. The above mixture was stirred fully first and sealed in a $23-\mathrm{mL}$ Teflon-lined stainless steel container, heated at $120^{\circ} \mathrm{C}$ for 3 days and then cooled to room temperature. Blue single crystals of $\left\{\left[\mathrm{H}_{3} \mathrm{O}\right]\left[\mathrm{Cu}_{2}(\mathrm{DSOA})(\mathrm{OH})\left(\mathrm{H}_{2} \mathrm{O}\right)\right] \cdot 9 \cdot 5 \mathrm{H}_{2} \mathrm{O}\right\}_{n}$ were isolated. Yield, $92 \%$ (based on Cu$)$. Anal. Calcd for $\left\{\left[\mathrm{H}_{3} \mathrm{O}\right]\left[\mathrm{Cu}_{2}(\mathrm{DSOA})(\mathrm{OH})\left(\mathrm{H}_{2} \mathrm{O}\right)\right] \cdot 9.5 \mathrm{H}_{2} \mathrm{O}\right\}_{n}$ (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 $\alpha$ radiation $(\lambda=0.71073 \AA$ ) 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.

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

| Temperature | 293 K |
| :--- | :---: |
| Formula | $\mathrm{C}_{14} \mathrm{H}_{9} \mathrm{Cu}_{2} \mathrm{O}_{13} \mathrm{~S}_{2}{ }^{a}$ |
| Formula weight | 576.41 |
| Crystal system | tetragonal |
| Space Group | $P 4 / n$ |
| Z | 8 |
| $a(\AA)$ | $24.1267(4)$ |
| $b(\AA)$ | $24.1267(4)$ |
| $c(\AA)$ | $11.3077(4)$ |
| $V\left(\AA^{3}\right)$ | $6582.2(3)$ |
| $\rho_{\text {calcd }}(\mathrm{g}$ cm |  |
| $\theta$ range $\left(^{\circ}\right)$ | 1.163 |
| $\mathrm{~F}(000)$ | 2.99 to 24.99 |
| $\mu\left(\right.$ mm $\left.{ }^{-1}\right)$ | 2296 |
| Refln.collected | 1.460 |
| Independent reflections | 12566 |
| Completeness | 5805 |
| Refinement Method | $99.8 \%$ |
| Data / restraints / parameters | Full-matrix least-squares on $\mathrm{F}^{\wedge} 2$ |
| $\mathrm{R}($ int $)$ | $5805 / 0 / 281$ |
| GOF | 0.0365 |
| $b \mathrm{R}_{1}[I>2 \sigma(I)]$, wR 2 | 1.005 |
| $\mathrm{R}_{1}[$ all data, wR 2 | $0.0509,0.1369$ |

${ }^{a}$ The program SQUEEZE was used to model the electron density in the pores from the disordered hydronium ion and crystalline water molecules.
${ }^{b} R_{1}=\Sigma| | F_{\mathrm{o}}\left|-\left|F_{\mathrm{c}}\right|\right| / \Sigma\left|F_{\mathrm{o}}\right|, w R_{2}=\left[\Sigma\left[w\left(F_{\mathrm{o}}{ }^{2}-F_{\mathrm{c}}{ }^{2}\right)^{2}\right] / \Sigma w\left(F_{\mathrm{o}}{ }^{2}\right)^{2}\right]^{1 / 2}$

Table S2. Selected bond lengths ( $\AA$ ) and bond angles $\left({ }^{\circ}\right)$ for $\mathbf{C u}-$ DSOA

|  | Bond lengths $(\AA 8)$ |  |  |
| :--- | :--- | :--- | :--- |
| $\mathrm{Cu}(1)-\mathrm{O}(2)$ | $1.912(3)$ | $\mathrm{Cu}(2)-\mathrm{O}(1)$ | $1.943(3)$ |
| $\mathrm{Cu}(1)-\mathrm{O}(3) \# 1$ | $1.925(3)$ | $\mathrm{Cu}(2)-\mathrm{O}(11)$ | $1.955(2)$ |
| $\mathrm{Cu}(1)-\mathrm{O}(11)$ | $1.972(2)$ | $\mathrm{Cu}(2)-\mathrm{O}(4) \# 4$ | $1.965(3)$ |
| $\mathrm{Cu}(1)-\mathrm{O}(11) \# 2$ | $1.9815(3)$ | $\mathrm{Cu}(2)-\mathrm{O}(1 \mathrm{~W})$ | $1.985(3)$ |
| $\mathrm{Cu}(1)-\mathrm{O}(10) \# 3$ | $2.422(3)$ | $\mathrm{Cu}(2)-\mathrm{O}(6) \# 3$ | $2.396(3)$ |
| $\mathrm{Cu}(1)-\mathrm{O}(8) \# 6$ | $2.482(3)$ |  |  |
| Bond |  |  |  |
|  | $\mathrm{Angles}\left({ }^{\circ}\right)$ |  |  |
| $\mathrm{O}(2)-\mathrm{Cu}(1)-\mathrm{O}(3) \# 1$ | $86.74(12)$ | $\mathrm{O}(11)-\mathrm{Cu}(1)-\mathrm{Cu}(1) \# 2$ | $41.79(8)$ |
| $\mathrm{O}(2)-\mathrm{Cu}(1)-\mathrm{O}(11)$ | $95.47(11)$ | $\mathrm{O}(11) \# 2-\mathrm{Cu}(1)-\mathrm{Cu}(1) \# 2$ | $41.56(7)$ |
| $\mathrm{O}(3) \# 1-\mathrm{Cu}(1)-\mathrm{O}(11)$ | $177.77(12)$ | $\mathrm{O}(10) \# 3-\mathrm{Cu}(1)-\mathrm{Cu}(1) \# 2$ | $84.31(4)$ |
| $\mathrm{O}(2)-\mathrm{Cu}(1)-\mathrm{O}(11) \# 2$ | $174.92(12)$ | $\mathrm{O}(8) \# 6-\mathrm{Cu}(1)-\mathrm{Cu}(1) \# 2$ | $82.91(0)$ |
| $\mathrm{O}(3) \# 1-\mathrm{Cu}(1)-\mathrm{O}(11) \# 2$ | $94.45(11)$ | $\mathrm{O}(1)-\mathrm{Cu}(2)-\mathrm{O}(11)$ | $93.99(11)$ |
| $\mathrm{O}(11)-\mathrm{Cu}(1)-\mathrm{O}(11) \# 2$ | $83.35(11)$ | $\mathrm{O}(1)-\mathrm{Cu}(2)-\mathrm{O}(4) \# 4$ | $171.74(12)$ |
| $\mathrm{O}(2)-\mathrm{Cu}(1)-\mathrm{O}(10) \# 3$ | $98.20(14)$ | $\mathrm{O}(11)-\mathrm{Cu}(2)-\mathrm{O}(4) \# 4$ | $94.12(11)$ |
| $\mathrm{O}(3) \# 1-\mathrm{Cu}(1)-\mathrm{O}(10) \# 3$ | $94.58(13)$ | $\mathrm{O}(1)-\mathrm{Cu}(2)-\mathrm{O}(1 \mathrm{~W})$ | $84.89(14)$ |
| $\mathrm{O}(11)-\mathrm{Cu}(1)-\mathrm{O}(10) \# 3$ | $84.91(11)$ | $\mathrm{O}(11)-\mathrm{Cu}(2)-\mathrm{O}(1 \mathrm{~W})$ | $178.69(14)$ |
| $\mathrm{O}(11) \# 2-\mathrm{Cu}(1)-\mathrm{O}(10) \# 3$ | $86.64(13)$ | $\mathrm{O}(4) \# 4-\mathrm{Cu}(2)-\mathrm{O}(1 \mathrm{~W})$ | $86.99(13)$ |
| $\mathrm{O}(10) \# 3-\mathrm{Cu}(1)-\mathrm{O}(8) \# 6$ | $164.82(4)$ | $\mathrm{O}(1)-\mathrm{Cu}(2)-\mathrm{O}(6) \# 3$ | $95.55(13)$ |
| $\mathrm{O}(11) \# 2-\mathrm{Cu}(1)-\mathrm{O}(8) \# 6$ | $78.08(3)$ | $\mathrm{O}(11)-\mathrm{Cu}(2)-\mathrm{O}(6) \# 3$ | $84.34(11)$ |
| $\mathrm{O}(3) \# 1-\mathrm{Cu}(1)-\mathrm{O}(8) \# 6$ | $88.99(2)$ | $\mathrm{O}(13) \# 4-\mathrm{Cu}(2)-\mathrm{O}(6) \# 3$ | $86.84(12)$ |
| $\mathrm{O}(2)-\mathrm{Cu}(1)-\mathrm{Cu}(1) \# 2$ | $137.05(8)$ | $\mathrm{O}(1 \mathrm{~W})-\mathrm{Cu}(2)-\mathrm{O}(6) \# 3$ | $96.43(16)$ |
| $\mathrm{O}(3) \# 1-\mathrm{Cu}(1)-\mathrm{Cu}(1) \# 2$ | $136.02(9)$ |  |  |

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

## 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: $1-x, 1-y, 1-z ; \mathrm{b}: x, y, 1+z ; \mathrm{c}: y, 1.5-x, 1+z ; \mathrm{d}: 1-y$, $0.5+x, 1-z$.


Fig. S4 Binodal (3,6)-connected topology network with Schäfli $\left\{4^{\wedge} 2 \cdot 6^{\wedge} 10.8^{\wedge} 3\right\}$. DSOA $^{4-}$ ligand and the tetrameric copper act as 3- and 6-connected nodes, respectively.


Fig. S5 View showing channel $\mathbf{A}$ and $\mathbf{B}$ 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 $3453 \mathrm{~cm}^{-1}$ 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 $\mathrm{CuK} \alpha$ irradiation $(\lambda=1.5418 \AA$ ).


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 $10^{\circ} \mathrm{C} \mathrm{min}^{-1}$ in the temperature range of $25^{\circ} \mathrm{C}-800^{\circ} \mathrm{C}$.


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 $12-14 \mathrm{M} \mathrm{Pa}$. 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 $10^{5}-1 \mathrm{~Hz}$. 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.


Fig. S9 Some of the Nyquist plots for at $98 \%$ relative humidity at different temperature (a) $40^{\circ} \mathrm{C}$ (b) $55^{\circ} \mathrm{C}$ (c) $70^{\circ} \mathrm{C}$ (d) $100^{\circ} \mathrm{C}$

Table S3: Proton conductivities at $25^{\circ} \mathrm{C}$ and various relative humidity as well as at $98 \%$ relative humidity and various temperatures.

| Temperature $\left({ }^{\mathbf{}} \mathbf{C}\right)$ | $\mathbf{R H}($ relative humidity | $\sigma\left[\mathbf{S ~ c m}^{-1}\right]$ |
| :---: | :---: | :---: |
| 25 | $\mathrm{RH}=35 \%$ | $1.40867 \mathrm{E}-9$ |
| 25 | $\mathrm{RH}=60 \%$ | $6.0592 \mathrm{E}-9$ |
| 25 | $\mathrm{RH}=75 \%$ | $1.45023 \mathrm{E}-8$ |
| 25 | $\mathrm{RH}=85 \%$ | $5.36147 \mathrm{E}-8$ |
| 25 | $\mathrm{RH}=98 \%$ | $1.36561 \mathrm{E}-6$ |
| 40 | $\mathrm{RH}=98 \%$ | $8.63066 \mathrm{E}-6$ |
| 55 | $\mathrm{RH}=98 \%$ | $6.47615 \mathrm{E}-5$ |


| 63 | $\mathrm{RH}=98 \%$ | $8.50618 \mathrm{E}-5$ |
| :---: | :---: | :---: |
| 70 | $\mathrm{RH}=98 \%$ | $2.40392 \mathrm{E}-4$ |
| 77 | $\mathrm{RH}=98 \%$ | $4.42321 \mathrm{E}-4$ |
| 85 | $\mathrm{RH}=98 \%$ | 0.00192 |
| 90 | $\mathrm{RH}=98 \%$ | 0.00164 |
| 95 | $\mathrm{RH}=98 \%$ | 0.0017 |
| 100 | $\mathrm{RH}=98 \%$ | 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: $50 \mathrm{mV} / \mathrm{s}$. (a) $25^{\circ} \mathrm{C}$, RH $=98 \%$ (b) $50^{\circ} \mathrm{C}, \mathrm{RH}=98 \%$

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 $\left(1^{\text {st }}\right)$ : cooling from room temperature to $-180^{\circ} \mathrm{C}$; the second step $\left(2^{\text {nd }}\right)$ : heating from $-180^{\circ} \mathrm{C}$ to $75^{\circ} \mathrm{C}$; the third step $\left(3^{\text {rd }}\right)$ : going on heating to $180^{\circ} \mathrm{C}$; the fourth step $\left(4^{\text {th }}\right)$ : and then cooling to room temperature.


Fig. S11 The dielectric constant $\left(\varepsilon^{\prime}\right)$ for Cu-DSOA measured as a function of temperature $\left(25^{\circ} \mathrm{C}\right.$ $\rightarrow-180{ }^{\circ} \mathrm{C}\left(1^{\text {st }}\right.$ step) $\rightarrow 75^{\circ} \mathrm{C}\left(2^{\text {nd }}\right.$ step) $\rightarrow 180^{\circ} \mathrm{C}\left(3^{\text {rd }}\right.$ step) $\rightarrow 25{ }^{\circ} \mathrm{C}\left(4^{\text {th }}\right.$ 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 <br> /guest cations | $\begin{aligned} & \text { Cu-DSOA } \\ & / \mathrm{H}_{3} \mathrm{O}^{+} \text {and } \mathrm{H}_{2} \mathrm{O} \end{aligned}$ | $\begin{aligned} & \left\{( \mathrm { EMI } ) _ { 2 } \left[\mathrm{Zn}_{3}(1,2,4,5-\right.\right. \\ & \left.\left.\mathrm{BTC})_{2}\right] \cdot 2 \mathrm{H}_{2} \mathrm{O}\right\}_{n}^{[3 b]} \\ & / \mathrm{EMI}^{+} \text {and } \mathrm{H}_{2} \mathrm{O} \end{aligned}$ | $\begin{aligned} & {\left[\left(\mathrm{CH}_{2}\right)_{3} \mathrm{NH}_{2}\right][\mathrm{Cu}} \\ & \left.(\mathrm{HCOO})_{3}\right]^{[3 \mathrm{c}]} \\ & /\left(\mathrm{CH}_{2}\right)_{3} \mathrm{NH}_{2}^{+} \end{aligned}$ | $\begin{gathered} \mathrm{Q}[8]^{[3 \mathrm{a}]} \\ / \mathrm{Cu}^{2+} \text { and } \mathrm{H}_{2} \mathrm{O} \end{gathered}$ | bulk water |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\begin{gathered} \varepsilon^{\prime} \\ \text { (temp., freq.) } \end{gathered}$ | $\varepsilon^{\prime}=5.1 \times 10^{4}$ <br> ( $75^{\circ} \mathrm{C}, 1 \mathrm{kHz}$ ) | $\begin{array}{r} \varepsilon^{\prime}=5.6 \times 10^{4} \\ \left(105.5^{\circ} \mathrm{C}, 1 \mathrm{kHz}\right) \end{array}$ | $\begin{gathered} \varepsilon^{\prime}>10^{4} \\ \left(0-47^{\circ} \mathrm{C}, 1 \mathrm{kHz}\right) \end{gathered}$ | $\begin{aligned} & \varepsilon^{\prime} \approx 1.5 \times 10^{3} \\ & \left(0^{\circ} \mathrm{C}, 10^{4} \mathrm{~Hz}\right) \end{aligned}$ | $\begin{aligned} & \varepsilon^{\prime} \approx 80-60 \\ & \left(25-80^{\circ} \mathrm{C}\right) \end{aligned}$ |



## 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.
[4] (a) X.-Y Dong, B. Li, B.-B. Ma, S.-J. Li, M.-M. Dong, Y.-Y. Zhu, S.-Q. Zang, Y. Song, H.-W. Hou and T. C. W. Mak, J. Am. Chem. Soc., 2013, 135, 10214; (b) J. Liu, X.-P. Zhang, T. Wu, B.-B. Ma, T.-W. Wang, C.-H. Li, Y.-Z. Li and X.-Z. You, Inorg. Chem., 2012, 51, 8649; (c) B. Zhou, A. Kobayashi, H.-B. Cui, L.-S. Long, H. Fujimori and H. Kobayashi, J. Am. Chem. Soc., 2011, 133, 5736; (d) Q. Ye, K. Takahashi, N. Hoshino, T. Kikuchi, T. Akutagawa, S. Noro, S. Takeda and T. Nakamura, Chem. Eur. J., 2011, 17, 14442; (e) H.-B. Cui, K. Takahashi, Y. Okano, H. Kobayashi, Z. Wang and A. Kobayashi, Angew. Chem. Int. Ed., 2005, 44, 6508.

## 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.

$$
\begin{gather*}
\hat{H}=J_{a}\left(\hat{S}_{1} \hat{S}_{2}+\hat{S}_{3} \hat{S}_{4}\right)+J_{b}\left(\hat{S}_{1} \hat{S}_{4}+\hat{S}_{2} \hat{S}_{3}\right)+J_{c}\left(\hat{S}_{1} \hat{S}_{3}\right)+g \mu_{B} H S_{T z}  \tag{eq1}\\
X m=\frac{N g^{2} \beta^{2}}{3 k T} \frac{A}{B} \tag{eq2}
\end{gather*}
$$

$$
\begin{aligned}
& A=6 \exp \left(\frac{3 J_{c}}{4 k T}\right)+6 \exp \left(-\frac{J_{c}-4 J_{a b}}{4 k T}\right)+6 \exp \left(-\frac{J_{c}}{4 k T}\right)+30 \exp \left(-\frac{J_{c}+4 J_{a b}}{4 k T}\right) \\
& B=\exp \left(\frac{3 J_{c}}{4 k T}\right)+\exp \left(-\frac{J_{c}-8 J_{a b}}{4 k T}\right)+3 \exp \left(\frac{3 J_{c}}{4 k T}\right)+3 \exp \left(-\frac{J_{c}-4 J_{a b}}{4 k T}\right) \\
& +3 \exp \left(-\frac{J_{c}}{4 k T}\right)+5 \exp \left(-\frac{J_{c}+4 J_{a b}}{4 k T}\right)
\end{aligned}
$$

The room temperature $(300 \mathrm{~K}) \chi_{\mathrm{M}} T$ value $\left(2.01 \mathrm{~cm}^{3} \mathrm{~K} \mathrm{~mol}^{-1}\right)$ is higher than the four uncoupled $\mathrm{Cu}($ II $)$ ions ( $\chi_{\mathrm{M}} T=0.375 \mathrm{~cm}^{3} \mathrm{~K} \mathrm{~mol}^{-1}$ for an $\mathrm{S}=1 / 2$ ion). Considering the structure of the tetranuclear Cu-DSOA, there are three different exchange-coupling parameters, viz. two different parameters between the peripheral $\mathrm{Cu}(2)$ and the two central $\mathrm{Cu}(1)$ and $\mathrm{Cu}(1 \#)\left(J_{\mathrm{a}}\right.$ and $\left.J_{\mathrm{b}}\right)$ and one parameter between the two central $\mathrm{Cu}(1)$ atoms ( $J_{\mathrm{c}}$ ) (Fig.4, inset). However, since the $\mathrm{Cu}(1)-\mathrm{O}(11)-\mathrm{Cu}(2)$ and $\mathrm{Cu}(1)-\mathrm{O}(11 \#)-\mathrm{Cu}(2 \#)$ angles are very close (119.41 and $122.38^{\circ}$, respectively), it is reasonable to assume that $J_{\mathrm{a}}=J_{\mathrm{b}}=J_{\mathrm{ab}}$. 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 $J_{\mathrm{ab}}=29.2 \mathrm{~cm}^{-1}$ and $J_{\mathrm{c}}=55.1 \mathrm{~cm}^{-1}$ with a reasonable $g$-factor (2.24).

## References:

[5] J. Li, C.-C. Ji, Z.-Z. Lu, T.-W. Wang, Y. Song, Y.-Z. Li, H.-G. Zheng, Z. Guo and S. R. Batten, CrystEngComm, 2010, 12, 4424.
[6] A. Mondal, Y. Li, M. A. Khan, J. H. Ross, Jr., and R. P. Houser, Inorg. Chem., 2004, 43, 7075.

