

**SUPPORTING INFORMATION**

**Mixed Valence Copper-sulfur Clusters of Highest Nuclearity: A Cu<sub>8</sub> Wheel and Cu<sub>16</sub> Nanoball**

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## Syntheses of Ligands L1<sup>S-S</sup>, L2<sup>S-S</sup> and their Copper Complexes:

**2,2'-disulfanediylbis(N-((3-methylthiophen-2-yl)methylene)aniline) (L1<sup>S-S</sup>):** A solution of 2,2'-disulfanediyl dianiline (2.0 g, 8.06 mmol) in 40 ml of CH<sub>3</sub>OH was added to a stirred solution of 3-methyl-2-thiophenecarbaldehyde (2.03 g, 16.12 mmol) in 40 ml CH<sub>3</sub>OH solution. Then the resulting solution was refluxed for 3 hrs and CH<sub>3</sub>OH was removed using rotary evaporator. The yellow solid of L1<sup>S-S</sup> was obtained which was recrystallized from CH<sub>3</sub>OH solution. (3.2 g, yield: 85 %). Elemental analysis calculated for C<sub>24</sub>H<sub>20</sub>N<sub>2</sub>S<sub>4</sub> (L1<sup>S-S</sup>): C 62.03, H 4.34, N 6.03; Found: C 61.86, H 4.28, N 5.84; IR frequencies (KBr disk, cm<sup>-1</sup>): 3078(w), 3060(w), 2950(w), 2915(w), 2873(w), 2848(w), 1602(v<sub>CN</sub>, s), 1570(s), 1464(m), 1439(m), 1423(s), 1385(m), 1337(m), 1289(w), 1263(m), 1194(m), 1160(w), 1128(w), 1094(w), 1053(w), 1039(m), 951(w), 933(w), 871(w), 840(m), 764(m), 753(s), 717(m), 710(m), 664(w), 616(w), 595(w), 549(w), 526(w), 484(w), 446(w); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.68 (2H, s, imine-CH), 7.63 (2H, d, J= 6.4 Hz, phenyl ring proton), 7.43 (2H, d, J=5.0 Hz, phenyl ring proton), 7.11 (4H, m, phenyl ring proton), 7.00 (2H, d, J=5.0 Hz, thiophene ring proton), 6.92 (2H, d, J=5.0 Hz, thiophene ring proton), 2.49 (6H, s, methyl proton of thiophene ring); ESI mass: m/z (%) = 464.05 (100)[M+H<sup>+</sup>]<sup>+</sup>.

**2,2'-disulfanediylbis(N-((3-methylthiophen-2-yl)methylene)ethanamine) (L2<sup>S-S</sup>):** To a stirred solution of 2,2'-diaminodiethyl disulfidedihydrochloride (0.37 g, 1.64 mmol) in 15 ml of CH<sub>3</sub>OH was added triethylamine (0.332 g, 3.28 mmol) and the solution was stirred for 30 mins. Then the resulting solution was added to a stirred solution of 3-methyl-2-thiophenecarbaldehyde (0.413 g, 3.28 mmol) in 10 ml CH<sub>3</sub>OH solution and refluxed for 6 hrs. Then CH<sub>3</sub>OH was removed using rotary evaporator. The resulting residue was dissolved in 30 ml of chloroform, washed with 100 ml (2 times) of water, brine water (100 ml) and again with 100 ml water. The organic layer was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and chloroform was removed using rotary evaporator, resulting yellow oil. (0.96 g, yield: 79%). Elemental analysis calculated for C<sub>16</sub>H<sub>20</sub>N<sub>2</sub>S<sub>4</sub> (L2<sup>S-S</sup>): C 52.14, H 5.47, N 7.60; Found: C 51.98, H 5.58, N 7.49; IR frequencies (KBr disk, cm<sup>-1</sup>): 3099(w), 3063(w), 2989(m), 2931(m), 2828(s), 1626(v<sub>CN</sub>, s), 1554(w), 1431(m), 1384(w), 1334(m), 1252(w), 1190(s), 1099(s), 1060(s), 972(m), 932(m), 901(m), 844(w), 809(w), 722(m), 606(w); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.44 (2H, s, imine-CH), 7.17 (2H, d, J= 5.4 Hz, thiophene ring proton), 6.81 (2H, d, J= 4.6 Hz, thiophene ring proton), 3.87 (4H, t, J= 6.8 Hz, methylene proton of -S-CH<sub>2</sub>-CH<sub>2</sub>-N-), 3.02 (4H, t, J= 6.8 Hz, methylene proton of -S-CH<sub>2</sub>-CH<sub>2</sub>-N-), 2.38(6H, s, methyl proton of thiophene ring); ESI mass: m/z (%) = 369.04 (100) [M+H<sup>+</sup>]<sup>+</sup>.

**[(L1)<sub>8</sub>Cu<sub>8</sub>](ClO<sub>4</sub>)<sub>2</sub>·DMF·0.5CH<sub>3</sub>OH (1·DMF·0.5CH<sub>3</sub>OH):** To a degassed solution of ligand L1<sup>S-S</sup> (0.298 g, 0.64 mmol) in 30 ml dry CH<sub>3</sub>OH was added solid [Cu(CH<sub>3</sub>CN)<sub>4</sub>]ClO<sub>4</sub> (0.419 g, 1.28 mmol), resulting a dark reddish purple solution. The solution was refluxed for 1hr. After cooling, the purple precipitate was collected by filtration. Slow diffusion of Et<sub>2</sub>O into the DMF

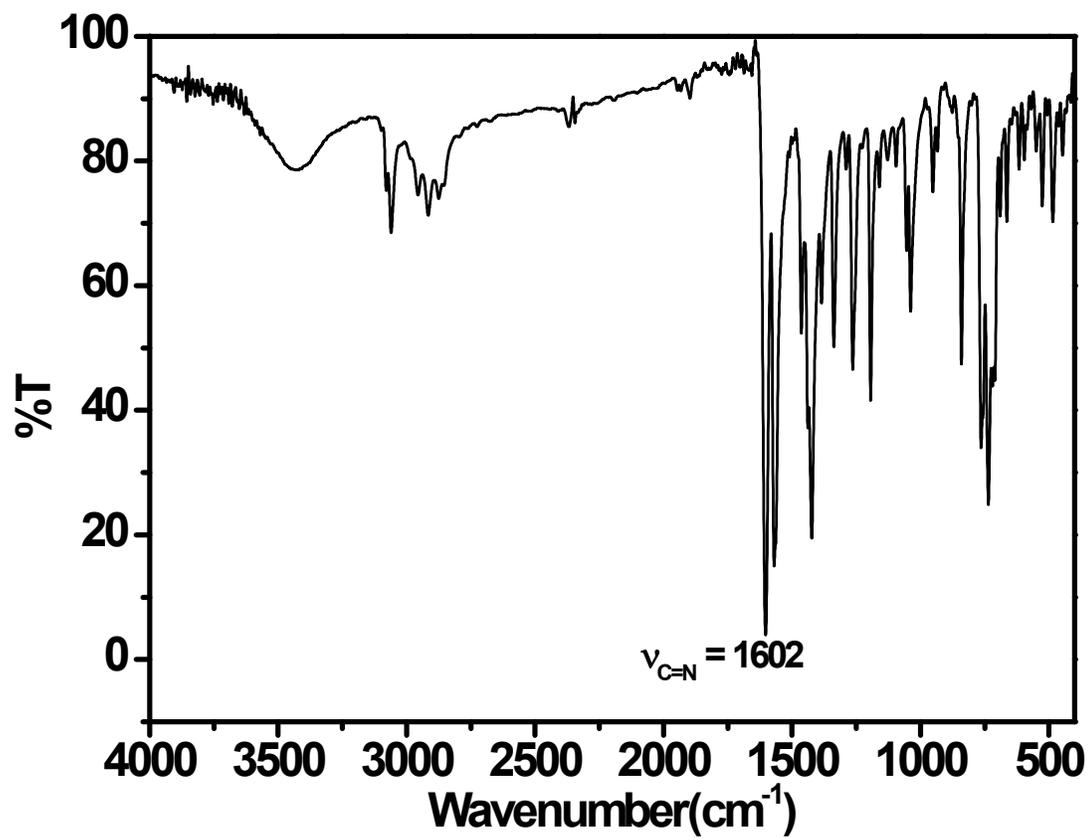
solution of purple precipitate afforded dark crystals of **1**·DMF·0.5CH<sub>3</sub>OH. (0.330 g, yield: 76 % based on Cu). Elemental analysis calculated for C<sub>99.5</sub>H<sub>87</sub>N<sub>9</sub>O<sub>9.5</sub>S<sub>16</sub>Cl<sub>2</sub>Cu<sub>8</sub> (**1**·DMF·0.5CH<sub>3</sub>OH): C 45.04, H 3.31, N 4.75; Found: C 44.91, H 3.19, N 4.61; IR frequencies (KBr disk, cm<sup>-1</sup>): 3442( $\nu_{\text{OH}}$ , s), 3047(w), 2956(w), 2925(m), 2850(w), 1654(m,  $\nu_{\text{C=O}}$  of DMF), 1581( $\nu_{\text{C=N}}$ , s), 1549(s), 1504(w), 1457(w), 1410(w), 1388(w), 1343(m), 1268(w), 1191(w), 1157(w), 1081( $\nu_{\text{ClO}_4}$ , s), 952(w), 844(w), 771(w), 742(m), 658(w), 623( $\nu_{\text{ClO}_4}$ , m), 549(w), 486(w); ESI mass: m/z (%) = 1182.81 (92) [(L1)<sub>8</sub>Cu<sub>8</sub>]<sup>2+</sup>, 823.93 (46) [2Cu+ 3(L<sup>-</sup>)]<sup>+</sup>, 526.97 (100) [Cu+2(L<sup>-</sup>)-H]<sup>+</sup>; Molar conductance,  $\Lambda_{\text{M}}$  in CH<sub>3</sub>CN = 240  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>; UV/Vis in CH<sub>3</sub>CN: 269(77250), 314(88875), 350(sh, 63320), 500(11170), 850(3104); Vis/NIR in CH<sub>3</sub>CN: 500(11820), 850(2510), 1175(8310), 1700(21930); Vis/NIR in DMF: 500(12170), 850(2565), 1175(8560), 1700(22485); Vis/NIR in DMSO: 500(11945), 850(2525), 1175(8450), 1700(21955).

#### **[(L2)<sub>12</sub>Cu<sub>16</sub>O<sub>6</sub>S](ClO<sub>4</sub>)·4H<sub>2</sub>O, (2.4 H<sub>2</sub>O):**

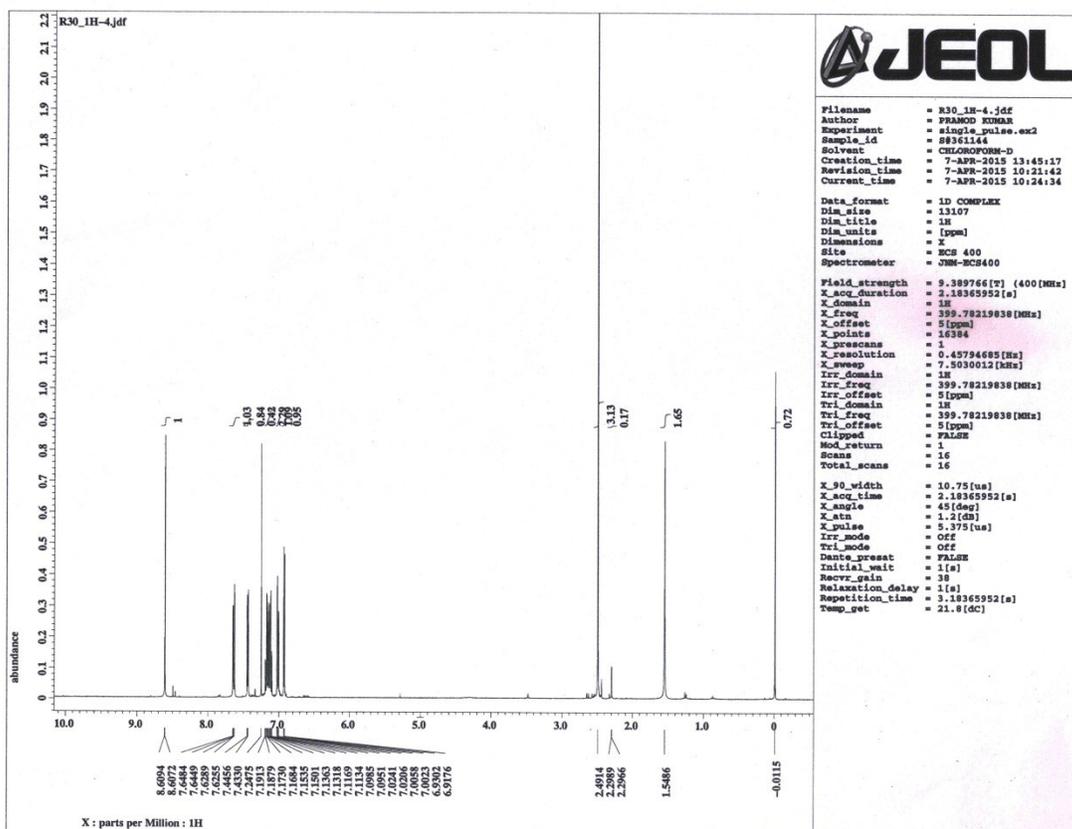
To a degassed solution of ligand L2<sup>S-S</sup> (0.50 g, 1.36 mmol) in 40 ml dry CH<sub>3</sub>OH was added solid [Cu(CH<sub>3</sub>CN)<sub>4</sub>]ClO<sub>4</sub> (0.89 g, 2.72 mmol), resulting a yellowish orange solution. The solution was refluxed for 1hr. After cooling, the yellow precipitate was collected by filtration. Slow diffusion of Et<sub>2</sub>O into the DMF solution of yellow precipitate afforded dark brown block crystals of **2.4 H<sub>2</sub>O**. (0.48 g, yield: 80 % based on Cu). Elemental analysis calculated for C<sub>96</sub>H<sub>128</sub>N<sub>12</sub>O<sub>14</sub>S<sub>25</sub>Cl<sub>1</sub>Cu<sub>16</sub> (**2.4H<sub>2</sub>O**): C 32.68, H 3.66, N 4.76; Found: C 32.52, H 3.59, N 4.86; IR frequencies (KBr disk, cm<sup>-1</sup>): 3448( $\nu_{\text{OH}}$ , br), 3097(w), 2920(w), 2856(w), 1602( $\nu_{\text{C=N}}$ , s), 1560(w), 1538(w), 1504(w), 1437(w), 1420(m), 1385(w), 1360(w), 1340(w), 1262(m), 1224(w), 1089( $\nu_{\text{ClO}_4}$ , s), 993(w), 930(w), 830(w), 802(w), 730(m), 623( $\nu_{\text{ClO}_4}$ , m), 558(w), 541(w), 494(w), 480( $\nu_{\text{Cu-O}}$ , w); ESI mass: m/z (%) = 1680.05 (30) {[(L2)<sub>12</sub>Cu<sub>16</sub>O<sub>6</sub>S]+3H}<sup>2+</sup>, 1086.70 (30) [10Cu+8(L<sup>-</sup>)+(S<sup>2-</sup>)+2(O<sup>2-</sup>)]<sup>2+</sup>, 805.79 (90) [8Cu+6(L<sup>-</sup>)+(S<sup>2-</sup>)+3(O<sup>2-</sup>)-3H]<sup>2+</sup>, 462.95 (45) [Cu+2(L<sup>-</sup>)+(S<sup>2-</sup>)]<sup>+</sup>; Molar conductance,  $\Lambda_{\text{M}}$  in CH<sub>3</sub>CN = 135  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>; UV/Vis in CH<sub>3</sub>CN: 269(98665), 355(25580), 455(13440), 760(1220); Vis/NIR in CH<sub>3</sub>CN: 455(14040), 760(1340), 1408(3380) 1460 (1645), 1535(1080); Vis/NIR in DMF: 455(14190), 770(1024), 1430(2905), 1560(1685); Vis/NIR in DMSO: 455(15980), 760(1110), 1430(3255), 1560(1840).

#### **Physical Measurements:**

The FTIR spectra of the complexes were recorded on a Thermo Nicolet iS10 spectrometer using KBr pellet in the range 4000 – 400 cm<sup>-1</sup>. The electronic spectra were recorded on an Agilent 8453 diode array spectrophotometer. The Vis-NIR spectra were recorded using Perkin Elmer spectrophotometer. Elemental analyses were carried out on a Perkin-Elmer 2400 series-II CHN Analyzer. Electron paramagnetic resonance (EPR) spectra were obtained using Bruker- EMX-1444 EPR spectrometer, ESI Mass spectra were recorded on Waters Q-ToF premier- HAB213 spectrometer. The <sup>1</sup>H NMR spectra were recorded on JEOL JNM LA 500 or on Bruker DPX-300. Redox potentials were measured using CHI 1120A spectro-electrochemical analyzer. The cyclic voltammograms (CV) were recorded in CH<sub>3</sub>CN using same cell set up. A three electrode cell set up such as platinum, saturated calomel electrode (SCE) and a platinum wire as a working, reference and auxiliary electrode respectively were used. The magnetic susceptibility of **1** and **2** were measured using Vibrating Sample Magnetometer (Cryogenic Inc. (UK) make) Operating at frequency 20.4 Hz.



**Figure S1:** FTIR spectrum of L1<sup>S-S</sup> in KBr disk, shown in the range 400 cm<sup>-1</sup>-4000 cm<sup>-1</sup>.



**Figure S2:**  $^1\text{H}$  NMR spectrum of  $\text{L}^1\text{S}^{\text{S}}$  in  $\text{CDCl}_3$  at RT.

Electrospray ionisation-MS

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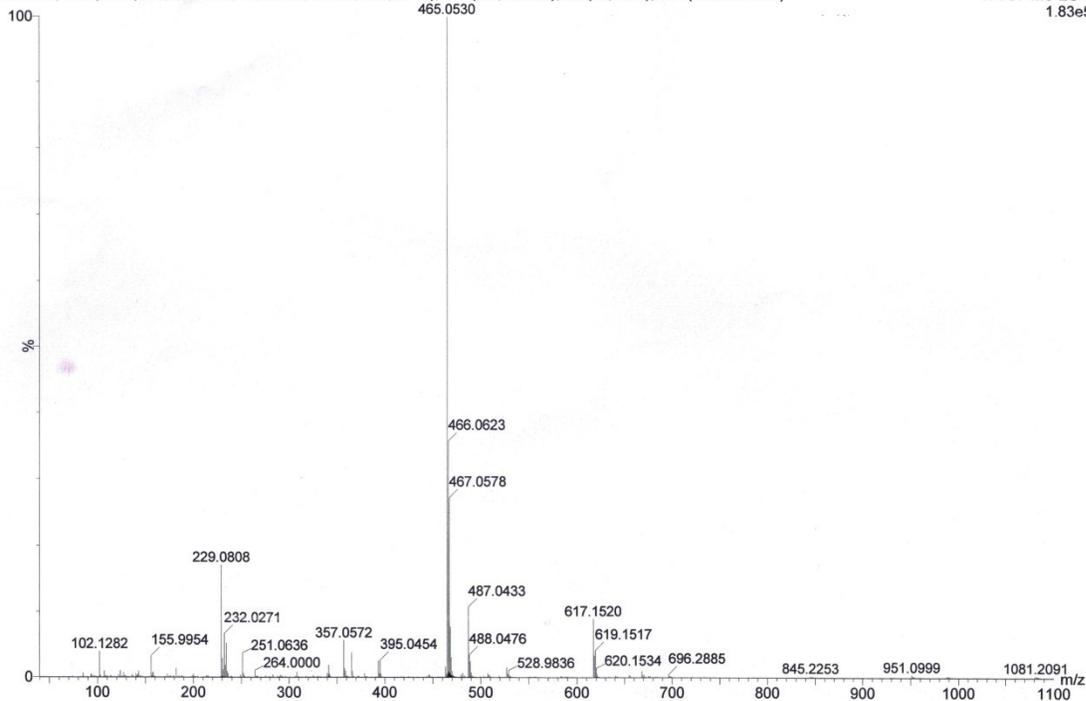
WATERS-Q-ToF Premier-HAB213

465.0530

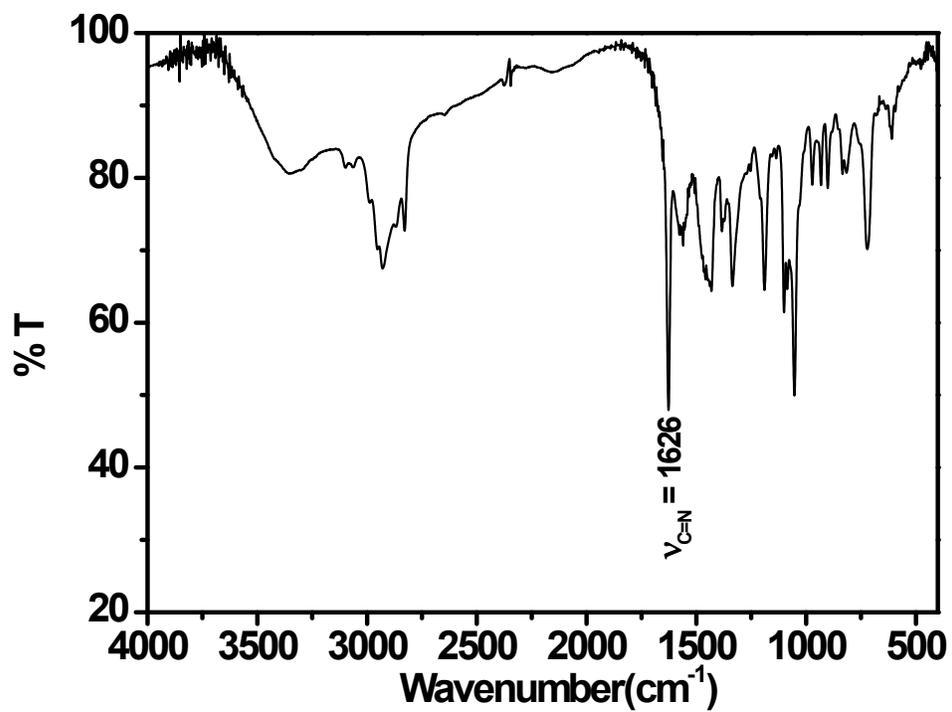
10:47:3015-Sep-2015

1: TOF MS ES+

1.83e5



**Figure S3:** ESI positive mass spectra of L1<sup>S-S</sup> taken in CH<sub>3</sub>CN, peak at m/z = 465.05 corresponds to [L1<sup>S-S</sup>+H<sup>+</sup>]<sup>+</sup>



**Figure S4:** FTIR spectrum of L2<sup>S-S</sup> in KBr disk, shown in the range 400 cm<sup>-1</sup>-4000 cm<sup>-1</sup>.

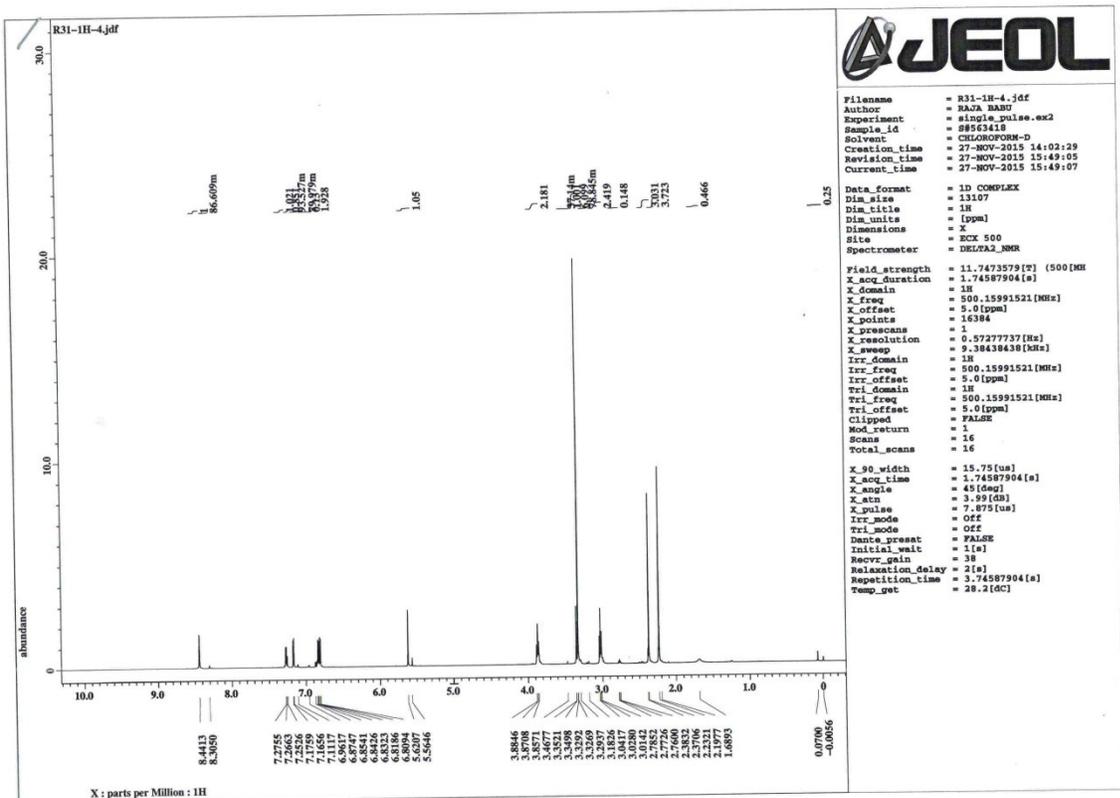


Figure S5:  $^1\text{H}$  NMR spectrum of  $\text{L2}^{\text{S-S}}$  in  $\text{CDCl}_3$  at RT.

Electrospray ionisation -MS

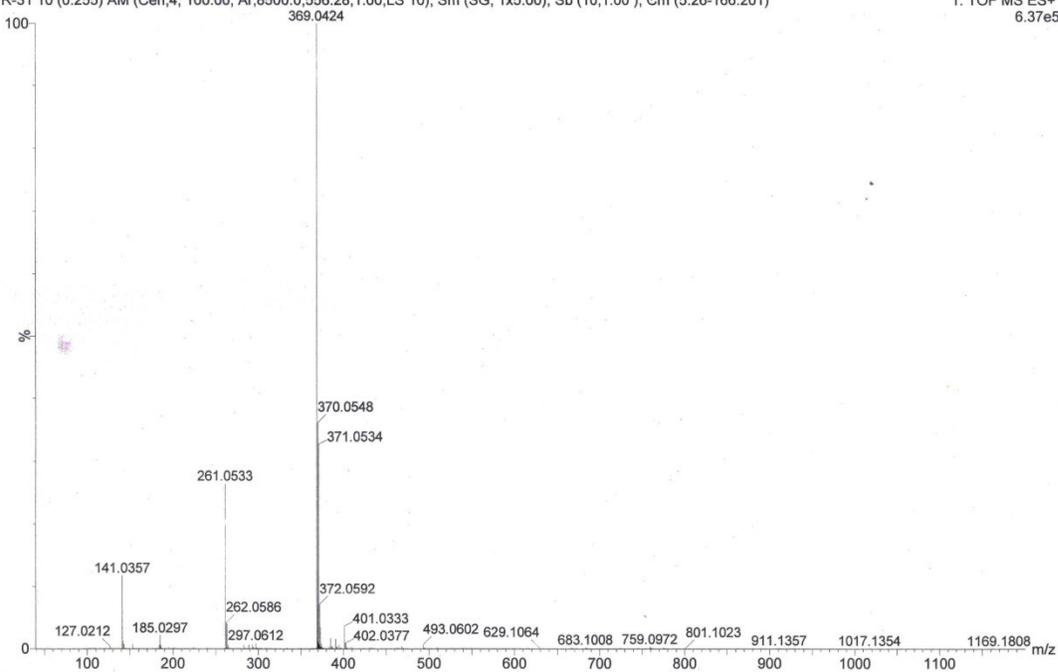
WATERS Q-TOF Premier-HAB213

30-Nov-2015

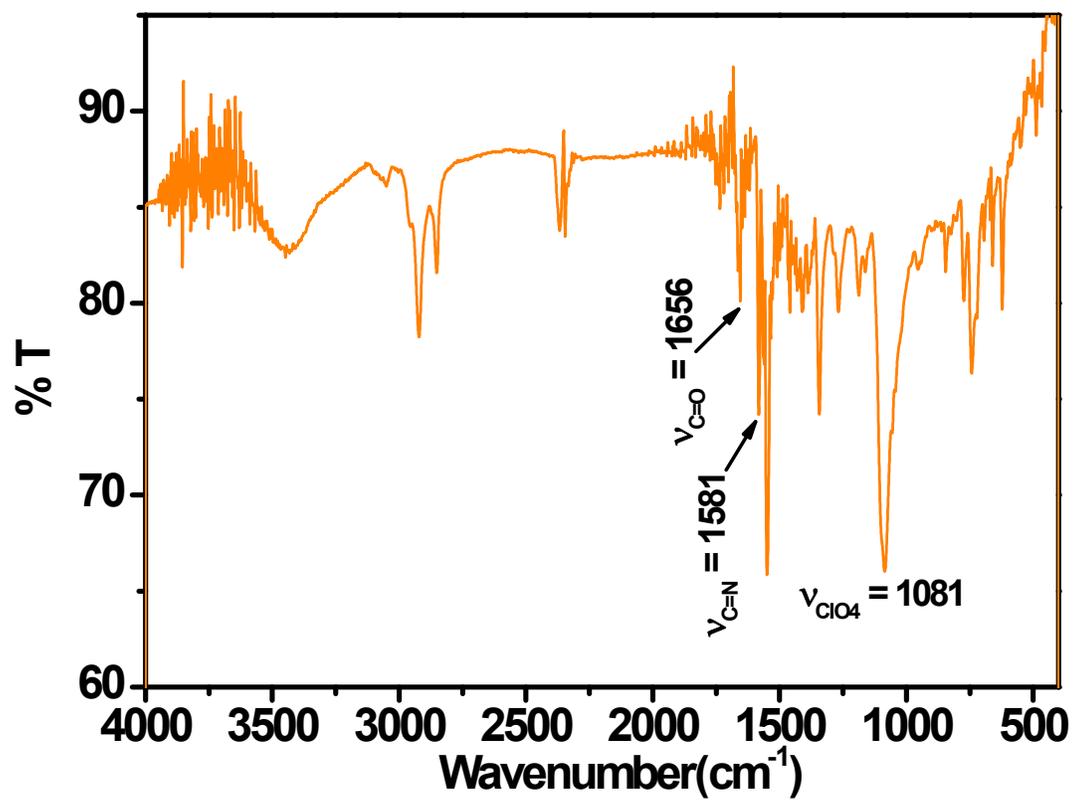
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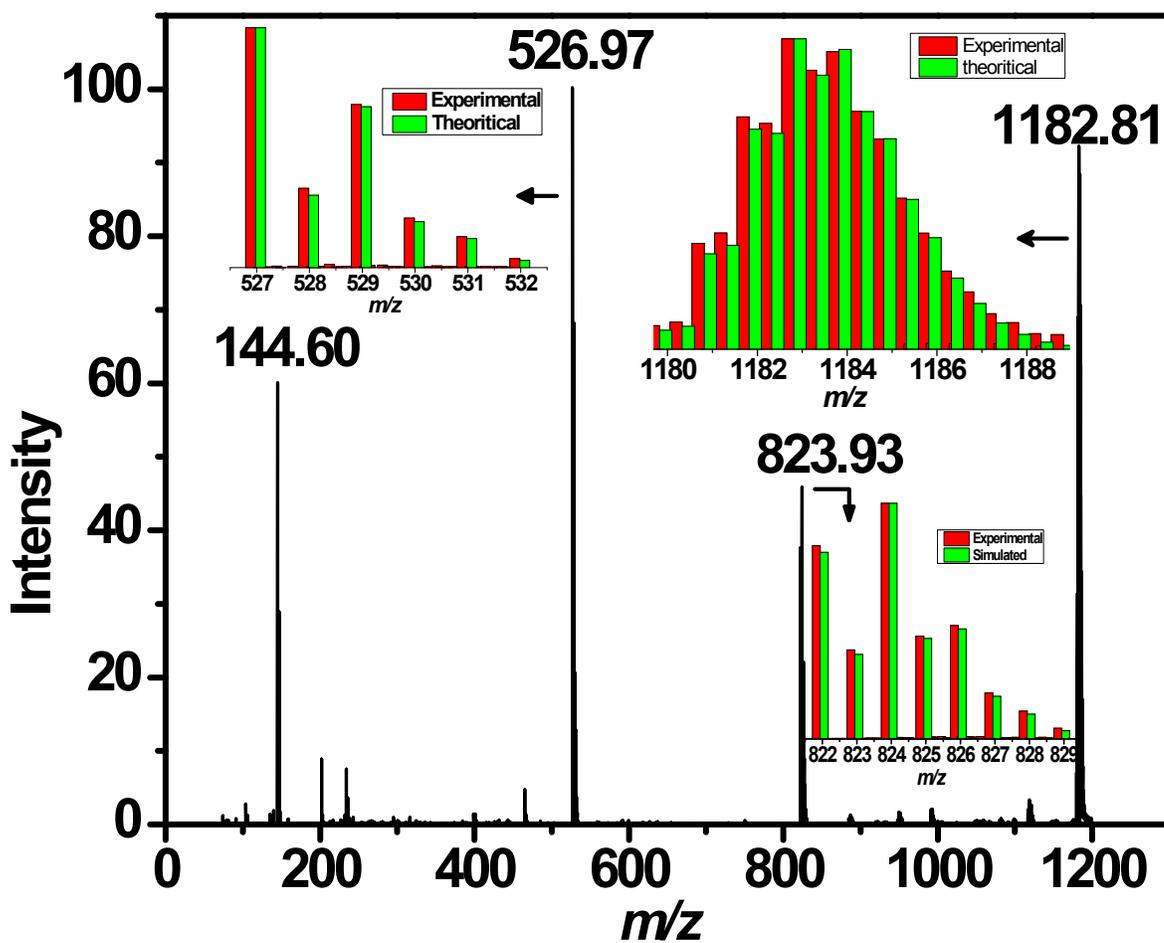
1: TOF MS ES+  
6.37e5



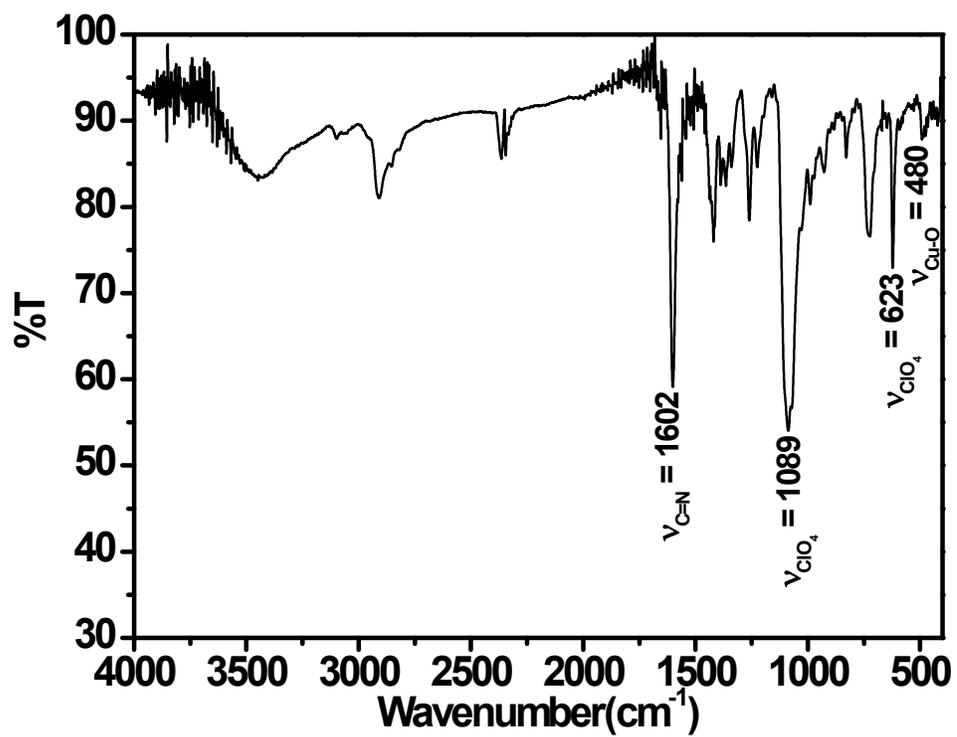
**Figure S6:** ESI positive mass spectra of  $L2^{S-S}$  taken in  $CH_3CN$ , peak at  $m/z = 369.04$  corresponds to  $[L2^{S-S}+H^+]^+$



**Figure S7:** FTIR spectrum of 1·DMF·0.5CH<sub>3</sub>OH in KBr disk, shown in the range 400 cm<sup>-1</sup>-4000 cm<sup>-1</sup>.



**Figure S8:** ESI positive mass spectra of **1** taken in  $\text{CH}_3\text{CN}$ , peak at  $m/z = 1182.81, 823.93, 526.97$  corresponds to  $[(\text{L}1)_8\text{Cu}_8]^{2+}, [2\text{Cu} + 3(\text{L}^-)]^+, [\text{Cu} + 2(\text{L}^-)\text{-H}]^+$ .



**Figure S9:** FTIR spectra of 2.4H<sub>2</sub>O in KBr disk, shown in the range 400 cm<sup>-1</sup> - 4000 cm<sup>-1</sup>.

Electrospray ionisation -MS

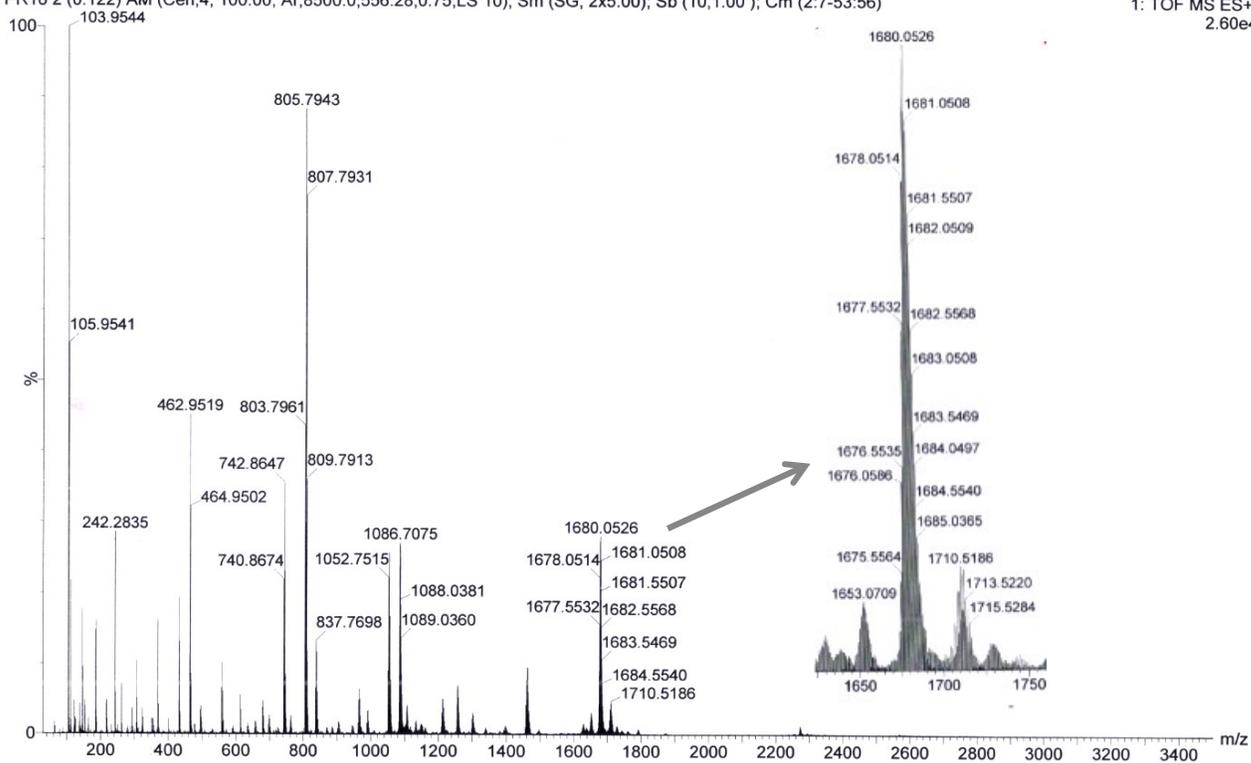
WATERS Q-TOF Premier-HAB213

08-Jun-2016

15:10:00

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1: TOF MS ES+  
2.60e4



**Figure S10:** ESI positive mass spectra of **2** taken in CH<sub>3</sub>CN, peak at m/z = 1680.05, 1086.70 , 805.79, 462.95 corresponds to  $\{[(L2)_{12}Cu_{16}O_6S]+3H\}^{2+}$ ,  $[10Cu+8(L^-)+S^{2-}+2O^{2-}]^{2+}$ ,  $[7Cu+6(L^-)+S^{2-}+2O^{2-}-3H]^{2+}$ ,  $[Cu+2(L^-)+(S^{2-})]^+$ .

Electrospray ionisation -MS

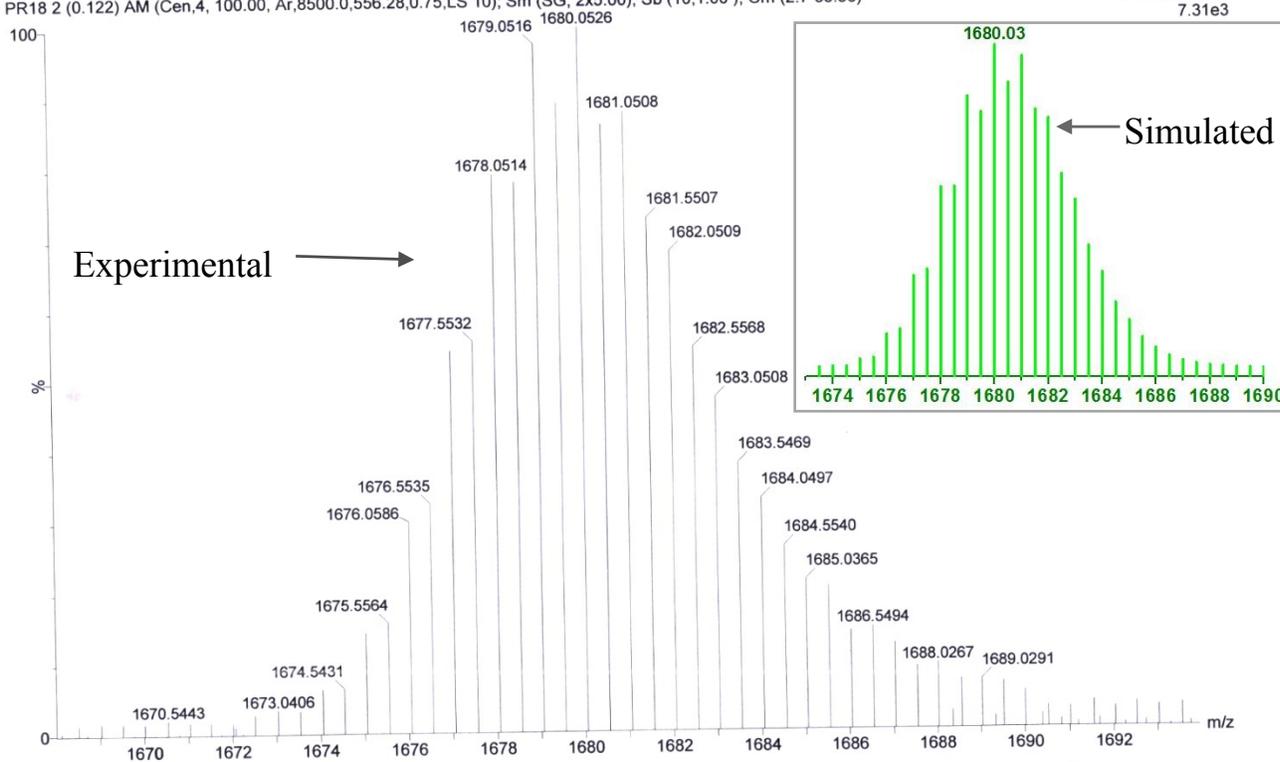
WATERS Q-TOF Premier-HAB213

08-Jun-2016

15:10:00

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1: TOF MS ES+  
7.31e3



**Figure S11:** Experimental (black) and Simulated (green) Mass distribution of peak at  $m/z = 1680.05$ , corresponds to  $\{[(L2)_{12}Cu_{16}O_6S]+3H\}^{2+}$ ,

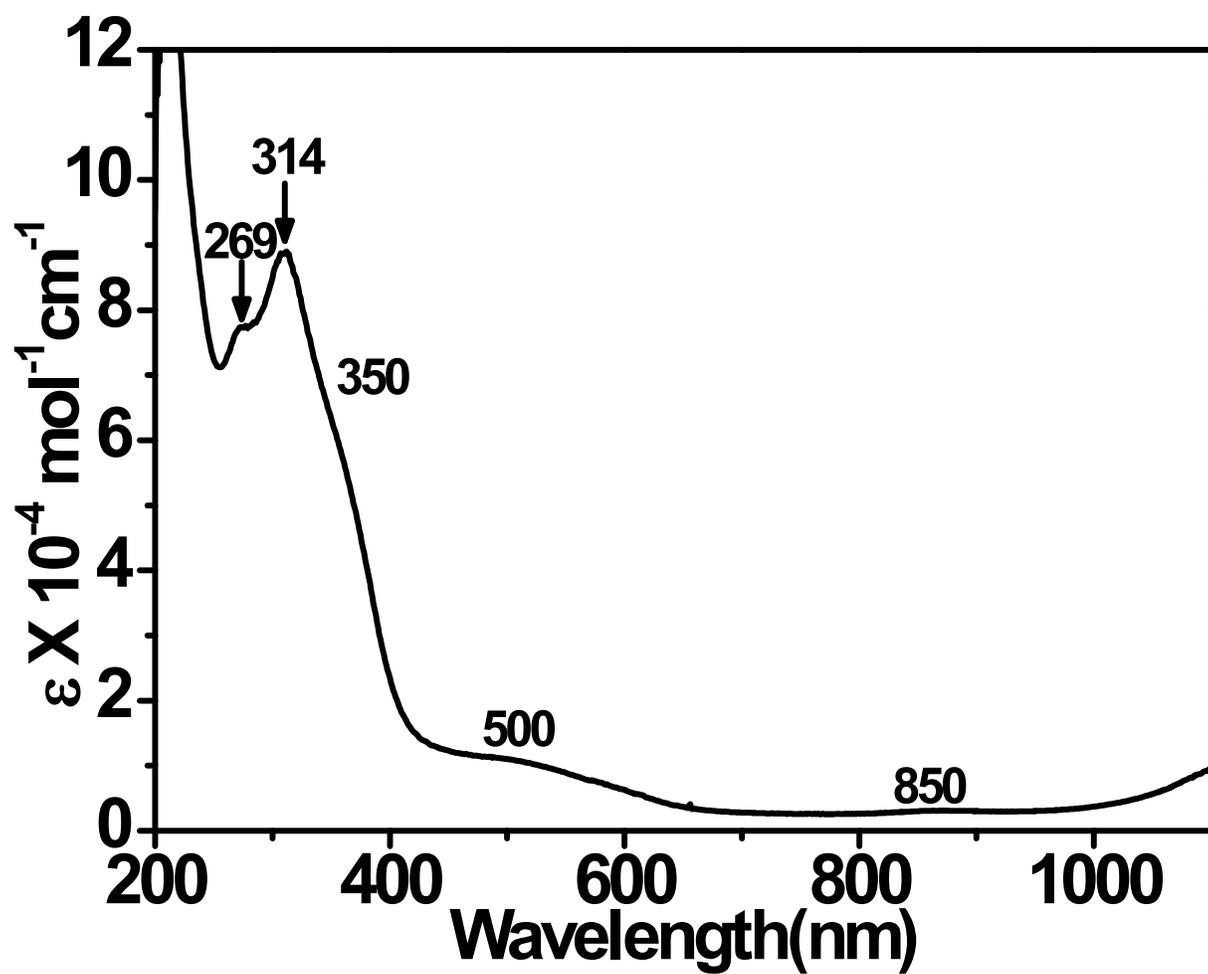
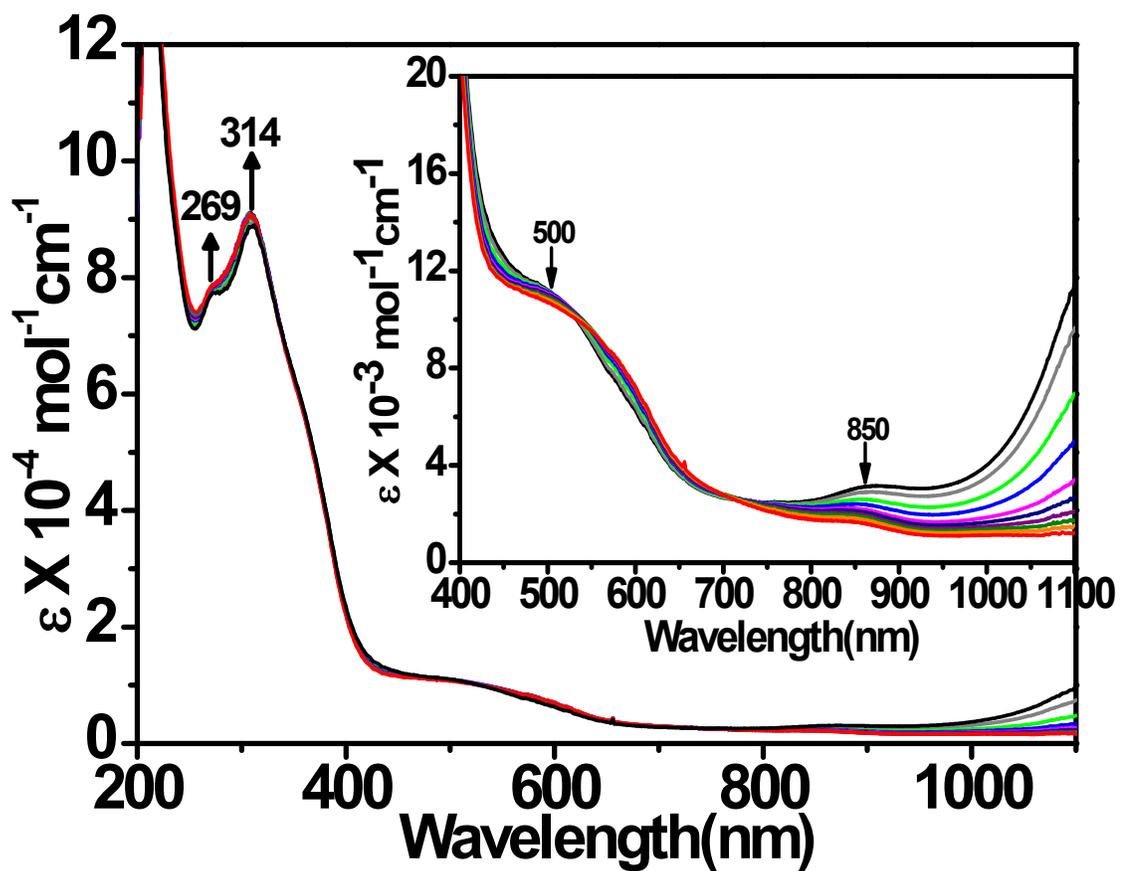
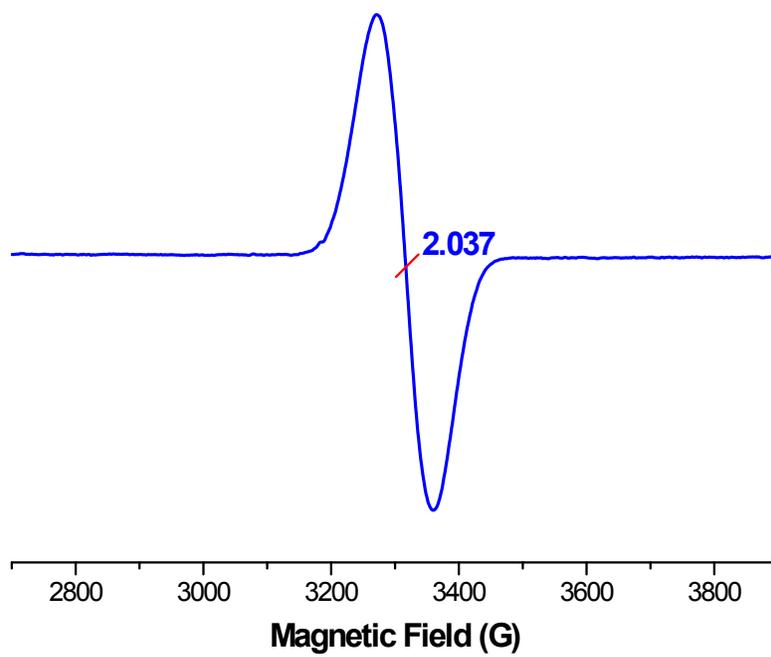


Figure S12: UV-Vis spectrum in CH<sub>3</sub>CN of 1.



**Figure S13:** UV-Vis spectral change during one electron reduction of **1** in  $\text{CH}_3\text{CN}$  (black trace complex **1**, red trace one electron reduce form of **1**). Inset:  $[\mathbf{1}] = 10^{-4} \text{ mol}$ .



**Figure S14:** EPR spectrum of one electron reduced form of **1** (i.e. of **1<sup>Red</sup>**) in CH<sub>3</sub>CN at 120 K.

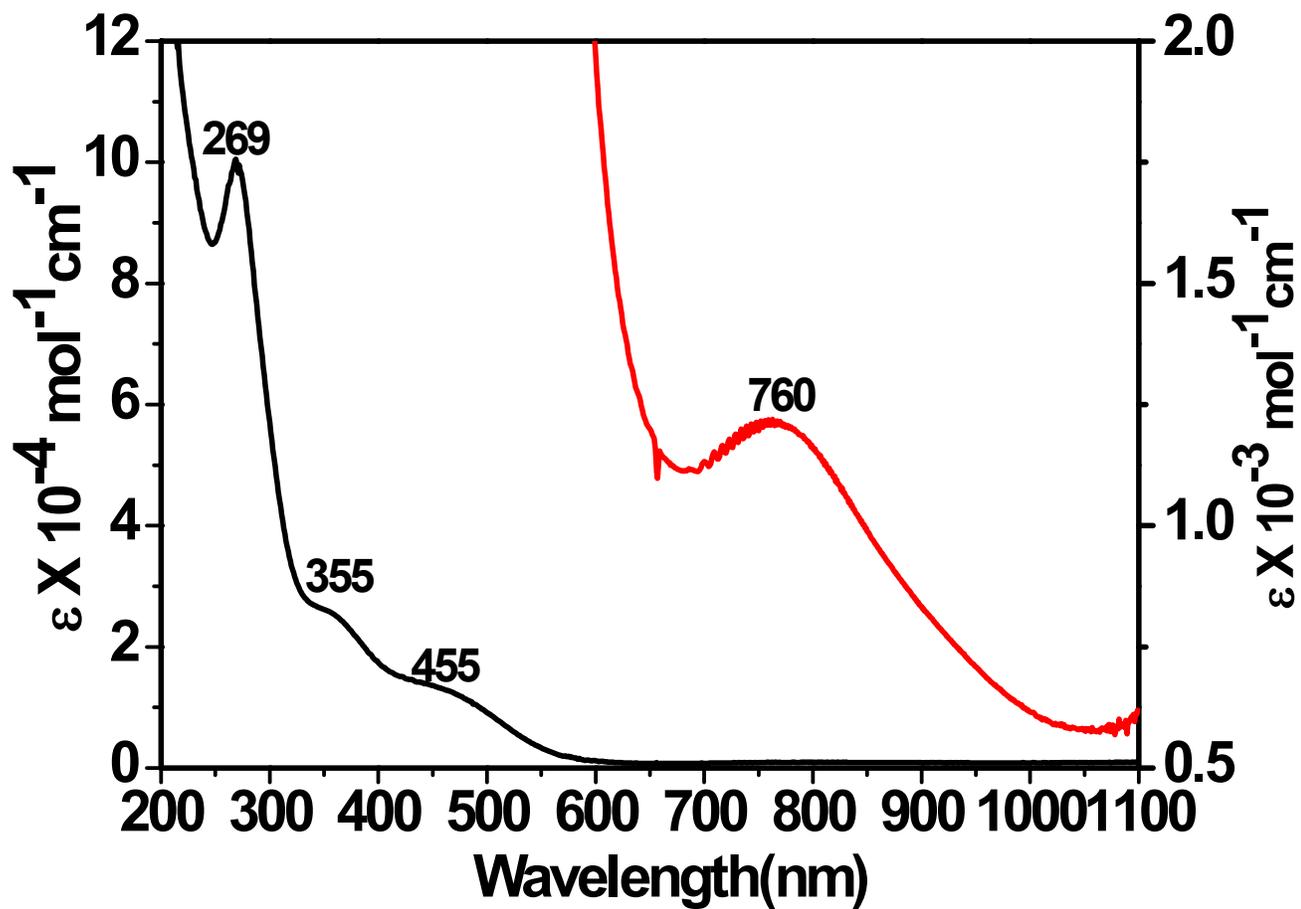


Figure S15: UV-Vis spectra in CH<sub>3</sub>CN of 2, [2] = 10<sup>-4</sup> mol.

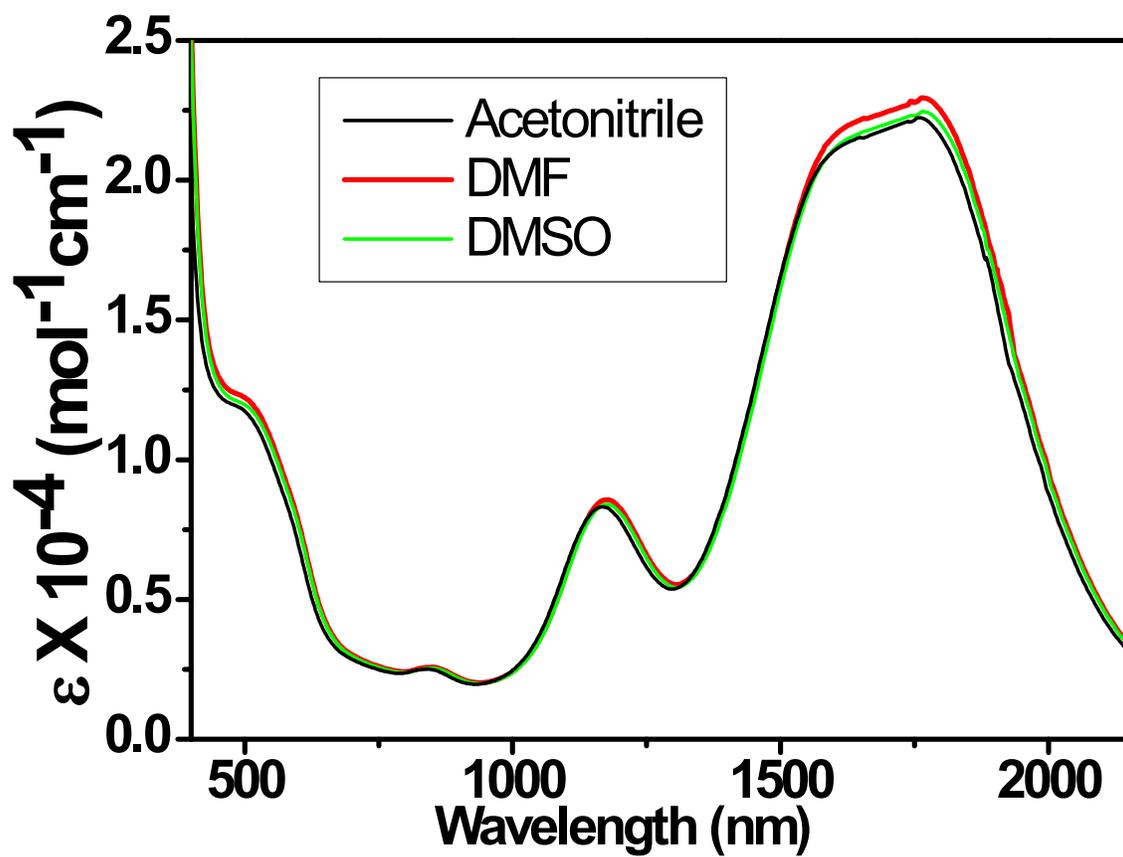
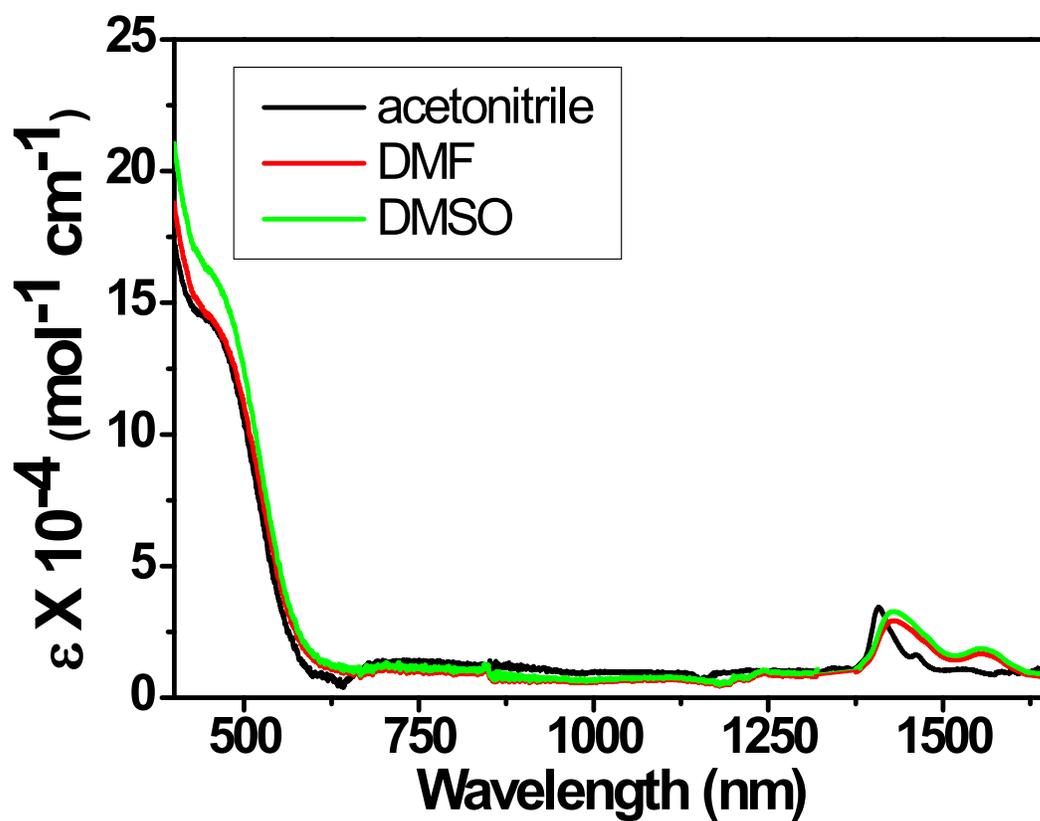
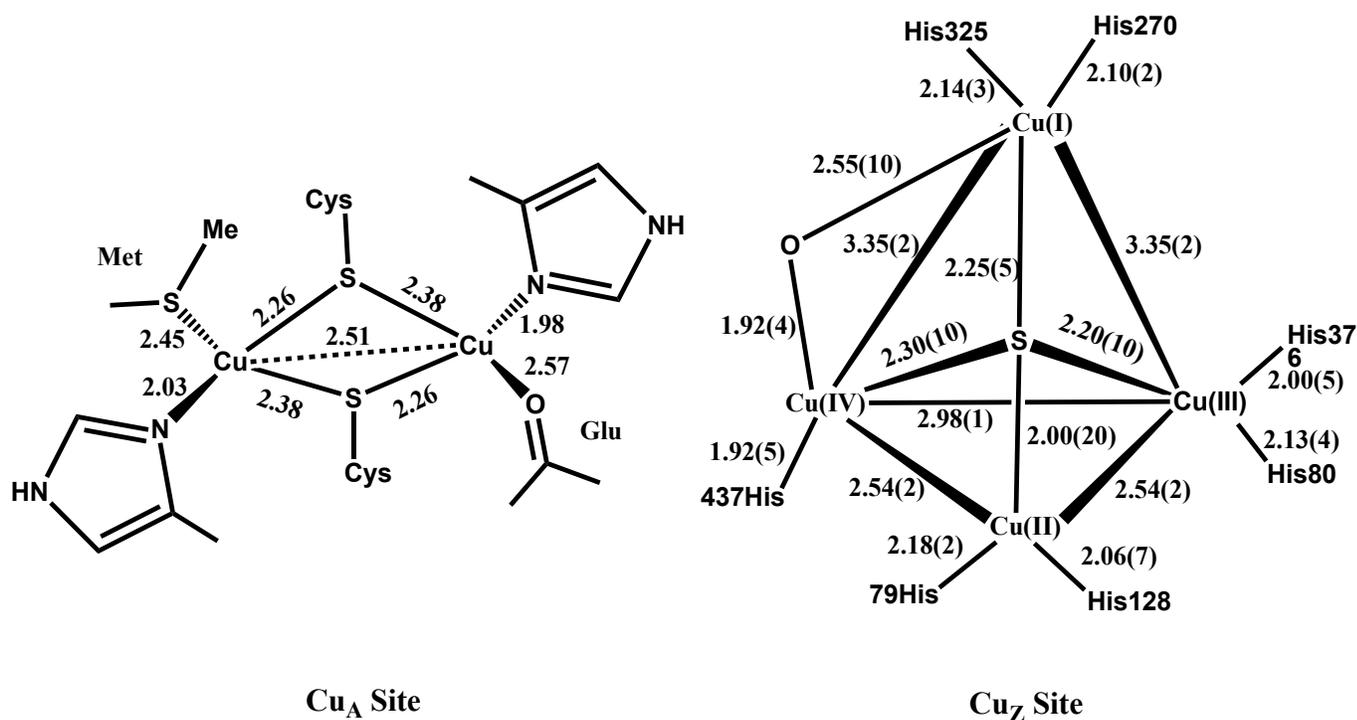


Figure S16: UV-Vis spectra of **1** in CH<sub>3</sub>CN (black trace), DMF (red trace), DMSO (green trace).



**Figure S17:** UV-Vis spectra of **2** in CH<sub>3</sub>CN (black trace), DMF (red trace), DMSO (green trace).



**Figure S18:** Bond distances of Cu<sub>A</sub> and Cu<sub>Z</sub> site adopted from the following references: 1) Haltia, T.; Brown, K.; Tegoni, M.; Cambillau, C.; Saraste, M.; Mattila, K.; Djinovic-Carugo, K. *Biochem. J.* **2003**, *369*, 77. 2) Brown, K.; Djinovic-Carugo, K.; Haltia, T.; Cabrito, I.; Saraste, M.; Moura, J. J. G.; Moura, I.; Tegoni, M.; Cambillau, C. *J. Biol. Chem.* **2000**, *275*(52), 41133.

CCDC number for the supplementary crystallographic data of **1** and **2**: **1494650** and **1494649** respectively. 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).

## Crystal Structure Determination

### The Cu<sub>8</sub> cluster, **1**

Crystals of **1** were large purple blocks. Data was collected at 100 K on a Bruker Apex II diffractometer. A multi-scan absorption correction was applied. The structure was solved by direct methods (SHELXS) and refined with SHELXL-2014. Crystallographic data are reported in Table S1.

The structure has some disorder that was treated with restraints. Most notable are the split perchlorate oxygen positions and two solvate DMF's that are evidently not at full occupancy. In addition, a solvate molecule of methanol was assigned occupancy of 0.5, and no hydrogen atoms were included for this species. A solvent accessible void with a maximum volume of 240 Å<sup>3</sup> and electron count maximum of 46 e<sup>-</sup> remained after all chemically reasonable solvate species were located. Therefore, the SQUEEZE routine (Spek, 2015) was applied, which resulted in a 0.007 reduction in *R*1. A few large difference map peaks remain which could not be assigned. Three reflections were omitted which were obscured by the beam stop.

### The Cu<sub>16</sub> cluster, **2**

A black block of [Cu<sub>16</sub>S)(L2)<sub>12</sub>O<sub>6</sub>](ClO<sub>4</sub>)•4H<sub>2</sub>O, **2**, was mounted in the 100 K nitrogen cold stream provided by an Oxford Cryostream low-temperature apparatus on the goniometer head of a Bruker D8 diffractometer equipped with a Photon 100 CMOS detector on beamline 11.3.1 at the Advanced Light Source (Lawrence Berkeley National Laboratory, Berkeley, CA). The data set was reduced with the use of Bruker SAINT, and a multi-scan absorption correction was applied with the use of SADABS. Structure solutions and refinements were conducted with SHELXS-2008 and SHELXL-2014, respectively.

Various types of disorder in the structure required some special refinement techniques. This dataset is the best that could be obtained out of numerous attempts in both India and the U.S. The set of Cu's is mixed valent by ESR, but the charge is evidently not localized. Two oxygen atoms, O1 and O2, with large displacement parameters have been assigned as O(oxide). There are two sites external to the cluster assigned as water (O1W and O2W). No attempt was made to locate and refine hydrogen positions for O1W and O2W. Very large thermal displacement parameters were observed for the peripheral 3-methylthiophene groups. In particular, the methyl groups were ill-behaved. In the final cycles of refinement, the N=C(H)-3-methylthiophene portion was refined as a rigid group in order for it to have a reasonable geometry. The coordinates for this group were taken from the structure with ref code LONSOX<sup>iv</sup> in the Cambridge Crystallographic Database. Thermal parameters were kept isotropic for carbon atoms. The Cu, S, and N atoms were anisotropic. One perchlorate anion occupies a special position of 3-fold symmetry. One of the four oxygens (O3) is also on the 3-fold axis, and the other (O4) is on a general position. This group is refined with restrained geometry of Cl-O

1.44(2) Å and O---O of 2.36(8) Å. Additionally, the oxygen isotropic thermal parameters are fixed at 0.10 Å<sup>2</sup>. The central sulphide-sulfur was anisotropic.

## References

- SAINT and SADABS: Bruker AXS Inc.: Madison, WI, **2014**.  
 SHELXS: Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112.  
 SHELXL: Sheldrick, G. M. *Acta Crystallogr., Sect. C* **2015**, *71*, 3.  
 SQUEEZE: Spek, A. L. *Acta Crystallogr., Sect. C*, **2015**, *71*, 9.  
 S. Wang, Z. Li, W. Wang, R.-J. Yu, X. Yu. *Z Crystallogr—New Cryst. Struct.* **2008**, *223*, 413.

**Table S1.** Crystal Data for [Cu<sub>8</sub>L<sub>18</sub>](ClO<sub>4</sub>)<sub>2</sub>•DMF•0.5MeOH, **1**, and [Cu<sub>16</sub>S](L<sub>2</sub>)<sub>12</sub>O<sub>6</sub>](ClO<sub>4</sub>)•4H<sub>2</sub>O, **2**

	<b>Cluster 1</b>	<b>Cluster 2</b>
chemical formula	C <sub>99.5</sub> O <sub>H<sub>87</sub></sub> Cl <sub>2</sub> Cu <sub>8</sub> N <sub>9</sub> O <sub>9.5</sub> S <sub>16</sub>	C <sub>96</sub> H <sub>120</sub> ClCu <sub>16</sub> N <sub>12</sub> O <sub>14</sub> S <sub>25</sub>
formula weight	2652.96	3519.62
radiation source, λ (Å)	sealed tube, 0.71073	synchrotron, 1.0332
crystal system	monoclinic	trigonal
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i> (No. 14)	<i>P</i> 31 <i>c</i> (No. 159)
T (K)	100(2)	100(2)
<i>a</i> (Å)	18.757(5)	18.1253(7)
<i>b</i> (Å)	30.586(5)	
<i>c</i> (Å)	20.498(5)	29.8697(14)
β (°)	92.805(5)	
<i>V</i> (Å <sup>3</sup> )	11746(5)	8498.3(8)
<i>Z</i>	4	2
<i>d</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.500	1.375
μ (mm <sup>-1</sup> )	1.805	6.41
<i>F</i> (000)	5380	3546
crystal size	0.20 x 0.30 x 0.30	0.08 x 0.10 x 0.14
reflections collected	94954	65370
data/parameters/restraints	21817/66/1295	10246/36/236
<i>R</i> (int)	0.1067	0.0769
<i>R</i> <sub>1</sub> [data with <i>I</i> > 2σ( <i>I</i> )]	0.0842 [12667]	0.1258 [7295]
<i>wR</i> <sub>2</sub> (all data)	0.2496	0.3727
largest diff peak, hole (e Å <sup>-3</sup> )	2.47, -0.81	1.81, -1.10

### Description of the structure of $[\text{Cu}_8(\text{L1})_8](\text{ClO}_4)_2(\text{DMF})\cdot 0.5(\text{MeOH}), 1$

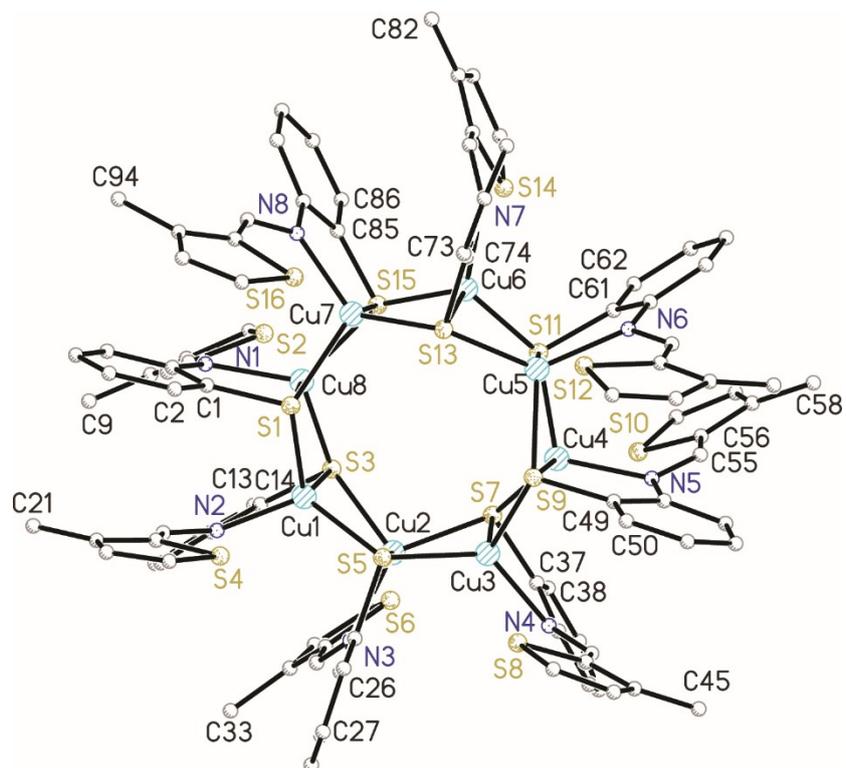
The cluster has no crystallographic symmetry. There are eight Cu's in a crown conformation and eight ligands (L1). The eight sulfide S atoms, S1, S3, S5, S7, S9, S11, S13, S15 form normal bonds to Cu whereas the thiophene S atoms are only weakly interacting. Bond distances and angles around Cu do not reveal whether the metal center is in the +1 or +2 oxidation state. A listing of selected distances and angles is given in Table S1 below.

Table 1. Selected bond lengths [Å] and angles [°] for  $[\text{Cu}_8(\text{L1})_8](\text{ClO}_4)_2(\text{DMF})\cdot 0.5(\text{MeOH}), 1$ .

Cu(1)-N(2)	2.048(9)	Cu(4)-Cu(5)	2.6051(19)
Cu(1)-S(6)	2.292(3)	Cu(5)-N(6)	2.057(9)
Cu(1)-S(1)	2.306(3)	Cu(5)-S(13)	2.306(3)
Cu(1)-S(3)	2.390(3)	Cu(5)-S(9)	2.315(3)
Cu(1)-Cu(2)	2.5836(18)	Cu(5)-S(11)	2.388(3)
Cu(1)-Cu(8)	2.6078(18)	Cu(5)-Cu(6)	2.5552(18)
Cu(2)-N(3)	2.033(9)	Cu(6)-N(7)	2.031(10)
Cu(2)-S(7)	2.293(3)	Cu(6)-S(11)	2.295(3)
Cu(2)-S(3)	2.314(3)	Cu(6)-S(15)	2.306(3)
Cu(2)-S(6)	2.412(3)	Cu(6)-S(13)	2.412(3)
Cu(2)-Cu(3)	2.5493(19)	Cu(6)-Cu(7)	2.5893(18)
Cu(3)-N(4)	2.053(9)	Cu(7)-N(8)	2.033(8)
Cu(3)-S(6)	2.300(3)	Cu(7)-S(13)	2.288(3)
Cu(3)-S(9)	2.342(3)	Cu(7)-S(1)	2.330(3)
Cu(3)-S(7)	2.426(3)	Cu(7)-S(15)	2.414(3)
Cu(3)-Cu(4)	2.5852(18)	Cu(7)-Cu(8)	2.5704(19)
Cu(4)-N(5)	2.052(9)	Cu(8)-N(1)	2.024(9)
Cu(4)-S(7)	2.286(3)	Cu(8)-S(15)	2.280(3)
Cu(4)-S(11)	2.312(3)	Cu(8)-S(3)	2.292(3)
Cu(4)-S(9)	2.367(3)	Cu(8)-S(1)	2.369(3)
N(2)-Cu(1)-S(6)	125.5(2)	S(1)-Cu(1)-S(3)	110.91(10)
N(2)-Cu(1)-S(1)	111.2(3)	N(2)-Cu(1)-Cu(2)	107.0(3)
S(6)-Cu(1)-S(1)	107.00(10)	S(6)-Cu(1)-Cu(2)	58.94(7)
N(2)-Cu(1)-S(3)	88.8(2)	S(1)-Cu(1)-Cu(2)	139.09(9)
S(6)-Cu(1)-S(3)	112.10(10)	S(3)-Cu(1)-Cu(2)	55.28(8)

N(2)-Cu(1)-Cu(8)	99.6(2)	S(7)-Cu(4)-S(11)	103.74(11)
S(6)-Cu(1)-Cu(8)	133.95(9)	N(5)-Cu(4)-S(9)	88.8(3)
S(1)-Cu(1)-Cu(8)	57.25(7)	S(7)-Cu(4)-S(9)	113.83(11)
S(3)-Cu(1)-Cu(8)	54.38(8)	S(11)-Cu(4)-S(9)	111.80(11)
Cu(2)-Cu(1)-Cu(8)	102.67(6)	N(5)-Cu(4)-Cu(3)	108.4(3)
N(3)-Cu(2)-S(7)	133.0(3)	S(7)-Cu(4)-Cu(3)	59.35(8)
N(3)-Cu(2)-S(3)	114.8(3)	S(11)-Cu(4)-Cu(3)	136.45(9)
S(7)-Cu(2)-S(3)	97.52(11)	S(9)-Cu(4)-Cu(3)	56.23(8)
N(3)-Cu(2)-S(6)	88.2(3)	N(5)-Cu(4)-Cu(5)	99.5(3)
S(7)-Cu(2)-S(6)	112.13(10)	S(7)-Cu(4)-Cu(5)	135.00(9)
S(3)-Cu(2)-S(6)	110.56(10)	S(11)-Cu(4)-Cu(5)	57.74(8)
N(3)-Cu(2)-Cu(3)	110.9(3)	S(9)-Cu(4)-Cu(5)	55.24(8)
S(7)-Cu(2)-Cu(3)	59.84(8)	Cu(3)-Cu(4)-Cu(5)	103.80(6)
S(3)-Cu(2)-Cu(3)	131.46(9)	N(6)-Cu(5)-S(13)	127.8(3)
S(6)-Cu(2)-Cu(3)	55.15(7)	N(6)-Cu(5)-S(9)	114.5(3)
N(3)-Cu(2)-Cu(1)	96.9(2)	S(13)-Cu(5)-S(9)	103.19(11)
S(7)-Cu(2)-Cu(1)	129.68(9)	N(6)-Cu(5)-S(11)	87.5(3)
S(3)-Cu(2)-Cu(1)	58.12(8)	S(13)-Cu(5)-S(11)	111.88(10)
S(6)-Cu(2)-Cu(1)	54.49(7)	S(9)-Cu(5)-S(11)	110.95(11)
Cu(3)-Cu(2)-Cu(1)	101.66(6)	N(6)-Cu(5)-Cu(6)	106.3(3)
N(4)-Cu(3)-S(6)	130.9(3)	S(13)-Cu(5)-Cu(6)	59.24(8)
N(4)-Cu(3)-S(9)	114.8(3)	S(9)-Cu(5)-Cu(6)	136.50(9)
S(6)-Cu(3)-S(9)	101.64(11)	S(11)-Cu(5)-Cu(6)	55.21(8)
N(4)-Cu(3)-S(7)	86.8(3)	N(6)-Cu(5)-Cu(4)	99.4(3)
S(6)-Cu(3)-S(7)	111.40(10)	S(13)-Cu(5)-Cu(4)	131.93(9)
S(9)-Cu(3)-S(7)	109.72(10)	S(9)-Cu(5)-Cu(4)	57.15(8)
N(4)-Cu(3)-Cu(2)	107.4(3)	S(11)-Cu(5)-Cu(4)	54.96(8)
S(9)-Cu(3)-Cu(2)	134.22(9)	Cu(6)-Cu(5)-Cu(4)	102.85(6)
S(7)-Cu(3)-Cu(2)	54.83(7)	N(7)-Cu(6)-S(11)	126.6(3)
N(4)-Cu(3)-Cu(4)	97.0(3)	N(7)-Cu(6)-S(15)	121.2(3)
S(6)-Cu(3)-Cu(4)	131.11(9)	S(11)-Cu(6)-S(15)	98.53(11)
S(9)-Cu(3)-Cu(4)	57.17(8)	N(7)-Cu(6)-S(13)	88.0(3)
S(7)-Cu(3)-Cu(4)	54.16(7)	S(11)-Cu(6)-S(13)	111.37(10)
Cu(2)-Cu(3)-Cu(4)	101.89(6)	S(15)-Cu(6)-S(13)	110.52(10)
N(5)-Cu(4)-S(7)	125.0(3)	N(7)-Cu(6)-Cu(5)	105.8(3)
N(5)-Cu(4)-S(11)	113.3(3)	S(11)-Cu(6)-Cu(5)	58.69(8)

S(15)-Cu(6)-Cu(5)	131.06(9)	S(1)-Cu(7)-Cu(6)	136.14(9)
S(13)-Cu(6)-Cu(5)	55.22(7)	S(15)-Cu(7)-Cu(6)	54.76(7)
N(7)-Cu(6)-Cu(7)	100.8(3)	Cu(8)-Cu(7)-Cu(6)	101.60(6)
S(11)-Cu(6)-Cu(7)	131.41(9)	Cu(7)-Cu(8)-Cu(1)	102.15(6)
S(15)-Cu(6)-Cu(7)	58.74(8)	N(1)-Cu(8)-S(15)	122.8(3)
S(13)-Cu(6)-Cu(7)	54.30(8)	N(1)-Cu(8)-S(3)	112.7(3)
Cu(5)-Cu(6)-Cu(7)	102.09(6)	S(15)-Cu(8)-S(3)	105.06(11)
N(8)-Cu(7)-S(13)	129.4(3)	N(1)-Cu(8)-S(1)	89.4(3)
N(8)-Cu(7)-S(1)	113.0(3)	S(15)-Cu(8)-S(1)	114.31(11)
S(13)-Cu(7)-S(1)	103.44(10)	S(3)-Cu(8)-S(1)	112.20(10)
N(8)-Cu(7)-S(15)	87.8(3)	N(1)-Cu(8)-Cu(7)	109.4(3)
S(13)-Cu(7)-S(15)	111.12(10)	S(15)-Cu(8)-Cu(7)	59.33(8)
S(1)-Cu(7)-S(15)	110.85(10)	S(3)-Cu(8)-Cu(7)	136.13(9)
N(8)-Cu(7)-Cu(8)	98.6(3)	S(1)-Cu(8)-Cu(7)	56.11(7)
S(13)-Cu(7)-Cu(8)	130.98(9)	N(1)-Cu(8)-Cu(1)	101.6(3)
S(1)-Cu(7)-Cu(8)	57.57(8)	S(15)-Cu(8)-Cu(1)	135.07(9)
S(15)-Cu(7)-Cu(8)	54.33(7)	S(3)-Cu(8)-Cu(1)	57.97(8)
N(8)-Cu(7)-Cu(6)	107.8(3)	S(1)-Cu(8)-Cu(1)	54.96(7)
S(13)-Cu(7)-Cu(6)	58.91(8)		



**Figure S19.** A view of the atom numbering for the cation of the cluster of  $[\text{Cu}_8(\text{L1})_8](\text{ClO}_4)_2 \cdot (\text{DMF}) \cdot 0.5(\text{MeOH})$ , **1**, as seen approximately down the  $b$  axis. Hydrogen atoms, anions, and solvate molecules have been omitted for clarity.

### **Description of the structure of [Cu<sub>16</sub>S)(O)<sub>6</sub>(L2)<sub>12</sub>](ClO<sub>4</sub>)(H<sub>2</sub>O)<sub>4</sub>, 2**

The compound crystallizes in the trigonal crystal system, space group *P31c* (No. 159), *Z* = 2. The overall Cu cluster has 16 Cu positions. However, the asymmetric unit has one Cu on a crystallographic 3-fold axis (Cu1) and five Cu's (Cu2–Cu6) on general positions. One unique S (S9) also resides on the 3-fold axis, and is considered to be sulfide. The sulfide atom constitutes a Cu<sub>4</sub>S core, shown in Figure S21. The asymmetric unit also contains two oxide O atoms at general positions. There are four ligands (L2) in the asymmetric unit. In each of these, there is a thiolate S (S1, S3, S5, S7) that bridges to three Cu's, with Cu-S bond distances in the range 2.250(6) to 2.377(6) Å. The four thiophene S's (S2, S4, S6, S8) are found in the periphery of the cluster and display weaker, non-bonded distances to the Cu's in the range 2.954 to 3.007 Å. Selected values for the bond distances and angles are given in Table S2.

Table S2. Selected bond lengths [Å] and angles [°] for **2**.

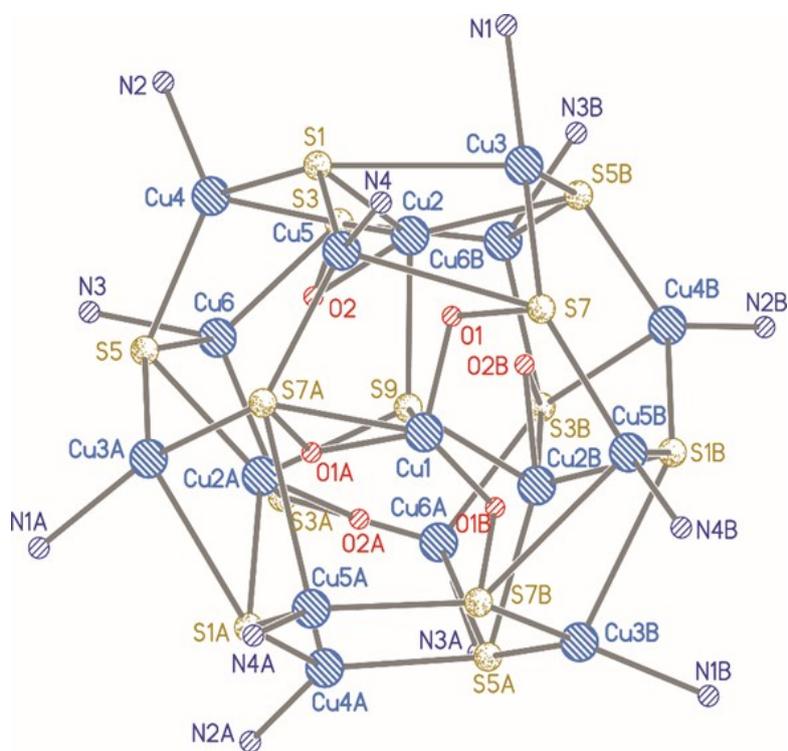
Cu(1)-O(1)	1.659(17)	Cu(4)-N(2)	1.897(19)
Cu(1)-S(9)	2.321(9)	Cu(4)-O(2)	2.03(5)
Cu(1)-S(7)	2.377(6)	Cu(4)-S(5)	2.250(6)
Cu(1)-Cu(5)#1	2.815(4)	Cu(4)-S(1)	2.271(7)
Cu(2)-O(2)	1.65(4)	Cu(4)-S(3)	2.843(6)
Cu(2)-S(9)	2.337(4)	Cu(4)-S(4)	2.954(9)
Cu(2)-S(3)	2.339(6)	Cu(5)-N(4)	1.938(19)
Cu(2)-S(5)#2	2.371(6)	Cu(5)-O(1)	2.234(18)
Cu(2)-S(1)	2.373(6)	Cu(5)-S(1)	2.252(7)
Cu(2)-O(2)#2	2.49(5)	Cu(5)-S(7)#1	2.295(7)
Cu(2)-O(1)	2.604(17)	Cu(5)-S(7)	2.857(7)
Cu(2)-Cu(4)	2.779(4)	Cu(6)-N(3)	1.862(15)
Cu(3)-N(1)	1.912(19)	Cu(6)-S(3)	2.271(6)
Cu(3)-O(1)	2.236(17)	Cu(6)-S(3)#1	2.300(6)
Cu(3)-S(7)	2.275(7)	Cu(6)-O(2)	2.31(4)
Cu(3)-S(5)#2	2.313(7)	Cu(6)-S(5)	2.831(7)
Cu(3)-S(1)	2.854(7)	Cu(6)-Cu(2)#1	2.847(4)
Cu(3)-S(2)	2.954(10)		
O(1)#1-Cu(1)-O(1)	105.4(7)	O(2)-Cu(2)-O(2)#2	93(3)
O(1)-Cu(1)-S(9)	66.7(6)	S(9)-Cu(2)-O(2)#2	54.5(10)
O(1)-Cu(1)-S(7)#1	99.2(6)	O(2)-Cu(2)-O(1)	105.0(16)
O(1)#1-Cu(1)-S(7)	145.5(6)	S(9)-Cu(2)-O(1)	54.1(4)
O(1)-Cu(1)-S(7)	43.7(6)	S(3)-Cu(2)-O(1)	157.4(4)
S(9)-Cu(1)-S(7)	102.7(2)	S(5)#2-Cu(2)-O(1)	82.6(4)
S(7)#1-Cu(1)-S(7)	115.29(16)	S(1)-Cu(2)-O(1)	67.5(4)
O(2)-Cu(2)-S(9)	64.9(17)	N(1)-Cu(3)-O(1)	143.6(7)
O(2)-Cu(2)-S(3)	53.8(15)	N(1)-Cu(3)-S(7)	136.4(8)
S(9)-Cu(2)-S(3)	104.9(2)	O(1)-Cu(3)-S(7)	42.7(5)
O(2)-Cu(2)-S(5)#2	154.4(16)	N(1)-Cu(3)-S(5)#2	112.7(8)
O(2)-Cu(2)-S(1)	90.2(16)	O(1)-Cu(3)-S(5)#2	92.5(5)
S(9)-Cu(2)-S(1)	102.7(2)	S(7)-Cu(3)-S(5)#2	108.9(2)
S(3)-Cu(2)-S(1)	115.4(2)	N(1)-Cu(3)-S(1)	84.4(3)

O(1)-Cu(3)-S(1)	64.6(5)	S(5)-Cu(4)-S(4)	89.0(3)
S(7)-Cu(3)-S(1)	100.2(2)	S(1)-Cu(4)-S(4)	92.5(3)
S(5)#2-Cu(3)-S(1)	101.0(2)	S(3)-Cu(4)-S(4)	157.6(2)
N(1)-Cu(3)-S(2)	72.2(3)	N(4)-Cu(5)-O(1)	120.2(6)
O(1)-Cu(3)-S(2)	132.6(5)	N(4)-Cu(5)-S(1)	130.0(7)
S(7)-Cu(3)-S(2)	90.8(3)	O(1)-Cu(5)-S(1)	76.3(5)
S(5)#2-Cu(3)-S(2)	96.6(3)	N(4)-Cu(5)-S(7)#1	117.9(8)
S(1)-Cu(3)-S(2)	154.8(2)	S(1)-Cu(5)-S(7)#1	109.3(2)
N(2)-Cu(4)-O(2)	127.7(12)	N(4)-Cu(5)-S(7)	85.2(3)
N(2)-Cu(4)-S(5)	129.1(7)	O(1)-Cu(5)-S(7)	35.0(5)
O(2)-Cu(4)-S(5)	72.7(13)	S(1)-Cu(5)-S(7)	100.7(2)
N(2)-Cu(4)-S(1)	116.7(7)	S(7)#1-Cu(5)-S(7)	101.9(3)
O(2)-Cu(4)-S(1)	84.3(12)	N(3)-Cu(6)-S(3)	126.5(7)
S(5)-Cu(4)-S(1)	110.9(2)	N(3)-Cu(6)-S(3)#1	120.6(6)
N(2)-Cu(4)-S(3)	85.7(3)	S(3)-Cu(6)-S(3)#1	109.9(3)
O(2)-Cu(4)-S(3)	42.0(12)	N(3)-Cu(6)-O(2)	135.6(13)
S(5)-Cu(4)-S(3)	101.8(2)	S(3)-Cu(6)-O(2)	49.1(11)
S(1)-Cu(4)-S(3)	101.7(2)	N(3)-Cu(6)-S(5)	87.0(3)
Cu(2)-Cu(4)-S(3)	49.14(13)	S(3)-Cu(6)-S(5)	101.6(2)
N(2)-Cu(4)-S(4)	72.4(3)	S(3)#1-Cu(6)-S(5)	99.6(2)
O(2)-Cu(4)-S(4)	158.8(13)	O(2)-Cu(6)-S(5)	58.2(11)

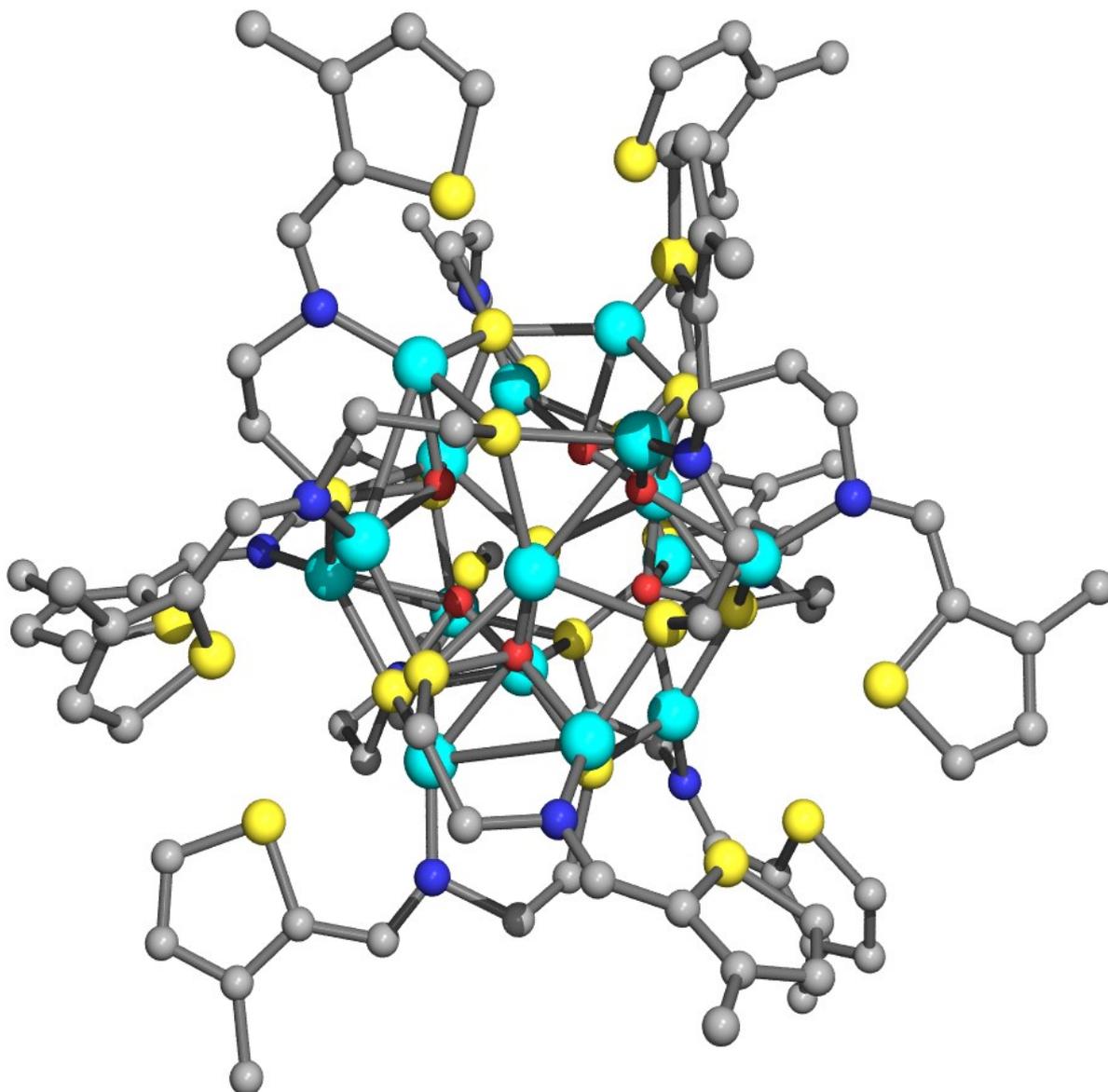
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Symmetry transformations used to generate  
equivalent atoms:

#1  $-y+1, x-y, z$  #2  $-x+y+1, -x+1, z$



**Figure S20.** A view of the cluster  $[\text{Cu}_{16}\text{S}(\text{L}2)_{12}\text{O}_6]^+$ , **2**, as seen approximately down the crystallographic 3-fold axis showing only the atoms coordinated to Cu together with atom numbering.



**Figure S21.** The  $[\text{Cu}_{16}\text{S}(\text{L}2)_{12}\text{O}_6]^+$  cluster excluding hydrogen atoms and water molecules. Copper atoms are green, sulfur are yellow, nitrogen are blue, oxygen are red and carbon are gray.

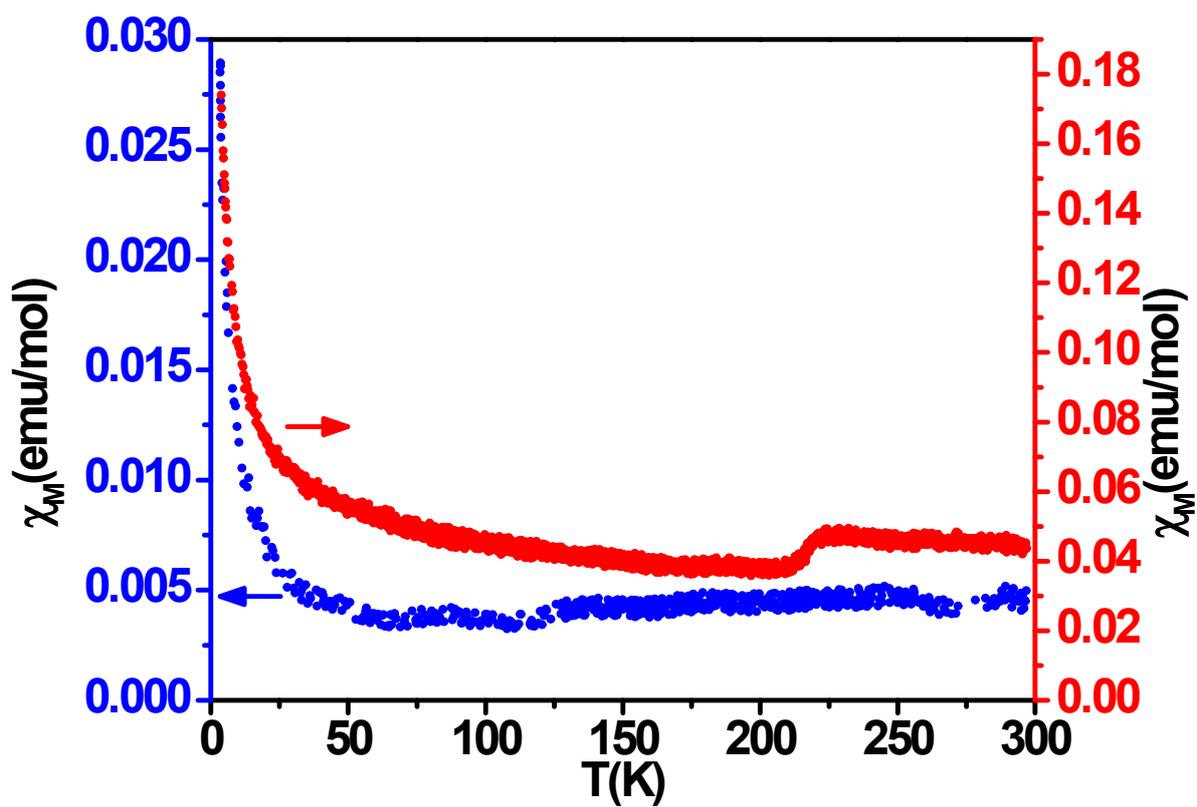


Figure S22:  $\chi_M$  Vs T plot of 1 (blue) and 2 (Red) at an external field of 500 Oe.