Coordination Frameworks

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# Self-Assembly of Nanometer-Scale $[Cu_{24}I_{10}L_{12}]^{14+}$ Cages and Ball-Shaped Keggin Clusters into a (4,12)-Connected 3D Framework with Photoluminescent and Electrochemical Properties**

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The design and construction of coordination polymers from preformed metal clusters,[1] such as metal carboxylate clusters[2] and chalcogenide supertetrahedral clusters,[3] to produce new materials with unique properties have been the focus of recent research interest. However, given the importance of cuprous iodide clusters in photochemistry and photophysics,[4] as well as their considerable variety of structural forms not encountered for other iodometalates,[5] it is surprising that relatively little progress has been made in using them as building blocks for the fabrication of multidimensional coordination frameworks.[6] On the other hand, polyoxometalates (POMs),[7,8] as a unique class of metal–oxide clusters, have many properties that make them attractive for applications in catalysis, biology, magnetism, optics, and medicine.[9] Impressive studies on linking of these well-defined metal–oxygen building blocks to generate giant discrete clusters and related extended structures have been performed.[10,11] However, up to now no reports have been made on the combination of these two interesting fields to prepare high-dimensional cluster-based compounds, although POM chemistry has touched an almost unprecedented number of other fields of chemistry.[9b] Such composite materials present the opportunity to generate high-dimensional nanoscopic assemblies from even larger multinanounits and also have vast potential for use in materials science by incorporation of their own physical and chemical properties.

Among the many different types of POMs, we chose the Keggin heteropolyanions, as they are the most widely recognized and thoroughly studied. Furthermore, we used the N-heterocyclic ligand 4-[3-(1*H*-1,2,4-triazol-1-yl)propyl]-4*H*-1,2,4-triazole (L, see the Supporting Information) for our synthetic strategy because 1) its clawlike donor atoms and bent coordination geometry offer the possibility of incorporating more metal atoms into high-nuclearity clusters, and 2) ligands containing a large number of N atoms could partially reduce $Mo^{VI}$ to $Mo^{V}$,[12] whereby the surface charge density of the polyanion is increased and the surface oxygen atoms are activated to facilitate formation of high-dimensional covalent networks. Herein we report the synthesis, structure, and luminescent and electrochemical properties of an unprecedented (4,12)-connected 3D network, namely, $(NH_4)[Cu_{24}I_{10}L_{12}][PMo^{V}{}_2Mo^{VI}{}_{10}O_{40}]_3$ (**1**), assembled by covalent connection of nanometer-scale $[Cu_{24}I_{10}L_{12}]^{14+}$ cages and ball-shaped Keggin anions.

Crystals of **1** were obtained by hydrothermal reaction of CuI, $H_3PMo_{12}O_{40}$, $NH_4Cl$, and L. Single-crystal X-ray analysis of **1**[13] showed the presence of two different nanocluster subunits (see the Supporting Information). One is the familiar Keggin cluster anion $[PMo^{V}{}_2Mo^{VI}{}_{10}O_{40}]^{5-}$ (ca. 10.5 Å in diameter), which consists of four internally edge sharing triads ($Mo_3O_{13}$) that share corners with each other and are disposed tetrahedrally around a central $T_d$ atom (Figure 1c). Valence-sum calculations based on bond lengths established that the Mo centers are in $+5/+6$ oxidation states (see the Supporting Information). The assignment of the oxidation state is also consistent with the charge requirement of the anion and the UV/Vis spectrum.[14]

The other subunit is an unprecedented, highly symmetrical $[Cu_{24}I_{10}L_{12}]^{14+}$ cluster (Figure 1a) built up of a tetrahedral $Cu_{12}I_{10}N_{12}$ core and twelve supporting copper(I) atoms (Figure 1b). As shown in Figure 1d, the linking mode of the $Cu_{12}I_{10}N_{12}$ core is very similar to that of the Keggin ion, that is, four $Cu_3I_4N_3$ triad clusters that result from the association of three edge-sharing $CuI_3N$ tetrahedra share corners to gen-

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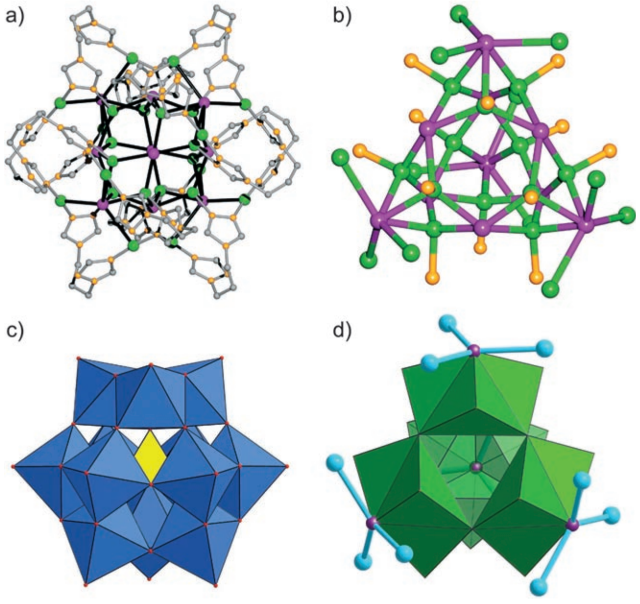

***Figure 1.*** a) Ball-and-stick representation of the highly symmetrical $[Cu_{24}I_{10}L_{12}]^{14+}$ cluster. The basic $[Cu_{24}I_{10}N_{12}]^{14+}$ unit is highlighted by thick black bonds. Cu green, I purple, N orange, C gray. b) Ball-and-stick representation of the $Cu_{24}I_{10}N_{12}$ cluster with bridging ligands omitted for clarity. c) Polyhedral representation of Keggin-type $[PMo^{V}_{2}Mo^{VI}_{10}O_{40}]^{5-}$ cluster. Blue polyhedra $MoO_6$, yellow polyhedron $PO_4$. d) Polyhedral representation of the $Cu_{12}I_{10}N_{12}$ core with twelve supporting copper atoms shown as cyan balls.

erate the $Cu_{12}$ core. All iodine atoms at the corners of the core are further bonded to three Cu atoms to give the novel $[Cu_{24}I_{10}L_{12}]^{14+}$ cluster. The arrangement of the central twelve $Cu^{I}$ atoms can be approximated as a cuboctahedron with $O_h$ symmetry, as found in the other two known species containing $Cu_{12}S_6$ clusters[15] (see the Supporting Information). Three adjacent Cu atoms that constitute a triad cluster form a perfect equilateral triangle with a Cu–Cu distance of 2.744(5) Å (Supporting Information). Such a short intermetallic distance, less than twice the van der Waals radius of $Cu^{I}$ of 1.4 Å, implies strong Cu–Cu interactions. All the $Cu^{I}$ centers and the inner six iodine atoms adopt tetrahedral coordination geometry, whereas the four remaining iodine atoms at the corners of the cluster have distorted octahedral geometry. The $[Cu_{24}I_{10}L_{12}]^{14+}$ cluster has a size of about 12.4 Å between corner metal sites and is the second largest iodocuprate(I) cluster made so far after the isolated cubic $[Cu_{36}I_{56}]^{20-}$ polyanion.[5b]

In coordination chemistry, it is quite rare that two different types of nanoclusters are directly assembled into crystalline solid-state materials.[16] Among the POM-based frameworks, we are aware of only two cases: $[\delta\text{-}Al_{13}O_4(OH)_{24}(H_2O)_{12}][XW_{12}O_{40}](OH)\cdot H_2O$ ($X = H_2$ or Co) in which $XW_{12}O_{40}{}^{6-}$ polyanions and $\delta\text{-}Al_{13}{}^{7+}$ polycations are packed alternately through intercluster hydrogen bonds and electrostatic interactions,[17] and a nanoring–nanosphere molecule with two K centers as hinge.[18] Compared to these species, the most important advance in **1** is the infinite and covalent assembly of the two types of nanoobjects. As illustrated in Figure 2, each $[Cu_{24}I_{10}L_{12}]^{14+}$ cluster is covalently bonded to twelve adjacent $[PMo_{12}O_{40}]^{5-}$ clusters via twelve peripheral copper atoms, and each $[PMo_{12}O_{40}]^{5-}$ cluster is connected with four $[Cu_{24}I_{10}L_{12}]^{14+}$ clusters via four $\mu_2$-O atoms. Therefore, the overall 3D framework can be rationalized as a (4,12)-connected net with Schläfli symbol $(4^{30}\cdot6^{30}\cdot8^{6})(4^{6})_3$ by assigning the $[Cu_{24}I_{10}L_{12}]^{14+}$ cluster as a twelve-connected node and the $[PMo_{12}O_{40}]^{5-}$ cluster as a four-connected node (Figure 3 and Supporting Information).[19] The trigonal-icosahedral coordination of the twelve-connected $[Cu_{24}I_{10}L_{12}]^{14+}$ cluster in **1** (see the Supporting Information) makes it exceptional in that the only two comparable examples both adopt cuboctahedral coordination.[15b,20] Notably, the heterocyclic ligand does not, as one might expect, act as network linker, but rather templates the formation of the iodocuprate(I) cluster. Considering that nearly all iodocuprate(I) clusters have been prepared as isolated clusters, the twelve-connected $[Cu_{24}I_{10}L_{12}]^{14+}$ cluster present in **1** not only has the highest connectivity known to date, but is also the first cuprous iodide cluster extended to 3D architectures.

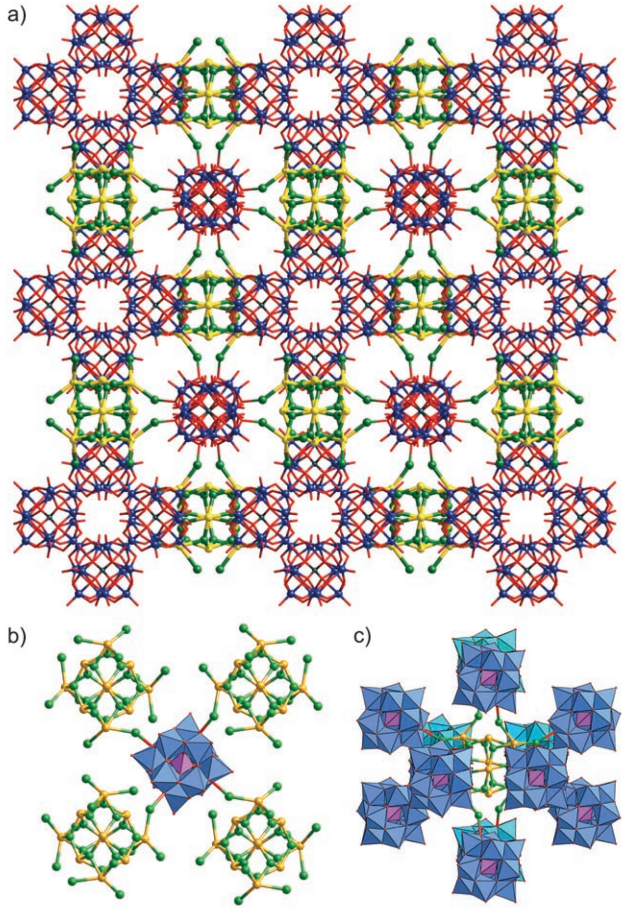

***Figure 2.*** a) Ball-and-stick representation of the three-dimensional framework of **1**. b, c) Local connections of the two types of nanoclusters. Cu green, I yellow, Mo blue, P purple, O red. For clarity, ligands and isolated $NH_4{}^{+}$ ions are omitted.

Compound **1** exhibits remarkably photoluminescent properties at ambient temperature. Two prominent emission peaks are observed at about 436 and 462 nm (excitation at 387 nm; see the Supporting Information). In accordance with the

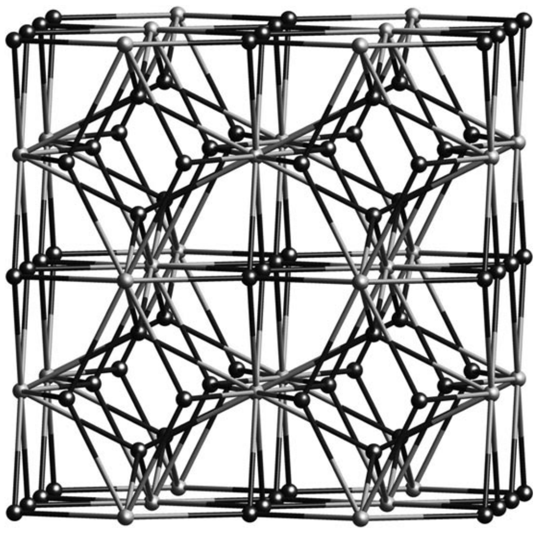

*Figure 3.* The (4,12)-connected $(4^{30}\cdot6^{30}\cdot8^{6})(4^{6})_3$ net. Dark gray: $[PMo_{12}O_{40}]^{5-}$ cluster; light gray: $[Cu_{24}I_{10}L_{12}]^{14+}$ cluster.

photoluminescent properties of cuprous halide clusters,[4] the two emissions may be attributed to a mixture of iodide-to-copper charge transfer and d–s transitions due to Cu–Cu interactions within the $Cu_3$ cluster.

The electrochemical behavior of **1**-modified carbon paste electrode (**1**-CPE) and its electrocatalytic reduction of nitrite were also studied (see the Supporting Information). Three well-defined redox couples can be observed in 1 M aqueous $H_2SO_4$ solution at a scan rate of 20 mV s$^{-1}$. The approximate proportionality of the reduction peak current to the scan rate up to 500 mV s$^{-1}$ indicates that the redox process is surface-controlled.[21] Moreover, **1**-CPE is highly stable. When the potential range is maintained at +800 to −120 mV, the peak currents remain almost unchanged over 500 cycles. When **1**-CPE was stored at room temperature for two months, the current only decreased by 4% and could be renewed by squeezing a little carbon paste out of the tube. This is especially useful for electrocatalytic studies, since the catalytic activity is known to decrease when the electrode is fouled. The electroreduction of nitrite requires a large overpotential[22] and so no obvious response is observed in the range +700 to −200 mV on a bare carbon paste electrode in 1 M $H_2SO_4$ containing 5 mM $NaNO_2$ (see the Supporting Information). However, **1**-CPE displays good electrocatalytic activity toward the reduction of nitrite. On addition of $NO_2^-$, the reduction peak currents increase and the corresponding oxidation peak currents decrease dramatically, and this suggests that nitrite is reduced. The results indicate that the three reduced species all have electrocatalytic activity for nitrite reduction. It was also noted that the third reduced species showed the best electrocatalytic activity, that is, the catalytic activity is enhanced with increasing extent of polyanion reduction.

In conclusion, a stable 3D covalent framework has been constructed by infinite assembly of two traditional but distinct nanoclusters. The novel nanoscale $[Cu_{24}I_{10}L_{12}]^{14+}$ cage building units and their covalent linkage with Keggin anions make this species an interesting solid-state rarity. More importantly, this framework generates a new kind of materials that combines the useful properties of the two clusters. Given the enormous structural diversity of POMs, this work opens new perspectives for the construction of fascinating multifunctional cluster-based networks. Work is continuing in this area.

## Experimental Section

**1**: A mixture of CuI (95 mg, 0.5 mmol), $H_3PMo_{12}O_{40}$ (183 mg, 0.1 mmol), $NH_4Cl$ (107 mg, 2 mmol), L (180 mg, 1 mmol), and water (10 mL) was sealed in a 20 mL teflon-lined autoclave and heated to 160 °C for 5 d. After slow cooling to room temperature, black crystals of **1** were obtained (yield: 139 mg, 40% based on Mo). Elemental analysis (%) calcd for $C_{84}H_{124}Cu_{24}I_{10}Mo_{36}N_{73}O_{120}P_3$: C 9.68, H 1.20, N 9.82, P 0.89, Mo 33.15, Cu 14.64; found: C 9.35, H 1.08, N 9.63, P 1.21, Mo 33.36, Cu 14.52. Materials and measurements are summarized in the Supporting Information.

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[13] Crystal data of **1**: $\mathrm{C_{84}H_{124}Cu_{24}I_{10}Mo_{36}N_{73}O_{120}P_3}$, $M_r = 10417.27$, cubic, space group $I\bar{4}3n$, $a = b = c = 22.4209(6)$ Å. $V = 11270.9(5)$ Å$^3$, $Z = 2$, $F(000) = 9764$. $\rho_{\mathrm{calcd}} = 3.070\ \mathrm{g\,cm^{-3}}$, $R1$ ($wR2$) = 0.0395 (0.1081) and $S = 1.056$ for 3216 reflections with $I > 2\sigma(I)$. The data were collected at 273(2) K on a Rigaku R-AXIS RAPID IP diffractometer with monochromated $\mathrm{Mo_{K\alpha}}$ radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods using SHELXS-97 and extended by Fourier techniques. CCDC 616371 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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