This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
An organic-inorganic hybrid semiconductor material based on lindqvist polyoxomolybdate and tetra-nuclear copper complex containing two different ligands

Zhi-Kun Qu,∗a Kai Yu,∗a,b Zhi-Feng Zhao,∗a,b Zhan-hua Su,∗a,b Jing-Quan Sha,c Chun-Mei Wang,a,b Bai-Bin Zhou,∗a,b

Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X

DOI: 10.1039/b000000x

A 3D organic–inorganic hybrid compounds based on the Lindqvist-type polyoxometallate, [[Cu(phen)]\{Cu\{μ-ox\}\}_{3}]\{Mo_6O_{19}\}\] (phen = 1,10-phenanthroline, ox = oxalate), has been synthesized under hydrothermal conditions and structurally characterized by elemental analysis, IR, TG, PXRD, XPS, UV-vis, and single-crystal X-ray diffraction. In compound 1, three C_2O_4\^2^- ligands bridge one Cu atom and three Cu(phen) fragments to form a tetra-nuclear copper(II) coordination complex [[Cu(phen)]\{Cu\{μ-ox\}\}_{3}]\{Mo_6O_{19}\}\] (phen = 1,10-phenanthroline, ox = oxalate). In compound 1, three C_2O_4\^2^- ligands bridge one Cu atom and three Cu(phen) fragments to form a tetra-nuclear copper(II) coordination complex. Compound 1 represents the highest connectivity of Lindqvist-type POM hybrid materials. The electrochemical behavior of I-CPE has been investigated in detail. Furthermore, diffuse reflectivity spectrum of I reveals presence of an optical band gap and the nature of organic units through secondary metal sites of coordination complex subunits. In contrast, hybrid materials derived from the latter method are still less common and only a minority of the kinds of hybrids have been reported. Hitherto only one monosubstituted,\(^7\) two disubstituted,\(^8\) one tetrasubstituted,\(^9\) and one hexadsubstituted derivatives\(^10\) of such kinds of hybrids have been synthesized and structurally characterized. Therefore, multiheterostituted covalent organic–inorganic hybrids have been rarely reported. The synthesis and exploration of 3D high-connected hybrids based on Lindqvist-type POM still remains a great challenge. On the other hand, the organic moieties play an important role in adjusting the structures of the inorganic–organic compounds. In recent years, the assembly system containing two or more organic bridging ligands has been widely adopted to generate new complexes with diversified topologies and interesting properties. As is known, Oxalate ligands bear more flexible coordination fashion and excellent coordination ability, which is favor to converge and bridge the transition metal ions forming multi-nuclear coordination polymers. Moreover, the introduction of a second aromatic organonitrogen ligand, such as 1,10-phen, often causes the system to produce many interesting structures. As a dicarboxyl ligand, 1,10-phenanthroline rings not only can make frameworks robust but also have the potential to form π-electron system. Furthermore, the transition metal copper(II) ions have been widely used as the linking units to construct the hybrid compounds due to their relatively strong coordination abilities with both terminal O atoms of POM and N atoms of organic ligand, as well as for their capacity to adopt various coordination number. In fact, Cu(II) ions containing paramagnetic spin-couple bearing interesting magnetic properties, which are easy to form unique magnetic clusters under the inducement of oxalate ligands.
Thus, it is possible to conduct unusual magnetic interaction between POMs building block and copper metal complex.

Based on aforementioned considerations, tetra-nuclear copper complex as linkers is introduced into \([\text{MoO}_4]^{2-}\) system under hydrothermal conditions via employing mixed ligand ox and Phen to assemble Bird’s Nest-likeed 3-D organic-inorganic hybrid, namely, \(\left[\text{Cu(phen)}\right]_3\left[\text{Cu(μ}_2\text{-ox)}\right]_3\left[\text{MoO}_4\right]_3\) (1). Our result further suggests that oxalate is an excellent template reagent and linking unit to induce new 3D multi-nuclear POM-based hybrid assemblies.

**Experimental**

**Materials and physical measurements**

All reagents were purchased commercially and used without further purification. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. Mo and Cu analyses were performed on a PLASMA-SPEC (I) inductively coupled plasma atomic emission spectrometer. The IR spectra were obtained on an Alpha Centaurt FT/IR spectrometer with KBr pellet in the 400-4000 cm⁻¹ region. The thermal gravimetric analyses (TGA) were carried out in N₂ on a Perkin-Elmer DTA 1700 differential thermal analyzer with a rate of 10 °C/min. XRD patterns were collected on a Rigaku Dmax 2000 X-ray diffractometer with graphite monochromatized Cu Kα radiation (λ= 0.154 nm) and 2θ ranging from 5 to 50°. X-ray photoelectron spectroscopy (XPS) analyses were performed on a VG ESCALAB MK II spectrometer with an MgKα (1253.6 eV) radiation (λ). The vacuum inside the analysis chamber was maintained at 6.2 × 10⁻⁶ Pa during analysis. The UV-vis-NIR absorption spectroscopy was measured with a Cary 500 spectrophotometer. Diffuse reflectivity spectrum was measured from 200 to 1500 nm using barium sulfate (BaSO₄) as a standard with 100% reflectance. Electrochemical measurements were performed with a CHI660 electrochemical workstation. A conventional three-electrode system was used. The working electrode was a carbon paste electrode (CPE), a Pt wire as the counter electrode and Ag/AgCl (3M KCl) electrode was used as a reference electrode.

Magnetic susceptibility data were collected over the temperature range of 2-300 K in a Quantum Design MPMS-5 SQUID magnetometer.

**Synthesis**

\(\left[\text{Cu(phen)}\right]_3\left[\text{Cu(μ}_2\text{-ox)}\right]_3\left[\text{MoO}_4\right]_3\) (1) A mixture of (NH₄)₂MoO₄·2H₂O (1.236 g, 1 mmol), CuCl₂·6H₂O (0.243 g, 1 mmol), 1,10-phenanthroline (0.180 g, 1 mmol), oxalic acid (0.180 g, 2 mmol) and water (18 ml, 1 mol) was stirred for 30 min. Then, the resulting suspension was sealed in a 30-ml Teflon reactor and heated at 160 °C for 3 days. After cooling to room temperature, Dark blue block crystals of 1 were isolated. The crystalline products were collected by filtration, washed with distilled water, and air-dried to give a yield of 45% (based on Mo). Elemental anal. Caled (%) for C₈₄H₄₈Cu₈Mo₁₂N₁₂O₆₂ (Mr = 3876.94) (%): C, 26.02; H, 1.25; N, 4.04; Cu, 13.11; Mo, 29.70; Found (%): C, 26.08; H, 1.21; N, 4.08; Cu, 13.07; Mo, 29.74. Selected IR (KBr pellet, cm⁻¹): 3083 (br), 1628 (sh), 1510 (m), 1418 (w), 1310 (s), 938 (s), 813 (s), 701 (s).

**X-ray crystallography**

The crystal structure of compound 1 was determined from single-crystal X-ray diffraction data. Intensity data were collected on a Bruker SMART CCD diffractometer equipped with a graphite monochromatized Mo-Kα radiation (λ= 0.71073 Å). The structure was solved by direct methods and difference Fourier map with SHELXL-97 program, and refined by full-matrix least-squares techniques on F². Anisotropic thermal parameters were used to refine all non-hydrogen atoms. The positions of hydrogen atoms of organic molecules were calculated theoretically, and refined using a riding model. Hydrogen atoms of water molecules were not treated. The crystal data and refinement parameters of compounds 1 are summarized in Table 1. The selected bond lengths and bond angles of compounds 1 are listed in Table S1.

| Compound |  
| --- | --- |
| Chemical formula | C₈₄H₄₈Cu₈Mo₁₂N₁₂O₆₂ |
| Formula weight | 3876.94 |
| T/K | 293(2) |
| λ/Å | 0.71073 |
| Crystall system | Trigonal |
| Space group | R-3c |
| a/Å | 14.9724(3) |
| b/Å | 14.9724(3) |
| c/Å | 80.713(3) |
| α/° | 90.00 |
| β/° | 90.00 |
| γ/° | 120.00 |
| V/Å³ | 15669.5(8) |
| Z | 6 |
| D_0calc/Mg m⁻³ | 2.465 |
| μ/mm⁻¹ | 3.090 |
| F(000) | 11208 |
| crystal size/mm | 0.18 x 0.18 x 0.16 mm |
| θ range/° | 1.65-28.27 |
| Reflections collected/ unique | 31117 / 4326 [R(int) = 0.0452] |
| Data/restraints/parameters | 4326 / 0 / 270 |
| GOF on F² | 1.007 |
| Final R indices (I > 2σ(I)) | R₁ = 0.0287, wR₂ = 0.0689 |
| R indices (all data) | R₁ = 0.0416, wR₂ = 0.0753 |

**Results and Discussion**

**Crystal Structure**

X-ray Single-crystal structural analyses reveal that compound 1 crystallizes in the trigonal system, space group R-3c. Compound 1 consists of \([\text{MoO}_4]^{2-}\) anions and the tetra-nuclear copper fragment \([\text{Cu(phen)}]_3\left[\text{Cu(μ}_2\text{-ox)}\right]_3\) (Fig. 1). The Linquist structure \([\text{MoO}_4]^{2-}\) consists of a central oxygen atom which is surrounded by six Mo atoms in an octahedral geometry. Each metal Mo has one terminal oxygen atom, and shares additional μ₂-oxygen atoms with adjacent metal atoms.
As shown in Fig.2(a), the tetra-nuclear copper fragment of 1 contains two kinds of crystallography independent copper atoms (Cu1 and Cu2), which exhibit the hexa-coordination environment. The Cu2 locating the centre of octahedral geometry is defined by six O atoms derived from three ox ligands, with the bond lengths of Cu2-O 2.080(2) Å. Cu1 exhibits distortional octahedral geometry which is defined by two N atoms from a phen, two O atoms from an ox ligand, and two terminal O atoms from two adjacent Mo6O192- anions with the distance of Cu2-Ot: 2.495(2) and 2.667(3) Å, Cu2-Oox: 1.952(2) and 1.957(2) Å, Cu2-N: 1.967(3) and 1.981(3). In such connection mode, three C2O42- ligands bridge one Cu atoms and three Cu(phen) fragments to form a tetra-nuclear copper(II) coordination complex unit. Each [Mo6O19]2- cluster serves as hexa-dentate ligand coordinating to six Cu1 centers through all the terminal oxygen atoms and further supports six tetra-nuclear complex ([Cu(phen)]3[Cu(μ2-ox)]3)2+ unit via Cu1 atoms (Fig.2(b)).

Figure 2. (a) Coordination environment of Mo6O192- and ([Cu(phen)]3[Cu(μ2-ox)]3)2+ in compound 1; (b) Each [Mo6O19]2- cluster supports six ([Cu(phen)]3[Cu(μ2-ox)]3)2+ via the six Cu1-O bonds (peripheral {Mo6O19} clusters are omitted for clarity); (c) Each [Mo6O19]2- cluster connects with six peripheral Lingquist-type cluster and six tetra-nuclear copper(II) complex unit via Cu1 atoms; (d) View of the topology of Coordination environment of each [Mo6O19]2-. Schematic illustration of the synthesis routes of complexes.
Moreover, each Cu1 links to two [Mo6O19]6− clusters, which result in each tetra-nuclear cooper complex joins to six Linquist clusters (Fig. S1). At the same time, each [Mo6O19]6− cluster connects with six peripheral Linquist-type cluster via Cu1 atoms (Fig. 2(c) and Fig. 2(d)). The six peripheral [Mo6O19]6− clusters make up two parallel equilateral triangles which are located at the two sides of the central [Mo6O19]6− cluster (Fig. 3). In addition, an important feature of the structure is that three Cu1 atoms, one Cu2 atoms, two C2O42− ligands and two [Mo6O19]6− polyoxoanions construct a polyhedron cavity with the dimension of 6.580×13.59 (Fig. 4). The apertures of the open network are filled by barrier-liked phen (shown in Fig.S2).

Figure 3. The six peripheral [Mo6O19]6− clusters make up two parallel equilateral triangles which are located at the two sides of the central [Mo6O19]6− cluster of the relationship between crystalline products of basket-type and different template reagent.

Figure 4. The polyhedron cavity constructed by three Cu1 atoms, one Cu2 atoms, two C2O42− ligands and two [Mo6O19]6− polyoxoanions.

Figure 5. The 3D Bird’s Nest-liked structure and 412•63-nbo (sodium chloride-type) topology of compound 1.
Most intriguing structural character is that the hexad-node \([\text{Mo}_6\text{O}_{19}]^{2-}\) clusters are interweaved by the 6-connected tetranuclear complexes unit into an intricate 3D network structure exhibiting a \(\alpha^{4}\beta^{6}\)-xbo (sodium chloride-like) topology (Fig. 5). In this simplification, the blue 6-connected nodes are \([\text{Mo}_6\text{O}_{19}]^{2-}\) cluster (O1 and O9 as central atom), the yellow 6-connected ones are tetranuclear complexes \([\text{Cu}(\text{phen})_2\{\text{Cu}(\beta\text{-citr})\}]^{2+}\) unit (Cu2 as central atom). The distances of Cu2-O1 are 9.416, 9.418, and 9.419 Å; the lengths of Cu2-O9 are 9.145, 9.147, and 9.148 Å. Compound I represents not only the highest connection Lindqvist-type hybrid but also the first 3D Lindqvist-type hybrid modified by tetra-nuclear copper(II) coordination complex. It is worth noting that \(\text{C}_2\text{O}_4^{2-}\) ligands play dual role as both pillar and crucial linkers of tetra-nuclear units, while phen ligands are located in the cavities of 3D hybrid materials to stabilize tetra-nuclear copper cluster and overall 3D open framework. Thus, the ligands are important template reagent to induce the formation of the tetra-nuclear copper segments and interlaced 3D network structure. According to bond valence calculation, all molybdenum atoms show +VI oxidation states and copper atoms are in +II oxidation states, which is also proved by charge neutrality.

**Spectroscopic and Thermal Analyses:**

In the IR spectrum of I (Fig. S3), the characteristic peaks at 802 and 941 cm\(^{-1}\) are attributed to the \(\nu(Mo-O-Mo)\) and \(\nu(Mo=O)\) of the \([\text{Mo}_6\text{O}_{19}]^{2-}\) polyanions, respectively. Bands in the 1640-1110 cm\(^{-1}\) region can be assigned to characteristic peaks of the ligands 1, 10-phen. The bands between 1430-1310 and 802-717 cm\(^{-1}\) are attributed to \(\nu(C-C)\) as(Cu-phen) and \(\nu(Cu-C)\) stretching vibrations, respectively. The data imply that the oxalate anion serve as symmetric bi-chelated oxalate donor ligand, which is in agreement with the result of the X-ray analysis. The bands in the range of 482-442 cm\(^{-1}\) can be assigned to \(\nu_{ad}(\text{Cu-O})\) and \(\nu_{ad}(\text{Cu-N})\) vibration.

The PXRD patterns for compound I are presented in Fig. S4. The diffraction peaks of both simulated and experimental patterns match in the key positions, indicating the phase purity of the compound. The differences in intensity may be due to the preferred orientation of the powder samples.

The oxidation states of Mo and Cu are further confirmed by X-ray photoelectron spectroscopy (XPS) measurements, which were carried out in the energy region of Mo3d\(_{3/2}\), Mo3d\(_{5/2}\), Cu2p\(_{1/2}\), and Cu2p\(_{3/2}\), respectively. The XPS spectrum of I presents two peaks at 932.7 eV and 953.2 eV in the Cu2p region which should be ascribed to Cu\(^{2+}\) (Fig. S5a). The XPS spectra give two sharp peaks at 232.5 and 235.6 eV in the Mo3d region, which attributed to Mo\(^{6+}\) ions (see Fig. S5b). All these results further confirm the valence sum calculations of compound I.

Thermogravimetric analysis (TGA) was performed at a rate of 10°C·min\(^{-1}\) in the range of 35–500°C on I (Fig. S6). In the TG curve of I, there exist two weight loss stages. In the temperature range of 150–200°C, the initial weight loss of 13.94% corresponds to the release of CO\(_2\) from reduction of oxalic acid ligand under oxidation action of Cu\(^{II}\), which in accordance with the calculated value of 13.25%. The second weight loss of 29.64% occurring between 225°C and 290°C is attributed to the release of the phen ligands (calcd. 29.81%). The whole weight loss (43.58%) is in good agreement with the calculated value (calcd. 43.06%).

**Optical Band Gap**

In order to explore the conductivity of compound I, the measurement of diffuse reflectivity for the powder sample was used to achieve its band gap (E\(_g\)). The band gap (E\(_g\)) was determined as the intersection point between the energy axis and the line extrapolated from the linear portion of the absorption edge in a plot of the Kubelka-Munk function \(F\) against energy \(E\). As shown in Fig. 6, for this compound, the corresponding well-defined optical absorption associated with band gap (E\(_g\)) can be assessed at 3.12 eV. The reflectance spectrum measurements reveal the presence of an optical band gap and the nature of semiconductivity with a wide band gap for compound I. The band gap of I is larger than that of \((n-\text{Bu}_4\text{N})_2\{\text{trans-}[\text{Mo}_6\text{O}_{17-80}\text{the literature.}\)

The cyclic voltammetry behavior for I-CPE in 1 M H\(_2\)SO\(_4\) aqueous solution at different scan rates was recorded in Fig. 7. As shown in Fig. S8, it can be clearly seen that three reduction peaks and two oxidation peaks appear in the potential range of +0.4 to -1.0 V at a scan rate of 20 mV·s\(^{-1}\). One couple of redox peaks (II-II') located at E\(_pa\) = 0.64 V and E\(_pc\) = 0.42 V are observed. These peaks correspond to one-electron oxidation and reduction steps involving Mo atoms, which are similar to analogous compounds reported in the literature. The voltammetric responses of \([\text{Mo}_6\text{O}_{19}]\{\text{Ni}(\text{C}_2\text{H}_3)_{2}\}\) electrode (denoted to 2-CPE) displays one couple of redox peaks at E\(_pa\) = 0.55 V and E\(_pc\) = 0.39 V, which similar to that of II-II' in I-CPE. This further indicates that redox reaction of II-II' in I-CPE originates from \([\text{Mo}_6\text{O}_{19}]\) (Figure S9). The last two reduction waves and their oxidation counterpart, a single oxidation process located at +0.12 V, are attributed to the redox processes of the Cu\(^{II}\) centers. The two reduction waves located at -0.09 and -0.06 V feature the reduction of Cu\(^{2+}\) to Cu\(^{+}\), possibly through Cu\(^{+}\) to Cu\(^{0}\). Moreover, the cathodic peak potentials shift toward the negative direction and the corresponding anodic peak potentials shift to the positive direction with increasing scan rates. Additionally, the peak-to-peak separations between the corresponding anodic and cathodic peaks increased, but the average peak potentials do not change on the whole.
Figure 6. K-M function versus energy (eV) curve of compound 1.

Figure 7. The cyclic voltammograms of the 1-CPE in 1 M H2SO4 at different scan rates (20, 50, 80, 110, 140, 170, 210, 240 mV•s⁻¹).

Magnetic Measurements

The variable temperature magnetic susceptibility of 1 were measured from 300 to 2 K at 1000 Oe and plotted as χM and χMT versus T, as shown in Figure 8. The χM increases continuously with decreasing temperature, and the curves of χM and χMT obey the Curie-Weiss law. The room temperature χMT value is 4.831 cm³•K•mol⁻¹, which is higher than the expected for four noncorrelated Cu²⁺ ions (1.67 cm³•K•mol⁻¹, considering g = 2.10). It can be viewed that it is the result of combined action of the spin coupling and orbital contribution of Cu²⁺ ions. When the systems is cooled, the χM product decreases to a value of 2.027 cm³•K•mol⁻¹ at 15 K. These behaviors indicate the presence of the antiferromagnetic coupling for 1. At relatively low temperature (15 K to 2 K), the χMT product increases with decreasing temperature (as inner of Fig.8a), which might be mainly attributed to the presence of zero-field splitting. The behavior suggests that there exist overall antiferromagnetic interactions with the presence of zero-field splitting for Cu²⁺ ions in the compound 1.

The magnetic mode of the tetra-nuclear copper(II) coordination fragment shown in Fig. 8(b) is an equilateral triangle, which is formed by the three equal isosceles triangles, and the isosceles parts are bridged by two oxalate ligands, respectively. The interactions of S₁-S₂ and S₁-S₃ are both described by the coupling constant J. The interaction of S₂-S₃ is given by the coupling constant J₁. In the presence of an external magnetic field, the spin Hamiltonian with S₁=S₂=S₃=1/2 for the tri-nuclear-copper fragment is given by H=-2J(S₁•S₂+S₁•S₃)-2J₁(S₂•S₃). The expression of χM for 1 is χM = (Ng²β²/4kT){1+exp[(2J₁-2J)/kT]+10exp[(2J₁+J)/kT]}/[1+exp[(2J₁-2J)/kT]+10exp[(2J₁+J)/kT]], where N, β, and k have their usual meaning, g is a factor.

The best-fitting parameters obtained from a simulation of the curve of χM versus T are J = -32.2 cm⁻¹, J₁ = 65.0 cm⁻¹ and g = 2.10 with the agreement factors, \( R = \frac{\sum (\chi_{\text{M, exp}} - \chi_{\text{M, calcd}})^2}{\sum (\chi_{\text{M, exp}})^2} = 6.60 \times 10^{-4} \).

Figure 8. (a) The Plot of χM and χMT versus T for compound 1. (b) The magnetic mode of tetra-nuclear copper (II) coordination fragment in compound 1. Schematic illustration of the synthesis routes of complexes.

Conclusion

In this paper, mixed ligand modified tetraneuclear copper (II) complex, was firstly introduced into the Lindqvist-type clusters
as linking units to weave a fascinating 3D network structure, which exhibits a 4\textsuperscript{4}3\textsuperscript{6}-nbo (sodium chloride-type) topology. Cyclic voltammetric behavior of \textbf{I} exhibits three reduction waves and their oxidation counterpart in 1M H\textsubscript{2}SO\textsubscript{4} aqueous solution, which can be ascribed to one-electron redox processes of Mo atoms and the redox processes of Cu(II) center. Furthermore, diffuse reflectivity spectrum of \textbf{I} shows its band gap being assessed as 3.02 eV, which could be applied as a wide gap semiconductor. Magnetic susceptibility study reveal predominant antiferromagnetic interactions between the Cu\textsuperscript{2+} bridge units. The ongoing efforts will be concentrated on the organic–inorganic hybrid materials contained multineural coordination complex.

**Acknowledgements**

This work was supported the National Natural Science Foundation of China (Grants Nos. 21271056 and 21371042), the Ministry of Education and Specialised Research Fund for the Doctoral Program of Higher Education (20122329110001), the Natural Science Foundation of Heilongjiang Province(B201216), Key Laboratory of Functional Inorganic Material Chemistry (Heilongjiang University), Ministry of Education, Doctoral initiation Foundation of Harbin Normal University (No.KGB201214), Ministry of Education, Doctoral initiation Foundation of Harbin Normal University (No.KGB201214), Program for Scientific and Technological Innovation Team Construction in Universities of Heilongjiang Province (No. 2011TD010).

**Notes and references**

*Key Laboratory for Photonic and Electronic Bandgap Materials, Ministry of Education, School of Chemistry and Chemical Engineering, Harbin Normal University, Harbin 150025, People’s Republic of China; E-mail: bzyu@163.com(K.Yu); zhou_bai_bin@163.com(B.B.Zhou)

† Electronic Supplementary Information (ESI) available: Summary of selected bond lengths and angles; IR spectrum, PXRD patterns, UV-vis spectrum, XPS spectrum, TG curve, part structural figures of compounds \textbf{I}, and cif files of \textbf{I}. CCDC reference numbers: 708957 (1) See DOI: 10.1039/b000000c


10 (a) G. M. Sheldrick, SHELXL 97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997; (b) G. M. Sheldrick, SHELXL 97, Program for Crystal Structure Solution, University of Göttingen, Germany, 1997.


Graphical Abstract

Mixed ligand modified tetranuclear copper (II) complex was firstly introduced into \{Mo_6O_{19}\} systems as linking units to weave a fascinating 3D Bird’s Nest-like structure, which exhibits a 4^{12}6^{3}-nbo (sodium chloride-type) topology. The compound display good redox properties, excellent semiconductive nature, and unique Magnetic activity.