Isolation of Ubiquitous Au$_{40}$(SR)$_{24}$ Clusters from the 8 kDa Gold Clusters

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Thiolate-protected Au nanoclusters have attracted considerable research interest due to their interesting optical, electronic, and charging properties as well as potential applications in catalysis, biomedicine, and nanoelectronics.[1–8] When the particle size is less than ~2 nm, their structure as well as physical and chemical properties exhibit fundamental differences from those of their larger counterparts, "nanocrystals"; such drastic changes are primarily caused by strong quantum confinement effects in clusters.[1,9,10] In recent years, a number of well-defined Au$_n$(SR)$_m$ clusters have been individually synthesized (or isolated from a mixture).[9–16] Early seminal work by Whetten and co-workers identified a series of gold clusters with core masses of 5, 8, 14, 22, and 29 kDa.[9] A major task is to determine the exact formula of each of these clusters and their structure; this is particularly important to fully understand the new physicochemical properties of these clusters. With the efforts of multiple research groups, the formula of 5, 8, 14, 22, and 29 kDa have been identified as Au$_{25}$(SR)$_{18}^{-}$, Au$_{38}$(SR)$_{24}$, Au$_{68}$(SR)$_{34}$, Au$_{102}$(SR)$_{44}$, and Au$_{144}$(SR)$_{60}$, respectively.[10,13–18] In addition, some other well-defined clusters have been attained, e.g., Au$_{20}$(SR)$_{16}$.[19] A great deal of theoretical work has been carried out on gold thiolate clusters.[20–24] On the basis of the currently available results, the particular stability of most of the Au$_n$(SR)$_m$ clusters seems to be consistent with electron-shell closing; that is, the 2, 8, 18, 20, 34, 40, and 58 "free" or valence electrons are critical numbers due to atomic-like electron shells in gold clusters.[20a]

Despite these impressive achievements, a number of major issues remain to be tackled.[1] From the viewpoint of critical sizes of Au$_n$(SR)$_m$ clusters, interesting questions are what additional sizes may exist as stable clusters and what number of free-electron counts these robust clusters possess.[1,25,26] A prerequisite for answering these questions is to prepare well-defined, robust Au$_n$(SR)$_m$ clusters. Herein, we report the identification and isolation of a new cluster, formulated as Au$_{40}$(SC$_2$H$_4$Ph)$_{24}$, based upon mass spectrometry analyses including matrix-assisted laser desorption ionization (MALDI) and electrospray ionization (ESI) methods.

This new cluster is found to coexist in good yield with Au$_{38}$(SC$_2$H$_4$Ph)$_{24}$ in the ~8 kDa clusters; note that 8 kDa refers to the core mass. In this work, we attained separation of this new species by size exclusion chromatography. The formula of Au$_{40}$(SC$_2$H$_4$Ph)$_{24}$ and its purity are further verified by ESI-MS, and its distinctive optical absorption spectrum is investigated and compared with its "twin" cluster Au$_{38}$(SC$_2$H$_4$Ph)$_{24}$.

The synthesis and isolation of Au$_{40}$(SC$_2$H$_4$Ph)$_{24}$ clusters involve three main steps (see Supporting Information for details). The synthetic procedure is as was previously reported for the synthesis of Au$_{38}$(SC$_2$H$_4$Ph)$_{24}$ with molecular purity.[27] In the first step, size-mixed Au$_n$(SG)$_m$ clusters (roughly 38 ≤ n ≤ 102, determined by MALDI-MS, —SG≡glutathionate) were prepared by reducing a Au(I)-SG polymer with NaBH$_4$ in an *acetone* solution. The Au$_n$(SG)$_m$ clusters were found to spontaneously precipitate out of solution and deposit onto the wall of the flask. This is due to the low solubility of Au$_n$(SG)$_m$ clusters in acetone. The solids were isolated for subsequent conversion.

In the second step, the Au$_n$(SG)$_m$ mixture is subject to thiol aerobic etching at 80 °C for a prolonged time using excess PhC$_2$H$_4$SH (a toluene solution, 50%v) as the etchant. Intact molecule ions of thiolated

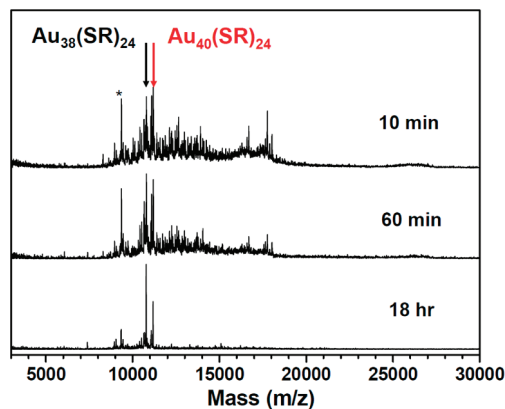**Figure 1.** MALDI mass spectra of Au$_n$(SC$_2$H$_4$Ph)$_m$ clusters after thermal thiol etching for different times. In all three spectra, the asterisk indicates a fragment[27a] of Au$_{38}$(SC$_2$H$_4$Ph)$_{24}$.

Au clusters were observed using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenyldidene] malononitrile (DCTB) as the matrix in MALDI-MS.[28] As shown in Figure 1, the initial stage (~10 min) showed size-mixed Au$_n$(SC$_2$H$_4$Ph)$_m$ clusters from ligand exchange/ phase transfer of water-soluble Au$_n$(SG)$_m$ to organic soluble Au$_n$(SC$_2$H$_4$Ph)$_m$. Interestingly, MALDI-MS analysis showed a distinct peak at ~11175.7 Da (highest intensity in the mass spectrum, Figure 1), which is readily assigned as Au$_{40}$(SC$_2$H$_4$Ph)$_{24}$ (theoretical FW: 11171.9) using Au$_{38}$(SC$_2$H$_4$Ph)$_{24}$ as a reference and by recognizing the 394 Da difference (i.e., 2Au atoms). After etching for ~18 h, only two main peaks are remaining at 10780.5 and 11175.7 in the mass spectrum (Figure 1); they are assigned Au$_{38}$(SC$_2$H$_4$Ph)$_{24}$ and Au$_{40}$(SC$_2$H$_4$Ph)$_{24}$, respectively. Thus, over the prolonged thermal thiol etching process (~18 h) the starting polydispersed Au$_n$(SR)$_m$ clusters are gradually converted to Au$_{38}$(SC$_2$H$_4$Ph)$_{24}$ and Au$_{40}$(SC$_2$H$_4$Ph)$_{24}$ clusters. This process seems to be driven by the particular stability of these two clusters.

Note that the small peaks in the range of 9341 to 10 780 Da in the mass spectrum (Figure 1) are fragments of Au$_{38}$(SC$_2$H$_4$Ph)$_{24}$, instead of genuine clusters in the sample; this is evident by observation that nearly identical fragments are observed in MALDI analysis of pure Au$_{38}$(SC$_2$H$_4$Ph)$_{24}$ clusters under similar conditions.[27a] The peak at 9341 is a main fragment assigned to Au$_{34}$(SC$_2$H$_4$Ph)$_{19}$S.[27a] Of further note, a longer time for etching (>18 h, 80 °C) results in decomposition of Au$_{40}$(SC$_2$H$_4$Ph)$_{24}$, and pure Au$_{38}$(SC$_2$H$_4$Ph)$_{24}$ clusters result; however, an even longer reaction time (>40 h) results in decomposition of Au$_{38}$(SC$_2$H$_4$Ph)$_{24}$ as well. These observations demonstrate Au$_{40}$(SC$_2$H$_4$Ph)$_{24}$ is slightly less stable than Au$_{38}$(SC$_2$H$_4$Ph)$_{24}$, but still much more stable than larger clusters of 40 < n ≤ 102, evidenced by the gradual conversion of Au$_n$ (40 < n ≤ 102) into Au$_{40}$ and Au$_{38}$ over the 18 h etching process. To obtain Au$_{40}$(SC$_2$H$_4$Ph)$_{24}$, we quenched the etching reaction at ~18 h.

The last step is to separate Au$_{40}$(SC$_2$H$_4$Ph)$_{24}$. We have attempted various methods. Isolation of Au$_{40}$(SC$_2$H$_4$Ph)$_{24}$ is not successful through the solvent extraction approach, mainly because they are too close in size and solubility. The hydrophobicity of these clusters also precludes
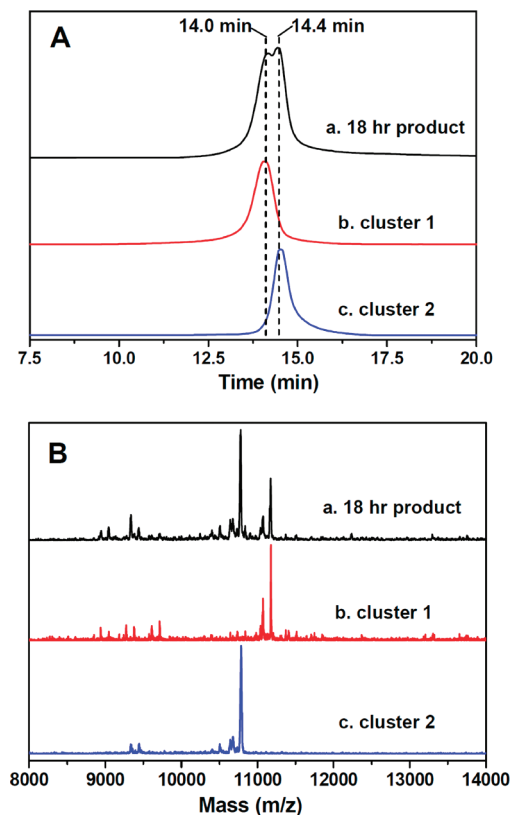
Figure 2. (A) SEC chromatograms of clusters (monitored by DAD at 750 nm wavelength). (B) MALDI mass spectra of the crude product and isolated clusters (**1** and **2**); see Figure S1 for wider mass range spectra.

isolation via gel electrophoresis, whereas this method was previously demonstrated in isolating $Au_n(SG)_m$ clusters.[9a,10] We finally resorted to size exclusion chromatography (SEC). In a previous work Tsukuda et al. employed recycling-SEC to separate Au clusters of core masses of 8, 11, 21, and 26 kDa.[29] In our work, we found that $Au_{38}(SC_2H_4Ph)_{24}$ and $Au_{40}(SC_2H_4Ph)_{24}$ are indeed separable by SEC.

Figure 2A (profile a) shows a typical size exclusion chromatogram of the 18 h etched product, and two peaks (14.0 and 14.4 min) were found. The online recorded UV−vis spectra (ranging from 12.5 to 14.0 min) are almost superimposable, indicating the high purity of the eluted clusters (species **1**), also evidenced by ESI-MS analysis (*vide infra*). Similarly, the optical spectra for the 14.4 to 15.6 min eluate also show no variations; hence, the eluate constitutes a second pure species (**2**). The in-between eluate (from 14.0 to 14.4 min) is a mixture, indicated by the evolving spectra with time (temporal resolution, 0.1s). Thus, we only collected the eluate from 12.5 to 14.0 min (**1**) and from 14.4 to 15.6 min (**2**), respectively. MALDI-MS analyses confirmed

that **1** is $Au_{40}(SC_2H_4Ph)_{24}$ while **2** is $Au_{38}(SC_2H_4Ph)_{24}$ (Figure 2B); note that some fragments are seen in the MALDI mass spectrum of $Au_{40}(SC_2H_4Ph)_{24}$, e.g. 11 069 as $Au_{40}(SC_2H_4Ph)_{23}S$ (see Figure S2 and Table S1). We have rerun the SEC of the isolated clusters (Figure 2A, profiles b and c). The Au_{40} and Au_{38} clusters show sharp peaks centered at 14.0 and 14.4 min, respectively. These retention times are consistent with the peak values from the mixture analysis (cf. profile a). The successful separation of these two clusters is attributed to their relatively narrow elution peaks. The relatively sharp elution peaks of Au_{40} and Au_{38} clusters render the 12.5−14.0 min eluate quite pure Au_{40} clusters, as Au_{38} clusters do not elute until 14.0 min (Figure 2A); similarly, the range of 14.4 to 15.6 min gives rise to pure Au_{38}, as Au_{40} elution stops at 14.4 min.

The isolated $Au_{40}(SC_2H_4Ph)_{24}$ cluster is further characterized by ESI-MS to verify its formula, as MALDI-MS tends to break clusters and a loss of gold atoms and/or ligands often occurs, even when the laser intensity is kept at a minimum. The core mass of **1** is determined to be ∼8.6 kDa (Figure S3), which is ∼0.4 kDa higher than the core mass of $Au_{38}(SR)_{24}$ clusters. In ESI analysis, to enhance cluster ionization CsOAc is added to a solution of clusters and Cs-adducts of Au clusters are typically formed.[14] As shown in Figure 3A, the ESI mass spectrum shows a single intense peak at 11 304.9 Da, assigned to $Au_{40}(SC_2H_4Ph)_{24}Cs$ (theoretical FW: 11 304.9). The single intense peak indicates the high purity of the chromatographically isolated $Au_{40}(SC_2H_4Ph)_{24}$ clusters. Taken together, both MALDI and ESI analyses confirm the assignment of the $Au_{40}(SC_2H_4Ph)_{24}$ formula of this new cluster and its purity.

We further investigated the optical absorption property of isolated $Au_{40}(SC_2H_4Ph)_{24}$ clusters. Unlike $Au_{38}(SC_2H_4Ph)_{24}$ clusters, which show multiple distinct absorption peaks at 1.18, 1.66, 2.0, 2.2, 2.39, and 2.53 (peaks >2.6 eV are not prominent, Figure S4), $Au_{40}(SC_2H_4Ph)_{24}$ clusters do not exhibit pronounced peaks; instead, only three steps at ∼2.2, 3.2, and 4.4 eV are observed in the optical spectrum (Figure 3B). By extrapolating the profile to zero absorbance, the HOMO−LUMO gap of $Au_{40}(SC_2H_4Ph)_{24}$ is estimated to be ∼1.0 eV, comparable to $Au_{38}(SR)_{24}$ (0.9 eV). Given the only two-atom difference between $Au_{40}(SC_2H_4Ph)_{24}$ and $Au_{38}(SC_2H_4Ph)_{24}$, the observed distinct differences in optical absorption are somewhat surprising. This behavior might indicate some major structural differences between Au_{40} and Au_{38} clusters.

To confirm the molecular formula of $Au_{40}(SR)_{24}$ clusters and also investigate if this cluster is ubiquitous (i.e., regardless of the type of thiolate), we replaced PhC_2H_4SH with other types of thiols in the etching process, such as 1-hexanethiol ($C_6H_{13}SH$) and 1-pentanethiol ($C_5H_{11}SH$). As shown in Figure 4, after etching the $Au_n(SG)_m$ mixture with $C_6H_{13}SH$ for 46 h, the predominant species are similar to the case of PhC_2H_4SH; that is, $Au_{40}(SC_6H_{13})_{24}$ (peak **a_1** at 10 691.2 Da, theoretical: 10 692.2) and $Au_{38}(SC_6H_{13})_{24}$ (peak **b_1** at 10 295.6 Da, theoretical: 10 298.3) are observed. Similarly, with 1-pentanethiol (46
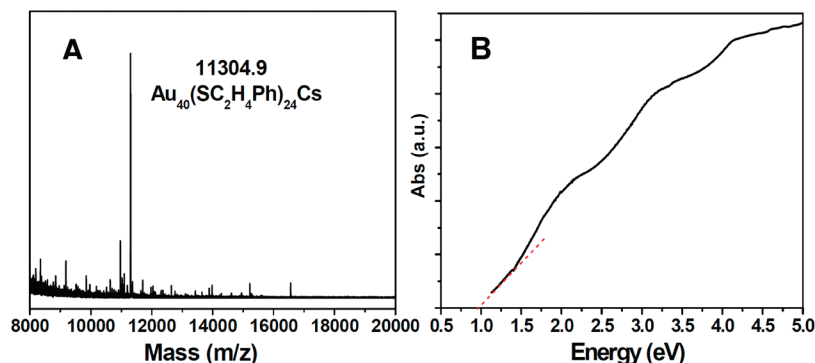

Figure 3. (A) ESI mass spectrum of isolated $Au_{40}(SC_2H_4Ph)_{24}$ clusters. (B) UV−vis spectrum of $Au_{40}(SC_2H_4Ph)_{24}$ clusters.
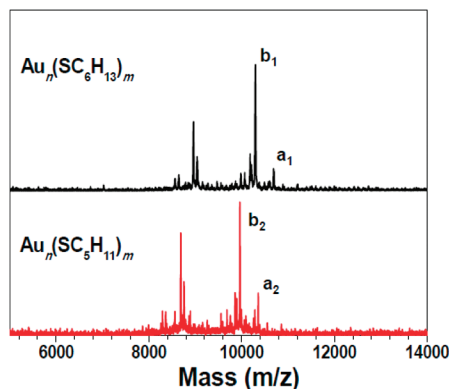
Figure 4. MALDI mass spectra of $Au_n(SC_6H_{13})_m$ and $Au_n(SC_5H_{11})_m$ (both etched for 46 h). Peak a is from $Au_{40}(SR)_{24}$; peak b is from $Au_{38}(SR)_{24}$.

Table 1. Possible Structural Models of $Au_{40}(SCH_2CH_2Ph)_{24}$ Clusters

Number of $Au_2(SR)_3$ staples	Number of $Au(SR)_2$ staples	Au core
8	0	Au_{24}
6	3	Au_{25}
4	6	Au_{26}
2	9	Au_{27}
0	12	Au_{28}

h etching) the final species are $Au_{40}(SC_5H_{13})_{24}$ (peak a_2 at 10 357.6 Da, theoretical: 10 355.7) and $Au_{38}(SC_5H_{11})_{24}$ (peak b_2 at 9962.4 Da, theoretical: 9961.6). The zoomed-in MALDI mass spectra and assignment of peaks are shown in Figure S5 and Table S2. Note that the lower mass peaks are fragments of $Au_{38}(SC_5H_{11})_{24}$ and $Au_{40}(SC_6H_{13})_{24}$ clusters, similar to the case of phenylethylthiolate as ligand. Taken together, all these data confirm the above assignment of the $Au_{40}(SR)_{24}$ formula and demonstrate that this cluster is ubiquitous, as is $Au_{38}(SR)_{24}$.

The $Au_{40}(SR)_{24}$ formula indicates that the cluster has 16 free electrons (assuming each thiolate consumes one 6s electron of gold). The electron count is 2e more than that of $Au_{38}(SR)_{24}$. Zeng et al.[22a] previously predicted that $Au_{38}(SR)_{24}$ should possess a face-fused biicosahedral Au_{23} core and that the core is further capped by three S−Au−S and six S−Au−S−Au−S staples residing on the Au_{23} waist and two ends, respectively. Based on their work and some empirical rules suggested by Tsukuda et al.,[15] several possibilities of the structural model of $Au_{40}(SR)_{24}$ are listed in Table 1; for example, one possibility would be a Au_{25} core plus three $Au(SR)_2$ and six $Au_2(SR)_3$ staples. Given the large differences in optical absorption spectrum of Au_{40} compared to Au_{38}, we also suspect a Au_{28} core capped by 12 $Au(SR)_2$. Note that herein we presume only dimeric $Au_2(SR)_3$ and monomeric $Au(SR)_2$ staples are present in the structure. DFT calculations should offer more details on the atomic arrangements of the core and staple motifs. The 16 free electron number is indeed not in the superatom series (e.g., critical free electrons of 2, 8, 18, 20, 34, 40, 58, and 92). It is worth noting that several reported clusters such as $Au_{44}(SPh)_{28}$ and $Au_{39}(SG)_{23}$ also possess 16e.[9c,10] The 16e indicates that the core may not necessarily be spherical, for the critical numbers are predicted on the basis of a spherical potential in the jellium model.[30]

In summary, we have identified a new gold−thiolate cluster and isolated it from the ~8 kDa clusters containing $Au_{38}(SC_2H_4Ph)_{24}$. The cluster formula is determined to be $Au_{40}(SC_2H_4Ph)_{24}$ by both MALDI- and ESI-MS. Unlike $Au_{38}(SC_2H_4Ph)_{24}$ clusters, the UV−vis spectrum of $Au_{40}(SC_2H_4Ph)_{24}$ clusters shows less prominent absorption peaks. This $Au_{40}(SR)_{24}$ cluster constitutes another robust and ubiquitous species in the potpourri of $Au_n(SR)_m$ clusters and is useful for future studies of their new properties and potential applications such as in catalysis. The successful isolation of $Au_{40}(SC_2H_4Ph)_{24}$ indicates that the previous 8 kDa (core mass) Au cluster species should contain two

stable clusters (Au_{38} and Au_{40}), though $Au_{38}(SR)_{24}$ is slightly more robust than $Au_{40}(SR)_{24}$. The distinct optical spectral differences between $Au_{40}(SC_2H_4Ph)_{24}$ and $Au_{38}(SC_2H_4Ph)_{24}$ imply a high sensitivity of the $Au_n(SR)_m$ optical properties to the composition and structure.

Supporting Information Available: Details of experimental procedures and characterization; MALDI mass spectra of $Au_n(SR)_m$ clusters; optical spectrum of $Au_{38}(SR)_{24}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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