

Heteroatom Tracing Reveals the 30-Atom Au–Ag Bimetallic Nanocluster as a Dimeric Structure

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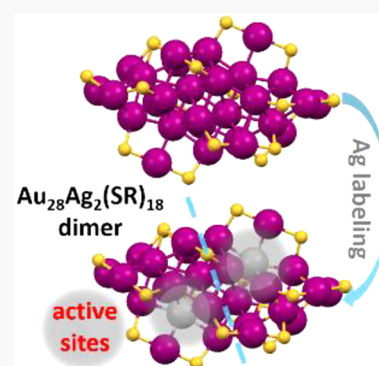
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ABSTRACT: Understanding the formation of face-centered cubic (fcc) nanostructures at the atomic level remains a major task. With atomically precise nanoclusters (NCs) as model systems, herein we devised an atom-tracing strategy by heteroatom doping into $\text{Au}_{30}(\text{SR})_{18}$ ($\text{SR} = \text{S}^-\text{C}_4\text{H}_9$) to label the specific positions in $\text{M}_{30}(\text{SR})_{18}$ NCs ($\text{M} = \text{Au}/\text{Ag}$), which clearly reveals the dimeric nature of M_{30} . Interestingly, the specific position is also consistent with the Ag-doping site in $\text{M}_{21}(\text{SR})_{15}$. Electronic orbital analysis shows intrinsic orbital localization at the two specific positions in M_{30} , which are decisive to the electronic structure of M_{30} , regardless of Au or Ag occupancy. The fcc dimeric NC, which would not be discovered without Ag tracing, provides a possible explanation for the wide accessibility of nonsuperatomic Au–SR NCs.



Atomically precise metal–thiolate (SR) nanoclusters (NCs) provide new opportunities to tackle some of the tough issues remaining in nanoscience research,^{1–4} e.g., how atoms are packed together in an efficient, energy-optimized pathway, the rules for nanoparticle assembly, and many other issues. In regard to the stability of NCs, the “noble-gas superatom” model⁵ had early success in explaining the stability of some spherical metal NCs via an electron shell closing picture.^{5–13} Other than the electronic factor, the geometric factor is also a major contributor to the stability of NCs;¹⁴ hence, determining the structures of NCs is of critical importance. The thermodynamic stability theory has explored homogold and doped NCs (both “superatomic” and “non-superatomic”) through the energetic stability between the shell and core regions of the NC.^{15–17}

Compared to the spherical Au–SR NCs, the rod-shaped ones do not follow the electronic shell-closing rule, and such NCs indeed outnumber the “superatomic” counterparts.^{18–22} This could be understood by the diatomic bonding concept for dimeric NCs, in which electrons on each half of the dimeric NC can delocalize on the whole, forming a cluster-molecule.²² Experimentally, Maran et al. revealed the fusion growth of $\text{Au}_{25}(\text{SR})_{18}$ into $\text{Au}_{38}(\text{SR})_{24}$ ²³ and the bi-icosahedral Au_{23} kernel in $\text{Au}_{38}(\text{SR})_{24}$ resembles the diatomic molecule.²⁴ Two or more 8e superatoms with icosahedral kernels can be bonded together.^{25–29} Although $[\text{Au}_{23}(\text{SR})_{16}]^-$ and $\text{Au}_{28}(\text{SR})_{20}$ NCs^{30–32} with face-centered cubic (fcc) kernels bear 8e, which seems electronic shell closure, they are actually “non-superatomic” as the frontier orbitals do not resemble s/p/d/f orbitals. Thus, there exist more electronic configurations

for the 8e case, as are the others. New electronic models for Au–SR NCs have been reported,^{33–35} in which the 4-centered 2-electron bonding for a tetrahedral (Au_4^{2+}) network can elucidate the electronic structures of the $\text{Au}_{20+8N}(\text{SR})_{16+4N}$ ($N \geq 1$) family.^{36–39}

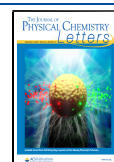
Compared to the icosahedron-based dimeric NCs,^{21–23} fcc dimeric NCs are not clear yet. Although the fcc $\text{Au}_{28}(\text{SR})_{20}$ was identified to possess an interpenetrated bicuboctahedral kernel,³² there is no evidence yet for dimerization growth. The reason for the intractability is due to the difficulty in distinguishing one atom from the other in the fcc kernel, unless some specific atom(s) can be labeled and traced.

In this work, $\text{Au}_{30-x}\text{Ag}_x(\text{S}^-\text{C}_4\text{H}_9)_{18}$ ($x = 2-4$) and $\text{Au}_{21-x}\text{Ag}_x(\text{S}^-\text{C}_4\text{H}_9)_{15}$ ($x = 2-4$) NCs with fcc kernels are obtained, and the crystal structure of $\text{Au}_{30-x}\text{Ag}_x(\text{SR})_{18}$ reveals the specific positions that the Ag atoms occupy. The Ag dopants serve as atomic “labels”, allowing us to reveal that $\text{M}_{30}(\text{SR})_{18}$ ($\text{M} = \text{Au}/\text{Ag}$) is a dimer NC. Silver tracing along with time-dependent density functional theory (TDDFT) demonstrates that the specific active site(s) (Ag vs Au) play an important role in the electronic structures of the two NCs, which also supports that M_{30} is a dimer, with its possible

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monomer to be M_{17} which can be derived from the structure of M_{21} and is observed at the initial stage of the synthesis.

The $Au_{30-x}Ag_x(SR)_{18}$ ($SR = S^tC_4H_9$, $x = 2-4$) was synthesized by two steps: step I, $Au^I-S^tC_4H_9$ and $Ag^I-S^tC_4H_9$ ($Au:Ag = 8:1$, molar ratio) were coreduced by $NaBH_4$; step II, the crude product from the first step was collected and then reacted with excess *tert*-butylthiol at 45 °C. The resulting NCs were a mixture of $Au_{30-x}Ag_x(SR)_{18}$ and $Au_{21-x}Ag_x(SR)_{15}$ (Figure S1a). Fortunately, pure $Au_{30-x}Ag_x(SR)_{18}$ was crystallized out of the mixture in dichloromethane/ethanol (Figure S1b), while $Au_{21-x}Ag_x(SR)_{15}$ remained in the supernatant (Figures S2 and S3). Plate-like crystals were obtained after 2 days and solved to be $Au_{30-x}Ag_x(SR)_{18}$ ($x = 2-4$) (Figure 1a) in space group $P_{21/n}$.

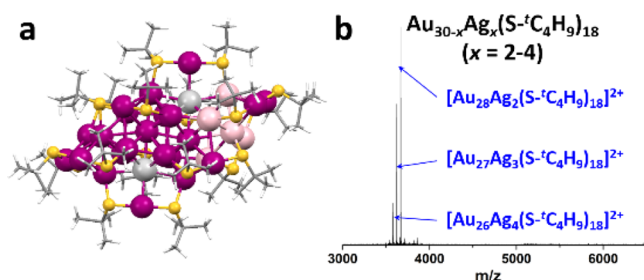


Figure 1. (a) Total structure and (b) ESI-MS spectrum of $Au_{30-x}Ag_x(SR)_{18}$ NCs. Color labels: magenta, Au; light gray, Ag dominant; pink, Au dominant; yellow, S; gray, C; and white, H.

The metal framework of $Au_{30-x}Ag_x(SR)_{18}$ is close to that of homogold $Au_{30}(SR)_{18}$,⁴⁰ which possesses an interpenetrating bicuboctahedral Au_{20} kernel (Figure S4b, two overlapped dashed frames) with two capping Au atoms at opposite sites (indicated by arrows). The sites for Ag atoms in $Au_{30-x}Ag_x(SR)_{18}$ are intriguing. The two symmetric positions in the kernel have 87% and 97% of Ag occupancy (Ag dominant), respectively (Figures 1a and S4d, marked in light gray), whereas other positions (Figure 1a, marked in pink) have much lower Ag percentages (10–20%, Table S1) and are thus Au dominant. The low Ag occupancy at these sites can be ascribed to the structural disorder at one side of Au_{30} ,⁴⁰ which increases the distribution of electron density.

ESI mass spectrometry (ESI-MS) analysis shows that the most abundant peak corresponds to two Ag dopants (Figure 1b, isotope patterns in Figure S2). It is noteworthy that when step II was performed at room temperature (as opposed to 45 °C), only $Au_{21-x}Ag_x(SR)_{15}$ ($x = 2-4$) was obtained (Figures S1 and S3). The 21-atom alloy is related to the homogold $Au_{21}(SR)_{15}$,⁴¹ which possesses a cuboctahedral Au_{13} kernel (Figure S4a, dashed frame) with one capping Au atom (indicated by arrow).⁴¹ Upon silver doping to $Au_{20}Ag_1(SR)_{15}$, the Ag atom goes to a specific position in the kernel without changing the structure (Figure S4c).^{42,43}

We note that the relation of $Au_{21}(SR)_{15}$ to $Au_{30}(SR)_{18}$ has long been missing. Herein, by Ag doping and crystallography analysis, we have explicitly revealed the missing correlation between the two NCs, i.e., an intricate dimeric relationship. In our $Au_{30-x}Ag_x(SR)_{18}$, there are two specific positions in the kernel with high Ag occupancy (marked as Ag in Figure S4d). The two Ag sites are consistent with the original Ag position in $Au_{20}Ag_1(SR)_{15}$. Thus, the special Ag atom(s) in the NCs can serve as “atomic label(s)”, just like the isotopic labeling technique widely used in NMR and MS studies. This indicates

that the kernel atoms in $M_{21}(SR)_{15}$ or $M_{30}(SR)_{18}$ are not equivalent as those in $[M_{25}(SR)_{18}]^-$, in the latter the Ag atoms are almost equally distributed in the icosahedral M_{12} shell.⁴⁴

To further demonstrate the merit of Ag tracing in $M_{21}(SR)_{15}$ and $M_{30}(SR)_{18}$, the optical absorption spectra of $Au_{20}Ag_1(SR)_{15}$, $Au_{21}(SR)_{15}$, $Au_{28}Ag_2(SR)_{18}$, and $Au_{30}(SR)_{18}$ are simulated by TDDFT based on their crystal structures solved herein plus the ones reported in the literature (Figures 2 and S5).⁴⁰⁻⁴² The $S^tC_4H_9$ ligand is simplified to $S-CH_3$ as is commonly done for TDDFT.^{20,31}

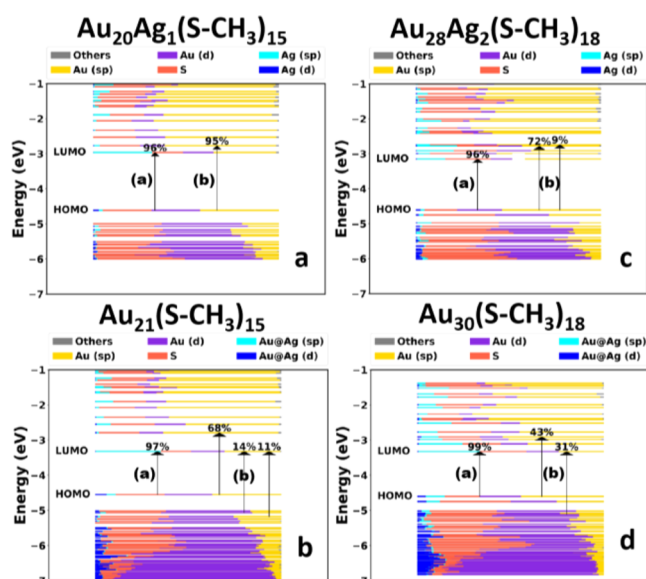


Figure 2. Kohn–Sham (KS) orbital energy level diagrams for (a) $Au_{20}Ag_1(S-CH_3)_{15}$, (b) $Au_{21}(S-CH_3)_{15}$ with the specific Au atom (at the Ag position in $Au_{20}Ag_1(S-CH_3)_{15}$) highlighted as Au@Ag, (c) $Au_{28}Ag_2(S-CH_3)_{18}$, and (d) $Au_{30}(S-CH_3)_{18}$ with the specific Au atoms (at Ag positions in $Au_{28}Ag_2(S-CH_3)_{18}$) highlighted as Au@Ag. Each KS orbital is drawn to indicate the relative contributions (line length with color labels) of the atomic orbitals.

We found that the Ag “tracer” in $Au_{20}Ag_1(S-CH_3)_{15}$ (Figure 2a) contributes greatly to the LUMO, but very little to the HOMOs. Accordingly, in the visualized diagrams (Figure S5c), the LUMO cloud aggregates around the tracing Ag, but the lobes of HOMO do not involve this specific atom. The experimental and simulated absorption spectra of $Au_{20}Ag_1$ (Figure S5a,b) show low-energy peaks (a and b) corresponding to $HOMO \rightarrow LUMO$ and $HOMO \rightarrow LUMO+1$, respectively (Figure 2a).

As silver tracing indicates there is a specific position in $M_{21}(SR)_{15}$, theoretical analysis of $M_{21}(SR)_{15}$ molecular orbitals is further performed in order to highlight the effect of the special Au atom in $Au_{21}(SR)_{15}$ (i.e., the special Au occupies the same position as the Ag does in $Au_{20}Ag_1(S-CH_3)_{15}$, i.e., Au@Ag). When the special Au atom at the equivalent Ag position is highlighted (marked in cyan, Figure 2b), it turns out that the Au@Ag atom is the major contributor to the LUMO, compared to the sum of all other Au atoms. Thus, the LUMO orbital of M_{21} is localized (shape-driven) at the specific position no matter whether it is occupied by Ag or Au.

When comparing the KS diagrams of the two M_{21} NCs (Figure 2a/b), the HOMO energies are found to be almost the same, while the LUMO energy of $Au_{20}Ag_1$ increases with respect to that of Au_{21} . This explains the distinct change in the

energy gaps of the two NCs, i.e., ~ 1.5 eV for $\text{Au}_{20}\text{Ag}_1$ and <1.2 eV for Au_{21} (Figure S5a,b vs d,e). The observation that the specific Ag in $\text{Au}_{20}\text{Ag}_1(\text{S}-\text{CH}_3)_{15}$ contributes greatly to LUMO (one Ag vs 20 Au atoms) explains why more Ag doping ($x \geq 2$) in $\text{Au}_{21-x}\text{Ag}_x(\text{SR})_{15}$ does not change the optical properties much.⁴²

The $\text{Au}_{28}\text{Ag}_2(\text{S}-\text{CH}_3)_{18}$ case is similar to $\text{Au}_{20}\text{Ag}_1(\text{S}-\text{CH}_3)_{15}$ that the tracing Ag atoms participate in the LUMO and change its energy, whereas they rarely affect the HOMOs (Figure 2c), indicating the character of frontier orbitals is inherited in the dimeric $\text{Au}_{28}\text{Ag}_2(\text{SR})_{18}$. The diagram of the LUMO of $\text{Au}_{28}\text{Ag}_2(\text{S}-\text{CH}_3)_{15}$ illustrates that the lobes are around the tracing Ag atoms at symmetric positions (Figure S5h), though they are less well-defined than the LUMO localization on the Ag in the $\text{Au}_{20}\text{Ag}_1(\text{S}-\text{CH}_3)_{15}$.

As the two special sites in $\text{Au}_{30}(\text{SR})_{18}$ are indicated by Ag tracing (supporting equation Au₃₀), we again calculated the specific Au atoms at the Ag positions in the $\text{Au}_{30}(\text{S}-\text{CH}_3)_{18}$ (Au@Ag). Indeed, the two specific Au atoms in $\text{Au}_{30}(\text{S}-\text{CH}_3)_{18}$ (marked in cyan, Figure 2d) constitute the major part of the LUMO compared to the sum of all other Au atoms, resembling the case of $\text{Au}_{21}(\text{S}-\text{CH}_3)_{15}$. Therefore, even in homogold $\text{Au}_{21}(\text{SR})_{15}$ and $\text{Au}_{30}(\text{SR})_{18}$, the LUMOs are mainly located on the intrinsically active site(s) identified by Ag tracing.

In M_{30} NCs, peaks a and b can be found in the experimental and simulated optical spectra (Figure S5f,g), in which peak a corresponds to the HOMO $\rightarrow$ LUMO transition (Figure 2c). By contrast, such a HOMO $\rightarrow$ LUMO transition (Figure 2d, peak a) is almost absent in the spectrum of Au_{30} (Figure S5i,j), although it is present in the discrete spectrum with very low intensity (at ~ 1.3 eV). The observable HOMO $\rightarrow$ LUMO transition (a) in the spectra of $\text{Au}_{28}\text{Ag}_2$ (Figure S5f,g, peak a) is attributed to the Ag interaction with the LUMOs, which increases the oscillator strength of the transition. The HOMO $\rightarrow$ LUMO transition mainly comprises Au(sp) $\rightarrow$ Ag(sp) and Au(d) $\rightarrow$ Ag(sp) transitions (Figure 2c).

We conclude that the two major advantages of the Ag tracing strategy are (1) acting as label(s) to identify the formation of dimeric M_{30} (where, $\text{M} = \text{Au}$ or Au/Ag) upon the structure determination by crystallography and (2) indicating the active site(s) that play a critical role in the electronic structure characteristics of M_{21} and M_{30} NCs. Although heteroatom doping has been applied to Au-SR NCs for almost two decades, such useful functions have not been utilized until now.

Although the calculation is about $\text{M}_{30}(\text{SR})_{18}$, the study is limited to S^tBu . The chemistry reported depends upon the accessibility to a given site and stabilization of a given product. These may depend upon the ligand significantly. Therefore, generalization to other ligands should be made with caution.

Energetic analysis is further performed via DFT to suggest the thermodynamic feasibility of dimerization for various NC pairs. The Au-SR NC pairs cover different structure types, including the icosahedral pair of $[\text{Au}_{25}(\text{SR})_{18}]^0$ versus $\text{Au}_{38}(\text{SR})_{24}$,^{21,45} the cuboctahedral pairs of $\text{Au}_{20}\text{Ag}_1(\text{SR})_{15}$ ^{42,43} versus $\text{Au}_{28}\text{Ag}_2(\text{SR})_{18}$ and $\text{Au}_{21}(\text{SR})_{15}$ versus $\text{Au}_{30}(\text{SR})_{18}$,^{40,41} and the tetrahedral-network pair of $\text{Au}_{28}(\text{SR})_{20}$ versus $\text{Au}_{44}(\text{SR})_{28}$.^{32,36}

The energetics of net-neutral intercluster reactions with only Au-SR reactants and byproducts is given in Figure 3, showing that dimers are favored in terms of Gibbs free energy (ΔG) and electronic energy (ΔE) for each proposed reaction pathway:

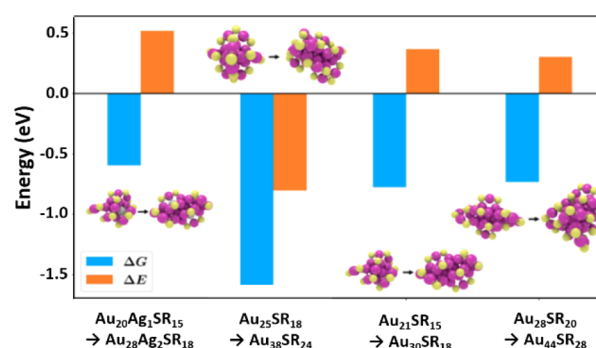
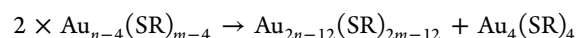


Figure 3. ΔG and ΔE of dimerization from DFT for different proposed dimerization pairs with Au_4SR_4 referenced as Au_nSR_m ($\text{R} = \text{CH}_3$) species. Color labels: magenta, Au; yellow, S.



$\text{Au}_4(\text{S}-\text{CH}_3)_4$ is used as the reference because it has been theoretically predicted⁴⁶ and experimentally verified.^{47,48} Considering that all of the free energies for dimerization are negative, the dimer is thermodynamically favorable even in solutions of atomically precise NCs. We note that the energy preference of the dimer is particularly pronounced for the $\text{Au}_{38}(\text{SR})_{24}$ cluster. Moreover, the reactions become non-favorable if only electronic energy is taken into account, and free-energy analysis is needed to capture entropic effects driving the dimerization process. These results suggest the reaction is feasible only from Au_{25} to Au_{38} but may not be feasible for other pairs. In view of the dynamics known in such systems, especially in solution, one wonders what makes the specific locations stable in $\text{M}_{30}(\text{SR})_{18}$ and $\text{M}_{21}(\text{SR})_{15}$. It is quite likely that reaction conditions are highly important in determining the product.

We attempted to isolate the $\text{M}_{21}(\text{SR})_{15}$ and react it with excess thiol at 45°C , but no reaction was observed. Hence, an intermediate phase, i.e., $\text{Au}_{n-4}(\text{SR})_{m-4}$, must be there before the dimer can be obtained. In our case, it should be $\text{Au}_{16}\text{Ag}_1(\text{SR})_{11}$, which is structurally shared by $\text{Au}_{20}\text{Ag}_1(\text{SR})_{15}$ and $\text{Au}_{28}\text{Ag}_2(\text{SR})_{18}$ (marked with “brick” artistic effect in Figure S4c,d), that is assumed during the formation of dimer.

To test the pathway, we monitored the step II process (thiol etching) by MALDI-MS. The crude product from step I was dissolved in mixed toluene and thiol (v:v = 1:1.5) and etched at 45°C (Figures S6 and S7) or room temperature (Figures S8 and S9). A set of peaks corresponding to intermediate $\text{M}_{17}(\text{SR})_{11}$ (e.g., $\text{Au}_{16}\text{Ag}_1(\text{SR})_{11}$) along with $\text{M}_{21}(\text{SR})_{15}$ was observed first. One hour after reaction at 45°C , a hump at doubled m/z of $\text{M}_{17}(\text{SR})_{11}$ indicated the appearance of $\text{M}_{34}(\text{SR})_{22}$ adduct. After 3 h, the peaks for $\text{M}_{30}(\text{SR})_{18}$ became more and more obvious, and the $\text{M}_{34}(\text{SR})_{22}$ adduct diminished to give rise to $\text{M}_{30}(\text{SR})_{18}$ (e.g., $\text{Au}_{28}\text{Ag}_2(\text{SR})_{18}$, Figures S6 and S7). By contrast, the formation of M_{30} was suppressed at RT because of the energy barrier (Figures S8 and S9), and the final product was M_{21} with some M_{17} intermediate.

We also found that the formation of $\text{Au}_{28}\text{Ag}_2(\text{SR})_{18}$ was more favored when increasing the amount of thiol (e.g., toluene/thiol = 1:3 (v:v), Figures S10 and S11). Changing the molar ratio of Au:Ag to 15:1 (closer to the stoichiometric ratio of the final product) rendered $\text{Au}_{16}\text{Ag}_1(\text{SR})_{11}$ as the intermediate, $\text{Au}_{28}\text{Ag}_2(\text{SR})_{30}$ as the major product, and $\text{Au}_{20}\text{Ag}_1(\text{SR})_{15}$ as a minor product (Figures S12 and S13).

Considering the experimental results, the possible monomer of the dimeric $M_{30}(SR)_{18}$ should be M_{17} , which was observed at the initial stage of the synthesis. The possible reaction process is proposed as shown in Figure 4. The structure of the

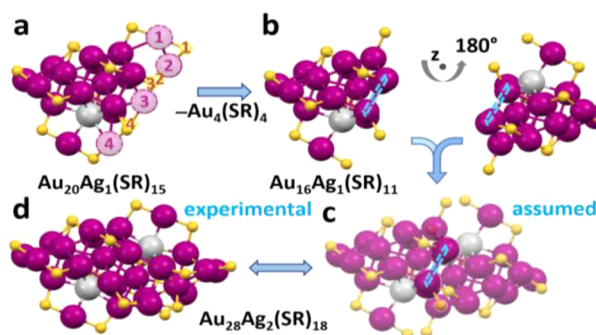


Figure 4. (a) $Au_{20}Ag_1(SR)_{15}$ with surface $Au_4(SR)_4$ eliminated (dashed circles) to give rise to $Au_{16}Ag_1(SR)_{11}$ intermediate; (b) rotating $Au_{16}Ag_1(SR)_{11}$ and (c) attaching two intermediates at the Au_4 plane (dashed square) to form $Au_{32}Ag_2(SR)_{22}$ dimer; (d) the experimental structure of $Au_{28}Ag_2(SR)_{18}$. Labels: magenta, Au; light gray, Ag; and yellow, S.

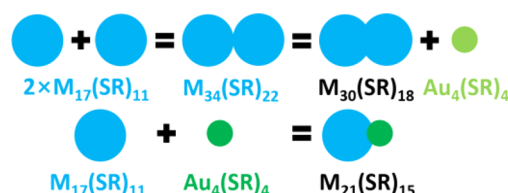
$Au_{16}Ag_1(SR)_{11}$ (M_{17}) intermediate is proposed on the basis of the experimental structure of $Au_{20}Ag_1(SR)_{15}$ by eliminating a $Au_4(SR)_4$ unit from the surface (Figure 4a dashed circles). By rotating the resultant $Au_{16}Ag_1(SR)_{11}$ by 180° along the z axis (Figure 4b, z axis is out of plane) and attaching two of them in a face-to-face manner (Figure 4b dashed squares), a $Au_{32}Ag_2(SR)_{22}$ (M_{34}) adduct could be obtained. Note, a second $Au_4(SR)_4$ unit is eliminated from the other $Au_{20}Ag_1(SR)_{15}$ that takes part in the fusion process. Finally, a third $Au_4(SR)_4$ unit is eliminated at the fusion Au_4 plane (Figure 4c dashed square) from the adduct, giving rise to a dimeric $Au_{28}Ag_2(SR)_{18}$ structure, which is exactly the experimentally observed structure (Figure 4d). In addition, the specific position that Ag takes in the $Au_{20}Ag_1(SR)_{15}$ maintains its location when the $Au_{28}Ag_2(SR)_{18}$ dimer is formed.

Given the above conversion of $Au_{20}Ag_1(SR)_{15}$ to $Au_{28}Ag_2(SR)_{18}$ with $Au_{16}Ag_1(SR)_{11}$ as the intermediate, i.e., $Au_{28}Ag_2(SR)_{18}$ NC is formed from dimerization of two building blocks, such as $Au_{16}Ag_1(SR)_{11}$, we suggest that the formation of a stable Au-SR NC could be trapped by a thermodynamic potential-well under a given condition (i.e., RT) and it can further evolve into a more stable NC by dimerization under appropriate conditions (i.e., $45^\circ C$). The relationship between the starting and the final NCs can also be understood by their coexistence in one pot. The fact that $Au_{28}Ag_2(SR)_{18}$ can be obtained only at higher temperature suggests that it is more thermodynamically favored, when made kinetically accessible.

Because $M_{30}(SR)_{18}$ is proposed to be obtained via dimerization of two $M_{17}(SR)_{11}$ intermediates (eliminating one $Au_4(SR)_4$ unit), $M_{21}(SR)_{15}$ might be formed via a termination process by capping the intermediate $M_{17}(SR)_{11}$ with $Au_4(SR)_4$ (Scheme 1). The valence-electron count doubles from 6e of $M_{21}(SR)_{15}$ to 12e of $M_{30}(SR)_{18}$. More evidence should be pursued in future work.

In summary, this work highlights the importance of the heteroatom tracing strategy which provides a signature in the dimeric $M_{30}(SR)_{18}$ NC, i.e., Ag atoms in the doped NCs serve

Scheme 1. Formation of $M_{30}(SR)_{18}$ via Dimerization and the Formation of $M_{21}(SR)_{15}$ via Termination



as labels to trace the specific positions when a dimer is formed. TDDFT reveals that the specific position(s) identified by Ag tracing in $M_{21}(SR)_{15}$ and $M_{30}(SR)_{18}$ are electronically active site(s), on which the LUMO is localized. The active site(s) are intrinsic in the NCs, regardless of applying Au or Ag occupancy. Thus, it is revealed with heteroatom doping that the electronic structure can be mainly correlated to specific position(s) in the NCs rather than taking all Au atoms equally. The dimerization insight from the current cuboctahedral $M_{21}(SR)_{15}$ -to- $M_{30}(SR)_{18}$ conversion, together with the earlier reported icosahedral $[Au_{25}(SR)_{18}]^0$ -to- $Au_{38}(SR)_{24}$ conversion,²³ may find more generality in future work. Dimerization is a specific aspect of reactivity; thus, the obtained insights may be applied to other known cases of chemical reactions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpclett.0c01977>.

Details on syntheses, characterization, MS measurements (Figures S1–S4); experimental absorption spectra (Figure S5); time-dependent MS (Figures S6–S13) (PDF)

X-ray crystallographic data for $Au_{38-x}Ag_x(S-^iC_4H_9)_{18}$ ($x = 2-4$) (CIF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Jin, R.; Zeng, C.; Zhou, M.; Chen, Y. Atomically Precise Colloidal Metal Nanoclusters and Nanoparticles: Fundamentals and Opportunities. *Chem. Rev.* **2016**, *116*, 10346–10413.
- (2) Chakraborty, I.; Pradeep, T. Atomically Precise Clusters of Noble Metals: Emerging Link between Atoms and Nanoparticles. *Chem. Rev.* **2017**, *117*, 8208–8271.
- (3) Li, Y.; Chen, Y.; House, S. D.; Zhao, S.; Wahab, Z.; Yang, J. C.; Jin, R. Interface Engineering of Gold Nanoclusters for CO Oxidation Catalysis. *ACS Appl. Mater. Interfaces* **2018**, *10*, 29425–29434.
- (4) Zeng, C.; Chen, Y.; Kirschbaum, K.; Lambright, K. J.; Jin, R. Emergence of Hierarchical Structural Complexities in Nanoparticles and Their Assembly. *Science* **2016**, *354*, 1580–1584.
- (5) Walter, M.; Akola, J.; Lopez-Acevedo, O.; Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.; Whetten, R. L.; Grönbeck, H.; Häkkinen, H. A Unified View of Ligand-Protected Gold Clusters as Superatom Complexes. *Proc. Natl. Acad. Sci. U. S. A.* **2008**, *105*, 9157–9162.
- (6) Zhu, M.; Aikens, C. M.; Hollander, F. J.; Schatz, G. C.; Jin, R. Correlating the Crystal Structure of a Thiol-Protected Au₂₅ Cluster and Optical Properties. *J. Am. Chem. Soc.* **2008**, *130*, 5883–5885.
- (7) Joshi, C. P.; Bootharaju, M. S.; Alhilaly, M. J.; Bakr, O. M. [Ag₂₅(SR)₁₈][−]: The “Golden” Silver Nanoparticle. *J. Am. Chem. Soc.* **2015**, *137*, 11578–11581.
- (8) Negishi, Y.; Kawawaki, T.; Imai, Y.; Suzuki, D.; Kato, S.; Kobayashi, I.; Suzuki, T.; Kaneko, R.; Hossain, H. Atomically Precise Alloy Nanoclusters. *Chem. - Eur. J.* **2020**, DOI: 10.1002/chem.202001877.
- (9) Yang, H.; Wang, Y.; Huang, H.; Gell, L.; Lehtovaara, L.; Malola, S.; Häkkinen, H.; Zheng, N. All-Thiol-Stabilized Ag₄₄ and Au₁₂Ag₃₂ Nanoparticles with Single-Crystal Structures. *Nat. Commun.* **2013**, *4*, 2422.
- (10) Desiredy, A.; Conn, B. E.; Guo, J.; Yoon, B.; Barnett, R. N.; Monahan, B. M.; Kirschbaum, K.; Griffith, W. P.; Whetten, R. L.; Landman, U.; Bigioni, T. P. Ultrastable Silver Nanoparticles. *Nature* **2013**, *501*, 399–402.
- (11) Harkness, K. M.; Tang, Y.; Dass, A.; Pan, J.; Kothalawala, N.; Reddy, V. J.; Cliffl, D. E.; Demeler, B.; Stellacci, F.; Bakr, O. M.; McLean, J. A. Ag₄₄(SR)₃₀^{4−}: A Silver-Thiolate Superatom Complex. *Nanoscale* **2012**, *4*, 4269–4274.
- (12) Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.; Bushnell, D. A.; Kornberg, R. D. Structure of a Thiol Monolayer-Protected Gold Nanoparticle at 1.1 Å Resolution. *Science* **2007**, *318*, 430–433.
- (13) Higaki, T.; Liu, C.; Zhou, M.; Luo, T.-Y.; Rosi, N. L.; Jin, R. Tailoring the Structure of 58-Electron Gold Nanoclusters: Au₁₀₃S₂(S-Nap)₄₁ and Its Implications. *J. Am. Chem. Soc.* **2017**, *139*, 9994–10001.
- (14) Negishi, Y.; Chaki, N. K.; Shichibu, Y.; Whetten, R. L.; Tsukuda, T. Origin of Magic Stability of Thiolated Gold Clusters: A Case Study on Au₂₅(SC₆H₁₃)₁₈. *J. Am. Chem. Soc.* **2007**, *129*, 11322–11323.
- (15) Taylor, M. G.; Mpourmpakis, G. Thermodynamic Stability of Ligand-Protected Metal Nanoclusters. *Nat. Commun.* **2017**, *8*, 15988.
- (16) Taylor, M. G.; Mpourmpakis, G. Rethinking Heterometal Doping in Ligand-Protected Metal Nanoclusters. *J. Phys. Chem. Lett.* **2018**, *9*, 6773–6778.
- (17) Cowan, M. J.; Mpourmpakis, G. Structure-Property Relationships on Thiolate-Protected Gold Nanoclusters. *Nanoscale Adv.* **2019**, *1*, 184–188.
- (18) Das, A.; Liu, C.; Byun, H. Y.; Nobusada, K.; Zhao, S.; Rosi, N.; Jin, R. Structure Determination of [Au₁₈(SR)₁₄]. *Angew. Chem., Int. Ed.* **2015**, *54*, 3140–3144.
- (19) Cowan, M. J.; Mpourmpakis, G. Towards Elucidating Structure of Ligand-Protected Nanoclusters. *Dalton Trans* **2020**, *49*, 9191–9202.
- (20) Das, A.; Li, T.; Li, G.; Nobusada, K.; Zeng, C.; Rosi, N. L.; Jin, R. Crystal Structure and Electronic Properties of a Thiolate-Protected Au₂₄ Nanocluster. *Nanoscale* **2014**, *6*, 6458–6462.
- (21) Qian, H.; Eckenhoff, W. T.; Zhu, Y.; Pintauer, T.; Jin, R. Total Structure Determination of Thiolate-Protected Au₃₈ Nanoparticles. *J. Am. Chem. Soc.* **2010**, *132*, 8280–8281.
- (22) Cheng, L.; Ren, C.; Zhang, X.; Yang, J. New Insight into the Electronic Shell of Au₃₈(SR)₂₄: A Superatomic Molecule. *Nanoscale* **2013**, *5*, 1475–1478.
- (23) Dainese, T.; Antonello, S.; Bogialli, S.; Fei, W.; Venzo, A.; Maran, F. Gold Fusion: From Au₂₅(SR)₁₈ to Au₃₈(SR)₂₄, the Most Unexpected Transformation of a Very Stable Nanocluster. *ACS Nano* **2018**, *12*, 7057–7066.
- (24) Liu, L.; Cheng, L.; Yang, J. The Superatomic Molecule Theory of Metal Clusters. *Zhongguo Kexue: Huaxue* **2018**, *48*, 143–153.
- (25) Shichibu, Y.; Negishi, Y.; Watanabe, T.; Chaki, N. K.; Kawaguchi, H.; Tsukuda, T. Biicosahedral Gold Clusters [Au₂₅(PPh₃)₁₀(SC_nH_{2n+1})₅Cl₂]²⁺ (n = 2–18): A Stepping Stone to Cluster-Assembled Materials. *J. Phys. Chem. C* **2007**, *111*, 7845–7847.
- (26) Jin, R.; Liu, C.; Zhao, S.; Das, A.; Xing, H.; Gayathri, C.; Xing, Y.; Rosi, N. L.; Gil, R. R.; Jin, R. Tri-icosahedral Gold Nanocluster [Au₃₇(PPh₃)₁₀(SC₂H₄Ph)₁₀X₂]⁺: Linear Assembly of Icosahedral Building Blocks. *ACS Nano* **2015**, *9*, 8530–8536.
- (27) Teo, B. K.; Zhang, H.; Shi, X. Cluster of Clusters: A Modular Approach to Large Metal Clusters. Structural Characterization of a 38-Atom Cluster [(p-Tol₃P)₁₂Au₁₈Ag₂₀Cl₁₄] Based on Vertex-Sharing Triicosahedra. *J. Am. Chem. Soc.* **1990**, *112*, 8552–8562.
- (28) Malola, S.; Lehtovaara, L.; Knoppe, S.; Hu, K.-J.; Palmer, R. E.; Bürgi, T.; Häkkinen, H. Au₄₀(SR)₂₄ Cluster as a Chiral Dimer of 8-Electron Superatoms: Structure and Optical Properties. *J. Am. Chem. Soc.* **2012**, *134*, 19560–19563.
- (29) Jin, S.; Zou, X.; Xiong, L.; Du, W.; Wang, S.; Pei, Y.; Zhu, M. Bonding of Two 8-Electron Superatom Clusters. *Angew. Chem., Int. Ed.* **2018**, *57*, 16768–16772.
- (30) Das, A.; Li, T.; Nobusada, K.; Zeng, C.; Rosi, N. L.; Jin, R. Nonsuperatomic [Au₂₃(SC₆H₁₁)₁₆][−] Nanocluster Featuring Bipyrimidyl Au₁₅ Kernel and Trimeric Au₃(SR)₄ Motif. *J. Am. Chem. Soc.* **2013**, *135*, 18264–18267.
- (31) Zeng, C.; Li, T.; Das, A.; Rosi, N. L.; Jin, R. Chiral Structure of Thiolate-Protected 28-Gold-Atom Nanocluster Determined by X-ray Crystallography. *J. Am. Chem. Soc.* **2013**, *135*, 10011–10013.
- (32) Xu, W. W.; Zhu, B.; Zeng, X. C.; Gao, Y. A Grand Unified Model for Liganded Gold Clusters. *Nat. Commun.* **2016**, *7*, 13574.
- (33) Cheng, L.; Yuan, Y.; Zhang, X.; Yang, J. Superatom Networks in Thiolate-Protected Gold Nanoparticles. *Angew. Chem., Int. Ed.* **2013**, *52*, 9035–9039.
- (34) Xu, W. W.; Zeng, X.-C.; Gao, Y. Application of Electronic Counting Rules for Ligand-Protected Gold Nanoclusters. *Acc. Chem. Res.* **2018**, *51*, 2739–2747.
- (35) Pei, Y.; Wang, P.; Ma, Z.; Xiong, L. Growth-Rule-Guided Structural Exploration of Thiolate-Protected Gold Nanoclusters. *Acc. Chem. Res.* **2019**, *52*, 23–33.

- (36) Zeng, C.; Chen, Y.; Iida, K.; Nobusada, K.; Kirschbaum, K.; Lambright, K. J.; Jin, R. Gold Quantum Boxes: On the Periodicities and the Quantum Confinement in the Au_{28} , Au_{36} , Au_{44} , and Au_{52} Magic Series. *J. Am. Chem. Soc.* **2016**, *138*, 3950–3953.
- (37) Ma, Z.; Wang, P.; Zhou, G.; Tang, J.; Li, H.; Pei, Y. Correlating the Structure and Optical Absorption Properties of $\text{Au}_{76}(\text{SR})_{44}$ Cluster. *J. Phys. Chem. C* **2016**, *120*, 13739–13748.
- (38) Xu, W. W.; Li, Y.; Gao, Y.; Zeng, X.-C. Unraveling a Generic Growth Pattern in Structure Evolution of Thiolate-Protected Gold Nanoclusters. *Nanoscale* **2016**, *8*, 7396–7401.
- (39) Pei, Y.; Lin, S.; Su, J.; Liu, C. Structure Prediction of $\text{Au}_{44}(\text{SR})_{28}$: A Chiral Superatom Cluster. *J. Am. Chem. Soc.* **2013**, *135*, 19060–19063.
- (40) Dass, A.; Jones, T.; Rambukwella, M.; Crasto, D.; Gagnon, K. J.; Sementa, L.; de Vetta, M.; Baseggio, O.; Aprà, E.; Stener, M.; Fortunelli, A. Crystal Structure and Theoretical Analysis of Green Gold $\text{Au}_{30}(\text{S}^t\text{Bu})_{18}$ Nanomolecules and Their Relation to $\text{Au}_{30}\text{S}(\text{S}^t\text{Bu})_{18}$. *J. Phys. Chem. C* **2016**, *120*, 6256–6261.
- (41) Xiong, L.; Yang, S.; Sun, X.; Chai, J.; Rao, B.; Yi, L.; Zhu, M.; Pei, Y. Structure and Electronic Structure Evolution of Thiolate-Protected Gold Nanoclusters Containing Quasi Face-Centered-Cubic Kernels. *J. Phys. Chem. C* **2018**, *122*, 14898–14907.
- (42) Yang, S.; Chai, J.; Song, Y.; Fan, J.; Chen, T.; Wang, S.; Yu, H.; Li, X.; Zhu, M. *In Situ* Two-Phase Ligand Exchange: A New Method for the Synthesis of Alloy Nanoclusters with Precise Atomic Structures. *J. Am. Chem. Soc.* **2017**, *139*, 5668–5671.
- (43) Li, Y.; Luo, T.-Y.; Zhou, M.; Song, Y.; Rosi, N. L.; Jin, R. A Correlated Series of Au/Ag Nanoclusters Revealing the Evolutionary Patterns of Asymmetric Ag Doping. *J. Am. Chem. Soc.* **2018**, *140*, 14235–14243.
- (44) Kumara, C.; Aikens, C. M.; Dass, A. X-ray Crystal Structure and Theoretical Analysis of $\text{Au}_{25-x}\text{Ag}_x(\text{SCH}_2\text{CH}_2\text{Ph})_{18}^-$ Alloy. *J. Phys. Chem. Lett.* **2014**, *5*, 461–466.
- (45) Zhu, M.; Eckenhoff, W. T.; Pintauer, T.; Jin, R. Conversion of Anionic $[\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}]^-$ Cluster to Charge Neutral Cluster via Air Oxidation. *J. Phys. Chem. C* **2008**, *112*, 14221–14224.
- (46) Mpourmpakis, G.; Caratzoulas, S.; Vlachos, D. G. What Controls Au Nanoparticle Dispersity during Growth? *Nano Lett.* **2010**, *10*, 3408–3413.
- (47) Luo, Z.; Nachammai, V.; Zhang, B.; Yan, N.; Leong, D. T.; Jiang, D.-e.; Xie, J. Toward Understanding the Growth Mechanism: Tracing All Stable Intermediate Species from Reduction of $\text{Au}(\text{I})$ –Thiolate Complexes to Evolution of Au_{25} Nanoclusters. *J. Am. Chem. Soc.* **2014**, *136*, 10577–10580.
- (48) Marbella, L. E.; Chevrier, D. M.; Tancini, P. D.; Shobayo, O.; Smith, A. M.; Johnston, K. A.; Andolina, C. M.; Zhang, P.; Mpourmpakis, G.; Millstone, J. E. Description and Role of Bimetallic Prenucleation Species in the Formation of Small Nanoparticle Alloys. *J. Am. Chem. Soc.* **2015**, *137*, 15852–15858.