

## Stabilizing subnanometer Ag(0) nanoclusters by thiolate and diphosphine ligands and their crystal structures†

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The combined use of thiolate and diphosphine as surface ligands helps to stabilize subnanometer Ag(0) nanoclusters, resulting in the successful crystallization of two Ag(0)-containing nanoclusters (Ag<sub>16</sub> and Ag<sub>32</sub>) for X-ray single crystal analysis. Both clusters have core-shell structures with Ag<sub>8</sub><sup>6+</sup> and Ag<sub>22</sub><sup>12+</sup> as their cores, which are not simply either fragments of face-centered cubic metals or their five-fold twinned counterparts. The clusters display UV-Vis absorption spectra consisting of molecule-like optical transitions.

Nanoclusters with well-defined structures in the size regime of a few sub-nanometers to several nanometers are readily crystallized into single crystals suitable for X-ray diffraction analysis. Such an important feature makes nanoclusters containing tens to hundreds of metal atoms an ideal system to provide molecular structure models for their nanocrystal counterparts having much larger sizes. For example, during the past several years, the total structure determination of thiolate-capped Au clusters (*e.g.*, Au<sub>102</sub>,<sup>1</sup> Au<sub>25</sub>,<sup>2,3</sup> and Au<sub>38</sub> (ref. 4)) has been making a growing impact on the field of metal nanocrystals. The presence of –RS–Au–SR– (SR = thiolate) or –RS–Au–SR–Au–SR– staple units is commonly revealed in the surface of the determined Au nanocluster structures. These revealed staple units have then been widely applied as a surface structure model for describing and predicting the structures of thiolate-covered Au and even Ag containing nanoclusters/nanocrystals.<sup>5–14</sup> However, very recently, the single-crystal analysis of a Ag<sub>14</sub> cluster co-capped by thiolate and phosphine ligands (XMC-1) has indicated that thiolate-protected Ag(0)-containing nanoclusters do not

necessarily adopt either core or surface structures of those reported thiolate-capped Au clusters.<sup>15</sup>

In general, Ag(0) is more prone to oxidation than Au(0). Under ambient conditions, thiolated Ag(0)-containing metal nanoclusters are not expected to have comparable stability to thiolated Au nanoclusters. Such an instability has resulted in the following fact: although the syntheses of thiolate-protected Ag clusters (*e.g.*, Ag<sub>7</sub>, Ag<sub>8</sub>, Ag<sub>9</sub>, Ag<sub>7</sub>Au<sub>6</sub>, Ag<sub>44</sub>, and Ag<sub>152</sub>) have been reported,<sup>16–25</sup> rare thiolated Ag(0)-containing clusters have been crystallized and structurally characterized *via* single-crystal diffraction.<sup>15</sup> Therefore, with chemical formulae determined by mass spectrometry, the structures of thiolate-protected Ag metal nanoclusters were mainly proposed through simulations by assuming their structural similarity to the reported thiolate-protected Au nanoclusters.<sup>24,26</sup> However, the proposed structures have not been confirmed by experiments yet. Such a situation would likely prevent us from deeply understanding the structure–property relationships of thiolate-protected Ag nanoclusters, many of which, for example, have been found to exhibit promising luminescence properties.

We report here the stabilization of subnanometer Ag(0) nanoclusters by the combined use of thiolate and diphosphine as surface ligands. The structures of two stabilized Ag(0)-containing nanoclusters, Ag<sub>16</sub>(DPPE)<sub>4</sub>(SC<sub>6</sub>H<sub>3</sub>F<sub>2</sub>)<sub>14</sub> (Xiamen Metal Cluster-2, XMC-2) and {Ag<sub>32</sub>(DPPE)<sub>5</sub>(SC<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>)<sub>24</sub>}<sup>2–</sup> (XMC-3), DPPE = 1,2-bis(diphenylphosphino)ethane, are determined by single crystal X-ray analysis. Both clusters have core-shell structures with a multinuclear Ag unit encapsulated in a shell containing Ag(I)-thiolate-diphosphine complex. In the complex shell, each Ag atom is tetrahedrally coordinated by three thiolates and one P from the diphosphine ligands. Moreover, the cores of the two clusters are not simply either fragments of face-centered-cubic (fcc) metals or their five-fold twinned counterparts. The coordination modes of both thiolate and metal atoms on the surface of XMC-2 and XMC-3 are distinct from those in the reported thiolate-protected Au nanoclusters.

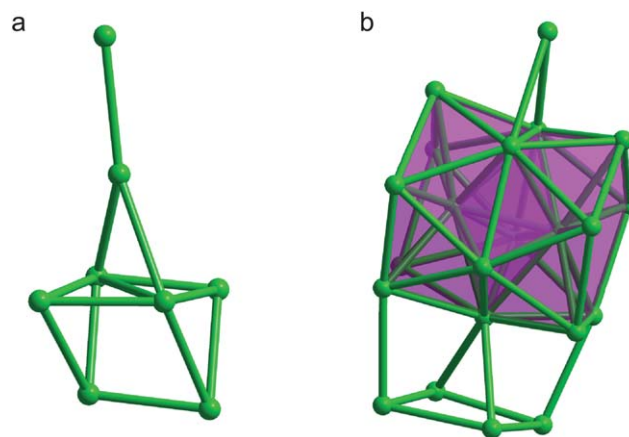
In a typical synthesis of XMC-2 (see ESI† for details), a silver salt AgBF<sub>4</sub> was dissolved in the mixture solution of

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dichloromethane and methanol. After the solution was cooled to 0 °C in an ice bath, DPPE, 3,4-difluorothiophenol and  $\text{PPh}_4\text{Br}$  were added. After 20 minutes, triethylamine and  $\text{NaBH}_4$  aqueous solution were added quickly to the mixture under vigorous stirring. After the reaction mixture was stirred at 0 °C for 12 hours, the aqueous phase was removed. The mixture in the organic phase was then washed several times with water. Red block crystals were crystallized from  $\text{CH}_2\text{Cl}_2$ -hexane at 4 °C after 10 days in a yield of ~20%. In some cases, XMC-2 was even crystallized into a single big piece of red crystal (Fig. S1†). A similar synthetic protocol was applied for the synthesis of XMC-3 by using 4-(trifluoromethyl)thiophenol instead of 3,4-difluorothiophenol.

The single crystal analysis revealed that both XMC-2 and XMC-3 clusters have core-shell structures with a multinuclear Ag unit encapsulated in a shell containing Ag(I)-thiolate-diphosphine complex.† As illustrated in Fig. 1, S2 and S3,† while XMC-2 has an overall cluster composition of  $\text{Ag}_{16}(\text{DPPE})_4(\text{SC}_6\text{H}_3\text{F}_2)_{14}$  with a  $\text{Ag}_8^{6+}$  unit encapsulated in a complex shell of  $\{\text{Ag}_8(\text{DPPE})_4(\text{SC}_6\text{H}_3\text{F}_2)_{14}\}^{6-}$ , XMC-3 has a composition of  $\{\text{Ag}_{22}@\text{Ag}_{10}(\text{DPPE})_5(\text{SC}_6\text{H}_4\text{CF}_3)_{24}\}^{2-}$  with a  $\text{Ag}_{22}^{12+}$  core unit. In XMC-3, the  $\text{Ag}_{22}^{12+}$  core is co-protected by one  $\{\text{Ag}_6(\text{DPPE})_3(\text{SC}_6\text{H}_4\text{CF}_3)_{12}\}^{6-}$ , two  $\{\text{Ag}_2(\text{DPPE})(\text{SC}_6\text{H}_4\text{CF}_3)_4\}^{2-}$  and four  $(\text{SC}_6\text{H}_4\text{CF}_3)^-$  units. Each XMC-3 cluster has thus a negative-two charge balanced by two  $\text{PPh}_4^+$  cations that are present in intercluster voids (Fig. S4†). While there are Ag–Ag interactions in the cores of both XMC-2 and XMC-3 clusters, no obvious Ag–Ag interactions are revealed among the Ag atoms in their complex shells. Such a core-shell structural feature of XMC-2

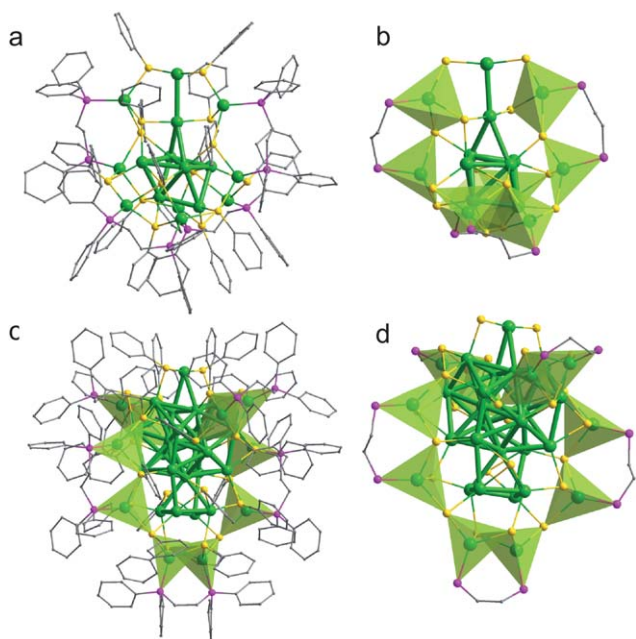


**Fig. 2** The structures of the  $\text{Ag}_8^{6+}$  (a) and  $\text{Ag}_{22}^{12+}$  (b) cores in XMC-2 and XMC-3 clusters. The bi(pentagonal antiprism)  $\text{Ag}_{17}$  unit in XMC-3 are highlighted in pink for better visualization.

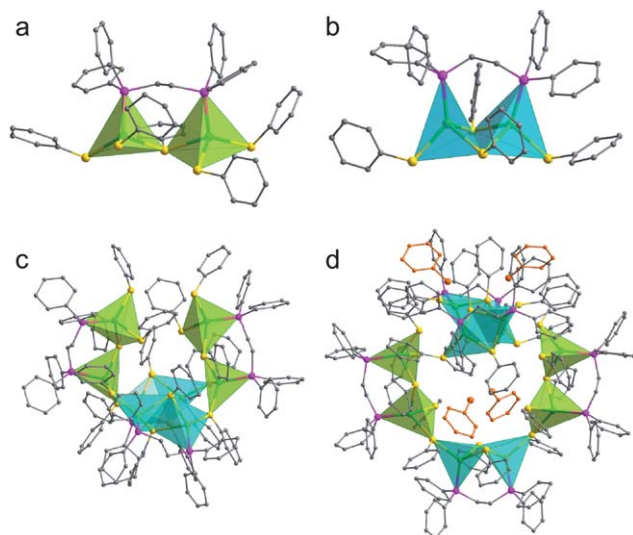
and XMC-3 was previously reported in XMC-1,<sup>15</sup> a silver cluster co-protected by thiolate and monodentate  $\text{PPh}_3$ .

As shown in Fig. 2, both the  $\text{Ag}_8^{6+}$  core unit of XMC-2 and the  $\text{Ag}_{22}^{12+}$  core of XMC-3 are not structural fragments of bulk Ag that has a face-centered cubic structure. While the Ag–Ag distances in the core of XMC-2 are distributed from 2.694 to 3.040 Å with an average of 2.845 Å, the Ag–Ag distances in XMC-3 are ranged from 2.657 to 3.089 Å with an average of 2.917 Å. The  $\text{Ag}_8^{6+}$  core of XMC-2 can be depicted as a nearly rhombus  $\text{Ag}_4$  unit capped by two  $\text{Ag}_2$  units above and below the rhombus (Fig. 2a). While the  $\text{Ag}_2$  unit above is bridging the short diagonal of the  $\text{Ag}_4$  rhombus using only one of the two Ag atoms, the  $\text{Ag}_2$  unit below is face capping the  $\text{Ag}_4$  rhombus using its both atoms. In comparison, XMC-3 has a much larger  $\text{Ag}_{22}^{12+}$  core unit which can be described as a pentagon face-sharing bi(pentagonal antiprism)  $\text{Ag}_{17}$  unit that is side-capped by one Ag atom and one near-square  $\text{Ag}_4$  unit at the opposite direction (Fig. 2b). While the one Ag atom bridges two Ag atoms, the  $\text{Ag}_4$  unit bonds to three Ag atoms from the bi(pentagonal antiprism). It should be noted that two Ag atoms at the center of the bi(pentagonal antiprism) are ten-coordinated, but not twelve-coordinated as in bulk Ag.

In the complex shells of XMC-2 and XMC-3, all Ag atoms are tetrahedrally coordinated by three thiolates and one P of the diphosphine ligand, similar to the coordination structure of surface Ag atoms in XMC-1. Each surface Ag atom in XMC-1 is coordinated to one monophosphine and three thiolate ligands. However, in both XMC-2 and XMC-3, each DPPE joints every two Ag tetrahedra together to form two types of  $\text{Ag}_2$  ditetrahedral units, corner-sharing (Fig. 3a) and edge-sharing (Fig. 3b) dimers. Similar surface structures have been previously found in Ag(I) clusters.<sup>27–29</sup> The eight Ag tetrahedra in XMC-2 are joined by four DPPE ligands to form two corner-sharing and two edge-sharing dimers (Fig. 3c). The two corner-sharing units are further connected by the two edge-sharing dimers to yield a pocket-like Ag(I)-thiolate-diphosphine complex shell with a composition of  $\{\text{Ag}_8(\text{DPPE})_4(\text{SC}_6\text{H}_3\text{F}_2)_{14}\}^{6-}$ . The shell caps the  $\text{Ag}_8$  core unit through Ag–thiolate bonds. Each Ag atom of the



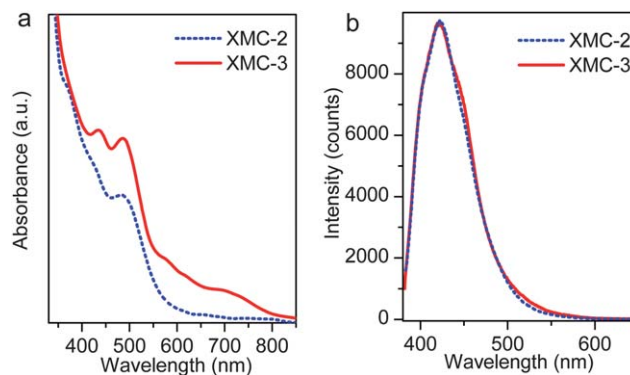
**Fig. 1** The crystal structures of  $\text{Ag}_{16}(\text{DPPE})_4(\text{SC}_6\text{H}_3\text{F}_2)_{14}$  (XMC-2) (a and b) and  $\{\text{Ag}_{32}(\text{DPPE})_5(\text{SC}_6\text{H}_4\text{CF}_3)_{24}\}^{2-}$  (XMC-3) (c and d) clusters. Color legend: green spheres, Ag; yellow spheres, S; pink spheres, P; gray spheres, C. In (a) and (c), all fluorine and hydrogen atoms are omitted for clarity. In (b) and (d), all phenyl groups are further omitted. The tetrahedrally coordinated Ag atoms are highlighted by tetrahedra in light green.



**Fig. 3** The structures of the corner-sharing (a) and edge-sharing (b)  $\text{Ag}_2$  ditetrahedral units in XMC-2, and the arrangements of  $\text{Ag}_2$  ditetrahedral units in the shells of XMC-2 (c) and XMC-3 (d). The corner-sharing and edge-sharing ditetrahedral units are in light green and cyan, respectively. In (d), four thiolates that are not from  $\text{Ag}_2$  ditetrahedral units are highlighted in golden color. All fluorine, hydrogen atoms and trifluoromethyl groups are omitted for clarity.

$\text{Ag}_8$  core unit is coordinated to two thiolate ligands from the  $\text{Ag}(\text{I})$ -thiolate-diphosphine shell. In XMC-3, five DPPE ligands link the ten surface 4-coordinated Ag atoms into five  $\text{Ag}_2$  dimers, two corner-sharing and three edge-sharing ditetrahedra (Fig. 3d). Two corner-sharing dimers are joined by an edge-sharing dimer to form an arc-like  $\{\text{Ag}_6(\text{DPPE})_3(\text{SC}_6\text{H}_3\text{F}_2)_{12}\}^{6-}$  unit. Together with this arc-like unit, the other two edge-sharing  $\{\text{Ag}_2(\text{DPPE})(\text{SC}_6\text{H}_4\text{CF}_3)_4\}^{2-}$  dimers and four thiolate  $(\text{SC}_6\text{H}_4\text{CF}_3)^-$  ligands are capping the  $\text{Ag}_{22}^{12+}$  core through Ag-thiolate interactions to form XMC-3.

In XMC-2 and XMC-3, the surface thiolates bind two, three and four Ag atoms, confirming the rich Ag-thiolate coordination chemistry that has been revealed in many  $\text{Ag}(\text{I})$ -thiolate clusters.<sup>28–32</sup> Such a situation is different from the reported structures of thiolated Au nanoclusters in which  $-\text{RS}-\text{Au}-\text{SR}-$  and  $-\text{RS}-\text{Au}-\text{SR}-\text{Au}-\text{SR}-$  staples are their common surface structural units. On the surface of thiolate-protected Au nanoclusters, each Au atom is linearly coordinated by two thiolates and each thiolate serves as a  $\mu_2$  bridging ligand. In XMC-2 and XMC-3, the presence of Ag atoms linearly coordinated by 2-fold bridging ( $\mu_2$ ) thiolates indeed leads to the formation of a  $-\text{RS}-\text{Ag}-\text{SR}-$  staple unit in each cluster. However, the preferential tetrahedral coordination of  $\text{Ag}(\text{I})$  makes Ag tetrahedra as the dominant surface structural units for the Ag nanoclusters. Since single-crystal structures of thiolate-protected Ag nanoclusters have been rarely reported, their structures were mainly theoretically modeled by assuming that Ag nanoclusters adopt similar core and surface structures of Au nanoclusters. Based on the total structure determination of XMC-2 and XMC-3, as well as our previously reported structure of XMC-1, such an assumption should be carefully assessed. Considering that each Ag ( $4d^{10}5s^1$ ) has one valence electron and the bonding to each thiolate anion consumes one valence electron, XMC-2 and



**Fig. 4** UV-Vis absorption (a) and emission (b) spectra of XMC-2 and XMC-3 in  $\text{CH}_2\text{Cl}_2$ . The emission spectra were collected by using an excitation wavelength of 360 nm.

XMC-3 clusters have 2 and 10 free valence electrons, respectively. Although XMC-2 has the smallest magic electronic number corresponding to the closed electron shell, XMC-3 is not the case of the closed-shell superatom.<sup>33,34</sup>

As illustrated in Fig. 4a, XMC-2 and XMC-3 in  $\text{CH}_2\text{Cl}_2$  exhibit distinct UV-Vis absorption spectra with molecule-like optical transitions. While both have an absorption peak at 485 nm, XMC-3 displays at least three distinguishable shoulder peaks at the wavelength longer than 550 nm. Upon excitation by UV light in either solid or solution form, unlike the small cluster XMC-1 which contains 14 Ag atoms and emits yellow light,<sup>15</sup> XMC-2 and XMC-3 give rather weak blue emissions. When excited at 360 nm at room temperature, XMC-2 and XMC-3 in  $\text{CH}_2\text{Cl}_2$  display only a prominent emission peak at  $\sim 440$  nm (Fig. 4b), significantly different from that of XMC-1. This result suggests that there might be a size threshold above which thiolated-Ag(0) nanoclusters are not as intensely photoluminescent as the reported smaller Ag clusters.<sup>18,19</sup>

To summarize, two Ag(0)-containing nanoclusters,  $\text{Ag}_{16}(\text{DPPE})_4(\text{SC}_6\text{H}_3\text{F}_2)_{14}$  (XMC-2) and  $\{\text{Ag}_{32}(\text{DPPE})_5(\text{SC}_6\text{H}_4\text{CF}_3)_{24}\}^{2-}$  (XMC-3), were synthesized and structurally characterized by single crystal X-ray analysis. The clusters have core-shell structures with a multinuclear Ag unit encapsulated in a shell containing  $\text{Ag}(\text{I})$ -thiolate-diphosphine complex. The co-presence of both thiolate and diphosphine ligands makes the coordination modes of both thiolate and metal atoms on the surface of both clusters highly distinct from those in the reported thiolated Au nanoclusters. Structural features reported here provide information that is significant and valuable for predicting the structure of thiolate-capped Ag clusters.

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## Notes and references

† Crystallographic data for XMC-2 (CCDC 916463):  $I4_1/a$ ,  $a = 25.3878(3)$  Å,  $b = 25.3878(3)$  Å,  $c = 72.3758(11)$  Å,  $V = 46\,649.2(10)$  Å<sup>3</sup>,  $Z = 8$ , Cu K $\alpha$ ,  $T = 100$  K,  $2\theta = 127.38^\circ$ . 48 569 reflections were measured, of which 19 090 were unique with  $R_{\text{int}} = 0.0438$ . Final  $R_1 = 6.84\%$ ,  $wR_2 = 0.2070$  for 1154 parameters and 13 710 reflections with  $I > 2\sigma(I)$ . Crystallographic data for XMC-3 (CCDC 916464):  $C2/c$ ,

$a = 49.221(10)$  Å,  $b = 22.630(5)$  Å,  $c = 40.889(8)$  Å,  $\beta = 120.01(3)^\circ$ ,  $V = 39\,437(14)$  Å<sup>3</sup>,  $Z = 4$ , Mo  $K\alpha$ ,  $T = 173$  K,  $2\theta = 49.42^\circ$ . 140 474 reflections were measured, of which 33 528 were unique with  $R_{\text{int}} = 0.1147$ . Final  $R_1 = 5.90\%$ ,  $wR_2 = 0.1734$  for 2129 parameters and 24 781 reflections with  $I > 2\sigma(I)$ .

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