Fathoming the principles underpinning the structures of monolayer-coated molecular metal nanoparticles remains an enduring challenge. Notwithstanding recent x-ray determinations, coveted veritable de novo structural predictions are scarce. Building on recent syntheses and de novo structure predictions of $M_n$Au$_{17-2x}$ (TBBT)$_{12}$, where $M$ is a counterion, $x = 0$ or 1, and TBBT is 4-tert-butylbenzenethiol, we report an x-ray–determined structure that authenticates an a priori prediction and, in conjunction with first-principles theoretical analysis, lends force to the underlying forecasting methodology. The predicted and verified $Ag_3(SR)_9$ monomer, together with the recently discovered $Ag_3(SR)_9$ dimer and $Ag_3(SR)_6$ trimer, establishes a family of unique mount motifs for silver thiolate nanoparticles, expanding knowledge beyond the earlier-known Au-S staples in thiol-capped gold nanoclusters. These findings demonstrate key principles underlying ligand-shell anchoring to the metal core, as well as unique T-like benzene dimer and cyclic benzene trimer ligand bundling configurations, opening vistas for rational design of metal and alloy nanoparticles.

INTRODUCTION

Knowledge and understanding of structure are keys to advancement in the physical sciences. This dictum is well captured by the writing reads, “What I cannot create, I do not understand.” (Quote can be found in a photograph in the Caltech Archives, http://archives-dc.library.caltech.edu/islandora/object/ct1%3A483/print_object). In general, a priori prediction of the structure of a materials is a vexing problem (1, 2) that presents major challenges in the exploration of novel materials. This problem is further exacerbated for nanomaterials where structural motifs differing from those found in bulk matter tend to emerge (3–6). In particular, although determination of the molecular formulas of small metal nanoparticles is possible with electrospray mass spectrometry and other techniques, a validated general strategy for predicting the structures of molecular metal nanoparticles is not yet available.

The development of reliable theoretical methodologies for structure prediction is an imperative that was recognized early on in a paper entitled “Nanocrystal gold molecules” (6), published two decades ago. A decade later, the first crystal structure of a gold molecular nanoparticle, namely, Au$_{102}$(SR)$_{44}$, which accurately forecasted all but the chiral pattern of the ligands (7). Other successfully verified structural predictions are limited to Au$_{44}$(SR)$_{20}$ which was a missing member of a previously known series (8), and to Au$_{130}$(SR)$_{50}$ (9, 10), which was motivated by electron microscopy imaging.

Most recently, we have begun to develop a structure prediction methodology (11) based on condensed-phase nucleation behavior (12, 13) and quantum mechanical principles (14–17) for the atomic and electronic structure of the metal core and on chemical principles for the ligand shell (18, 19). We used our model in a de novo prediction (11) of the structure of a new silver nanoparticle, $M_3$Ag$_{17}$(TBBT)$_{12}$, and a heteroatom-substituted analog, $M_3$AuAg$_{16}$(TBBT)$_{12}$. This work included the prediction of the structure of the metallic component of the nanocluster as well as the forecasting of a novel capping motif for the thiolate ligands, namely, the Ag(SR)$_3$ mount. This new capping motif can be viewed as completing the series Ag$_m$(SR)$_m$ with $(n, m) = (1, 3)$ (11), $(2, 5)$ (5), and $(3, 6)$ (20).

Here, we present an experimental x-ray total structure determination and theoretical optimization and analysis of the atomic arrangement in (TOA)$_2$AuAg$_{16}$(TBBT)$_{12}$, where TOA$^+$ is the tetraoctylammonium counterion. Along with the aforementioned emergence of the novel family of mount motifs for silver thiolate nanoparticles, the present investigation compares in detail the observed and predicted structural, electronic, and spectral properties of the monolayer-protected silver nanoparticle; confirms our de novo structure prediction; validates our methodology; and provides impetus for further experimental and theoretical developments. Furthermore, the identification of intramolecular ligand bundling (21), with the emergence of perennial noncovalent phenyl ring assemblies in the form of cyclic trimers and T shape-like diners (22), is relevant to molecular recognition, self-assembled supramolecular architecture, crystal packing, biomolecule (DNA and protein) structures, and quantum chemistry benchmark studies (22, 23).

RESULTS

The synthesis of $M_3$AuAg$_{16}$(TBBT)$_{12}$ nanoparticles has been previously reported (11) (see Materials and Methods). Clean solutions of (TOA)$_2$AuAg$_{16}$(TBBT)$_{12}$ nanoparticles were crystallized from acetonitrile under nitrogen gas, forming orange orthorhombic-shaped crystals (see fig. S1). The crystals diffracted x-rays to 0.85 Å resolution, yielding a solvable data set with a completeness of 96.9% (see the Supplementary Materials), and were found to be composed of orthorhombic unit cells with four (TOA)$_2$AuAg$_{16}$(TBBT)$_{12}$ nanoparticles per unit cell.

Structure: Comparison of x-ray determination with de novo prediction

A global view of the nanoparticle structure, including the three TOA$^+$ cations, is displayed in Fig. 1A, where we also show the x-ray–determined structure for (TOA)$_2$AuAg$_{16}$(TBBT)$_{12}$, optimized through

1Department of Chemistry, University of Toledo, Toledo, OH 43606, USA. 2School of Physics, Georgia Institute of Technology, Atlanta, GA 30332–0430, USA. 3School of Solar and Advanced Renewable Energy, University of Toledo, Toledo, OH 43606, USA.

*Corresponding author. Email: uzi@gatech.edu (U.L.); terry.bigioni@utoledo.edu (T.P.B.)
first-principles density functional theory (DFT) relaxation; see Materials and Methods. Details of the optimized structure were found to be highly insensitive to the inclusion of van der Waals interactions in the DFT calculations (see Materials and Methods and the Supplementary Materials). A hierarchical buildup (aufbau) of the molecule, from the inner core going outward, illustrates the high degree of similarity between the predicted and x-ray–determined structures, as shown in Fig. 1 (B to G). The structure of \((\text{TOA}_3\text{AuAg}_{16}\text{TBTT})_{12}\) has a 13-atom icosahedral core with a central Au atom surrounded by 12 Ag atoms. The measured bond lengths for the icosahedron range from 2.75 to 2.78 Å for the Au–Ag bonds and from 2.83 to 3.00 Å for the Ag–Ag bonds. The 13-atom metallic core is capped by four silver atoms forming a regular tetrahedron (Fig. 1, B and C). Each of these Ag atoms is the center of a quasi-planar \(\text{Ag}(\text{SR})_3\) capping mount, where \(\text{SR}\) is a thiol ligand (here, \(\text{TBTT}\)). The measured Ag–S bond lengths in the capping motifs range from 2.49 to 2.55 Å. The predicted and measured metal cores and capping motifs are depicted in Fig. 1 (D and E, respectively), showing only the first carbon atom (bonded directly to the S atom). The striking similarity between the predicted and measured structures is evident.

The sole variance between the predicted and measured structures is in the conformational sense (angular orientation) of the ligands, which are anchored at the mounts. This most likely originates from the packing of nanoparticles in the crystalline superlattice (24) used in the current x-ray measurements [whereas the forecasted structure was constructed for an isolated nanoparticle (11)], as well as from effects arising from the difference between the counterions used in the de novo prediction paper (11) (three small sodium cations) and in the current study (three bulky TOA+ cations). The ligands in the predicted structure were all arranged in a clockwise manner (see Fig. 1D); on the other hand, in the measured structure, the ligands of one of the capping mounts (see white arrow in Fig. 1E) maintained the clockwise conformational sense, whereas a counterclockwise sense was found in the other three mounts (see lighter blue C atoms in Fig. 1E).

Further information about the two different ligand conformational senses is provided by the total energy difference calculated for the predicted and measured conformations of the \(\text{AuAg}_{16}\text{TBTT})_{12}^3\) cluster, in the presence of a uniform neutralizing positive (+3e) background. This calculation, which allows us to isolate the conformational effect from the effects arising from the difference in counterions and lattice environment, shows a rather small energetics difference between the two conformations, with a total energy difference of \(\Delta = 0.458\,\text{eV}\) (or 0.037 eV per ligand). In this case, the measured conformation had a lower total energy than the predicted one (by \(\delta = 0.026\%\) relative to the total energy of the optimized measured configuration); the conformational difference is even smaller when van der Waals interactions are included in the DFT calculations (see Materials and Methods), with \(\Delta = 0.281\,\text{eV}\) (0.023 eV per ligand) and \(\delta = 0.016\%\). The calculated small energy differences between the two ligand conformations (differing mainly by their rotational sense) reflect the rather flat, shallow nature of the multidimensional energy surface associated with the accessible conformations of the capping ligands. These characteristics, together with the likely influence of the “bulky” TOA+ counterions used in the synthesis of the current (x-ray–analyzed) material and in superlattice packing, underlie the aforementioned difference between the de novo prediction (11) and the measured structure and serve to highlight some of the difficulties that need to be overcome to achieve reliable structural predictions of these nanocrystalline systems.
**Electronic structure**

The stability of the nanocluster can be inferred from the optical absorption spectrum and the density of states (DOS) calculated with first-principles DFT (see Fig. 2, A and B, and the Supplementary Materials), on the basis of the measured structure. The DFT-calculated projections of the wavefunctions onto their angular momentum components [giving a projected DOS (PDOS)] for the relaxed x-ray-determined structure show a superatom closed-shell structure [see Fig. 2, A and B], with occupied 1S 2 (at ~6.97 eV, showing 88.3% L = 0, S character) and 1P 6 levels (at ~2.12, 1.23, and -1.13 eV, showing a majority, that is, 58.4% L = 1, P contribution, with a threefold splitting of the degeneracy, owing to the nanocrystalline environment), and unoccupied 1D (at 0.99, 1.03, 1.04, 1.06, and 1.09 eV), showing a dominant, that is, 74% L = 2, D contribution, with a fivefold crystal-field splitting, and mixed 2S and 1F (at 1.42 eV, showing 31.8% S and 61.5% F character) delocalized molecular orbitals, in agreement with our earlier prediction (11) (see wavefunction portraits in Fig. 2B; for a detailed analysis of the superatom orbitals, see table S1). The PDOS also shows the formation of a pronounced peak of mostly d character (~74% at 7.9 eV, showing 88.3% L = 3, D character, with a sixfold crystal-field splitting), originating from the metal (Au and Ag) atoms. The nodal structures of the delocalized orbitals exhibit 1S, 1P, and 1D superatom states. The HOMO states (~1.98 eV) and the LUMO states (~1.86 eV) are well-defined in the PDOS, as are the transitions from occupied metal and sulfur levels (~1.6 eV), and to transitions from unoccupied states lying on the ligands (~1.6 eV), and to transitions from occupied metal and sulfur levels (~1.75 to ~1.55 eV) to the LUMO+1 empty states localized on the methyl groups of the ligands (1.314 to 1.374 eV). For the assignment of other (minor) spectral features in the absorption spectrum, see the Supplementary Materials.

**Optical absorption**

As compared in Fig. 2C, the measured and calculated optical absorption spectra (using TDDFT; see the Supplementary Materials) illustrate good correspondence. The experimental spectrum was measured in an acetonitrile solution, whereas the calculation was carried out under vacuum; therefore, the energy axis of the calculated spectrum was scaled by a factor of 1.095 to simulate a solvatochromic shift, such that the main prominent absorption features in the measured and calculated spectra (near 400 nm) matched (see Fig. 2C). The measured spectrum from M1AuAg(16)(TBBT)+4 NC2H3 in Fig. 2C bears obvious similarity to the spectrum in fig. S5 of a previous report (11), as expected for similar preparations of the cluster. However, we note that the previous spectrum was measured in dimethylformamide (DMF), whereas, the one reported here was measured in acetonitrile, as noted above. Furthermore, the methods used to prepare the cluster in our previous work (11) and in our present study are similar. In particular, the method used here was modified in such a way as to enable the preparation of a more pure sample for crystallization; most importantly, it included a precipitation step. The differences in purity of the two samples involved species (that is, unused reactants, borohydride byproducts, etc.) that absorbed outside of the range of the spectrum shown in Fig. 2C; consequently, the effects arising from differences in purity are not apparent upon comparing the two spectra.

The main experimentally observed spectral feature, between 2.91 and 3.17 eV, was found to originate from several transitions. This feature is mainly attributed to transitions from the 1P superatom HOMO states (~1.0 eV) to states that are primarily located on the phenyl rings (~1.7 eV), to transitions between the HOMO–1 states localized on the sulfur atoms (~1.253 to ~1.278 eV) and the aforementioned unoccupied states lying on the ligands (~1.6 eV), and to transitions from occupied metal and sulfur levels (~1.75 to ~1.55 eV) to the LUMO+1 empty states localized on the methyl groups of the ligands (1.314 to 1.374 eV). For the assignment of other (minor) spectral features in the absorption spectrum, see the Supplementary Materials.

**Capping ligands and mount motif**

In analogy with the case of gold, where the capping motifs can be thought of as fragments of the linear gold thiolate polymer, p-(AuSR) n (that is, monomer staples, dimer staples, etc.) (4, 25–27), the newly found silver capping motifs (Fig. 1, D and E) can be thought of as fragments of the two-dimensional (2D) silver thiolate polymer, p-(AgSR) n (18, 19). Accordingly, our verified prediction of the Ag(SR)
capping motif may be regarded as the introduction of a “monomer mount” (11), four of which cap the $M_3AuAg_{18}(TBBT)_{12}$ structure presented here (Fig. 1, D to G). The monomer mount is the smallest member of a series of capping motifs based on the 2D silver thiolate polymer (Fig. 3). The $M_4Ag_{34}(SR)_{30}$ nanocluster can be thought of as being capped by dimer mounts, Ag$_2$(SR)$_5$, six of which protect the metal core (5, 28). Similarly, the recently reported (20) $M_3Ag_{29}(SPhS)_{12}(TPP)_{4}$ nanocluster, where TPP is triphenylphosphine, can be thought of as being capped by trimer mounts, Ag$_3$(SR)$_6$, four of which protect the metal core.

It is cogent to conjecture that the capping mount systematics outlined above would apply to other metals, where once the monomer unit for a metal thiolate is identified, a corresponding series may be constructed by considering the possible topological combinations for that coordination. In this way, two-coordinate gold thiolate bonding underlies the well-known linear staple series. It might then be expected that three-coordinate copper thiolate bonding would follow the above-described silver mount series (see Fig. 3) and that four-coordinate platinum and palladium thiolate bonding would correspond to a yet undiscovered series of capping motifs, likely based on Pt(SR)$_4$ and Pd(SR)$_4$ monomers with square-planar geometry. Such motifs might also appear in the interfacial structures of surface coatings on metals (29).

### Ligand bundling

The predicted (isolated single nanocluster) structure shows six dimer bundles (11) (Fig. 1F), whereas the ligands’ arrangement in the measured structure (Fig. 1G) reflects the properties of the superlattice made from the assembly of these nanoclusters (24). The aforementioned variation in the ligands’ conformational sense (Fig. 1, D and E) is expressed in the ligand bundling patterns (21), evident from comparing Fig. 1F and Fig. 1G. The observed bundling order is addressed in Fig. 4, where we identify three doubly bundled ligand assemblies (L2; in pink, green, and red) along with one triply bundled assembly (L3; in blue) and three unbundled ligands (L1; in gray). The L2 bundling involves three pairs of ligands, each composed of one clockwise- and one counterclockwise-oriented ligand, located on neighboring capping mounts. In each of the L2 bundles, the ligands are oriented with respect to each other in a way that brings the two aromatic phenyl groups into a T-like configuration (see Fig. 4 and the geometrical analysis in the section “Analysis of ligand bundling” in the Supplementary Materials). The L3 bundle is made of three ligands located on the opposite side of the nanocluster forming a cyclic trimer. As aforementioned, the structural parameters describing the nanoclusters and particularly the geometry of the ligand bundling were found to be insensitive to the inclusion of van der Waals interactions in the DFT structural optimization (see fig. S2 and table S2).

This is the first ligand-protected nanocluster found to exhibit ligand bundling that corresponds to specific intermolecular orientations (T-type and cyclic ring-like), characteristic of π–π interactions between aromatic rings; deviations from the predicted geometries of the gas-phase benzene dimer and trimer (22) are the consequence of the limited conformational freedom available to the ligands due to their being anchored to the metal core. Improving fundamental knowledge of these noncovalent interactions is important to many fields, including supramolecular, biomolecular, and theoretical chemistry (22, 23), and our findings usher the opportunity to enhance understanding of the contributing forces, which include electrostatic, induction, dispersion, and exchange-repulsion effects. Modeling of these complex intermolecular interactions presents exceptional challenges, even with the employment of advanced ab initio quantum mechanical methods (22), and consequently adding ligand-protected clusters to the gallery of systems for exploration brings experimental and theoretical advantages. The opportunity to explore these forces on such well-defined atomically precise systems promises benchmark confrontation of theory and experiments.

### DISCUSSION

The above structure forecasting and analysis manifest the key importance played by the bonding geometries of the organic ligands to the metal atoms in the capping shell in the attempt to model nanoparticle structures. The structural elements that enter the description of these bonding geometries are ligand mount motifs, ligand conformations, and interligand bundling configurations. As an illustration of the structural role of the ligand shell, we recall the present $M_3AuAg_{18}(SR)_{12}$ cluster case (and Ag$_{17}$ analog) with the Ag(SR)$_4$ monomer mounts, the MAu$_{23}(SR)_{18}$ case with the Au$_3(SR)_3$ dimer staples (25, 26), and the $M_4Ag_{34}(SPhS)_{12}(TPP)_{4}$ case with the Ag$_4$(SPhS)$_6$ trimer mounts (and phosphines) (20). These three cases share an icosahedral $M_{13}$ core; however, the marked differences in bonding at the metal-ligand interface result in decidedly different nanoparticle compositions and structures.

The principles underlying the ligand shell structure also imply that the structure of bimetallic nanoparticles will be affected by the coordination of the metal atoms in the ligand shell. For example, if the coordination of the heteroatoms is not compatible with the ligand shell structure, then those heteroatoms will tend to be located in the metal core (11, 28); heteroatom substitution can be used in this sense as a structural probe (11). However, if the incompatible metal atoms are located in the ligand shell, then the structure of the nanoparticle will not be conserved because of the structural changes in the ligand shell necessitated by the different heteroatom bonding requirements (30).

---

**Fig. 3. Silver mount motifs.** (A) Silver thiolate polymer, from which each mount is derived; (B) Ag$_3$ monomer; (C) Ag$_3$ dimer; and (D) Ag$_3$ trimer mount. For (B) to (D), top and side views are shown, whereas for (A), only the former is displayed.
Notably, diethiols and sterically crowded ligands can force unexpected structures to emerge [for example, MAg_{25}(SR)_{18}] \(^{(31)}\), with further structural variations likely to occur through the use of other capping agents (for example, phosphines). Other variations include mixed ligand shells and bimetallic clusters \(^{(30)}\) with stoichiometries that force atoms of different chemical identity to occupy the ligand shell, bringing about tapestries of coexisting ligand capping motifs. These systems require further systematic studies, with the current ones being mere forerunners, which provide impetus for future endeavors.

In closing, we reiterate that structure predictions, particularly for complex materials systems, such as the ligand-capped metal nanocluster discussed here, made of chemical constituents of varying electronic properties, bonding modes, and bonding strengths \(\text{that is, metal atoms (here, Au and Ag), aromatic thiol ligands (here, TBBT), and counterions (here, TOA\(^{+}\)),}\) remain as extreme challenges. Physical factors encountered and highlighted in this study that compound the difficulties of structure predictions include varying metal core structures and their isomers, ligand-to-core bonding and mount motifs, ligand conformations \(\text{(here, rotational conformers with close-in-energy isomeric forms), and interligand bundling and their geometries (here, T-like dimers and cyclic trimers can be found).}\)

Fig. 4. Ligand (TBBT) bundling. (A and B) Views along the threefold axis from the front (A) and back (B) of the nanocluster, showing the L3 (trimer) bundle \(\text{(dark blue), the three L2 (dimers) bundles \(\text{(in pink, green, and red), and the unbundled three ligands \(\text{(gray/white spheres).}\)}\) C} View showing the T-like orientation of the two phenyl rings in each of the L2 dimers. Also shown in light blue are the three trapped acetonitrile solvent molecules. The silver atoms are depicted as gray spheres, the central Au atom is shown in orange, and the S atoms are colored yellow. For further details, see the Supplementary Materials \(\text{(particularly fig. S2, where the definitions and values of geometrical parameters describing the T-like dimers and cyclic trimers can be found).}\)

### Chemicals

Silver nitrate \((\text{AgNO}_3)\), hydrogen tetrachloroaurate(III) trihydrate \((\text{HAuCl}_4-3\text{H}_2\text{O})\), TBBT, TPP, tetraphenylphosphonium bromide \((\text{TPPB})\), potassium borohydride \((\text{KBH}_4)\), tetraoctylammonium bromide \((\text{TOAB})\), \(\text{N}_2\text{N}\)-DMF, methanol, and cesium hydroxide \((\text{CsOH})\) were all purchased from Sigma-Aldrich. Acetonitrile was purchased from Fisher. Paratone oil was purchased from Hampton Research. All the reagents were used without further purification. Deionized water \((18.2\text{ megohm-cm})\) from a Millipore Synergy system was used.

### Synthesis

Briefly, 50 mg of \(\text{HAuCl}_4-3\text{H}_2\text{O} \) \((0.125\text{ mmol})\) was dissolved into 50.0 ml of DMF and stirred vigorously for 5 min to produce a clear yellow solution. Next, 216 \(\mu\)l of TBBT \((1.25\text{ mmol})\) was added to the solution, and the reaction was stirred for 5 min. Then, 170 mg of silver nitrate \((1.0\text{ mmol})\) was added to the solution and stirred for 10 min to form an insoluble white metal thiolate precursor. The metal thiolate precursor was solubilized by the addition of 943 mg of TPPB \((2.25\text{ mmol})\) to yield a clear yellow solution. Next, 557 mg of TPP \((2.25\text{ mmol})\) was added to form a clear colorless solution. An ice bath was used to cool the solution before the addition of the reducing agent. A separate solution containing 3.0 ml of ice-cold \(\text{H}_2\text{O}\) and 122 mg of \(\text{KBH}_4\) \((2.25\text{ mmol})\) was added dropwise to reduce the metal thiolate precursor and then stirred for 5 hours.

After the reaction was completed, the dark yellow solution was centrifuged for 5 min and separated from the insoluble products by decanting. The supernatant was precipitated with \~50 ml of \(7:4\text{ H}_2\text{O}/\text{methanol solution that had its } p\text{H adjusted to 12 with CsOH. The precipitated product was collected by centrifugation and redissolved in acetonitrile. Dissolving the precipitate into acetonitrile allowed } M_3\text{AuAg}_{16}(\text{TBBT})_{12} \text{ to be selectivity separated.}\)

### Crystallization

A freshly prepared solution of \(M_3\text{AuAg}_{16}(\text{TBBT})_{12}\) in acetonitrile had trace amounts of TOAB added and dissolved into the solution. The solution was sealed with a rubber septum, and nitrogen gas was used to evaporate the solvent. Orange orthorhombic-shaped crystals were formed after 12 hours of drying, as shown in fig. S1. The crystals were removed from the crystallization vial and suspended in paratone oil for the separation and inspection of the quality of the crystals.

### Density functional theory

The DFT calculations and Bader \((33, 34)\) charge analysis \(\text{(see Supplementary Materials)}\) were performed using the VASP DFT package with a plane-wave basis with a kinetic energy cutoff of 400 eV, the PAW pseudopotentials \((35)\), and the PW91 generalized gradient approximation
for the exchange-correlation potential (36–38). For structure optimization, convergence was achieved for forces smaller than 0.001 eV Å⁻¹. As aforementioned, inclusion of van der Waals interactions (39) between the ligands had minimal influence on the structural parameters of the metal cluster and the capping ligands (see fig. S2 and table S2).

TDDFT calculations of the absorption spectrum

The calculations of the absorption spectra were carried out following the TDDFT method with the formalism described by Casida (40, 41), implemented in the real-space Octopus code (42, 43). These calculations used the norm-conserving nonlocal soft Troullier-Martins pseudopotentials (44) with scalar-relativistic corrections for the electrons of the Au and Ag atoms and have included the valence electrons for the elements in the molecule: Au (5d¹⁰ 6s¹), Ag (4d¹⁰ 5s¹), S (3s² 3p⁴), C (2s² 2p²), N (2s² 2p²), and H (1s¹). The generalized gradient-corrected PBE exchange–correlation (xc) potential (45) has been used.

The (TOA)₃AuAg₁₆(TBBT)₁₂ structure was optimized (starting from the x-ray structure, relaxed with the VASP DFT program) through the use of the Born-Oppenheimer DFT code (46), using the above soft pseudopotentials and PBE xc potential. In the subsequent absorption spectra calculations, the system was placed in a sphere of radius 27 Å, such that the electron vanishes outside of that sphere. The grid spacing was taken as 0.2 Å, which corresponded to a 70 Rydberg plane-wave kinetic energy cutoff. The calculation involved 1592 valence electrons. In the TDDFT calculations, we used all states in the interval E_F – 3.49 eV to E_F + 2.56 eV, where the lower limit was chosen to coincide with a minimum in the DOS. This interval included 45 occupied states and 74 unoccupied states, and therefore, 330 electron-hole (occupied–unoccupied) pairs. Convergence was tested by varying the number of states included in the spectral calculations.

Detailed interpretation of the optical absorption spectrum (see the Optical absorption section and the Supplementary Materials) requires analysis of the states and matrix elements contributing to the optical transition probabilities; in our analysis of TDDFT results, we have adopted a method developed on the basis of time-dependent density functional perturbation theory, which allows analysis of correlations between single-particle transitions within a given energy range (28).

Supporting materials

Additional details regarding the syntheses, complete x-ray data, and theoretical analysis are supplied in the Supplementary Materials.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/2/11/e1601609/DC1

fig S1. Optical micrograph of a typical orange colored orthorhombic crystal of (TOA)₃AuAg₁₆(TBBT)₁₂.
fig S2. Definitions of distances and angles used in analysing the bundling geometries (fig. 4).
detailed interpretation of the TDDFT optical absorption (fig. 2C).
comparison of x-ray determined and theoretically optimized structures.
Bader charge distribution.

Analysis of the superatom peaks in the PDOS (fig. 2A).

Analysis of ligand bundling.

Single-crystal x-ray diffraction and analysis.

Structural analysis of (TOA)₃AuAg₁₆(TBBT)₁₂.
table S1. Contributions of different angular momentum components (s, p, d, ... ) to the superatom peaks in the calculated PDOS (fig. 2A).
table S2. Geometrical parameters describing the cyclic trimer formed by the L3 bundled ligands (upper part of table) and the T-like L2 ligand dimers (lower part of table).

REFERENCES AND NOTES

1. C. L. Cleveland, U. Landman, The energetics and structure of nickel clusters: Size dependence. J. Chem. Phys. 94, 7376–7396 (1991).
2. D. J. Wales, H. A. Scheraga, Global optimization of clusters, crystals, and biomolecules. Science 285, 1368–1372 (1999).
3. N. T. Tran, D. R. Powell, L. F. Dahl, Nanosized Pd₄₇(CO)₃(PPh₃)₇ containing a capped three-shell 145-atom metal-core geometry of pseudo icosahedral symmetry. Angew. Chem. Int. Ed. 39, 4121–4125 (2000).
4. P. J. Dzidzinski, G. Calero, C. J. Ackerson, D. A. Bushnell, R. D. Kornberg, Structure of a thiol monolayer-protected gold nanoparticle at 1.1 Å resolution. Science 318, 430–433 (2007).
5. A. Desiderddy, B. E. Conn, J. Guo, B. N. Barnett, B. M. Monahan, K. Kirschbaum, W. P. Griffith, R. L. Whetten, U. Landman, T. P. Bigioni, Ultrastable silver nanoparticles. Nature 501, 399–402 (2013).
6. R. L. Whetten, J. T. Khoury, S. Murthy, I. Vezmar, Z. L. Wang, P. W. Stephens, C. L. Cleveland, W. D. Luedtke, U. Landman, Nanocrystalline gold molecules. Adv. Mater. 8, 428–433 (1996).
7. Y. Pei, Y. Gao, X. C. Zeng, Structural prediction of thiolate-protected Au₁₅₄. A face-fused bi-icosahedral Au core. J. Am. Chem. Soc. 130, 7830–7832 (2008).
8. C. Zeng, Y. Chen, G. Li, R. Jin, Synthesis of a Au₆₅(SR)₃₄ nanocluster: Structure prediction and evolution from Au₁₃₄(SR)₆ₐ to Au₁₅₄(SR)₆ₑ. Chem. Commun. 50, 55–57 (2014).
9. A. Tlahuice-Florres, U. Santiago, D. Bahena, E. Vinigradova, C. V. Conroy, T. Ahuja, S. B. H. Bach, A. Ponce, G. Wang, M. José-Yacamán, R. L. Whetten, Structure of the thiolated Au₁₅₄ cluster. J. Phys. Chem. A 117, 10470–10476 (2013).
10. Y. Negishi, C. Sakamoto, T. Ohyama, T. Tsukuda, Synthesis and the origin of the stability of thiolate-protected Au₁₅₄ and Au₂₁₄ clusters. J. Phys. Chem. Lett. 3, 1624–1628 (2012).
11. S. Wickramasinghe, A. Atanagulov, B. Yoon, R. N. Barnett, W. P. Griffith, U. Landman, T. P. Bigioni, M₃Au₉(SPH₃)₉ nanoparticles and their structure prediction. J. Am. Chem. Soc. 137, 11550–11553 (2015).
12. F. C. Frank, Supercooling of liquids. Proc. Roy. Soc. Lond. Ser. A 215, 43–46 (1952).
13. K. F. Kelton, G. W. Lee, A. K. Gangopadhyay, R. W. Hyers, T. J. Rathz, J. R. Rogers, M. B. Robinson, D. S. Robinson, First x-ray scattering studies on electrostatically levitated metallic liquid: Demonstrated influence of local icosahedral order on the nucleation barrier. Phys. Rev. Lett. 90, 195504 (2003).
14. S. B. Zhang, M. L. Cohen, M. Y. Chou, Electronic shell structure of simple metal heteroclusters. Phys. Rev. B 36, 3455–3458 (1987).
15. C. Yannoulas, P. Jena, S. N. Khanna, Optical resonances in bimetallic clusters and their relation to the electronic structure. Phys. Rev. B 46, 9751–9760 (1992).
16. W. D. Knight, K. Clemenger, W. A. de Heer, W. A. Saunders, M. Y. Chou, M. L. Cohen, Electronic shell structure and abundances of sodium clusters. Phys. Rev. Lett. 52, 2141–2143 (1984).
17. B. Yoon, P. Koshkin, B. Huber, O. Kostko, B. van Issendorff, H. Hakkinen, M. Moslehi, U. Landman, Size-dependent structural evolution and chemical reactivity of gold clusters. ChemPhysChem 8, 157–161 (2007).
18. I. G. Dance, The structural chemistry of metal thiolate complexes. Polyhedron 5, 1037–1104 (1986).
19. I. G. Dance, K. J. Fisher, R. M. H. Banda, M. L. Scudder, Layered structure of crystalline compounds silver thiolates (AgSR). Inorg. Chem. 30, 183–187 (1991).
20. L. G. Abdulhalim, M. S. Boothajaru, Q. Tang, S. Del Gobbo, R. G. Abdulhalim, M. Eddaoudi, D.-e. Jiang, O. M. Bakr, Ag₈₉(BDT)₁₄(TPP)₁₄ A tetavalent nanocluster. J. Am. Chem. Soc. 137, 11970–11975 (2015).
21. W. D. Luedtke, U. Landman, Structure, dynamics, and thermodynamics of passivated gold nanocrystallites and their assemblies. J. Phys. Chem. 100, 13323–13329 (1996).
22. M. O. Sinnokrot, C. D. Sherrill, High-accuracy quantum mechanical studies of π–π interactions in benzene dimers. J. Phys. Chem. A 110, 10656–10668 (2006).
23. S. R. Gadre, S. D. Yeole, N. Sahar, Quantum chemical investigations on molecular clusters. Chem. Rev. 114, 12132–12173 (2014).
24. B. Yoon, W. D. Luedtke, R. N. Barnett, J. Guo, A. Desiderddy, B. E. Conn, T. Bigioni, U. Landman, Hydrogen-bonded structure and mechanical chiral response of a silver nanoparticle superlattice. Nat. Mater. 13, 807–811 (2014).
25. M. W. Heaven, A. Dass, P. S. White, K. M. Holt, R. W. Murray, Crystal structure of the gold nanoparticle [NiC2H3]+[Au14]+[HCH2Ph]+. J. Am. Chem. Soc. 130, 3754–3755 (2008).
26. M. Zhu, C. M. Aikens, F. J. Holland, G. C. Schatz, R. Jin, Correlating the crystal structure of a thiol-protected Au125 cluster and optical properties. J. Am. Chem. Soc. 130, 5883–5885 (2008).
27. H. Qian, W. T. Eckenhoff, Y. Zhu, T. Pintauer, R. Jin, Total structure determination of thiolate-protected Au154 nanoparticles. J. Am. Chem. Soc. 132, 8280–8281 (2010).
28. H. Yang, Y. Wang, H. Huang, L. Gell, L. Lehtovaara, S. Malola, H. Häkkinen, N. Zheng, All-thiol-stabilized Ag34 and Au127Ag32 nanoparticles with single-crystal structures. Nat. Commun. 4, 2422 (2013).
29. R. L. Whetten, R. C. Price, Chemistry: Nano-golden order. Science 318, 407–408 (2007).
30. H. Yang, Y. Wang, J. Yan, X. Chen, X. Zhang, H. Häkkinen, N. Zheng. Structural evolution of atomically precise thiolated bimetallic [Au12+nCu12+SR]1+ (n=0,2,4,6) nanoclusters. J. Am. Chem. Soc. 136, 7197–7200 (2014).
31. C. P. Joshi, M. S. Bootharaju, M. J. Alhiliy, O. M. Bakr, [Ag32(SR)12]−: The “golden” silver nanoparticle. J. Am. Chem. Soc. 137, 11578–11581 (2015).
32. J. Barhen, V. Protopopescu, D. Reister, TRUST: A deterministic algorithm for global optimization. Science 276, 1094–1097 (1997).
33. R. F. W. Bader, Atoms in Molecules: A Quantum Theory (Oxford Univ. Press, 1990).
34. J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, C. Fiolhais, The octopus project. J. Phys. Condens. Matter 24, 233202 (2012).
35. G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method. Phys. Rev. B 43, 1993–2006 (1991).
36. J. P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple. Phys. Rev. Lett. 77, 3865–3868 (1996).
37. R. N. Barnett, U. Landman, Born-Oppenheimer molecular dynamics simulations of finite systems: Structure and dynamics of (H2O)n. Phys. Rev. B 48, 2081–2097 (1993).

Acknowledgments: Computations were carried out at the Georgia Institute of Technology Center for Computational Materials Science. Funding: Work at the University of Toledo was supported by NSF grant CBET-0955148, the School of Solar and Advanced Renewable Energy, and the School of Graduate Studies. B.Y. and U.L. were supported by grant FA9550-14-1-0005 from the Air Force Office of Scientific Research, and R.N.B. was supported by the Office of Basic Energy Sciences of the U.S. Department of Energy under contract no. FG05-86ER45234. Author contributions: T.P.B. and U.L. conceived this work and directed the experimental and theoretical studies, respectively. B.E.C. and A.A. carried out the synthesis and sample preparation and measurements, and B.E.C. made the x-ray diffraction measurements and structure determination. B.Y. carried out electronic structure calculations and structural relaxations, and R.N.B. performed calculations of the optical absorption. All authors contributed to the analysis of the data. U.L. and T.P.B. wrote the paper, and all authors contributed to the editing of the manuscript. Competing interests: The authors declare that they have no competing interests. Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

Submitted 13 July 2016
Accepted 25 October 2016
Published 25 November 2016
10.1126/sciadv.1601609

Citation: B. E. Conn, A. Atanagulov, B. Yoon, R. N. Barnett, U. Landman, T. P. Bigioni, Confirmation of a de novo structure prediction for an atomically precise monolayer-coated silver nanoparticle. Sci. Adv. 2, e1601609 (2016).
Confirmation of a de novo structure prediction for an atomically precise monolayer-coated silver nanoparticle
Brian E. Conn, Aydar Atnagulov, Bokwon Yoon, Robert N. Barnett, Uzi Landman and Terry P. Bigioni

Sci Adv 2 (11), e1601609
DOI: 10.1126/sciadv.1601609

ARTICLE TOOLS
http://advances.sciencemag.org/content/2/11/e1601609

SUPPLEMENTARY MATERIALS
http://advances.sciencemag.org/content/suppl/2016/11/21/2.11.e1601609.DC1

REFERENCES
This article cites 42 articles, 4 of which you can access for free
http://advances.sciencemag.org/content/2/11/e1601609#BIBL

PERMISSIONS
http://www.sciencemag.org/help/reprints-and-permissions

Use of this article is subject to the Terms of Service

Science Advances (ISSN 2375-2548) is published by the American Association for the Advancement of Science, 1200 New York Avenue NW, Washington, DC 20005. The title Science Advances is a registered trademark of AAAS.
Copyright © 2016, The Authors