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# Luminescent 2-D Double-layered Polymer, $[(CuI)_4(CH_3SCH_3)_3]_\infty$, Containing Helical Chains Constructed by Flower-Basket-Shaped $Cu_4I_4$ Clusters

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A new route for the synthesis of coordination compounds with dimethyl sulfide ligand is reported; the prepared compound is a novel 2-D framework with a 1-D right-handed and left-handed helical structure, which is unique in the sense that the fundamental units are unusual $Cu_4I_4$ clusters.

Supramolecular assembly, using clusters of metal chalcogenides or halides as building blocks, has attracted much attention. Many of these compounds not only are of the intriguing structural diversities in architectures but also display potentially useful properties, including ion-exchange capacity, electronic, and optical properties.[1] A number of cluster-based materials have been obtained by such a self-assembly process. For instance, a large supramolecular cube[1b] was achieved by a combination of $Cp^*WS_3Cu_3$ clusters and cyanide anions; a 3-D photoluminescent superlattice (UCR-9)[1c] was formed by linking $[Cd_8(SPh)_{12}]^{4+}$ clusters; a 3-D cubic framework was based on edge-bridged $[Nb_6Cl_{12}]^{2+}$ clusters and CN−Mn−NC bridges.[1h]

The iodine atom can bind to Cu metal by a variety of bonding modes, so it has been extensively used as component of cuprous clusters and polymers.[2,3] Noteworthy examples of polymeric compounds including $Cu_xI_y$ clusters are those cubane-like tetramers linked by various organic ligands.[3] For example, a 1-D zigzag chain of $\{[(C_2H_5)_2S]_3[CuI]_4\}_\infty$ is constructed by $Cu_4I_4$ clusters and diethyl sulfide;[3a] a 2-D polymer is formed by $Cu_4I_4$ clusters and bis(4-pyridyl)-disulfide,[3b] and a 3-D polymer is tetrahedrally connected by $Cu_4I_4$ junctions.[3c] As an extension of these studies, we have successfully isolated a novel compound $[(CuI)_4(CH_3SCH_3)_3]_\infty$ (**1**) which is an unusual 2-D double-layered inorganic−organic hybrid polymer constructed by cluster units as building blocks.

The title polymer **1** was synthesized by the solvothermal method in a mixed solvent of toluene and DMSO.[4] The compound was characterized by single crystal X-ray analysis (Supporting Information). Interestingly, it is not only a polymeric structure self-assembled from building units of unusual $Cu_4I_4$ clusters but also a bridging ligand, dimethyl sulfide (DMS), formed from the reduction of dimethyl sulfoxide (DMSO).

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(4) The reactants CuI (38.1 mg, 0.2 mmol), $P_2S_5$ (88.9 mg, 0.4 mmol), and $(CH_3CH_2)_4NBr$ (42 mg, 0.2 mmol) were added to a mixed solvent of 2 mL of toluene and 0.5 mL of DMSO in a Teflon-lined steel autoclave (15 mL). The reaction was carried out at 145 °C for 4 days. A bright yellow solution was obtained, which was layered with $Et_2O$ and afforded colorless brick crystals of $[(CuI)_4(CH_3SCH_3)_3]_n$ in about 32% yield (based on Cu metal) after 3 weeks.

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$$\mathrm{CuI + DMSO + P_2S_5 \xrightarrow{Et_4NBr} [Cu_4I_4(CH_3SCH_3)_3]_n + S_8 + PO\ byproducts} \quad (1)$$

Among the most studied results, DMSO acts as reagent, solvent, and/or ligand. One of the fundamental chemical properties of DMSO is the ability to undergo deoxygenation to give the corresponding sulfide. There are three well-demonstrated methods for the deoxygenation of $R_2SO$ ligands. The first is the combination of an electrophilic activator and a reducing agent.[5] The activator binds to the O atom, increases the partial positive charge on the S atom, and thus promotes the deoxygenating reaction. For instance, the reaction of $R_2SO$ with the reducing agent NaI[5b] in the presence of $PCl_5$ (activator) yields $OPCl_3$ and $R_2S$. The second is metal-catalyzed oxygen transfer reactions.[6] Re(O)C1$_3$(PPh$_3$)[6b] reacting with DMSO to form $OPPh_3$ and Re(O)C1$_3$(DMS)(OPPh$_3$) is one of the good examples. The third is metal−acid mediated deoxygenations in the presence of HCl.[7] The deoxygenation promoted by acids and related complexes of Pt(II), which is accompanied by the oxidation of Pt(II) to Pt(IV) and the reduction of DMSO to dimethyl sulfide. In this communication, we found a new deoxygenating reaction using $P_2S_5$ reagent.[4]

The deoxygenation reaction has been further confirmed by the preparation of $[CuCl(CH_3SCH_3)]_\infty$ and $[CuBr(CH_3SCH_3)]_\infty$ in a similar method (Supporting Information). Their crystal structures were characterized using single-crystal X-ray analysis. The 2-D polymeric structure formed by $Cu_2X_2$ clusters, however, had been described by Maelger's group.[8] The mechanism of the new reaction is still unclear, and it should relate to the phosphorus atoms of $P_2S_5$ possessing of a strong affinity to oxygen. In the reaction of $P_2S_5$ with molar equivalent of DMSO in toluene solution, an instantaneous reaction occurred with a sulfide odor evolved. During the reaction, yellow crystals of $S_8$ were synchronously obtained as a byproduct. They enable us to speculate that the deoxygenating process is followed by oxidation of $S^{2-}$ to $S_8$ and reduction of DMSO to dimethyl sulfide in the reaction with an oxygen transfer from S to P centers. By consulting the reported mechanisms of deoxygenation of $R_2SO$,[5−7] the proposed reaction might be written as eq 1.

Single-crystal X-ray analysis of compound **1** shows that it is a two-dimensional inorganic−organic hybrid coordination polymer with a substructure of $Cu_4I_4$ clusters (Figure 1). In the $Cu_4I_4$ cluster (flower-basket-shaped), three Cu atoms (2, 3, and 3A) are presented in an isosceles trigonal arrangement, which is located in the waist positions of the flower basket. The I2 atom caps the triangle at the bottom, forming a $[Cu_3I]$ trigonal pyramid. Three iodine ligands bridge three Cu···Cu edges respectively, resulting in a roughly trigonal petaline $[Cu_3I_3]$ structure. The fourth Cu atom (Cu1) that lies at the handle position of the flower basket bridges I1 and I1A atoms.

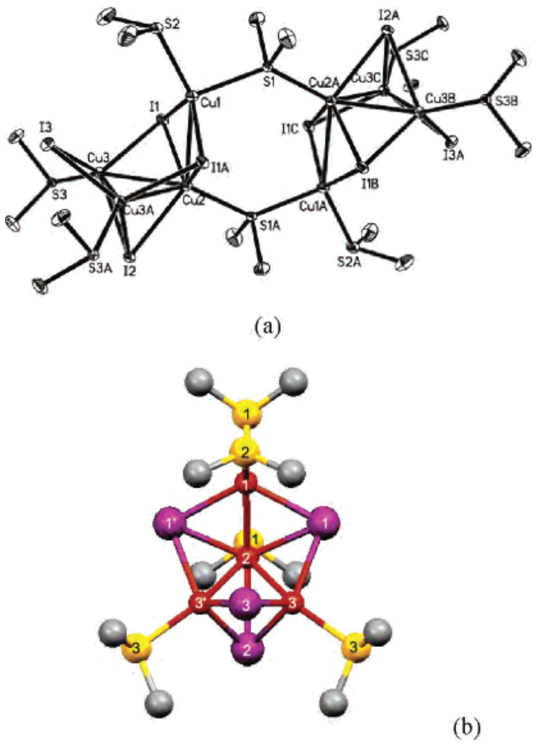

**Figure 1.** (a) Twin unit of the flower-basket-shaped clusters of **1**, showing 30% probability displacement ellipsoids and the atom-numbering scheme. All hydrogen atoms are omitted for clarity. [Symmetry codes: A: $-x + 1$, $y$, $z$; B: $-x + 1$, $-y + 1$, $-z + 1$; C: $-x + 3/2$, $y$, $-z + 3/2$]; (b) The unusual $Cu_4I_4$ cluster of **1**.

Among cuprous iodic $Cu_4$ clusters, most of the reported structures have a cubane-like $Cu_4I_4$ arrangement with an internal tetrahedral $Cu_4$ core.[3,9] Rectangular $Cu_4I_4$ clusters[10] and step or 'chair' structural $Cu_4I_4$ clusters[11] have also been reported. A very significant structure feature of the so-called flower-basket-shaped structure of **1** is that it is an opened structure of the cubane-like $Cu_4I_4$ cluster. The Cu1 and I3 are separated with a distance of 4.347 Å, showing the cubane-like $Cu_4I_4$ structure is opened at Cu1 and I3 site. Because two sites of the tetrahedral coordinated Cu1 atom are occupied by two $CH_3SCH_3$ molecules, the cubic $Cu_4I_4$ cluster is opened and turned to a flower-basket-shaped cluster that is significantly different from other cuprous iodic $Cu_4$ clusters.

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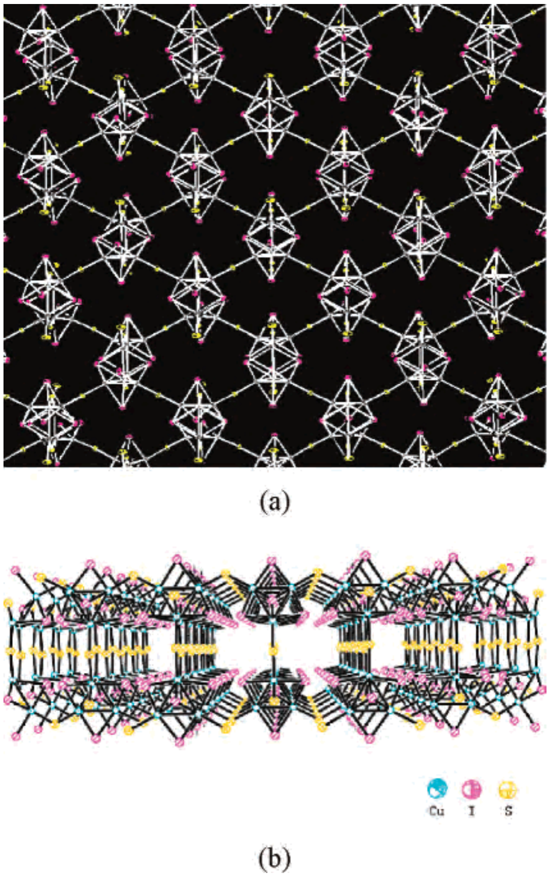
(a)

(b)

**Figure 2.** (a) View of the 2-D network of **1** along the *b* axis. All hydrogen and carbon atoms are omitted for clarity. (b) View down the *c* axis of **1** showing double-layered structure and 1-D channels. Hydrogen and carbon atoms are omitted for clarity.

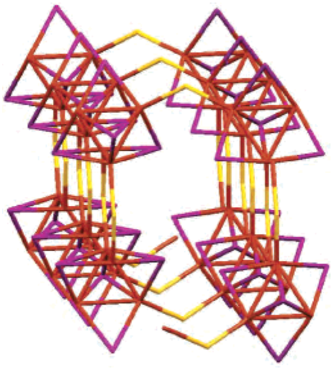
**Figure 3.** Fundamental $Cu_4I_4$ clusters of **1** are linked by sulfur bridges to form a helical structure.

Two adjacent flower-basket-shaped $Cu_4I_4$ fragments are bridged by two $CH_3SCH_3$ molecules to form a cluster dimer (Figure 1a). When viewed down the *b* direction, the twin units are rhombic arranged and connected to each other by $CH_3SCH_3$ bridges to form a 2-D network within the *ac* plane (Figure 2a). This is distinct from the cases of the reported other corresponding polymeric species having $Cu_xI_y$ cores.[2,3] The title 2-D polymeric compound is an absolutely new structural motif. Figure 2b depicts the double-layered structure viewed along the *c* axis. The remarkable structural feature of **1** is that the double-layered structure is constructed by 1-D channels, which is assembled by helically linked $Cu_4I_4$ clusters along the *c* axis (Figure 3). The 1-D infinite helices are arranged alternately by right-handed helices and left-handed helices. Organic and inorganic polymers existing in helical structures are of great practical and theoretical significance.[12] Most of the previously reported helical coordination compounds are generated by complexation of the ligands around the simple metal ions. The helical structure of **1** is unique in a sense that the fundamental units are clusters that are linked by sulfur bridges to form a helical pearl-necklace-like structure.

Upon excitation at 290 nm, intense emission of compound **1** in the solid state has been found at 545 nm at room temperature (see Figure SI-3). The emission is from a triplet "cluster centered" (CC) excited state and might be assigned to a combination of iodine−copper charge transfer (XMCT) and metal cluster centered transition [MCC, $d_{Cu} \rightarrow (s,p)_{Cu}$] in orbital parentage.[13] The existence of a MCC contribution is supported by Cu−Cu distances, 2.6681(9)−2.7138(12) Å, less than twice the van der Waals radius of Cu (i.e., less than 2.8 Å), consistent with the previous reported results for $Cu_xI_y$ clusters.[2c,14] In contrast, a compound where the Cu−Cu distance is substantially longer than 2.8 Å is not emissive due to its very weak Cu−Cu interaction.[15]

In summary, a novel luminescent 2-D double-layered polymer with a substructure of unusual $Cu_4I_4$ clusters has been synthesized. This new and relatively rare cluster with opened cubane-like $Cu_4I_4$ cluster is further assembled to form a 2-D polymer with unique helical structure. The results are significant not only for the preparation of a new luminescent polymeric compound with $Cu_xI_y$ blocks but also for a new route for synthesis of coordination compounds with DMS by using DMSO as a starting material instead of the disfavored DMS.

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**Supporting Information Available:** Experimental preparation, CIF table, Powder X-ray diffraction pattern, fluorescent spectrum and TG result of compound **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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