Deciphering synergetic core-shell transformation from \([\text{Mo}_6\text{O}_{22}@\text{Ag}_{44}]\) to \([\text{Mo}_8\text{O}_{28}@\text{Ag}_{50}]\)

Zhi Wang \(^1\), Hai-Feng Su \(^2\), Chen-Ho Tung \(^1\), Di Sun \(^1\) & Lan-Sun Zheng \(^2\)

The structural transformation of high-nuclearity silver clusters from one to another induced by specific stimuli is of scientific significance in terms of both cluster synthesis and reactivity. Herein, we report two silver-thiolate clusters, \([\text{Mo}_6\text{O}_{22}@\text{Ag}_{44}]\) and \([\text{Mo}_8\text{O}_{28}@\text{Ag}_{50}]\), which are templated by isopolymolybdates inside and covered by \(\text{PrS}^-\) and \(\text{PhCOO}^-\) ligands on the surfaces. Amazingly, the \([\text{Mo}_8\text{O}_{28}@\text{Ag}_{50}]\) can be transformed from \([\text{Mo}_6\text{O}_{22}@\text{Ag}_{44}]\) by adding \(\text{PhCOOH}\) which increases the degree of condensation of molybdates template from \(\text{Mo}_6\text{O}_{22}^8^-\) to \(\text{Mo}_8\text{O}_{28}^8^-\), then enlarging the outer silver shell from \(\text{Ag}_{44}\) to \(\text{Ag}_{50}\). The evolution of solution species revealed by time-dependent electrospray ionization mass spectrometry (ESI-MS) suggests a breakage-growth-reassembly (BGR) transformation mechanism. These results not only provide a combined assembly strategy (anion-template + induced transformation) for the synthesis of silver-thiolate clusters but also help us to better understand the complex transformation process underpinning the assembly system.
With regard to their ubiquitous argentophilicity and variable coordination fashions\textsuperscript{1–3}, Ag(I) coordination complexes, especially for silver clusters, are gorgeous in structural diversity and physicochemical properties\textsuperscript{4–6}. However, the synthesis of high-nuclearity silver clusters is always tedious and frankly a trial-and-error process. Overwhelming these synthesis barriers has promoted the appearance of exquisite assembly strategies including anion templation and geometric polyhedral principle\textsuperscript{7,8}, which have pushed the assembly of silver clusters to a higher level of sophistication\textsuperscript{9,10}. From the known largest silver(I) solid cluster (Ag\textsubscript{90}emo\textsubscript{41})\textsuperscript{11} to the largest silver(I) cage (Ag\textsubscript{81}emo\textsubscript{42})\textsuperscript{12}, we have witnessed the fruitful advances in this field. However, there is still vast room for improvement to realize the manipulation over such clusters at the molecular level, not just synthesizing them randomly. Inspired by the LEIST (ligand-exchange-induced size/structure transformation) methodology widely used in Aun(SR)\textsubscript{m} nanoclusters\textsuperscript{6}, we would like to study whether the similar stories can be observed in their silver cousins. In 2012, Mak et. al., reported the reaction of a famous Cl@Ag\textsubscript{14} clusters to AgClO\textsubscript{4}, which gave a larger Cl\textsubscript{6}Ag\textsubscript{6}@Ag\textsubscript{30} cluster, thus realizing the cluster enlargement\textsuperscript{13}. Following this, a polyoxovanadate-templated Ag\textsubscript{50} cluster was subjected to acid/base stimulations, which only resulted in the reversible conversion of [V\textsubscript{V}I\textsubscript{V}O\textsubscript{12}]\textsuperscript{4−} from D\textsubscript{4}d to C\textsubscript{3v}, however, the silver shell was kept invariable\textsuperscript{14}. These sporadic reports indicated the structural transformation of silver clusters inside and out by specific stimuli is still a challenging task.

In order to achieve structural transformation of silver clusters, two prerequisites are needed: (i) flexible silver shells and (ii) variable anion templates. Installing monocarboxylate ligands on the surface of silver clusters will endow the silver clusters some flexibility because the carboxylate belongs to hard base with respect to thiolate, thus forming relatively weak bonding with soft acid Ag(I) atoms\textsuperscript{15}. As such, when the stimuli-induced post-reaction proceeds in solution, the carboxylates can partially disassociate and thus realize the rearrangement of surface silver atoms. For variable anion templates, polyoxometalates (POMs) are the best candidates due to their mutable forms depending on pH values\textsuperscript{16}.

With all above considerations in mind, herein we use thiol and benzoic acid as mixed ligands to construct a silver cluster, [Mo\textsubscript{6}O\textsubscript{22}@Ag\textsubscript{44}(Pr\textsubscript{5}S)\textsubscript{24}(PhCOO)\textsubscript{18}(CH\textsubscript{3}CN)\textsubscript{2}]2CH\textsubscript{3}CN (SD/Ag\textsubscript{44}; SD = SunDi), which can be transformed to another larger silver cluster, [Mo\textsubscript{6}O\textsubscript{22}@Ag\textsubscript{50}(Pr\textsubscript{5}S)\textsubscript{22}(PhCOO)\textsubscript{18}(CH\textsubscript{3}CN)\textsubscript{2}]: 4CH\textsubscript{3}CN (SD/Ag\textsubscript{50}) by the reaction with additional PhCOOH. The reaction proceeds in solution, the carboxylates can partially disassociate then induce the rearrangement of surface silver atoms. For variable anion templates, polyoxometalates (POMs) are the best candidates due to their mutable forms depending on pH values\textsuperscript{16}.

Fig. 1 Synthesis and transformation routes for SD/Ag\textsubscript{44} and SD/Ag\textsubscript{50}. The scale bar is 1 mm

**Results**

**Structures of SD/Ag\textsubscript{44} and SD/Ag\textsubscript{50}**. The SD/Ag\textsubscript{44} was synthesized by solvothermal reaction of polymeric (Pr\textsubscript{5}S)\textsubscript{n} precursor, PhCOOAg and (Bu\textsubscript{4}N)\textsubscript{4}(Mo\textsubscript{6}O\textsubscript{22})\textsubscript{n} in CH\textsubscript{3}CN at 65 °C (Fig. 1). After the reaction, the yellow tufted crystals can be collected as the bulk sample of SD/Ag\textsubscript{44}. If adding another portion of PhCOOH (0.32 mmol) into above reaction mother liquor without removing crystals of SD/Ag\textsubscript{44}, then continuing to react again under the same condition will produce yellow block crystals of SD/Ag\textsubscript{50}.

The molecular structures of SD/Ag\textsubscript{44} and SD/Ag\textsubscript{50} were determined by single-crystal X-ray diffraction (SCXRD) analysis (Supplementary Table 1). Both of them crystallize in triclinic P-1 space group with a complete cluster in the asymmetric unit. As shown in Fig. 2a, the overall structure of SD/Ag\textsubscript{44} is a slightly squashed spheroid composed of 44 silver atoms and covered by 20 PrS\textsuperscript{−}, 16 PhCOO\textsuperscript{−} ligands and two CH\textsubscript{3}CN molecules. Interiory, an unusual Mo\textsubscript{6}O\textsubscript{22}\textsuperscript{8−} anion in situ generated from (Bu\textsubscript{4}N)\textsubscript{4}(α-Mo\textsubscript{6}O\textsubscript{22}) supports the outer Ag\textsubscript{44} shell. The diameter of SD/Ag\textsubscript{44} is roughly 1.2 nm, if removing the organic shell. On the other hand, the synthetic SD/Ag\textsubscript{50} [Mo\textsubscript{6}O\textsubscript{22}@Ag\textsubscript{50}] (Fig. 2c) is a slightly squashed spheroid composed of 50 silver atoms and covered by 34 PrS\textsuperscript{−}, 34 PhCOO\textsuperscript{−} ligands, and two CH\textsubscript{3}CN molecules. SD/Ag\textsubscript{50} features a larger shrunk spheroid with an added four silver atoms and covered by 34 PhCOO\textsuperscript{−} ligands.

**Fig. 2** Single-crystal X-ray structure of SD/Ag\textsubscript{44}. a The molecular structure of SD/Ag\textsubscript{44}. The inner POM anion template is shown in polyhedral mode (Color legend: Ag: purple; S: yellow; Mo: green; O: red; C: gray; N: blue). b The distributions of PrS\textsuperscript{−} ligands on the Ag\textsubscript{44} shell sorted by different coordination modes individually colored. Black: \(\mu_2\); yellow: \(\mu_3\). The polyhedral (c) and ball-and-stick (d) modes showing the inner Mo\textsubscript{6}O\textsubscript{22}\textsuperscript{8−} anion.
Notably, a Mo$_6$O$_{22}^{8-}$ anion was trapped into the Ag$_{50}$ cluster and should be in situ transformed from α-Mo$_6$O$_{22}^{8-}$. Bond-valence sum (BVS) calculations for six Mo atoms were performed and confirmed all of them are +6 oxidation state (Mo1-Mo6: 5.744, 5.455, 5.792, 5.531, 5.766, and 6.173$^{19}$). This indicates that no redox reaction occurs under the reaction condition. The Mo$_6$O$_{22}^{8-}$ in SD/Ag$_{44}$ is constructed from five edge-shared MoO$_6$ octahedra adding one MoO$_4$ tetrahedron by sharing one vertex (Fig. 2c). Alternatively, it can be seen as three Mo$_3$O$_4$ in classic POM chemistry$^{20}$. Using the valence sum (BVS) calculations for six Mo atoms were performed (5.744, 5.455, 5.792, 5.531, 5.766, and 6.173$^{19}$) This indicates that the structure might be related to Mo$_6$O$_{22}^{8-}$ anions in classic POM chemistry$^{20}$. Using the μ$_1$ and μ$_2$ bridging O atoms, Mo$_6$O$_{22}^{8-}$ binds total 30 Ag atoms around it with the Ag-O-POM bond lengths ranging from 2.255(4) to 2.793(5 Å (Supplementary Table 3). To date, only three isomeric Mo$_6$O$_{22}^{8-}$ anion templates have been reported in silver clusters such as face-sharing MoO$_4$ double cubanes$^{21,22}$, two MoO$_4$ opened cubanes sandwiching a Mo$_6$O$_4$ cubane by face-sharing$^{23}$, and three face-shared Mo$_6$O$_4$ opened cubanes$^{24}$, as summarized in Supplementary Table 2. By comparing, the Mo$_6$O$_{22}^{8-}$ in SD/Ag$_{44}$ is the fourth isomer trapped by silver cluster. Moreover, such Mo$_6$O$_{22}^{8-}$ is also different from those observed in POM-based inorganic–organic hybrids (Supplementary Table 3)$^{25-27}$, suggesting a new Mo$_6$O$_{22}^{8-}$ structure.

When adding another portion of PhCOOH to the mixture after the synthesis of SD/Ag$_{44}$ for second step reaction, we can isolate a larger silver cluster, SD/Ag$_{50}$. SCXRD analysis revealed that it is a larger cluster than SD/Ag$_{44}$. The overall structure of SD/Ag$_{50}$ comprised of 50 Ag atoms, forming a nearly ball-like shape with a diameter of ca. 1.4 nm, which is co-protected by 24 PhCOO$^-$ ligands, 18 PhCOO$^-$ ligands, and two CH$_3$CN molecules (Fig. 3a). The ratio of μ$_5$/μ$_6$/PhCOO in SD/Ag$_{50}$ is slightly larger than that in SD/Ag$_{44}$, indicating the re-organization of two kinds of ligands on the surface after structural transformation. As shown in Fig. 3b, 24 μ$_{5}^{−}$ ligands show μ$_4$ and μ$_5$ binding modes, whereas PhCOO$^-$ ligands show μ$_2$-$κ$-$1$,$ μ$_1$-$κ$-$3$,$ μ$_4$-$κ$-$3$,$ or μ$_4$-$κ$-$κ$ modes. The Ag$^+$ and Ag$-$O$_{enolate}$ bond lengths fall in the ranges of 2.248(7)−2.917(4) and 2.238(13)−2.771(12) Å, respectively. Due to the lack of regular silver polygons on the surface, such Ag$_{50}$ cluster doesn’t exhibit any geometrical polyhedron feature. The Ag$_{50}$ shell was further consolidated by rich Ag−Ag interactions falling in the range of 2.851(2)−3.431(2) Å.

This 50-nucleus cluster is also templated by a novel rod-like POM, formulated as Mo$_{28}^{8-}$, which can be seen as three Mo$_3$O$_4$ cubanes fused together by sharing two Mo$_2$O$_2$ rhombus faces (Fig. 3c), or described to eight edge-shared Mo$_6$O$_{22}^{8-}$ octahedra (Fig. 3d). The BVS$^{19}$ also verified +6 oxidation state of eight Mo atoms (Mo1-Mo8: 5.865, 5.431, 5.648, 5.889, 5.868, 5.748, 6.092, and 5.738). The surface of Mo$_{28}^{8-}$ has 20 terminal, 4 μ$_2$, bridging and 4 μ$_4$ bridging O atoms. Among these O atoms, only 20 terminal O atoms participate to the coordination with Ag atoms (Supplementary Fig. 4). Compared to the starting material α-Mo$_6$O$_{22}^{8-}$, Mo$_6$O$_{28}^{8-}$ has higher negative charges and more O atoms, which endow it as a better template for assembly of silver clusters. The Mo$_6$O$_{22}^{8-}$ in SD/Ag$_{50}$, to the best of our knowledge, has never been reported in POM-templated silver clusters and classic POM chemistry. Inspired by the above discussed structure features of SD/Ag$_{44}$, both PhCOO$^-$ ligands and weakly coordinated CH$_3$CN molecules are the potential reaction active sites, and the POM template can be also varied depending on the solution acidity. In fact, we found the transformation of SD/Ag$_{44}$ to SD/Ag$_{50}$ can facilely work by adding additional PhCOOH without changing any other reaction conditions. Based on the comparisons of their structures, such cluster-to-cluster structural transformation is a rare occurrence that simultaneously involved inner anion template (Mo$_6$O$_{28}^{8-} \rightarrow$ Mo$_6$O$_{28}^{8-}$) and outer silver shell (Ag$_{44} \rightarrow$ Ag$_{50}$). In this transformation process, the degree of condensation of molybdate was increased, resulting in the growth of Mo$_6$O$_{28}^{8-}$ to Mo$_6$O$_{28}^{8-}$. The larger POM template thus enlarges the outer silver shell from Ag$_{44}$ to Ag$_{50}$. We also tried to synthesize SD/Ag$_{50}$ without the transformation step by directly adding more PhCOOH into the reaction system, however, the SD/Ag$_{50}$ can be only isolated with a quite low yield (< 5%), whereas using the transformation synthesis route, it can reach up to more than 50%. Thus, PhCOOH-induced structural transformation might provide a new method for the high-yield synthesis of some silver clusters that are otherwise difficult to access. Moreover, this transformation reaction should be a thermodynamics controlled reaction, so SD/Ag$_{50}$ should be more stable than SD/Ag$_{44}$.

ESI-MS of SD/Ag$_{44}$ and SD/Ag$_{50}$. In order to investigate solution behaviors of both clusters, the ESI-MS of SD/Ag$_{44}$ and SD/Ag$_{50}$ dissolved in dichloromethane were measured in the positive ion mode. As shown in Fig. 4a, there are a series of +2 species (1a–1k) centered at the m/z range of 2000–8000. The most dominant peak centered at 4392.48 (1e) was assigned to [Δ(μ$_5^{−}$P$_{5}^-$)(PhCOO)$_8$(CH$_3$Cl)$_2$(H$_2$O)]$^{2+}$ based on the superimposable observed and simulated isotope patterns (Cal. 4392.49; Δ = Mo$_6$O$_{22}^{8-}$@Ag$_{44}$ hereafter). Similar formula assignment for each labeled species in ESI-MS was also performed as listed in Supplementary Table 4. Based on the assigned formula, we found the core of SD/Ag$_{44}$ is quite stable just with some surface ligand exchange between PhCOO$^-$ and μ$_5^{−}$P$_{5}^-$ such as those observed in paired species of 1b and 1c, 1g and 1h, and 1j and 1k. The 11 identified species existed in the solution, suggesting a typical coordination-disassociation equilibrium state, which may be broken by introducing some exotic stimuli, then producing some new species.
the Mo₉O₄₈⁻ being transformed from the residual molybdate species in mother liquor, we also used fresh crystals of SD/Ag44 and clean CH₃CN as solvent to do the transformation reaction and SD/Ag50 can also be formed, which suggested the Mo₉O₄₈⁻ must be transformed from the interior Mo₉O₂₂⁸⁻ in SD/Ag44. Meanwhile, this result also unambiguously indicated that the smaller-to-larger silver nanocluster conversion from SD/Ag44 to SD/Ag50 genuinely started from SD/Ag44 instead of other silver precursors.

As we know, ESI-MS is a promising analytical tool that provides considerable speciation information in solution 29–32. Cronin group have contributed largely to this field by using ESI-MS to detect new POM species and track transformation of POMs 33–35. This technique was also profoundly used by Xie group to study growth mechanism of gold nanoclusters or reactivity 36–40. However, using ESI-MS to study transformation or reactivity of silver clusters has remained a black box to date. To shed light on the details of transformation process from Ag₄₄ to Ag₅₀, we tracked the solution species evolution over the course of 240 min upon addition of PhCOOH (0.32 mmol, 39.1 mg) in the CH₂Cl₂ solution of Ag₄₄ cluster by time-dependent ESI-MS. In order to guarantee comparable intensity of signals for each species at different times, a generalized operation for the sampling and analysis was established and uniform instrument parameters were maintained. At scheduled time intervals, 500 μL aliquots of the reaction solution were extracted, and immediately infused (240 μL/h) to the mass spectroscope without dilution for subsequent measurement. To set the baseline and finishing line for this monitoring process, we also incorporated the ESI-MS spectra of Ag₄₄ (black line) and Ag₅₀ (dark green line) in CH₂Cl₂ into Fig. 5, respectively, although in-source fragmentation of them under our chosen ESI source parameters have been studied in above section. All formulae of labeled species in the ESI-MS in this section are listed in Supplementary Table 6 and hereafter only inner core compositions are shown below for clarity. Zoom-in ESI-MS including the simulated isotope distributions of all these species are shown in Supplementary Fig. 5. As depicted in Fig. 5a (0 min), once adding PhCOOH, four doubly charged species 11-1o appeared in the lower m/z range of 3600–4200 which are absent in original ESI-MS of Ag₄₄ solution. The assigned formulae for 11-1o are [Mo₉O₄₈@Ag₄₉]⁺ (II), [Mo₉O₄₈@Ag₄₉]⁻ (1m), and [Mo₉O₄₈@Ag₄₉]⁺ and 1o. In the higher m/z range of 4600–5300, the other five larger divalent species (1p, 1q, 1r, 2d, and 2e) are observed and can be assigned to [Mo₉O₄₈@Ag₄₆]⁺ (1p), [Mo₉O₄₈@Ag₄₆]⁻ (1q), [Mo₉O₄₈@Ag₄₇]⁺ (1r), [Mo₉O₄₈@Ag₄₇]⁻ (2d), and [Mo₉O₄₈@Ag₄₇]⁻ (2e). Of note, the 2e species is the parent cluster of SD/Ag₅₀. All these intermediates are smaller or larger than original Ag₄₄ cluster and their formations are intensely dependent on the addition of PhCOOH. The evolutions of species were further represented by the plots of signal intensity vs. time as shown in Fig. 5b. Upon adding PhCOOH, we observed the original species 11-1o smaller than Ag₄₄, indicating the breakage of Ag₄₄ shell was initiated by PhCOOH. As time going on (5–240 mins), the signal intensities of [Mo₉O₄₈@Ag₄₅]⁺ (II), [Mo₉O₄₈@Ag₄₅]⁻ (1m), and [Mo₉O₄₈@Ag₄₅]⁺ and 1o gradually decrease, whereas those of [Mo₉O₄₈@Ag₄₉]⁺ (2d) and [Mo₉O₄₈@Ag₅₀]⁺ (2e) become more intense, which suggested that the formation of Ag₅₀ cluster is at the expense of smaller intermediate species such as 11-1o at this stage. Moreover, we also noted the POM template encapsulated in silver shell undergo a condensation reaction from Mo₉O₂₂⁸⁻ to Mo₉O₈₂⁸⁻ and the excess oxygen coordination sites permit for the linkage of more silver atoms, thus forming the cluster larger than Ag₄₄.

Based on above observations, we speculated that the outer silver shell was attacked and partially broken by PhCOOH during
the initial stage, which resulted in the breakage of Ag$_{44}$ shell in some extent, followed by the growth of inner Mo$_8$O$_{28}$$^{8-}$ anion to Mo$_8$O$_{28}$$^{8-}$. Due to the addition of PhCOOH, the solution becomes more acidity, thus larger Mo$_8$O$_{28}$$^{8-}$ was formed via condensation reaction. The decomposed fragments further reassemble around the new template to form final large Ag$_{50}$ cluster. Finally, the overall breakage-growth-reassembly (BGR) mechanism was established for this transformation process (Fig. 6).

Universality of acid-induced transformation. We also introduced different substituted benzoic acids such as 4-methylbenzoic acid (4-MePhCOOH) and 3-methylbenzoic acid (3-MePhCOOH) into above transformation process (Supplementary Fig. 1) to check the universality of transformation. Of note, the similar Ag$_{50}$ clusters can be also isolated after acid induction and characterized by SCXRD analysis, which showed their structures are quite similar with inner Mo$_8$O$_{28}$$^{8-}$ and outer Ag$_{50}$ shell but just with different substituted degree of benzoates on the surface. The details of molecular structures and crystallography tables were shown in Supplementary Figs. 6–8 and Supplementary Table 1, respectively. Their formulae were determined as [Mo$_8$O$_{28}$@Ag$_{50}$($^{i}$PrS)$_{24}$(4-MePhCOO)$_{14}$(PhCOO)$_{4}$(CH$_3$CN)$_{4}$](SD/Ag$_{50}$a), [Mo$_8$O$_{28}$@Ag$_{50}$($^{i}$PrS)$_{24}$(4-MePhCOO)$_{16.5}$(PhCOO)$_{1.5}$(SD/Ag$_{50}$b), and [Mo$_8$O$_{28}$@Ag$_{50}$($^{i}$PrS)$_{24}$(3-MePhCOO)$_{18}$(3-MePhCOOH)(CH$_3$CN)$_{2}$(SD/Ag$_{50}$c). The degree of substitution reaction between substituted benzoates and PhCOO$^{-}$ is intensely depended on the dose of substituted benzoates. For example, when increasing amount of 4-MePhCOOH from 0.3 to 0.6 mmol, the SD/Ag$_{50}$b can be formed instead of SD/Ag$_{50}$a. These results not only justified a universal acid-induced transformation fashion to synthesize larger sized silver clusters but also may bring new functionalities for silver clusters by ligand exchanges.

UV-Vis absorption spectra and luminescence properties. The solid state UV/Vis absorption spectra of SD/Ag$_{44}$, SD/Ag$_{50}$, and ($^{i}$PrSAg)$_n$ precursor were measured at room temperature. As shown in Supplementary Fig. 19, SD/Ag$_{44}$ and SD/Ag$_{50}$ exhibit one intense absorption centered at 344 and 356 nm in the UV region. The UV absorption peaks can be attributed to the $n \rightarrow \pi^*$ transition of $^{i}$PrS$^{-}$, as similar observed in the spectrum of the precursor ($^{i}$PrSAg)$_n$. The HOMO–LUMO gaps were determined as 2.35, 2.33, and 2.52 eV for SD/Ag$_{44}$, SD/Ag$_{50}$, and ($^{i}$PrSAg)$_n$ precursor by using the transformed Kubelka–Munk plots, respectively (Supplementary Fig. 20), which are consistent with their yellow appearances.

We also checked the emission behaviors of SD/Ag$_{44}$ and SD/Ag$_{50}$ at both 298 and 77 K using hand-held UV light.
Phosphorescent triplet excitation state. It is worth noting microsecond scale (Supplementary Fig. 21), suggesting the state under the excitation of 463 nm. Insets: the photographs of 193 K along with obvious decrease of emission intensity. For attribution to the ligand-to-metal charge transfer (LMCT, charge transfer from S to Ag 5s) perturbed by Ag–Ag interaction. The temperature-dependent emissions should be in the connection with the variations of molecule rigidity and argentophilicity under different temperatures. The emission lifetimes of both SD/Ag44 and SD/Ag50 at 93 K fall in the microsecond scale (Supplementary Fig. 21), suggesting the phosphorescent triplet excitation state. It is worth to noting that the emission intensities have good linearity correlation with respect to temperature in the low temperature regions (Supplementary Fig. 22). The linearity equations can be described as $I_{\text{max}} = -1461T + 294270$ (correlation coefficient = 0.979) for SD/Ag44 (93–213 K) and SD/Ag50 (93–193 K), respectively.

**Discussion**

In conclusion, we synthesized and characterized two thiolate/benzoate co-protected Ag44 and Ag50 clusters. The latter can be facilely synthesized by PhCOOH-induced transformation reaction, resulting in the enlargement of both inner anion template (Mo6O228– $\rightarrow$ Mo8O288–) and outer silver shell (Ag44 $\rightarrow$ Ag50). The solution behaviors of Ag44 and Ag50 clusters were studied in details using ESI-MS technique. The overall breakage-growth-reassembly (BGR) transformation mechanism was also established based on the time-dependent ESI-MS, which revealed several small fragmented species ([Mo6O18@Ag38]– [Mo6O18@Ag40]) and large intermediates ([Mo8O28@Ag40]– [Mo8O28@Ag50]), as well as their abundance evolutions along with reaction going on. To our knowledge, this is the first example of the transformation of a smaller silver cluster into a larger one via anion template growth. This work not only revealed the important reactivity of silver clusters with acids but also provide a novel method for synthesizing larger silver clusters that are otherwise difficult to obtain.

**Methods**

**Synthesis of ([PrSAg]n).** ([PrSAg]n), was prepared by the following reported procedure. The solution of AgNO3 (30 mmol, 5.1 g) in 75 ml acetonitrile was mixed with 100 ml ethanol containing PrSH (30 mmol, 2.8 mL) and 5 mL Et3N under stirring for 3 h in the dark at room temperature, then the yellow powder of ([PrSAg]n), was isolated by filtration and washed with 10 mL ethanol and 20 mL ether, then dried in the ambient environment (yield: 97 %, based on AgNO3).

**Synthesis of SD/Ag44.** Typically, the mixture of PhCOOH (0.1 mmol, 22.9 mg), ([PrSAg]n), (0.05 mmol, 9.2 mg), and ([BuNO3]4-MoO3) (0.0002 mmol, 4.2 mg) was added in 5 ml acetonitrile then stirred for 3 h at room temperature, then this mixture was again sealed into 25 ml Teflon-lined autoclave and heated at 65 °C under autogenous pressure for 200 min. After cooling to room temperature, yellow crystals were isolated with a yield of 45 % (based on ([PrSAg]n)). Elemental analyses calc. (found) for SD/Ag44 ([C115H113Ag44Mo8N6O64S24]): C, 23.30 (23.18); H, 2.52 (2.47); N 0.60 (0.52) %. Selected IR peaks (cm−1): 3682 (w), 2961 (m), 1589 (w), 1523 (m), 1454 (w), 1371 (s), 1241 (w), 1149 (w), 1032 (s), 1014 (m), 811 (w), 715 (m), 675 (m), 588 (w).

**Synthesis of SD/Ag50.** Another portion of PhCOOH (0.32 mmol, 39.1 mg) was added into the mother liquor after the synthesis of SD/Ag44 but without removing crystals of SD/Ag44, then this mixture was again sealed into 25 mL Teflon-lined autoclave and heated at 65 °C under autogenous pressure for 200 min. After cooling to room temperature, yellow crystals were isolated with a yield of 50% (based on ([PrSAg]n)). Elemental analyses calc. (found) for SD/Ag50 ([C120H113Ag50Mo8N6O64S24]): C, 23.09 (23.18); H, 2.52 (2.47); N 0.60 (0.52) %. Selected IR peaks (cm−1): 3682 (w), 2961 (m), 1589 (w), 1523 (m), 1454 (w), 1371 (s), 1241 (m), 1144 (w), 1046 (m), 910 (w), 880 (m), 830 (m), 800 (m), 714 (s), 671 (m), 635 (m), 610 (m).

**Synthesis of SD/Ag50a.** The synthesis conditions were similar to those described for SD/Ag50 except using 4-MePhCOOH (0.33 mmol, 44.9 mg) instead, yellow crystals were isolated with a yield of 56 % (based on ([PrSAg]n)). Elemental analyses calc. (found) for SD/Ag50a ([C107H105Ag50Mo8N6O64S24]): C, 24.12 (23.97); H, 2.74 (2.58); N 0.979 (0.96) %. Selected IR peaks (cm−1): 3670 (w), 2949 (w), 2912 (w), 1584 (w), 1520 (m), 1453 (w), 1368 (s), 1242 (m), 1169 (m), 1148 (m), 1052 (m), 916 (m), 876 (m), 831 (m), 796 (s), 759 (s), 712 (m), 632 (m), 606 (s).

**Synthesis of SD/Ag50b.** The synthesis conditions were similar to those described for SD/Ag50 except using 4-MePhCOOH (0.57 mmol, 77.6 mg) instead, yellow crystals were isolated with a yield of 30 % (based on ([PrSAg]n)). Elemental analyses calc. (found) for SD/Ag50b ([C108H107Ag50Mo8N6O64S24]): C, 23.80 (23.59); H, 2.71 (2.58) %. Selected IR peaks (cm−1): 3674 (w), 2971 (w), 2905 (w), 1584 (w), 1524 (m), 1453 (w), 1368 (s), 1237 (m), 1173 (w), 1149 (w), 1047 (s), 911 (m), 877 (s), 834 (m), 798 (m), 763 (s), 712 (m), 632 (m), 605 (s).

**Synthesis of SD/Ag50c.** The synthesis conditions were similar to those described for SD/Ag50 except using 3-MePhCOOH (0.57 mmol, 77.6 mg), yellow crystals were isolated with a yield of 33 % (based on ([PrSAg]n)). Elemental analyses calc. (found) for SD/Ag50c ([C220H291Ag50Mo8O64S24]): C, 25.12 (24.98); H, 2.86.
Data availability

The X-ray crystallographic coordinates for structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre, under deposition number CCDC: 1837115–1837119 for SD/Ag44, SD/Ag50, and SD/Ag50a-SD/Ag50c. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Received: 21 May 2018 Accepted: 4 September 2018
Published online: 23 October 2018

References

1. Young, A. G. & Hanton, L. R. Square planar silver(I) complexes: a rare but increasingly observed stereochemistry for silver(I). Coord. Chem. Rev. 252, 1346–1386 (2008).

2. Schmidbaur, H. & Schier, A. Argentophilic interactions. Angew. Chem. Int. Ed. 54, 7464–7485 (2015).

3. Liu, J.-W. et al. Anisotropic assembly of Ag52 and Ag76 nanoclusters. J. Am. Chem. Soc. 140, 1600–1603 (2018).

4. Corrigan, J. F., Fuhr, O. & Fenske, D. Metal chalcogenide clusters on the border between molecules and materials. Adv. Mater. 21, 1867–1871 (2009).

5. Xie, Y.-P., Jin, J.-L., Duan, G.-X., Lu, X. & Mak, T. C. W. High-nucleity silver (I) chalcogenide clusters: a novel class of supramolecular assembly. Coord. Chem. Rev. 331, 54–72 (2017).

6. Jin, R. C., Zeng, C. J., Zhou, M. & Chen, Y. X. Atomically precise colloidal metal nanoclusters and nanoparticles: fundamentals and opportunities. Chem. Rev. 116, 10346–10413 (2016).

7. Rais, D. et al. Anion-templated syntheses of rhombohedral silver-alkynyl cage compounds. Angew. Chem. Int. Ed. 40, 3464–3467 (2001).

8. Li, X.-Y. et al. A platonic solid templating Archimedean solid: an unprecedented nanometre-sized Ag12 cage. Nanoscale 7, 8284–8288 (2015).

9. Wang, Q.-M., Lin, Y.-M. & Liu, K.-G. Role of anions associated with the formation and properties of silver clusters. Acc. Chem. Res. 48, 1570–1579 (2015).

10. Li, S. et al. Atom-precise modification of silver(I) thiolate cluster by shell ligand substitution: a new approach to generation of cluster functionality and chirality. J. Am. Chem. Soc. 140, 594–597 (2018).

11. Anson, C. E. et al. Synthesis and crystal structures of the ligand-stabilized over border between molecules and materials. Angew. Chem. Int. Ed. 54, 7464–7485 (2015).

12. Wang, Z. et al. Assembly of silver trigons into a buckyball-like Ag180 nanocluster. Angew. Chem. Int. Ed. 47, 1326–1331 (2008).

13. Wang, Z. et al. Assembly of silver trigons into a buckyball-like Ag180 nanocluster. Angew. Chem. Int. Ed. 47, 1326–1331 (2008).

14. Hau, S. C. K., Cheng, P.-S. & Mak, T. C. W. Enlargement of globular silver alkynyl cluster by core formation. J. Am. Chem. Soc. 134, 2922–2925 (2012).

15. Hau, S. C. K., Cheng, P.-S. & Mak, T. C. W. Enlargement of globular silver alkynyl cluster by core formation. J. Am. Chem. Soc. 134, 2922–2925 (2012).

16. Chu, L. H. et al. Acid-base-triggered structural transformation of a polyoxometalate core inside a dodecahedrane-like silver thiolate shell. Angew. Chem. Int. Ed. 55, 3699–3703 (2016).

17. Pairs, R. G. & Pearson, R. G. Absolute hardness-companion parameter to absolute electronegativity. J. Am. Chem. Soc. 105, 7512–7516 (1983).

18. Chalmera, R. A. & Sinclair, A. G. Organic molybdate complexes. J. Inorg. Nucl. Chem. 29, 2065–2080 (1967).

19. Huang, R.-W. et al. Hypersensitive dual-function luminescence switching of a silver-chalcogenolate cluster-based metal-organic framework. Nat. Chem. 9, 689–697 (2017).

20. Dhamay, R. S. et al. [Ag2(S2C4H10)2]−: an eight-electron superatom. Angew. Chem. Int. Ed. 54, 3702–3706 (2015).

21. Brown, I. D. & Alterman, D. Bond-valence parameters obtained from a systematic analysis of the inorganic crystal-structure database. Acta Crystallogr. B 41, 244–247 (1985).

22. Li, Y.-W. et al. Two unprecedented POM-based inorganic organic hybrids with concomitant heteropolytungstate and molybdate. Inorg. Chem. 56, 2481–2489 (2017).

23. Li, X.-Y. et al. Atom-precise polyoxometalate-Ag5S core-shell nanoparticles. Chem. Asian J. 10, 1295–1298 (2015).

24. Li, X.-Y. et al. Atom-precise polyoxometalate-Ag5S core-shell nanoparticles. Chem. Asian J. 10, 1295–1298 (2015).

25. Qiao, J., Shi, K. & Wang, Q.-M. A giant silver alkynyl cage with sixty silver(I) ions clustered around polyoxometalate templates. Angew. Chem., Int. Ed. 1765–1767 (2010).
Additional information
Supplementary Information accompanies this paper at https://doi.org/10.1038/s41467-018-06755-4.

Competing interests: The authors declare no competing interests.

Reprints and permission information is available online at http://npg.nature.com/reprintsandpermissions/

Publisher’s note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.