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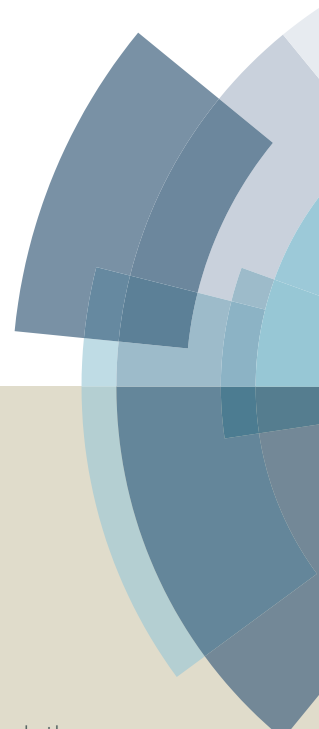
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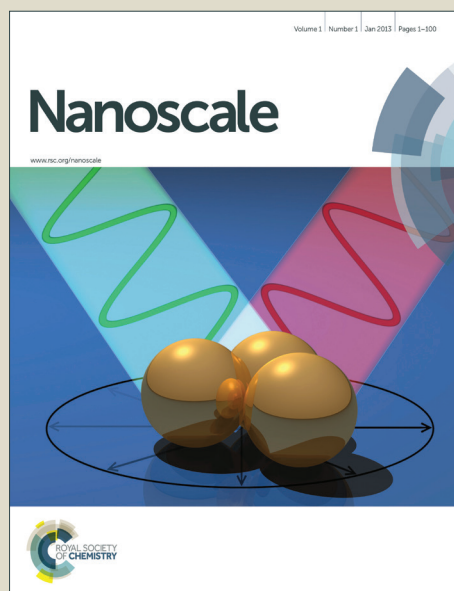
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ARTICLE TYPE

Self-assembly of an unprecedented polyoxomolybdate anion $[\text{Mo}_{20}\text{O}_{66}]^{12-}$ in a giant peanut-like 62-core silver-thiolate nanoclusterRen-Wu Huang,^a Qing-Qing Xu,^a Hong-Lin Lu,^a Xiao-Kang Guo,^a Shuang-Quan Zang,^{*a} Guang-Gang Gao,^{*b,d} Ming-Sheng Tang^a and Thomas C. W. Mak^c⁵ Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
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A polyoxometalate-templated silver thiolate nanocluster, $[\text{Ag}_{62}(\text{S}^t\text{Bu})_{40}(\text{Mo}_{20}\text{O}_{66})(\text{Mo}_6\text{O}_{19})_3(\text{CH}_3\text{CN})_2] \cdot (\text{CF}_3\text{SO}_3)_4$ (**1**), has been isolated, in which a giant peanut-like silver(I)-thiolate cluster $[\text{Ag}_{62}(\text{S}^t\text{Bu})_{40}]^{22+}$ encapsulates an unprecedented $[\text{Mo}_{20}\text{O}_{66}]^{12-}$ polyoxoanion core. It opens a new approach to the synthesis of both elusive polyoxometalates and high-nuclearity silver(I)-thiolate nanoclusters.

¹⁵ In recent years, high-nuclearity gold and silver clusters have been studied extensively not only due to their fascinating structures but also owing to their luminescent or catalytic properties.¹⁻⁴ A variety of high-nuclearity silver clusters have been synthesized by using various template anions, such as halide,⁵ carbonate⁶ and chromate⁷ etc. Considering that polyoxometalate (POMs) have shown diverse structures and potential applications in a range of fields such as electronics, catalysis, and materials design,⁸ more attention has been paid to synthesize POM-based high-nuclearity metal clusters.⁹
²⁵ Among these, a series of impressive POM-templated silver-ethynide and -thiolate clusters have been reported.¹⁰⁻¹⁴ All these compounds indicate that POM anion has become an effective template to induce diverse high-nuclearity silver(I)-ethynide or -thiolate clusters but also may transfer their functional characteristics to the silver(I) shell.

However, it remains a great challenge to synthesize giant POM-templated silver(I) nanoclusters due to that only limited small size POMs can be used so far. Most efforts were restricted to take advantage of some known polyoxoanion to regulate and control silver clusters skeletons. Noteworthy, it was reported previously that the transformation of POM precursors for adapting to the peripheral silver(I) atoms were often observed.^{11a,11d,12a} That is, there is great potential to synthesize new POM family members while also to induce fascinating high-nuclearity silver(I) nanoclusters by using conventional and soft synthesis method. This clue inspired us to explore more reactions of polyoxoanions with mixed silver(I) salts, forming new structurally determined and nanosized POM-templated silver(I)-thiolate clusters.

⁴⁵ In view that polymolybdate template silver(I)-thiolate cluster has not been explored yet, we recently devote our effort to investigate polymolybdate induced silver(I)-thiolate

compounds. We tried to synthesize a core-shell nanocluster featuring as silver(I)-thiolate shell with $[\text{Mo}_6\text{O}_{19}]^{2-}$ core. Fortunately, a fascinating POM-templated silver nanocluster, $[\text{Ag}_{62}(\text{S}^t\text{Bu})_{40}(\text{Mo}_{20}\text{O}_{66})(\text{Mo}_6\text{O}_{19})_3(\text{CH}_3\text{CN})_2] \cdot (\text{CF}_3\text{SO}_3)_4$ (**1**), has been acquired by the reaction of Lindquist polyoxometalate of $(^t\text{Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{19}]$ with AgS^tBu , $\text{CF}_3\text{SO}_3\text{Ag}$ and $\text{CF}_3\text{SO}_3\text{H}$ in the mixed solvent of acetonitrile and methanol. The self-assembly of POM-based silver(I)-clusters often lead to unpredictable structures which is due to the flexible polyoxoanion template and versatile coordination modes of thiol ligands. Surprisingly, incorporation of polyoxomolybdate stabilizes the silver(I) cluster and makes it insensitive to light. This is the first case that a new icosamolybdate $[\text{Mo}_{20}\text{O}_{66}]^{12-}$ has been isolated in a silver thiolate cage, in which $[\text{Mo}_6\text{O}_{19}]^{2-}$ polyoxoanion underwent a self-assembly process to form a new polyoxometalate species.

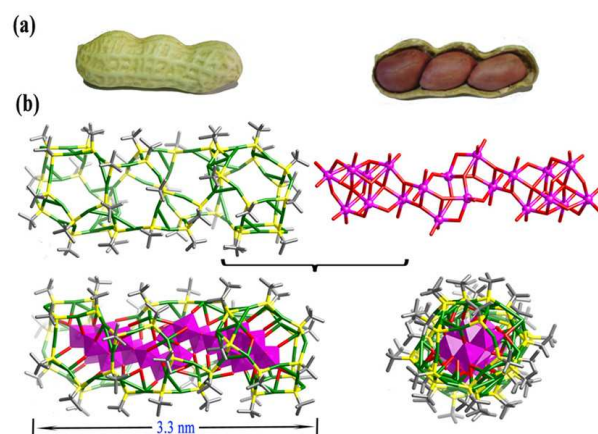


Fig. 1 (a) Pictures of real peanut. (b) The peanut-like nanocluster structure illustrating the silver-POM interactions in **1**. All H atoms, CH_3CN and CF_3SO_3^- are omitted for clarity. Color legend: green, Ag; pink, Mo; yellow, S; red, O; gray, C.

Complex **1** was successfully isolated as a peanut-like skeleton with $[\text{Ag}_{62}(\text{S}^t\text{Bu})_{40}]^{22+}$ shell and a $[\text{Mo}_{20}\text{O}_{66}]^{12-}$ core. As shown in Fig. 1, forty S^tBu ligands adopt $\mu_3\text{-}\eta^1$, η^1 , η^1 and $\mu_4\text{-}\eta^1$, η^1 , η^1 , η^1 ligation modes to link adjacent silver ions.

The whole shell is stabilized by the Ag–S covalent bonds and argentophilic Ag⋯Ag interactions with Ag–S and Ag⋯Ag bond lengths in the ranges of 2.329(9)–2.662(6) Å and 2.855(4)–3.324(2) Å, respectively. The interesting structural feature of **1** is its nanoscale core-shell configuration. The [Ag₆₂(S'Bu)₄₀]²²⁺ shell in **1** is large enough (3.3×1.7 nm) to accommodate one [Mo₂₀O₆₆]^{12−} polyoxoanion (2.5×0.8 nm). The TEM image reveals that **1** exists as discrete particle (Fig. 2), and the size of the identified particles is about 3.0 nm close to the size of the above described.

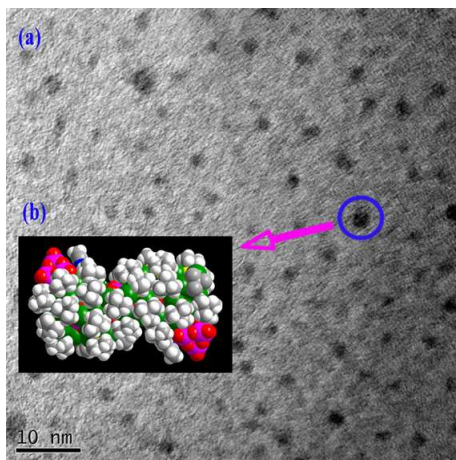


Fig. 2. (a) TEM image of **1** in acetone. (b) Single cluster unit of **1**. Color code: green, Ag; pink, Mo; yellow, S; red, O; dark blue, N; gray, C; white, H.

Structural analysis indicates that the Lindqvist-type precursors [Mo₆O₁₉]^{2−} transformed into [Mo₂₀O₆₆]^{12−} via self-assembly process. Such unusual peanut-like [Mo₂₀O₆₆]^{12−} can be considered as two [Mo₇O₂₄]^{6−} heptamolybdate anions that linked by bridging [Mo₆O₁₈] subunit (Fig. S1, ESI†). It is well-known that the classical Lindqvist-type [Mo₆O₁₉]^{2−} anion has 6 terminal oxygen atoms (O_t), 12 μ₂-bridging oxygen atoms (O_b), and one central μ₆-O atom (O_c). While the strip-like [Mo₂₀O₆₆]^{12−} anion is equipped with abundant terminal oxygen atoms, which has 34 O_t atoms, 16 μ₂-O atoms, 12 μ₃-O atoms, 2 μ₄-O atoms, and 2 μ₅-O atoms. Generally speaking, an increase in the number of the terminal oxygen atoms of polyoxoanion is more favorable to improve its coordination ability. To verify this theory, the atom charges of [Mo₆O₁₉]^{2−} and [Mo₂₀O₆₆]^{12−} were calculated by a natural bond orbital (NBO) calculation at the BP86¹⁵ level involving the effective core potential (ECP) on the Mo atom, using Gaussian 09 package (Fig. S3 and S4, ESI†).¹⁶ The LANL2DZ basis set associated with the pseudopotential was used to describe the Mo atom, and the 6-31G (d) basis set was used to describe the oxygen atom. The natural charge of Mo atoms are 1.173 ~ 1.179e and 0.911 ~ 1.170e in [Mo₆O₁₉]^{2−} and [Mo₂₀O₆₆]^{12−}, respectively. The charge of O_t are −0.436 ~ −0.582e in [Mo₂₀O₆₆]^{12−} (Table S3 and S4, ESI†), which are larger than those of [Mo₆O₁₉]^{2−}. It indicates that the nucleophilic activities of terminal atoms O_t in [Mo₂₀O₆₆]^{12−} are stronger than those of [Mo₆O₁₉]^{2−}. In addition, the unique core-shell configuration reflects that the polyoxoanions with higher

charge densities make it easier to induce the formation of thiolate silver (I) shell via multiple Ag–O bonds^{12a}. As a result, the [Mo₂₀O₆₆]^{12−} polyoxoanion not only acts as template for the formation of the cationic silver(I)-thiolate cluster, but also consolidates the peanut structure by virtue of its surface O atoms with Ag–O distances ranging from 2.375(12) to 2.743(5) Å, which are comparable to the Ag–O distances in the intercluster compounds.¹³ Despite of the fact that POM chemistry has developed more than 180 years, the self-assembly process of most of polymolybdates remains elusive for POM chemists. The successful synthesis of **1** opens a new route to discover the new polymolybdates that are difficultly synthesized by the usual synthetic method in acid water solution. In addition, there are two kinds of [Mo₆O₁₉]^{2−} anions, of which one is located between two neighbouring clusters with the weak Ag⋯O contacts to improve the stability of the crystals of **1**; while the other one directly coordinates to the silver shell with the Ag–O bonds of 2.612(12) Å (Fig. S2, ESI†).

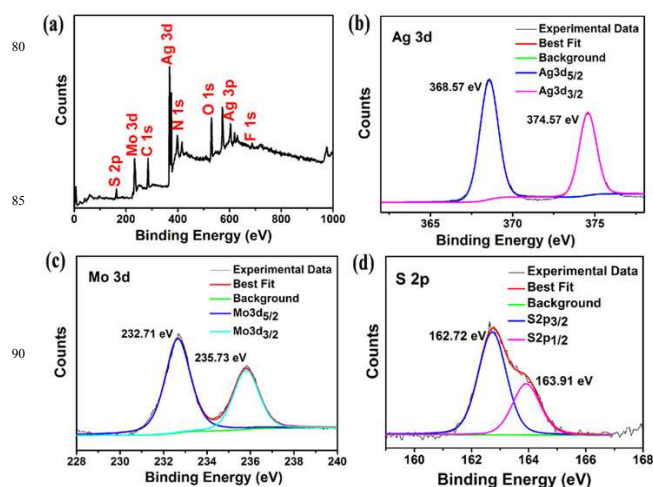


Fig. 3. (a) XPS survey of complex **1**, (b) Ag 3d, (c) Mo 3d, (d) S 2p high-resolution XPS spectra.

The composition of **1** was also supported by FT-IR spectrum (Fig. S5, ESI†), in which the absorption characteristic bands of 960 and 797 cm^{−1} are similar to those of [Mo₆O₁₉]^{2−}, while the bands at 921, 892, and 686 cm^{−1} should be ascribed to Mo–O vibrations for [Mo₂₀O₆₆]^{12−}.¹⁷ Its phase purity, stability in air and light stability were confirmed by powder X-ray diffraction (PXRD) (Fig. S6, ESI†). XPS survey spectra reveal the presence of Ag, Mo, S, C, N, O, F, and no other elements were detected (Fig. 3a). High-resolution XPS measurements were performed in order to qualitatively and quantitatively analyse the elements Ag, Mo and S. The integration of the area under Ag3d, Mo3d and S2p peaks gave 44.5% Ag, 25.8% Mo and 30.7% S atomic concentration, and in reasonably good match with the values calculated for compound **1**, where there is 43.7% Ag, 26.7% Mo and 29.6% S. In addition, for Ag, the peaks around 368.57 and 374.57 eV in the energy regions of Ag3d_{5/2} and Ag3d_{3/2} correspond to Ag⁺ bonding with S'Bu[−] (Fig. 3b). The Mo

element presents the peaks around 232.71 and 235.73 eV, which are in agreement with the energy regions of Mo3d_{5/2} and Mo3d_{3/2} ascribed to Mo⁶⁺ centers as shown in Fig. 3c. As for sulfur, the S2p_{3/2} peak is observed at 162.72 eV (Fig. 3d). This value does not correspond neither to free thiols nor to disulfides, whose expected binding energy values (BEs) are higher than 163 eV; moreover, the reported value of metal sulphides (161.1–162.2 eV) is also smaller.¹⁸ Therefore, the difference of S2p peak may be due to the special ligation modes of S'Bu[−] (μ_3 - η^1 , η^1 , η^1 and μ_4 - η^1 , η^1 , η^1 , η^1). These results agree well with the single-crystal structural analysis.

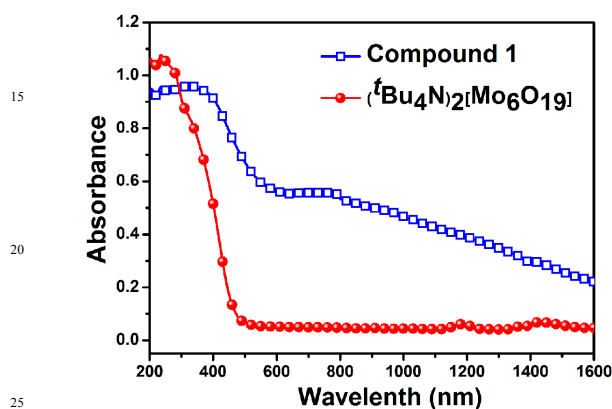


Fig. 4. UV-vis diffuse reflectance spectra of (tBu₄N)₂[Mo₆O₁₉] and compound 1.

The diffuse reflectance spectra of compound 1 and the POM precursor are shown in Fig. 4. Compound 1 displays a broad absorption starting from 610 nm and tailing to near-IR regions in the solid state, which is similar to compounds reported in the literature.¹⁹ According to Mulliken theory,²⁰ the near-IR absorption bands can be ascribed to charge-transfer transitions between the [Ag₆₂(S'Bu)₄₀(Mo₂₀O₆₆)]¹⁰⁺ donors and [Mo₆O₁₉]^{2−} acceptors. It should be noted that the charge-transfer behavior was observed for the first time in POM-templated silver(I)-thiolate cluster. In addition, a weak absorption band at ca. 526 nm was observed in the UV-vis absorption spectrum of the acetone solution of 1 ($\epsilon = 4.6 \times 10^3$ M^{−1} cm^{−1}) (see Fig. S7, ESI†).

In summary, an giant POM-templated silver(I)-thiolate nanocluster has been synthesized and structurally characterized. For the first time, polyoxoanion of [Mo₂₀O₆₆]^{12−} has been isolated as template located in a peanut-like silver(I)-thiolate nano-cage via self-assembled process. The synthesis of 1 paves a promising route to the isolation of new polyoxometalate and high-nuclearity silver(I)-thiolate nanoclusters, which makes the synthetic strategy of silver(I) nanocluster be realized by a bottom-up design.

Notes and references

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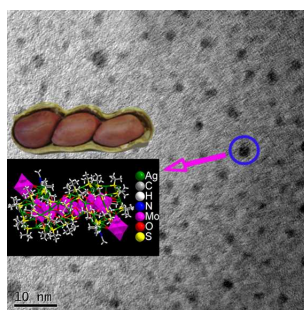
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†Electronic Supplementary Information (ESI) available: Details of measurements, experimental and theoretical calculated details, additional structural figure and characterization data. CCDC No. (1025476). See DOI:10.1039/b000000x/

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A giant peanut-like silver(I)-thiolate nanocluster $[\text{Ag}_{62}(\text{S}^t\text{Bu})_{40}]^{22+}$ encapsulating an unprecedented $[\text{Mo}_{20}\text{O}_{66}]^{12-}$ polyoxoanion has been successfully assembled.