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Communication

Copper-sulfide cluster assembled architecture *via in situ* reaction

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ABSTRACT

A new copper-thiolate cluster assembled framework $[Cu_2(\mu_4\text{-}SCH_3)Cl]_n$ (**1**), has been solvothermally synthesized through *in situ* reaction *viz.*, *in situ* ligand generation and metal reduction. Compound **1** represents the first 3D framework based on Atlas-sphere functionalized by single μ_2-Cl^- groups. DOS calculation reveals the interaction of electronic structures. It is found that the HOMO is mainly distributed on Cl, Cu and S bonding orbitals, while the LUMO is dominated by Cu-Cl antibonding orbitals.

Metal-thiolate cluster species, among the large family of chalcogenides, represents a topical area of crystal engineering [1–9]. By introduction of different coordinating atoms, types of metal-sulfide clusters, such as binary, ternary, quaternary, could be achieved [10]. The unique range of structural versatility and tunable properties make this field an attractive prospect [11–19]. Scientists have pioneered routes during the past decades, and two predominant structural types have been documented: discrete chalcogenide clusters and extended cluster networks. For metal-thiolate cluster discovery, *in situ* strategy is a promising solution under which the synthons could be gradually generate, and oligomeric structures with rapid aggregation could be prevented [20]. As ongoing effort of cluster chemistry, we have explored approaches for new chalcogenide clusters. In this work, we focus our study intensively on how a stable cluster can be created by "simple components", and yet cluster assembled architecture. For this purpose, a simple reaction based on copper and dimethyl sulfoxide (DMSO) is set up. Copper ion is a widespread precursor for chalcogenides. DMSO is used as a potential sulfide source *via in situ* decompositon [21,22]. After numerous attempts, optimized conditions were obtained. Solvothermal reaction of DMSO-$Cu(OAc)_2$ solution at 160 produced yellow crystals of $[Cu_2(\mu_4\text{-}SCH_3)Cl]_n$ (**1**).

X-ray single-crystal analysis shows that compound **1** crystallizes in a highly symmetric hexagonal system with space group *R*-3. The neutral framework is constructed by copper sulfide core $[Cu_{12}(\mu_4\text{-}SCH_3)_6]^{6+}$ with a known Atlas-sphere configuration [23,24]. Connected by μ_2-Cl^- ligands in three dimensions of the crystal (Fig. 1a), the overall formula of Atlas-sphere is $[Cu_{12}(\mu_4\text{-}SCH_3)_6(\mu_2\text{-}Cl)_{12}]^{6-}$ (abbreviated as $Cu_{12}S_6Cl_{12}$). Considering the surface modification *via* functional groups, two main kinds of Atlas-spheres are observed. The first one is different subunits modified cluster [23,25–27], features types of fragments appended to outer Atlas-surface (*e.g.*, halide anion, Cu-halide, Cu-thiolate). The second one is single group functionalized structure [24]. In this work, each of the twelve Cu atoms in the Atlas-sphere core is uniformly coordinated to a μ_2-Cl^- ligand. Compound **1** is the first 3D framework based on Atlas-sphere functionalized by single μ_2-Cl^- groups. Only one similar Atlas-cluster has been reported to our knowledge, in which the bonded Cl^- anion acts as capping ligand [28]. In **1**, a centrosymmetric $\{Cu_{12}\}$ cubo-octahedron for $\{Cu_{12}S_6Cl_{12}\}$ with an outer diameter of ~5.90 Å is observed (Fig. 1b, left). Each SCH_3^- ligand is μ_4-bonded to four Cu atoms, and six μ_4-SCH_3^- are arranged into a regular octahedron, with its bearing methyl groups pointing outwards. Each edge of the octahedron has bridged by a CuCl unit, then a $\{Cl_{12}\}$ cubo-octahedron (with an outer diameter of ~10.40 Å), similar with

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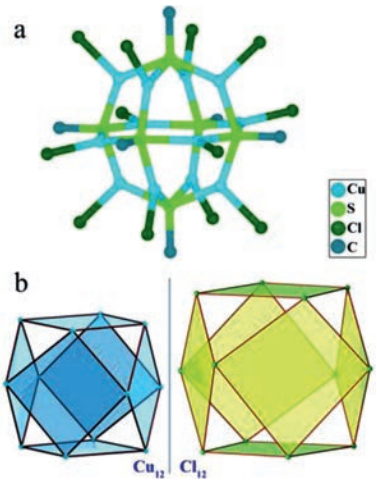

Fig. 1. (a) Ball-stick representation of $\{Cu_{12}S_6Cl_{12}\}$ cluster. (b) Cubo-octahedron of $\{Cu_{12}\}$ and $\{Cl_{12}\}$, respectively.

$\{Cu_{12}\}$ unit, has been observed (Fig. 1b, right). Three mutually perpendicular, coplanar, eight-membered $\{Cu_4S_4\}$ rings intersect at the sulfur atoms, giving birth to the known Atlas-sphere (Fig. S1 in Supporting information). Both of the crystallographically independent Cu centers (Cu1 and Cu2) lie in a trigonal coordination sphere that completed by one μ_2-Cl^- and two μ_4-SCH_3^- ligands. Bond distances around the Cu centers are normal. The μ_4-S center adopts a square-pyramidal $[SCCu_4]$ geometry, with one carbon atom at the apex and four Cu atoms in the equatorial plane. Note that, distance of Cu1···Cu2 (2.762 Å) observed within the $[SCCu_4]$ moiety is slightly shorter than the sum of the van der Waals radius of two Cu atoms (2.80 Å) [29,30], indicating a weak Cu···Cu interaction.

In compound **1**, each $\{Cu_{12}S_6Cl_{12}\}$ cluster is six-connected to adjacent ones by twelve μ_2-Cl^- ligands, as shown in Fig. 2a. The central $\{Cu_{12}S_6Cl_{12}\}$ unit is octahedral surrounded (Fig. 2b), and the regular octahedral arrangement leads to a high crystallographic symmetry of **1**. Self-assemble of $\{Cu_{12}S_6Cl_{12}\}$ clusters and extending infinitely in all three directions of space leads to a 3D microporous framework (Fig. 2c), which contains 17.7% void space (422.7 $Å^3$ of the 2388.5 $Å^3$ unit cell volume) that is accessible to solvent molecules, as calculated by PLATON [31]. A better insight into the nature of this intricate framework is provided by a topology analysis. Herein, each $\{Cu_{12}S_6Cl_{12}\}$ cluster can be defined as a 6-connected node, then the whole framework can be classified as a uninodal ***pcu*** net with Schläfli symbol of $4^{12}\cdot6^3$ (Fig. 2d).

Worth to mention here is the *in situ* reactions, including ligand generation ($DMSO/SCH_3^-$) and metal reduction (Cu^{2+}/Cu^+). To trigger this target, harsh reaction conditions are exploited in our approach. Experimental factors of relative high temperature, small filling capacity, long reaction time, and solution acidification are applied. Optimized conditions drive the *in situ* process and induces the aggregation of *in situ* synthons towards the formation of specific $\{Cu_{12}S_6Cl_{12}\}$ cluster. The FT-IR spectrum confirms the existence of SCH_3^- ligands (Fig. S2 in Supporting information). The CH-stretching mode is observed in region of 3200–2800 cm^{-1}, CH_3 deformation locates in 1500–1300 cm^{-1}. A strong band at 945 cm^{-1} is assigned to the CH_3-wagging mode. Characteristic bands at 755 and 708 cm^{-1} are assigned to the C–S stretching vibrations [32,33]. Scanning electron microscopy-energy-dispersed X-ray spectroscopy (SEM-EDX) reveals the presence of C, O, S, Cl and Cu elements (Fig. 3a). Atomic molar ratio of Cu/S/Cl calculated from EDX is about 2.0:1.0:0.9, which is close to the theoretical value (2:1:1). Bond valence sum (BVS) calculations show that the Cu centers are +1 valences [34].

Cyclic voltammetry (CV) study of **1** was carried out in 1 mol/L Na_2SO_4 solution (Fig. 3b). It can be seen that no voltammetric

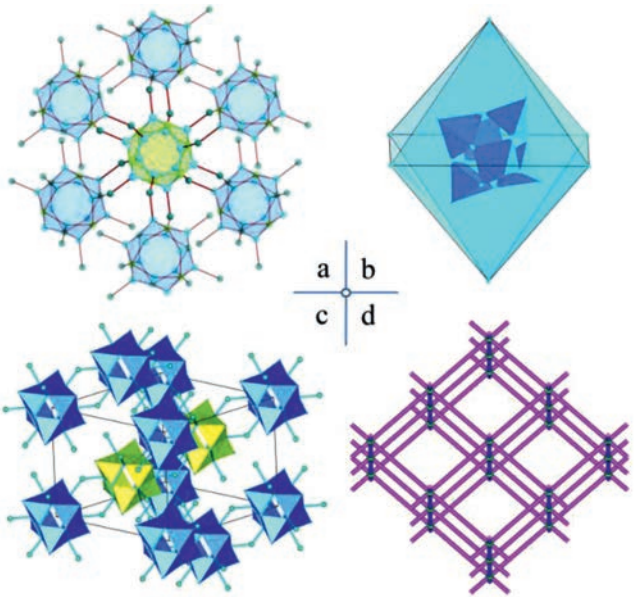

Fig. 2. (a) Highlighting the central $\{Cu_{12}S_6Cl_{12}\}$ cluster bonded with adjacent ones. (b) Octahedron arrangement of six-connected $\{Cu_{12}S_6Cl_{12}\}$. (c) Cluster assembled architecture. (d) Topological representation of the ***pcu*** net.

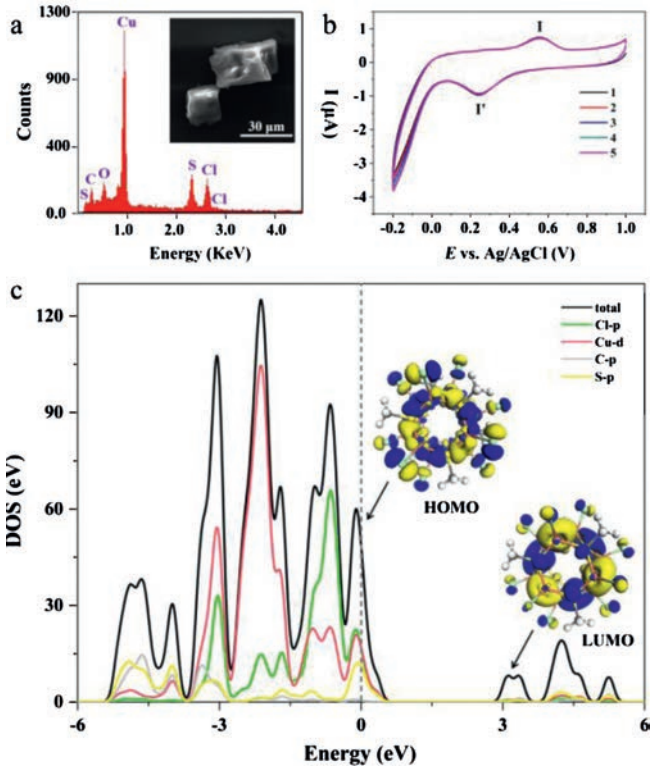

Fig. 3. (a) EDX spectrum and SEM image of **1**. (b) Cyclic voltammetry in 1 mol/L Na_2SO_4 solution at scan rate of 50 mV/s. (c) The state density and molecular orbitals of $\{Cu_{12}S_6Cl_{12}\}$ cluster. The Fermi level is set to zero.

characteristics were changed after several successive cycles, indicating the structural stability of **1** under the studied conditions. In the potential range from +1.0 V to −0.2 V, a couple of reversible redox peaks *I*/*I*' at 0.562 and 0.244 V are observed (scan rate: 50 mV/s), which can be ascribed to monoelectronic process of Cu atoms.

To gain a deeper understanding of the interaction of electronic structures, the isodensity surfaces and energy levels for **1** were calculated by Materials Studio software (Accelrys Inc.). Fig. 3c shows the density of states (DOS) of $\{Cu_{12}S_6Cl_{12}\}$ cluster. It can be seen that the energy area of -6.0 to -3.8 eV is basically contributed by the S-p, C-p and Cu-d orbitals. For orbitals with energies around -3.0 eV to -1.0 eV, the higher peaks of Cu-d and Cl-p orbitals indicate that these orbitals are contributed by Cu and Cl atoms. In addition, a peak appears near the Fermi level, indicating that the system has high activity, and this orbital is contributed by Cl-p, Cu-d, and S-p, which is consistent with the results of the orbital isosurface. The highest occupied molecular orbital (HOMO) is mainly distributed on Cl, Cu and S atoms. The binding of electrons is relatively relaxed, thus playing the role of electron donor. The lowest unoccupied molecular orbital (LUMO) is mainly distributed on Cu-Cu bonds and Cl atoms. It has a strong affinity for electrons and has the nature of an electron acceptor. The interaction of the two orbitals plays an important role in the chemical reaction.

In summary, we demonstrate here a new copper-thiolate cluster $\{Cu_{12}S_6Cl_{12}\}$ constructed by an *in situ* strategy, including *in situ* ligand generation and metal reduction. Compound **1** represents the first 3D framework based on Atlas-sphere functionalized by single μ_2-Cl^- groups, combining both cluster chemistry and extended architectures. DOS calculation reveals the contribution of certain atomic orbitals in **1**. The HOMO is mainly distributed on Cl, Cu and S bonding orbitals, while the LUMO is dominated by Cu-Cl antibonding orbitals. By applying the approach established in this study, we expect that a new family of metal-thiolate species to be discovered in the future.

Declaration of competing interest

The authors report no declarations of interest.

Acknowledgments

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.cclet.2020.08.025.

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