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Chromatographic Isolation of “Missing” Au_{55} Clusters Protected by Alkanethiolates

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Since the pioneering work by Schiffrin and co-workers,[1] thiolate-protected gold (Au:SR) clusters have been the focus of numerous studies.[2] One of the unique features of Au:SR clusters is that they can be isolated as stable chemical entities according to core size through fractional crystallization,[3] chromatography,[4] and electrophoresis.[5] For example, Whetten and co-workers have isolated alkanethiolate-protected gold (Au:SC_x) clusters with a core mass of 8 kDa (∼38 atoms), 14 kDa (∼75 atoms), 22 kDa (∼101 atoms), and 28 kDa (∼146 atoms) through elaborative fractional crystallization[3a,c] and studied the size dependence of the core geometries, electronic structures, optical, and electrochemical properties.[6] Preferential formation of these distinct clusters may stem from stabilities of packed geometries of the Au cores as supported by Landman:[7] truncated octahedral and decahedral geometries have been theoretically predicted for the 8 and 14 kDa clusters, respectively. This explanation is further supported by the fact that the corresponding Au_{39},[8] Au_{32-36},[9] and Au_{75} clusters[10] stabilized by phosphines have been isolated. However, the Au_{55}:SC_x cluster compound, which is a counterpart of the well-known $Au_{55}(PR_3)_{12}Cl_6$,[11] has not been isolated so far.[12,13] Very recently, Murray and co-workers have observed a small amount of 10 kDa clusters (most likely, Au_{55}) in Au:SC_6 clusters prepared by the ligand exchange reaction of $Au_{55}(PPh_3)_{12}Cl_6$ with hexanethiol.[14] This hints at the possibility that the Au_{55}:SC_x clusters can be synthesized via a route different from that of the conventional Brust method.[1] In the present paper, we report on the first synthesis of Au_{55}:SC_x clusters (x = 12, 18) by high-resolution chromatographic fractionation of Au:SC_x clusters prepared by thiolation of polymer-stabilized Au clusters (∼1.3 nm). Some structural characterization is also presented.

The Au:SC_x clusters (x = 12, 18) were prepared by a two-phase method. Briefly, Au clusters (ϕ = 1.3 ± 0.3 nm) stabilized by poly(*N*-vinyl-2-pyrrolidone) (PVP, K-30, M_w = 40 kDa) (Au:PVP) were first prepared by chemical reduction as reported previously.[15] Then, the toluene solution of C_xSH (5 mM, 50 mL) was poured onto a hydrosol of the Au:PVP (1 mM, 50 mL). The mixture was stirred vigorously for 2 h under ambient conditions. The brown color of the Au clusters was completely transferred from the aqueous layer to the organic layer without any formation of floccules. The organic phase was separated and evaporated in vacuo to yield Au:SC_x having a waxy texture. The Au:SC_x clusters were incubated at 80 °C for 24 h in neat C_xSH liquid under air. Free C_xSH was removed by repeated purification with ethanol.

In the following, GPC fractionation will be described in detail with a focus on the Au:SC_{18} clusters.[16] Figure 1 shows a typical recycling chromatogram of the Au:SC_{18} clusters (60 mg in 2.5 mL of toluene) obtained using two columns with a total exclusion limit of 5×10^4.[17] The efficiency of the elution estimated from the optical absorbance was 90−100%.[16] After repeated passages through the column, the peak separates into two. Although the relative intensities of the two peaks varied with batches of the cluster samples, their retention times were highly reproducible. In contrast, the chromatogram of clusters prepared without incubation in neat $C_{18}SH$ exhibits a broad and featureless peak (the dotted line in Figure 1a). This remarkable difference indicates that the etching treatment is essential to enhance the population of certain stable clusters.[16,18] Namely, two Au:SC_{18} having distinct hydrodynamic diameters are formed by the preparation method employed here. To isolate these two dominant clusters, the eluent at the fifth recycle was separated into two fractions (**I** and **II**). These crude fractions were then reinjected into the column individually. Figure 1b shows the recycling chromatograms of fractions **I** and **II**.

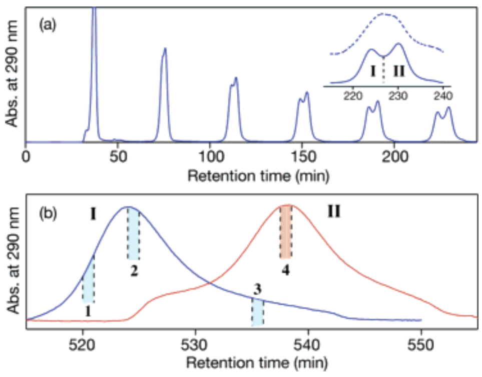

Figure 1. (a) Chromatogram of recycling GPC of the Au:SC_{18} clusters. Dotted curve in the inset is the data for the sample without etching treatment. (b) Recycling chromatograms of two fractions **I** and **II**.

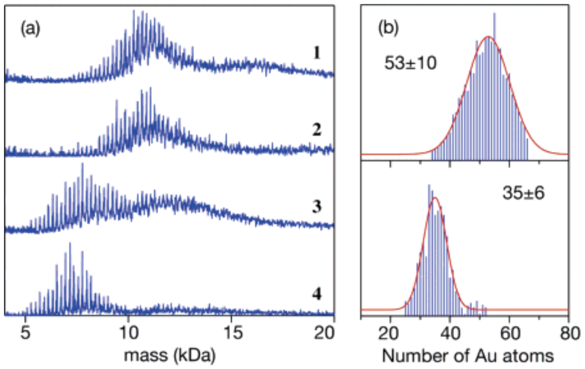

Figure 2. (a) LDI mass spectra of fractions **1**−**4** in the positive ion mode. (b) Histograms of the core numbers for fractions **2** and **4**.

The Au:SC_{18} clusters contained in the eluent were characterized by laser-desorption ionization (LDI) mass spectrometry, which has been used as a reliable tool for the core-size evaluation of the Au:SR clusters.[19] Typical mass spectra of fractions **1**−**4** are displayed in Figure 2a. The peaks are assigned to $Au_nS_m^+$.[16,19] The mass distributions reflect the core sizes in the samples since they do not change appreciably with the laser fluence in the range of 0.3−3.0 mJ/pulse.[16] As expected from the GPC separation mechanism, the

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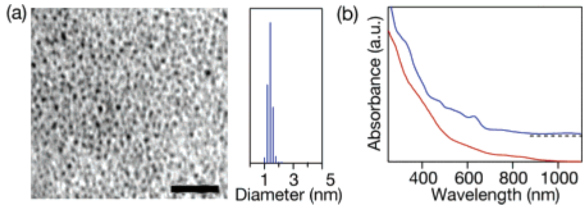

Figure 3. (a) TEM image and core-size distribution of Au_{55}:SC_{18}. The scale bar represents 20 nm. (b) Optical absorption spectra of Au_{55}:SC_{18} (red) and the 8 kDa clusters (blue).

cluster size decreases in going from **1** to **3**. Fraction **2** contains only 11 kDa clusters, while fractions **1** and **3** are contaminated by ~16 and ~8 kDa clusters, respectively. Fraction **4** is dominated by the 8 kDa clusters, which have a higher purity than those obtained previously by fractional crystallization.[3a,c] To evaluate the size of Au:SC_{18} contained in fractions **2** and **4** more quantitatively, the integrated intensities $I(n) = \sum_m I(n, m)$ are plotted as a function of n in Figure 2b, where $I(n, m)$ represents the intensity of $Au_nS_m^+$ in the mass spectrum. Clearly, fractions **2** and **4** contain Au_n:SC_{18} with an average core number of $n = 53 \pm 10$ and 35 ± 6, respectively. Since the 11 kDa clusters are formed more abundantly as compared with their neighbors, we conclude that they correspond to highly stable Au_{55} clusters with a closed-shell structure. The Au_{55}:SC_{12} clusters could be isolated in a similar manner.[16]

Some results of the characterization of the newly isolated Au_{55}:SC_{18} clusters are presented here. TEM analysis confirms that the Au_{55}:SC_{18} clusters we isolated are highly monodisperse in size and are of reasonable sizes, namely, in the 1.2−1.4 nm range (Figure 3a). Thermogravimetric analysis suggests that the chemical composition can be represented as $Au_{55}(SC_{18})_{32}$.[16] The $C_{18}S$ monolayers of Au_{55}:SC_{18} in toluene dispersion are highly disordered: (1) the symmetric and anti-symmetric CH_2 stretching modes were 2853 and 2924 cm^{-1}, respectively, which suggest liquid-like structures;[16,20] (2) the nominal monolayer thickness of ~2.0 nm, evaluated from the hydrodynamic diameter of Au_{55}:SC_{18} (5.4 nm),[16] was significantly smaller than the molecular length in the all-trans form (2.5 nm). The disordered monolayer structures are probably due to the large curvature and/or small facets of the underlying Au_{55} core. Figure 3b shows the optical spectra of Au_{55}:SC_{18} and the 8 kDa clusters, with the latter closely corresponding to results reported by Whetten.[3c] The spectrum of Au_{55}:SC_{18} is more or less structured, suggesting a rather molecular behavior when compared to larger clusters.[3]

Successful isolation of the 11 kDa (Au_{55}:SC_x) clusters is enabled by the following key features of the present study:

(1) Murray's group has reported that the Au_{55}:SC_6 clusters are obtained as a minor species in the reaction of $Au_{55}(PPh_3)_{12}Cl_6$ with hexanethiol.[14] This finding and the present results suggest that the thiolate ligation of Au cluster samples containing preformed Au_{55} yields novel Au_{55}:SC_x compounds, not obtained by the conventional reduction of Au(I)−SC_x polymer. This preparation route in combination with subsequent etching with free thiols enabled us to selectively populate the Au_{55}:SC_x clusters.

(2) The recycling GPC allows size separation of the Au:SC_x clusters with high reproducibility, resolution, and throughput. It allows the separation of $Au_{\sim 38}$ and $Au_{\sim 55}$, whose diameters differ by only 0.1−0.2 nm. The quantity we obtained by our preparative GPC system was typically ~10 mg, which is sufficient for most measurements and applications.

In summary, we have succeeded in isolating unprecedented Au_{55} clusters protected by alkanethiolates. We owe this to our preparation technique based on thiolation of Au:PVP (~1.3 nm) and subsequent etching treatment and high-resolution size separation by GPC. We believe that stable Au_{55}:SC_x clusters will constitute a prototype for fundamental studies and applications.

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Supporting Information Available: Details of the synthesis, separation, and characterization of the Au:SC_x clusters. This material is available free of charge via the Internet at http://pubs.acs.org.

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