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Communication

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COMMUNICATIONS

Origin of Magic Stability of Thiolated Gold Clusters: A Case Study on $Au_{25}(SC_6H_{13})_{18}$

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Mass spectrometric studies have revealed that thiolate-protected gold (Au:SR) clusters with specific compositions show extraordinarily high stability.[1−5] However, the origin of the magic stability, a topic of fundamental importance to nanomaterials science, remains unclear. This is partly because hitherto-isolated Au:SR clusters do not always correspond to inherently stable species, but rather to metastable species kinetically trapped during growth process.[3e−g] It is natural to expect that the inherent stability of magic Au:SR clusters can be explained in terms of closing of electronic and/or geometric shells. Since, to a first approximation, gold can be regarded as an s^1-electron system, the electronic shell model explains the stability of Au clusters in the gas phase[6] and those stabilized by phosphines.[7] Isolation of negatively charged Au:SR clusters (e.g., $[Au_{147}:SC_6H_{13}]^{1-}$ (ref 8), $[Au_{44}(SPh)_{28}]^{2-}$ (ref 1c), and $[Au_{25}(SC_2H_4Ph)_{18-x}(S\text{-PEG})_x]^{1-}$ (ref 2d)) has raised the possibility that their stability is also governed by such electronic factors. In contrast, size-selective synthesis of larger Au:SR clusters has been ascribed to preferential formation of highly symmetrical Au cores.[9] A new structural motif has been proposed for $Au_{38}(SCH_3)_{24}$, in which a Au_{14} core is fully protected by six $Au_4(SCH_3)_4$ cyclic oligomers.[10] Such a core−shell structure may be responsible for the stability of small Au:SR clusters.

We recently discovered that $Au_{25}(SG)_{18}$ has the highest resistance to core etching reactions[3c,g] and spontaneous decomposition[3b] among the series of glutathionate-protected gold (Au:SG) clusters. Iwasa and Nobusada have predicted theoretically that the geometrical structure of the most stable isomer of $[Au_{25}(SCH_3)_{18}]^+$ is constructed from a nearly planar Au_7^{1+} core and a cage made of one $Au_{12}(SCH_3)_{12}$ and two $Au_3(SCH_3)_3$ cyclic oligomers.[11] This "core-in-cage" structure could reproduce several experimental observations of $Au_{25}(SG)_{18}$, such as its optical spectrum (Figure 1a),[3b] X-ray diffraction pattern,[11] X-ray magnetic circular dichroism,[12a] and ^{197}Au Mössbauer spectrum.[12b] The present work aims to investigate the effect of charge state on the stability of $Au_{25}(SG)_{18}$ and thereby shed light on the origin of the magic stability. Here, we studied by ESI mass spectrometry the charge state of $[Au_{25}(SC_6H_{13})_{18}]^x$ that has no charging site in the organic layer instead of $Au_{25}(SG)_{18}$ having the deprotonation sites. We further probed the stability of $[Au_{25}(SC_6H_{13})_{18}]^0$ against redox reactions by voltammetric measurement and by mass spectrometric analysis of the oxidized and reduced products. These studies revealed that $[Au_{25}(SC_6H_{13})_{18}]^x$ is stable regardless of the charge state for $x = 1-$, 0, and $1+$. This result suggests that the magic stability of $[Au_{25}(SC_6H_{13})_{18}]^x$, or more generally $Au_{25}(SR)_{18}$, is attributable to geometric rather than electronic factors.

The preparation method of the $[Au_{25}(SC_6H_{13})_{18}]^x$ samples is summarized in Scheme 1.[13] According to the Schiffrin method,[14] $Au(I)-SC_6H_{13}$ polymers extracted by tetraoctylammonium (TOA^+) into the toluene phase were allowed to react with an aqueous solution of sodium borohydride ($NaBH_4$). After 3 h, the clusters in the organic phase were collected. Then, clusters **1** and **2** were obtained by extraction of the product by acetonitrile and subsequently by 1:1 acetonitrile/acetone, respectively. Typical yield of **2** is 1.5 times higher than that of **1** in weight.

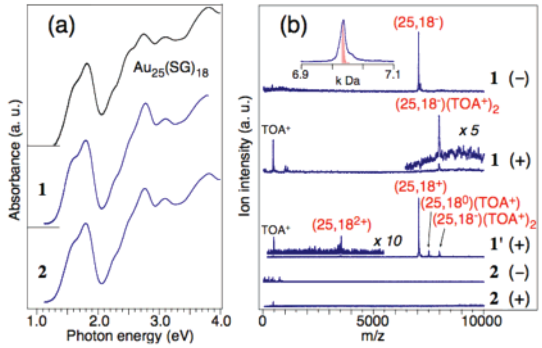
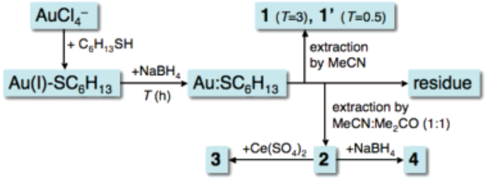


Figure 1. (a) Optical absorption spectra of $Au_{25}(SG)_{18}$, **1**, and **2**. (b) Positive and negative ESI mass spectra of **1**, **2**, and **1′**. The notation (n, $m^{-/+}$) represents $[Au_n(SC_6H_{13})_m]^{-/+}$.

Scheme 1. Preparation of Cluster Samples **1**−**4**



The optical spectra of **1** and **2** exhibit characteristic profiles that are very similar to that of $Au_{25}(SG)_{18}$ (Figure 1a).[3b,c,g] The negative ESI mass spectrum of **1** exhibits a single $[Au_{25}(SC_6H_{13})_{18}]^{1-}$ peak, whose assignment was confirmed by comparison with the mass spectrum of $[Au_{25}(SC_{12}H_{25})_{18}]^{1-}$ (Figure S1).[13] Interestingly, $[Au_{25}(SC_6H_{13})_{18}]^{1-}$ was detected also in the positive ESI mass spectrum of **1** in the form of $[Au_{25}(SC_6H_{13})_{18}]^{1-}(TOA^+)_2$ (Figure 1b), demonstrating that TOA^+ acts as a counterion. To the best of our knowledge, this is the first ESI mass spectrum of $Au_{25}(SR)_{18}$ utilizing the net charge of the core, rather than the charge of the ligands.[1a,b,2d,3b,c] In contrast, ion signals due to $[Au_{25}(SC_6H_{13})_{18}]^{1+/1-}$ were observed in neither the positive nor the negative ESI mass spectra of fraction **2** (Figure 1b), suggesting the formation of "neutral" $[Au_{25}(SC_6H_{13})_{18}]^0$. These results indicate that some of the neutral Au:S cores were reduced by $NaBH_4$ in the Schiffrin methods.[14] Thus, the tenacious remnant of TOA^+ that is often observed in Au:SR clusters[15] is thought to be due to the fact that TOA^+ acts as a counterion to stabilize the negatively charged clusters. What then determines the branching fraction between $[Au_{25}(SC_6H_{13})_{18}]^{1-}$ (**1**) and $[Au_{25}(SC_6H_{13})_{18}]^0$ (**2**)? One can easily

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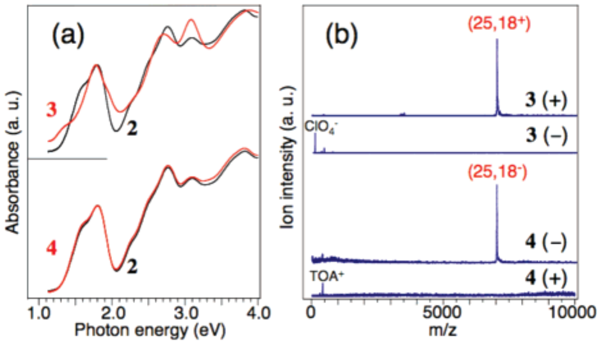

Figure 2. (a) Optical spectra and (b) ESI mass spectra of **3** (top) and **4** (bottom). The optical spectrum of **2** is superimposed in panel (a).

expect that the charge distribution is associated with the time of exposure of the clusters to the reducing agent. To check this possibility, we mass-analyzed the extracts by acetonitrile (**1′**) from the products obtained after a shorter reduction time (30 min). The positive ESI mass spectrum of **1′** clearly shows the presence of $[Au_{25}(SC_6H_{13})_{18}]^{1+}$ and $[Au_{25}(SC_6H_{13})_{18}]^{2+}$ (Figure 1b). This indicates that the cationic clusters are present at the early stage of the reaction and the charge distribution of $[Au_{25}(SC_6H_{13})_{18}]^x$ shifts toward negative values as the reduction proceeds. Thus, $Au_{25}(SC_6H_{13})_{18}$ is produced in various charge states whose distribution is determined by the reduction time.

Next, the stability of $[Au_{25}(SC_6H_{13})_{18}]^0$ (**2**) upon ionization and reduction was studied. Cluster **2** was allowed to react with $Ce(SO_4)_2$ (ref 16) and $NaBH_4$ to generate ionic products **3** and **4**, respectively (Scheme 1). A single peak assigned to $[Au_{25}(SC_6H_{13})_{18}]^{1+}$ was observed in the positive-ion mass spectrum of **3**, whereas no anions were detected (Figure 2b). In contrast, the negative-ion mass spectrum of **4** is dominated by a single species, $[Au_{25}(SC_6H_{13})_{18}]^{1-}$, and no cations were detected (Figure 2b). Note that the spectral profiles of **2** and **3** are consistent with those observed in electrochemical reactions of $[Au_{38}(SC_6H_{13})_{24}]^x$ (ref 2b), which have been recently reassigned to $[Au_{25}(SC_6H_{13})_{18}]^x$ (ref 2d). The absence of the $C_6H_{13}S^-$ anion in the mass spectrum suggests that the reductive desorption of thiolates ($Au{:}SR + 1e^- \rightarrow Au(0) + RS^-$) observed in self-assembled monolayers on a flat surface[17] and on a Au_{147} cluster[18] does not take place. These results indicate that $[Au_{25}(SC_6H_{13})_{18}]^0$ (**2**) can be oxidized to $[Au_{25}(SC_6H_{13})_{18}]^{1+}$ (**3**) by $Ce(SO_4)_2$ and reduced to $[Au_{25}(SC_6H_{13})_{18}]^{1-}$ (**4**) by $NaBH_4$ without any degradation. In other words, $[Au_{25}(SC_6H_{13})_{18}]^x$ is stable regardless of its charge state between 1− and 1+. The high tolerance of **2** to the redox reactions is in sharp contrast to phosphine-stabilized gold clusters, which favor specific charge states that fulfill the electron counting scheme.[7] Voltammetric measurements confirmed that redox reactions of cluster **2** proceed reversibly, while those of $Au_{11}(PPh_3)_8Cl_3$ do not (Figure S2). These results lead us to conclude that *electronic structure is not a direct cause of the magic stability of* $Au_{25}(SC_6H_{13})_{18}$. A recent DFT study of $[Au_{25}(SCH_3)_{18}]^x$ ($x = 3+$ to $3-$) showed that the electronic charge is localized at the Au_7 core while pertaining the core-in-cage framework.[19] Thus, we propose that the full coverage of $[Au_7]^x$ by robust [−Au−S−] oligomers imparts high stability to $[Au_{25}(SC_6H_{13})_{18}]^x$ against electrical charging. We found that the charge state of $[Au_{25}(SC_6H_{13})_{18}]^x$ is reflected by conditions of the preparation and storage because once formed they can survive at least against decomposition. This situation hinders the determination of which charge state is energetically the most favorable.

In summary, we have revealed that the Schiffrin method yields magic $[Au_{25}(SC_6H_{13})_{18}]^x$ clusters with a distribution in charge states that shifts toward negative values with reduction time. The stable ions $[Au_{25}(SC_6H_{13})_{18}]^{1+}$ and $[Au_{25}(SC_6H_{13})_{18}]^{1-}$ can be prepared by chemical oxidation and reduction of $[Au_{25}(SC_6H_{13})_{18}]^0$, respectively. These findings, together with DFT results,[11,19] lead us to conclude that geometric rather than electronic factors are responsible for the magic stability of $[Au_{25}(SC_6H_{13})_{18}]^x$ ($x = 1-, 0, 1+$). The striking similarity between the optical spectrum of $Au_{25}(SG)_{18}$ and those of **2** and **4** suggests that the head groups of thiolates have little impact on the electronic and geometric structures of the Au:S cores of $Au_{25}(SR)_{18}$.[20] Finally, we note that the mass spectrometric approach employed here is highly effective in determining the chemical compositions and charge states of hydrophobic Au:SR clusters.

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Supporting Information Available: Experimental procedures and characterization (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) The charge state of $Au_{25}(SG)_{18}$ (ref 3b) is 0 or 1− or a mixture thereof on the basis of a comparison of the optical spectra of **2**−**4**.

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