

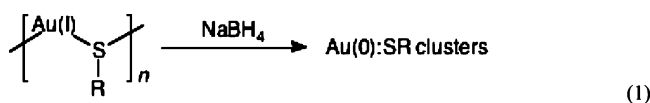
## Kinetic Stabilization of Growing Gold Clusters by Passivation with Thiolates

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Small gold clusters (<1 nm), protected by monolayers of glutathione, *N*-(2-mercaptopropionyl)glycine, or mercaptosuccinic acid, were prepared by reducing the corresponding Au(I)-thiolate polymers and were fractionated by size using polyacrylamide gel electrophoresis (PAGE). Mass analysis of the fractionated clusters revealed that their core sizes varied with the molecular structures of the thiolates. This finding indicates that the reduction of the Au(I)-thiolate polymers yields small clusters whose growth is kinetically hindered by passivation with thiolates. Optical spectra of the clusters with identical compositions exhibited different profiles depending on the thiolate molecular structures. This observation implies that deformation of the underlying gold cores is induced by interligand interactions.

## Introduction

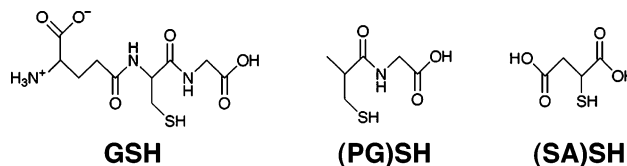
Gold clusters protected by thiolate monolayers (Au:SR clusters) have aroused significant scientific interest as prototype systems to study size-dependent properties and as building blocks for the fabrication of nanostructured materials or devices.<sup>1</sup> Conventionally, Au:SR clusters have been prepared by chemical reduction of Au(I)-SR polymers formed from Au(III) ions and thiol RSH:<sup>2</sup>



The resulting Au:SR clusters have been separated into distinct chemical entities according to core size by fractional crystallization,<sup>3</sup> chromatography,<sup>4</sup> and electrophoresis.<sup>5</sup> Extensive previous studies have revealed that the numbers of core atoms in relatively large (>1.5 nm) Au:SR clusters were limited to certain fixed values regardless of the thiolate ligands. For example, gold clusters with a core mass of 8 kDa (~38 atoms), 22 kDa (~101 atoms), and 28 kDa (~146 atoms) have been commonly isolated by protection with monolayers of alkanethiolate (SC<sub>n</sub>),<sup>3a,b,d,4e</sup> phenylthiolate (SPh),<sup>3e</sup> and phenylethanethiolate (SC<sub>2</sub>Ph).<sup>3c</sup> The preferential formation of these gold cores can be explained in terms of the high stability of the underlying cores having closed-shell geometries.<sup>6</sup>

On the other hand, one may anticipate that the structures and properties of smaller-sized gold clusters are influenced significantly by the ligation of thiols, since most of the constituent

## CHART 1: Thiols Used for Passivation of Gold Clusters



gold atoms are located at a core surface and are subject to covalent interactions with thiolates. Although several groups have succeeded in the synthesis of Au:SR clusters with well-defined chemical compositions,<sup>5a–e,7</sup> their core numbers could not be explained solely in terms of the stability of the underlying gold cores. For example, the formation of a series of Au<sub>n</sub> clusters (*n* = 10, 15, 18, 22, 25, 29, 33, 39) protected by glutathione (GSH; Chart 1)<sup>5d</sup> can be ascribed neither to the geometrical structure of the gold cores nor to the total number of valence electrons of the cores, in contrast to the cases of free<sup>8</sup> and phosphine-stabilized<sup>9</sup> gold clusters. This observation suggested that the thiolate structure plays a nontrivial role in the stabilization of specific-sized clusters formed during reaction 1. In addition, it has been reported that the thiolate ligation significantly modifies basic properties of Au:SR, such as photoluminescence,<sup>7f</sup> redox potentials,<sup>7h</sup> magnetic properties,<sup>10</sup> and optical activity,<sup>5a,b,f,11</sup> through charge transfer at the Au–S interface and deformation of the core geometry.

The objective of the present study was to clarify the effects of thiolate structure on the size and electronic structure of the cores in the subnanometer region. To this end, we prepared small gold clusters protected by carboxylated thiols, as shown in Chart 1, via reaction 1, fractionated them by core size, and determined their core sizes by mass spectrometry. The thiols used were glutathione (GSH), *N*-(2-mercaptopropionyl)glycine ((PG)SH), and mercaptosuccinic acid ((SA)SH). In contrast to relatively large Au:SR clusters, the core size varied with the thiolate

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structure. Comparison of the optical spectra of identical chemical compositions showed that the electronic structures of the subnanometer-sized gold clusters are greatly influenced by the thiolate structures.

### Experimental Section

**Size Selective Synthesis.** The gold clusters protected by thiolates shown in Chart 1 were prepared using reaction 1.<sup>12</sup> First, a methanol solution (50 mL) containing  $\text{HAuCl}_4$  (0.25 mmol) and thiol (1.5 mmol) was cooled to  $\sim 0^\circ\text{C}$  in an ice bath for 30 min. Then, an aqueous solution of  $\text{NaBH}_4$  (0.2 M, 12.5 mL) at  $\sim 0^\circ\text{C}$  was injected rapidly into the mixture under vigorous stirring to form  $\text{Au:SG}$  and  $\text{Au:S(SA)}$  clusters. For the preparation of  $\text{Au:S(PG)}$ , a methanol solution of  $\text{NaBH}_4$  (0.2 M, 12.5 mL) was added dropwise over a period of 5 min. After the mixture was allowed to react for 1 h, the resulting precipitate was collected and washed repeatedly with methanol to remove impurities. The precipitate was then dried in vacuo to yield  $\text{Au:SR}$  clusters in the form of a dark brown powder. Finally, the crude samples of the  $\text{Au:SR}$  clusters were fractionated using polyacrylamide gel electrophoresis (PAGE).<sup>5c,d</sup> The PAGE separation was performed at  $\sim 4^\circ\text{C}$  in a regular refrigerator to minimize the possibility of thermal decomposition of the clusters.<sup>13</sup>

**Characterization.** The chemical compositions of the fractionated clusters were probed using a homemade electrospray ionization (ESI) mass spectrometer, which has been described in detail previously.<sup>5d</sup> Typically, 50% (v/v) water–methanol solutions of the clusters with a concentration of 0.5 mg/mL were electrosprayed into an ambient atmosphere through a stainless steel needle of a syringe biased at ca.  $-3\text{ kV}$ . The highly charged liquid droplets were fed into a capillary which was located coaxially and resistively heated to ca.  $180^\circ\text{C}$  to form intact cluster ions via a desolvation process. A portion of the ions exiting the capillary was pulse-extracted perpendicular to the initial beam, accelerated up to 12–14 keV (130 Hz), and detected by the time-of-flight (TOF) mass spectrometer with a reflectron. The resolution of the mass spectrometer ( $m/\Delta m$ ) was typically 1000.

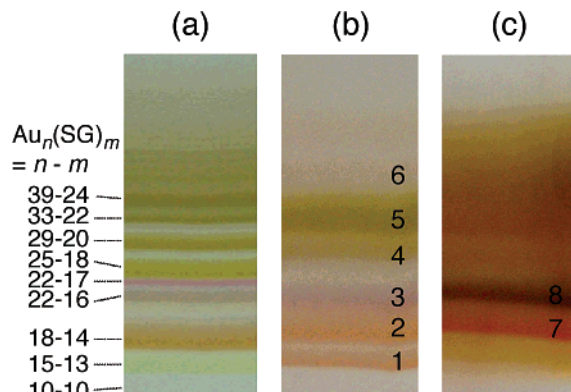
UV–vis absorption spectra of aqueous solutions of the clusters were recorded at ambient temperature with a spectrophotometer (HITACHI, U-210). The wavelength-dependent optical data,  $I(w)$ , were converted to energy-dependent data,  $I(E)$ , according to the following relation so that the integrated spectral areas were conserved:

$$I(E) = I(w)/(\partial E/\partial w) \propto I(w) \times w^2 \quad (2)$$

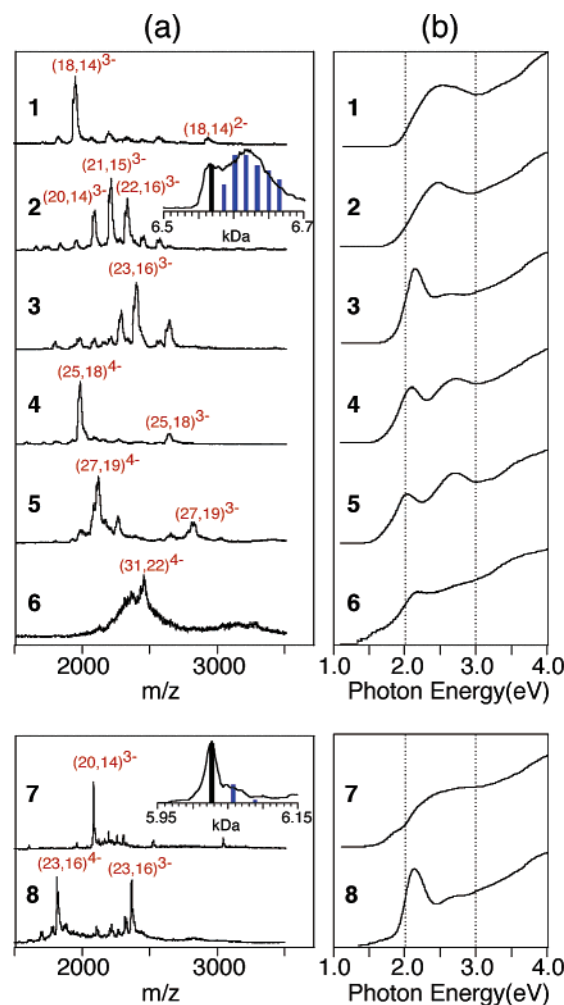
### Results and Discussion

**Chemical Compositions.** As-prepared clusters of  $\text{Au:S(PG)}$  and  $\text{Au:S(SA)}$  were separated into six bands (1–6 in Figure 1b) and two bands (7 and 8 in Figure 1c) using PAGE. The PAGE separation for the  $\text{Au:S(PG)}$  and  $\text{Au:S(SA)}$  clusters was less clear as compared to that for the  $\text{Au:SG}$  clusters, as shown in Figure 1a.<sup>5d</sup> This may be due to the fact that the  $\text{Au:S(PG)}$  and  $\text{Au:S(SA)}$  clusters are less stable compared to the  $\text{Au:SG}$  clusters and tend to slowly degrade into smaller clusters<sup>13</sup> during the PAGE separation.

Figure 2a displays the negative-ion ESI mass spectra of the  $\text{Au:S(PG)}$  (bands 1–6) and  $\text{Au:S(SA)}$  (bands 7 and 8) clusters recorded using our spectrometer. Only small Au thiolate fragment ions were observed using commercially available ESI mass spectrometers employing a nebulizer gas and an orthogonal extraction scheme.<sup>5d</sup> Thus, it is crucial to introduce large droplets containing the water-soluble  $\text{Au:SR}$  clusters directly into a heated capillary in order to vaporize them nondestructively. As



**Figure 1.** PAGE separation of (a)  $\text{Au:SG}$ , (b)  $\text{Au:S(PG)}$ , and (c)  $\text{Au:S(SA)}$  clusters.



**Figure 2.** (a) Negative-ion ESI mass spectra and (b) optical absorption spectra of  $\text{Au:S(PG)}$  (1–6) and  $\text{Au:S(SA)}$  (7 and 8) clusters. The deconvoluted spectra of the main peaks of 2 and 7 are shown in the insets of panel a. The peaks at the lower mass sides can be explained by  $\text{Au}_{21}(\text{S(PG)})_{15}$  and  $\text{Au}_{20}(\text{S(SA)})_{14}$  whose calculated molecular weights are indicated by black bars. The blue bars represent mass spectra of clusters whose thiolate ligands are replaced with impurities contained in the thiol samples used in the synthesis (ref 13). The mass peaks are assigned to  $[\text{Au}_n(\text{S(PG)})_m - \text{pH}^+]^{p-}$  and  $[\text{Au}_n(\text{S(SA)})_m - \text{pH}^+]^{p-}$  and are denoted as  $(n, m)^{p-}$ .

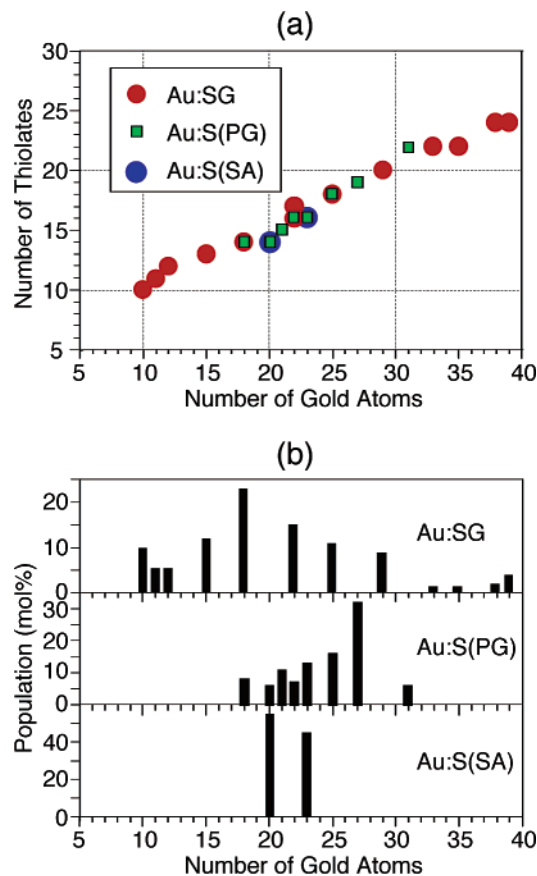
in the case of  $\text{Au:SG}$  clusters, it is reasonable to assign a series of peaks for 1–8 to multiple-charged anions originating from deprotonation of the carboxyl moieties of the corresponding thiolates,  $[\text{Au}_n(\text{S(PG)})_m - \text{pH}^+]^{p-}$  and  $[\text{Au}_n(\text{S(SA)})_m - \text{pH}^+]^{p-}$ , although the mass resolution itself is insufficient to detect the

deprotonation. Nevertheless, mass assignment for **1–8** was not as straightforward as that for Au:SG clusters<sup>5d</sup> and we encountered two difficulties. First, there was concern regarding the appearance of side peaks on the higher mass sides of the main peaks. For example, the deconvoluted spectra of the main peaks of **2** and **7** are shown in the insets of Figure 2a. The peaks at the lower mass sides can be assigned to Au<sub>21</sub>(S(PG))<sub>15</sub> and Au<sub>20</sub>(S(SA))<sub>14</sub> whose calculated molecular weights are indicated by black bars. We then calculated the mass spectra of Au<sub>21</sub>(S(PG))<sub>15</sub> and Au<sub>20</sub>(S(SA))<sub>14</sub> whose thiolate ligands are statistically replaced with impurities contained in the (PG)SH and (SA)SH samples.<sup>13</sup> The mass spectra thus calculated (shown as blue bars) reproduced quite well the spectral profiles observed experimentally. We thus ascribed the relatively broad peaks to impurities contained in the thiols used in the synthesis.<sup>14</sup> The second difficulty arises from coincidence of mass numbers. For example, although the molecular weight determined experimentally for **7** strongly suggests Au<sub>20</sub>(S(SA))<sub>14</sub> ( $M_w = 6028$ ), Au<sub>23</sub>(S(SA))<sub>10</sub> and Au<sub>17</sub>(S(SA))<sub>18</sub> yield similar molecular weights of 6035 and 6023, respectively. The assignment to Au<sub>17</sub>(S(SA))<sub>18</sub> is impossible because it gives unrealistic surface coverage. The weight percentage of Au calculated for Au<sub>20</sub>(S(SA))<sub>14</sub> (65%) agrees well with that for 1.0 nm Au:S(SA) clusters (61%) determined previously by thermogravimetric analysis,<sup>12b</sup> whereas the weight percentage for Au<sub>23</sub>(S(SA))<sub>10</sub> (75%) is significantly larger. On the basis of these considerations, we conclude that clusters **1–8** can be assigned to Au<sub>18</sub>(S(PG))<sub>14</sub>, Au<sub>21±1</sub>(S(PG))<sub>15±1</sub>, Au<sub>23</sub>(S(PG))<sub>16</sub>, Au<sub>25</sub>(S(PG))<sub>18</sub>, Au<sub>27</sub>(S(PG))<sub>19</sub>, Au<sub>31</sub>(S(PG))<sub>22</sub>, Au<sub>20</sub>(S(SA))<sub>14</sub>, and Au<sub>23</sub>(S(SA))<sub>16</sub>, respectively. Because of the lower stabilities of Au:S(PG) and Au:S(SA), the purities of fractions **1–8** were not as high compared to those of the Au:SG clusters.<sup>5d</sup> Nevertheless, these results demonstrate that fractionation by PAGE and mass analysis is a versatile approach for precise and systematic synthesis of gold clusters protected by thiolates bearing negatively charged functional groups. For practical purposes, it is crucial to use a high purity thiol sample.

**Kinetic Competition between Core Growth and Passivation.** The numbers of gold atoms and thiolate ligands for **1–8** are plotted in Figure 3a together with those of the Au:SG clusters.<sup>5d</sup> The data show that the gold-to-thiolate ratios are nearly the same regardless of the thiolate structure. The relative molar populations are shown as a function of the core size by bar graphs in Figure 3b. It is apparent that the core sizes do not always have common values but vary according to the thiolate structures. This indicates that the core sizes of the isolated clusters are not governed solely by the intrinsic stability of the gold cores but are affected by thiolate ligation, in contrast to the Au:SR clusters with relatively large cores (> 1.5 nm).<sup>3</sup> In reaction 1, the growth of gold clusters proceeds irreversibly and strongly competes with surface protection by thiolates. Under such circumstances, the consecutive core growth is kinetically hindered at every stage where the core is completely surrounded by the thiolate ligand shell. Thus, we interpret the variety of chemical compositions of the isolated Au:SR clusters to indicate that they correspond to trapped intermediates of the growing clusters whose surfaces are fully passivated. The stage at which growth is terminated may be determined by the monolayer structures of the thiolates having different molecular frameworks and/or sticking probability of the thiolates with different  $pK_a$  values to the gold cores.

Here, we raise two concerns regarding the origin of the stability of Au:SR clusters.

(1) The stabilities of the Au:SR clusters kinetically trapped in reaction 1 acutely depend on the core sizes. Some of them



**Figure 3.** (a) Chemical composition of **1–8** and (b) core-size distribution of Au:SG, Au:S(PG), and Au:S(SA) clusters. The data for the Au:SG clusters are taken from ref 5d.

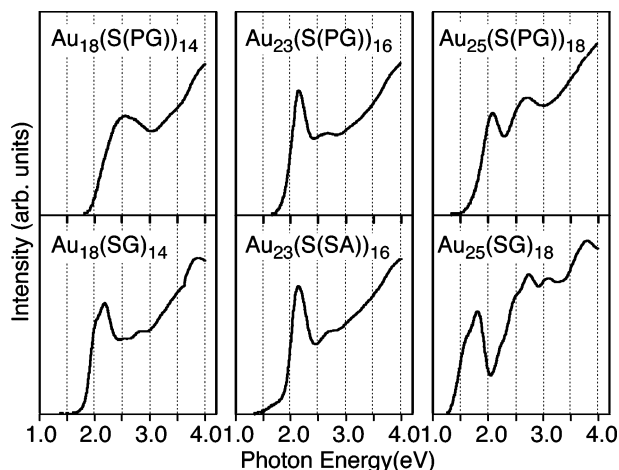
exhibit higher stability than others against core-size reduction by spontaneous decomposition in water dispersion and by etching with free thiols.<sup>15</sup> For example, Au<sub>25</sub>(SG)<sub>18</sub> clusters were found to be stable in aqueous solution while other Au:SG clusters degraded into smaller clusters.<sup>5d</sup> Selective formation of Au<sub>25</sub>(SG)<sub>18</sub> in the reaction of phosphine-stabilized gold clusters with an excess (400 equiv) amount of GSH<sup>7i</sup> suggests that Au<sub>25</sub>(SG)<sub>18</sub> exhibits the highest stability against size reduction by etching. Similar situations have been encountered in mass spectrometric studies of free metal clusters produced by laser vaporization: the abundance of magic-number clusters is prominent in the mass spectra, reflecting their higher stability against chemical reactions and dissociation than their neighbors.<sup>16</sup> We believe at this moment that the chemical tolerance of the Au:SR clusters, namely, stability against size-reduction processes, correlates well with the origin of their stabilities.

(2) There is a possibility that formation of some stable cores is skipped in reaction 1. We recently found that alkanethiolate-protected Au<sub>55</sub> clusters not formed via reaction 1 can be synthesized by thiolation of “preformed” gold clusters ( $\phi = 1.3 \pm 0.3$  nm) stabilized by polymers.<sup>4e</sup> This suggests that unique Au:SR clusters missing in reaction 1 can be obtained by decoupling the core formation and thiolate protection processes.

Thus, to understand the origin of the stability of the Au:SR clusters, it is vitally important to survey a series of “magic core sizes” by monitoring the stability of the clusters formed by various methods against size-reduction processes.

**Effect of Thiolate Ligation on Electronic Structures.** As shown in Figure 2b, the optical spectra clearly show that the electronic structures of **1–8** are well quantized and the HOMO–LUMO gap evolves with the core size.<sup>13</sup> In our previous paper,<sup>5d</sup>





**Figure 4.** Effect of thiolate structure on the absorption spectra.

we demonstrated, using the optical spectra of  $\text{Au}_{22}(\text{SG})_{16}$  and  $\text{Au}_{22}(\text{SG})_{17}$ , that the degree of thiolate ligation also affects the electronic structures of gold clusters. In the present study, we found a more surprising effect of thiolate ligation on the electronic structures of the Au:SR clusters. Figure 4 compares the optical spectra of three sets of the Au:SR clusters with identical chemical compositions:  $\text{Au}_{18}(\text{S(PG)})_{14}/\text{Au}_{18}(\text{S(G)})_{14}$ ,  $\text{Au}_{23}(\text{S(PG)})_{16}/\text{Au}_{23}(\text{S(SA)})_{16}$ , and  $\text{Au}_{25}(\text{S(PG)})_{18}/\text{Au}_{25}(\text{S(G)})_{18}$ . Figure 4 clearly shows that the optical spectra exhibit different profiles for the clusters with the above identical chemical compositions. According to a density functional theory (DFT) study on the optical properties of  $[\text{Au}_{13}(\text{SCH}_3)_8]^{3+}$ ,<sup>17</sup> the modulation of the spectral profiles observed in Figure 4 is associated with metal-centered optical transitions. This implies that the electronic structures of the  $\text{Au}_{18}$ ,  $\text{Au}_{23}$ , and  $\text{Au}_{25}$  cores are different, reflecting the molecular structures of the thiolates. Two possible mechanisms may contribute to the modification of the electronic structures of the gold cores. One is that the subnanometer-sized gold cores having large surface-to-volume ratios are deformed as a result of noncovalent interaction (e.g. hydrogen bonding)<sup>12</sup> between adjacent thiolates. The other is that the degree of electron transfer from the gold core to the thiolate layer varies with the  $\text{p}K_{\text{a}}$  values of the corresponding thiols. At any rate, Figure 4 affords an example wherein the electronic structures of the small gold clusters can be manipulated externally by proper design or precise control of thiolate headgroups.<sup>5a,b,f,7f–h,10,11</sup>

## Summary

We report the chemical compositions of gold clusters protected by various carboxylated thiolates. It was revealed that the core sizes of Au:SR clusters preferentially formed by the reductive decomposition of Au(I)-SR are dependent on the thiolate structures, and consequently are not predictable. This finding demonstrates that completion of the protecting shell leads to kinetic trapping of the Au:SR clusters with specific core sizes. Remarkable effects of the molecular structures of the thiolates on optical properties offer a strategy for fine-tuning of the fundamental properties of the Au:SR clusters through precise control of thiolate ligation as well as core size.

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**Supporting Information Available:** Details of the mass spectral assignment and time-dependent behaviors and optical data of isolated clusters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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