

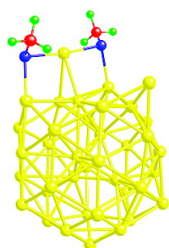
Communication

The “Staple” Motif: A Key to Stability of Thiolate-Protected Gold Nanoclusters

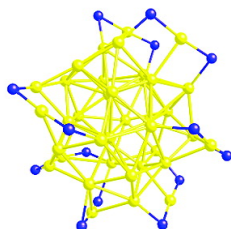
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J. Am. Chem. Soc., **2008**, 130 (9), 2777-2779 • DOI: 10.1021/ja710991n

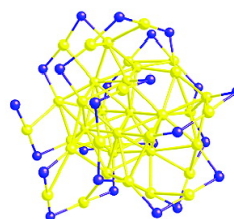
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$\text{Au}_{38}(\text{SCH}_3)_2$



$\text{Au}_{38}(\text{SCH}_3)_{14}$



$\text{Au}_{38}(\text{SCH}_3)_{24}$

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The “Staple” Motif: A Key to Stability of Thiolate-Protected Gold Nanoclusters

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Bonding between a gold surface and thiolate groups is the key to three research areas: thiolate-protected Au clusters,¹ self-assembled monolayers,² and Au-electrode-based molecular electronics.³ Despite tremendous efforts into the three areas, detailed molecular structures at the Au–thiolate interface have been unclear until recently. Maksymovych et al.⁴ studied adsorption of methylthiolate (MT) on Au(111) with scanning tunneling microscopy and density functional theory (DFT) calculations and found Au-adatom-induced self-assembly via formation of a linear RS–Au–SR bonding motif (Figure 1a and 1b). Coincidentally, Jadzinsky et al.⁵ succeeded in crystallizing Au₁₀₂(SR)₄₄ clusters and found that all 44 thiolate groups form linear RS–Au–SR motifs on the cluster surface, which they termed the “staple” motif (Figure 1c). These two reports highlight the importance of the “staple” motif at the gold–thiolate interface.

Given the huge amount of chemical research based on thiolate-protected Au clusters,⁶ the Au-cluster–thiolate interface is especially important and the work by Jadzinsky et al. is a great breakthrough because it offers atomic resolution at the cluster–thiolate interface. Inspired by their work, we hypothesize that the “staple” motifs are preferred at Au-nanocluster–thiolate interfaces. This hypothesis is in contrast with previous models that proposed Au–thiolate polymers as a protective layer for the Au clusters.⁷ Given the extensive recent experimental efforts on small Au clusters⁸ such as Au₂₅(SR)₁₈ and Au₃₈(SR)₂₄ (whose structures are not yet known), here we seek to understand the formation of “staple” motifs and how it affects the geometry, electronic structure, and energetics of the Au cluster by modeling the MT groups on the Au₃₈ surface from zero to full coverage with first-principles DFT simulations.⁹ We will show for the first time that the “staple” motif should indeed be the preferred structural unit for the Au₃₈(MT)_x clusters. We will also propose a new method for making “educated guesses” for structures of thiolate-protected Au clusters by adding “staples” to the cluster surface. These results will provide an initial step toward proving our hypothesis.

We started with a bare Au₃₈ cluster in the *O_h* symmetry,¹⁰ which has two shells: an inner shell of Au₆ octahedron and an outer shell of Au₃₂ consisting of six isolated squares and eight connected hexagons (Figure 2a). Next we added one MT group on the surface at different sites and found that the most stable site is at the square bridge (Figure 2b), which gives an adsorption energy of -2.77 eV/MT (relative to a bare cluster and an isolated MT group). This adsorption is stronger than that on Au(111), where a bridge adsorption (the so-called “standard” adsorption model^{5b}) yields -1.88 eV/MT and a “staple” motif as in Figure 1a and 1b yields -2.22 eV/MT.

To facilitate the formation of a “staple” motif on Au₃₈, we put the second MT next to the first one (Figure 2c) and then optimized the structure. Interestingly, the Au atom in-between the MT groups

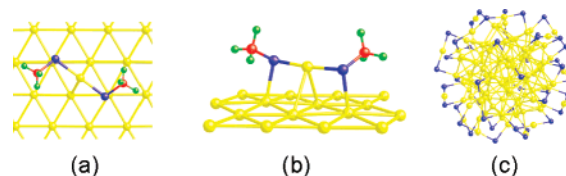


Figure 1. Linear CH₃S–Au–SCH₃ “staple” motif on Au(111) [(a) top view and (b) side view] and on Au₁₀₂ (c). Au in yellow, S in blue, C in red, and H in green. Same color scheme is used in all subsequent figures. Only the top Au layer is shown in (a) and (b), and only Au and S are shown in (c).

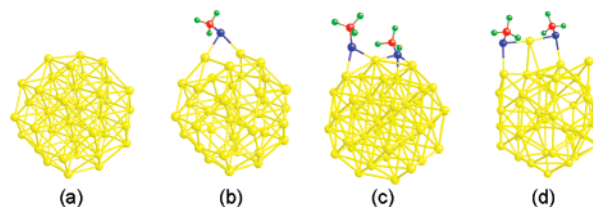


Figure 2. (a) Bare Au₃₈ in the *O_h* symmetry; (b) most stable site for one methylthiolate (MT) on Au₃₈; (c) initial guess for two MTs on Au₃₈; (d) optimized structure of (c).

is pulled out of the outer shell, and a “staple” motif emerges (Figure 2d), which dramatically changes the structure of the underlying cluster. Now the core shell becomes a Au₄ tetrahedron, the outer shell consists of Au₃₀, and the squares disappear and pentagons appear in the outer shell. Interestingly, this Au₄@Au₃₀ structure is quite similar to the global minimum found for Au₃₄[−].¹¹ Figure 2d also shows that formation of the “staple” generates an adatom on the cluster surface. The energetic change is similarly striking: now the adsorption energy is at -3.44 eV/MT. This great energy gain highlights the difference between a “staple” on Au₃₈ and such a motif on a flat surface such as Au(111); namely, forming a “staple” motif on a cluster can cause a greater structural change to the underlying cluster, thereby achieving more energetic gain.

It is well-known that Au(I) forms linear complexes when coordinated by two ligands, and the famous example is Au(CN)₂[−]. So it is convenient to think the Au atom in the “staple” motif (Figure 2d) as Au(I). However, our atom-in-molecule analysis⁹ yields a charge of -0.16 and $+0.15$ electron on S and Au of the “staple” motif, respectively, indicating that the Au atom in the “staple” motif cannot be viewed as Au(I). This is not surprising because we found that an isolated neutral CH₃S–Au–SCH₃ molecule also has a linear S–Au–S bond. Local density of states (see Figure S-1 in the Supporting Information) of the “staple” motif (Figure 2d) shows that the interaction between Au *5d* and S *3p* dominates the Au–S bond, followed by the interaction between Au *6s* and S *3p*. The *p*-orbital bonding of S has directionality, so the two S legs of the “staple” motif are anchored to the cluster surface at about the right angle for Au–S–Au.

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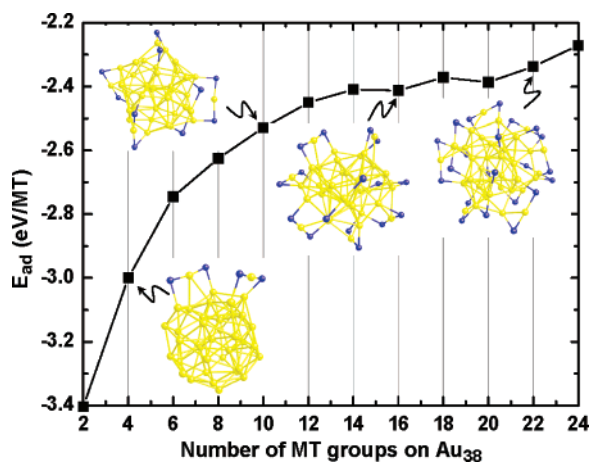


Figure 3. Adsorption energy versus methylthiolate (MT) coverage on Au_{38} and several optimized structures (methyl groups not shown in this and all subsequent figures).

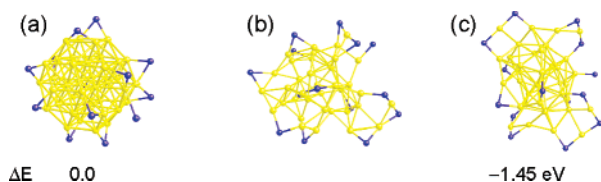


Figure 4. Simulated annealing of $\text{Au}_{38}(\text{MT})_{14}$ (a) at 700 K leads to (c), and (b) is a snapshot of the system at 5 ps. Relative energy between (a) and (c) is also shown.

Based on the optimized structure for $\text{Au}_{38}(\text{MT})_2$ (Figure 2d), we next “artificially” created the second “staple” motif by sandwiching the Au adatom with two MT groups and optimized the structure. Likewise, we generated staple-covered $\text{Au}_{38}(\text{MT})_x$ clusters for $x = 6-24$. We call this method of generating structural models for $\text{Au}_m(\text{SR})_n$ “stapling”. Figure 3 displays the adsorption energy versus the MT coverage, together with several optimized structures. One can see that the averaged adsorption energy per MT decreases in magnitude with the coverage quite sharply in the low coverages and slowly in the high coverages. For $\text{Au}_{38}(\text{MT})_{22}$, we obtained an adsorption energy of -2.34 eV/MT, similar to -2.35 eV/MT computed for $\text{Au}_{102}(\text{MT})_{44}$, based on the single-crystal structure.^{5a} In the process of adding “staples” to the cluster and optimizing the structure, we found that $x = 20$ is approximately the maximum coverage for isolated “staples” to exist on Au_{38} . Beyond 20, we observed dimerization of “staple” motifs. For example, one can see a “staple” dimer on the optimized structure of $\text{Au}_{38}(\text{MT})_{22}$ in Figure 3 (near the top of the structure). Interestingly, the single-crystal structure of $\text{Au}_{102}(\text{SR})_{44}$ also has staple dimers on the surface (one of the two can be seen near the top of Figure 1c). Hence, higher coverage of thiolate groups on the cluster surface can lead to dimerization of “staple” motifs.

To further demonstrate the energetic preference for the “staple” motif, we applied a first principles simulated annealing approach by using constant temperature DFT-based molecular dynamics to heat up, equilibrate, and then cool down an initial configuration of $\text{Au}_{38}(\text{MT})_{14}$ with all MT groups at the square bridge sites (Figure 4a). We found that several “staple” motifs evolve out within a relatively short time frame (~ 10 ps) and do not dissociate once formed at the prescribed equilibrating temperature (700 K). Therefore, formation of “staple” motifs helps pin surface Au atoms and stabilize the cluster. Figure 4b shows a snapshot at 5 ps, and we see that one “staple” monomer (at upper right) and one dimer (at lower right) formed. The final configuration (Figure 4c) has three monomers and one dimer and is 1.45 eV more stable than

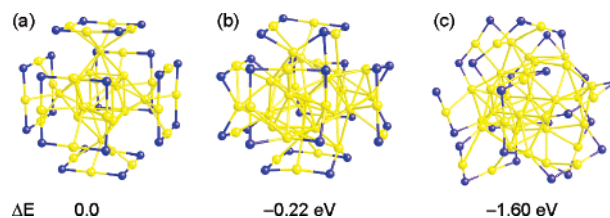


Figure 5. Three optimized structures for $\text{Au}_{38}(\text{MT})_{24}$ and their relative energies: (a) from ref 7c; (b) from ref 13; (c) the present work.

the initial structure. Due to limitation of simulation time, there are still five isolated MT groups in Figure 4c that have not had enough time to meet and form “staples”.

The role of the “staples” to stabilize the gold cluster is reflected not only in the geometry and energetics but also in the electronic structure. In Figures S-2 and S-3, we show the electronic density of states (DOS) for Au_{38} , $\text{Au}_{38}(\text{MT})_2$, $\text{Au}_{38}(\text{MT})_{14}$, and $\text{Au}_{38}(\text{MT})_{24}$. One can see that the bare Au_{38} cluster has a significant DOS at E_{Fermi} , indicating a metallic character. But after only one “staple” is formed on the surface, the DOS at the E_{Fermi} is reduced to nearly zero. With more “staples” on the surface, a HOMO–LUMO gap is developed and widened with the coverage, indicating an increased stability and a molecule-like character. This metal-to-insulator transition caused by the thiolate ligands is in line with the experimental observation that chemically active ligands such as chlorine cause a metal-to-insulator transition for Au_{55} .¹²

Now we focus our discussion on $\text{Au}_{38}(\text{SR})_{24}$. Despite a plethora of experiments,^{8a,b,d,e,g,i} structures of $\text{Au}_{38}(\text{SR})_{24}$ have not been determined and several candidate models have been proposed. Using DFT at the GGA (generalized-gradient approximation) level, Häkkinen et al.^{7b} obtained a high-symmetry configuration that has a Au_8 cube core, a Au_6 middle shell with one Au at each of the cube face centers, and an outer shell of six cyclic Au–thiolate tetramers (Figure 5a). An earlier, structurally similar and slightly more stable configuration was obtained by Garzon et al.¹³ (Figure 5b). This structure has a disordered core, two monomers, three dimers, and two trimers of the “staple” motif, and three separate MT groups. In contrast, our “stapling” method yielded an optimized structure of 1.60 eV more stable (Figure 5c) than that of Häkkinen et al. Besides a disordered core, our structure is dominated with “staple” monomers (six) and dimers (four) and has no Au–thiolate oligomers such as trimers or tetramers or cyclic structures. The energetic preference for more “staple” monomers may indicate a rule that governs the configuration selectivity; that is, given a certain number of thiolate groups, the cluster achieves a more stable configuration by simultaneously maximizing the number of “staples” and minimizing the number of gold atoms participating in formation of those “staples”. This rule enables the cluster to lower its energy from both formation of “staples” and retaining as much as possible Au–Au bonding. Further verification of this rule is planned for the future.

To compare with experiment for $\text{Au}_{38}(\text{SR})_{24}$, we computed the optical spectrum for $\text{Au}_{38}(\text{MT})_{24}$ with the time-dependent DFT method. In a recent experiment, Tsunoyama et al.¹⁴ isolated *n*-octadecanethiolate-protected gold clusters with a core mass of 8 kDa, which was assigned a composition of $\text{Au}_{38}(\text{SR})_{24}$. They measured the cluster’s optical spectrum down to near IR region (0.6 eV) and obtained an optical gap of 0.9 eV. Our computed optical band-edge energy for the structure in Figure 5c is 0.8 eV (see Figure S-4 in SI), in good agreement with experiment. Although this agreement may be fortuitous and a characteristic experimental peak at 2 eV¹⁴ is not reproduced in our computed optical spectrum, our structure and the method to arrive at our structure may point

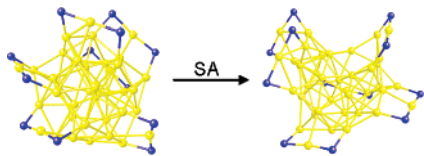


Figure 6. Simulated annealing (SA) of a pre-optimized “staple-covered” $\text{Au}_{38}(\text{MT})_{12}$ leads to a more stable configuration by 1.22 eV.

toward a direction that can lead to structures in better agreement with experiment.

Although a global minimum is difficult to reach from first principles calculations, the present work indicates that a reasonable way to guess initial structures for $\text{Au}_{38}(\text{MT})_x$ clusters is to put “staple” motifs on the surface and optimize the structure, thanks to the energetic preference to form a “staple”. However, there are still many ways to “staple” the surface, especially for medium coverages. One way to obtain configurations of further lower energy is to perform simulated annealing on structures from the “stapling” method. For example, we achieved a 1.22 eV energy gain for the “stapled” $\text{Au}_{38}(\text{MT})_{12}$ cluster by simulated annealing (Figure 6). One can see that the six “staples” survived the annealing at 700 K and the cluster core underwent a dramatic structural change.

In summary, we have used first principles DFT simulations to show that “staple” motifs of linear RS–Au–SR bonding with two S legs anchored to the cluster surface are energetically favored on gold nanoclusters and stabilize the cluster by pinning the surface Au atoms and increasing the HOMO–LUMO gap. “Staple” motifs were also found to cause dramatic structural change to the cluster. A way to obtain reasonable structural models for $\text{Au}_{38}(\text{SR})_x$ clusters was devised by adding “staple” motifs to the surface. The resultant model for $\text{Au}_{38}(\text{SCH}_3)_{24}$ is significantly lower in energy than previously proposed structures, and the computed optical band-edge energy for this model is in good agreement with experiment. The “staple” models can be further improved by simulated annealing. Our work aids understanding the recently reported single-crystal $\text{Au}_{102}(\text{SR})_{44}$ cluster and provides a theoretical underpinning and a structure-generation method for further examination of thiolate-protected Au clusters whose structures are not yet known.

Acknowledgment. This work was supported by the Office of Basic Energy Sciences, U.S. Department of Energy under Contract No. DE-AC05-00OR22725 with UT-Battelle, LLC. The authors thank Prof. H. Häkkinen, Prof. I. L. Garzon, and Prof. K. Nobusada for providing structural files for $\text{Au}_{38}(\text{MT})_{24}$ and $\text{Au}_{25}(\text{MT})_{18}$ clusters. The authors also thank Prof. D. Lee and Prof. T. Tsukuda for helpful discussions. This research used resources of the National Energy Research Scientific Computing Center, which is supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

Supporting Information Available: Density of states plots, computational details for optical spectra, computed optical spectra, and coordinates for all cluster structures shown in figures (PDF). This information is available free of charge via the Internet at <http://pubs.acs.org>.

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- (9) Vienna Ab Initio Simulation Package (VASP)¹⁵ was used to perform DFT calculations with planewave bases and periodic boundary conditions and within the generalized-gradient approximation (GGA)¹⁶ for electron exchange and correlation. Projector augmented wave (PAW) method was employed to describe the electron-core interaction.¹⁷ Scalar relativistic PAW potentials and a converged 450 eV kinetic energy cutoff were used. An Au fcc lattice parameter from a previous study¹⁸ was employed ($a = 4.170$ Å). The (111) surface was modeled with four layers of atoms together with a 12-Å thick vacuum layer and a (4×2) rectangular lateral cell (along the $\langle 110 \rangle$ and $\langle 112 \rangle$ directions). A $2 \times 2 \times 1$ Monkhorst–Pack grid of k-mesh was used to sample the Brillouin zone. The top two substrate layers were allowed to relax with the adsorbed thiolate layer. $\text{Au}_{38}(\text{MT})_x$ and $\text{Au}_{102}(\text{MT})_{44}$ clusters were placed in a cubic box of $a = 25$ and 30 Å, respectively, and only the Gamma-point was used for the k-sampling. The force tolerance for structural optimization was set at 0.025 eV/Å. Simulated annealing was performed by constant-temperature molecular dynamics via the Nöse thermostat with a time step of 1 or 3 fs (a larger time step was used when we set equal mass for atoms in the cluster). A cluster was heated up in steps to 700 K, allowed to equilibrate, and then slowly cooled down to 0 K. Total time frame was ~ 10 ps. Formal charges on atoms were determined according to Bader’s atom-in-molecule method, as implemented by Henkelman et al.¹⁹ Computational details for optical spectra by the time-dependent DFT method are in the Supporting Information.
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JA710991N