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Separation of Precise Compositions of Noble Metal Clusters Protected with Mixed Ligands

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Ⓢ *Supporting Information*

ABSTRACT: This report describes the precise and systematic synthesis of $PdAu_{24}$ clusters protected with two types of thiolate ligands (-SR1 and -SR2). It involved high-resolution separation of metal clusters containing a distribution of chemical compositions, $PdAu_{24}(SR1)_{18-n}(SR2)_n$ (n = 0, 1, 2, ..., 18), to individual clusters of specific n using high-performance liquid chromatography. Similar high-resolution separation was achieved for a few ligand combinations as well as clusters with other metal cores, such as Au_{25} and Au_{38}. These results demonstrate the ability to precisely control the chemical composition of two types of ligands in thiolate-protected mono- and bimetallic metal clusters. It is expected that greater functional control of thiolate-protected metal clusters, their regular arrays, and systematic variation of their properties can now be achieved.

Small metal clusters (≤2 nm core diameter) are attracting attention as new functional materials because they have size-specific physical/chemical properties that are not present in their corresponding bulk metals. Among these metal clusters, thiolate-protected metal clusters ($M_n(SR)_m$) have the potential to be useful materials because they are stable chemical substances. Since the first report of thiolate-protected gold clusters ($Au_n(SR)_m$) in 1994,[1] research on $M_n(SR)_m$ has been pursued across a wide range of fields. Through those studies, synthetic methodology for the production of metal clusters, especially $Au_n(SR)_m$, has developed rapidly. Multiple high-resolution size separation methods and techniques for evaluating chemical composition have been established, and it is now possible to treat $Au_n(SR)_m$ as a compound with a well-defined chemical composition.[2−5] Stable clusters (magic clusters) such as $Au_{25}(SR)_{18}$, $Au_{38}(SR)_{24}$, and $Au_{144}(SR)_{60}$ have been reported,[2−5] and methods for size-selective and bulk-scale synthesis have been established.[6−9] Successes in single-crystal X-ray structure analysis[10−13] have clarified the geometrical structure of $Au_n(SR)_m$, and these experimental results, along with theoretical studies,[14] have shown that some types of $Au_n(SR)_m$ have optical isomers. Methods have been established to separate the optical isomers of $Au_{38}(SR)_{24}$.[15] The structural rules for stabilizing $Au_n(SR)_m$ have also been elucidated,[16−19] and design guidelines for producing new stable clusters are emerging. In addition, a number of reports describing precise syntheses of silver clusters[20−22] and alloy clusters[23−27] have been published. Thus, the science of precise and efficient synthesis of metal clusters is becoming more established.

Controlling the chemical composition of the ligands surrounding the metal core of $M_n(SR)_m$ is an effective method for the functionalization of clusters. Changing the physical/chemical properties of $M_n(SR)_m$ can be accomplished by replacing some of its ligands with other thiolates.[9,28−30] In addition, conferring or changing functional properties (e.g., molecular recognition ability, catalytic activity, or fluorescence resonance energy transfer)[31−33] and forming regular arrangements[34] become possible by the introduction of functional thiolates. However, in cluster synthesis, where multiple types of thiolates are used as ligands, a distribution of ligands with varying chemical compositions is formed,[35] with a few limited exceptions.[36] Thus, to achieve precise control of the function and specific arrangement of $M_n(SR)_m$, development of a new methodology for precisely separating clusters, which also controls the chemical composition of the ligands, is needed.[37−41]

This report describes the precise and systematic creation of $PdAu_{24}$ clusters[23,42] with two types of thiolate ligands, -SR1 and -SR2. This was achieved through the separation of metal clusters with ligands having a distribution of chemical compositions using high-performance liquid chromatography (HPLC). This method is applicable to clusters incorporating various ligand combinations, as well as to clusters with other metal cores; therefore, it has broad application potential.

$PdAu_{24}$ clusters[23,42] protected by two types of thiolate ligands were synthesized as described in Supporting Information I. Briefly, $PdAu_{24}(SC_{12}H_{25})_{18}$ with dodecanethiolate ligands was placed in a solution with other thiols (4-*tert*-butylbenzylmercaptan (BBSH), $C_6H_{13}SH$, $C_{10}H_{21}SH$, $C_{16}H_{33}SH$, and PhC_2H_4SH) and made to undergo ligand-exchange reaction.[9,43−47] For $PdAu_{24}$ clusters synthesized in this way, the chemical composition of the ligands had a wide distribution (Figure 1a).[47] For these clusters, the polarities are expected to be different, depending on the chemical composition of the ligands. HPLC with a reverse-phase column is an effective method for separating metal clusters with different polar-

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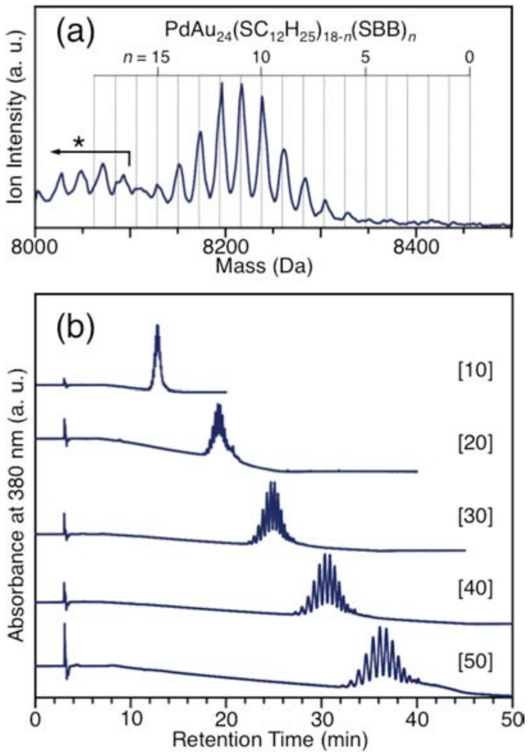

Figure 1. (a) Negative-ion MALDI mass spectrum of $PdAu_{24}(SC_{12}H_{25})_{18-n}(SBB)_n$ (n = 6−16). The asterisk indicates laser-induced fragments.[35] (b) Chromatograms of $PdAu_{24}(SC_{12}H_{25})_{18-n}(SBB)_n$ (n = 6−16) at each gradient program (see the text). The peak observed at 3.0 min was confirmed to be due to the solvent, THF.

ities.[48−50] We separated $PdAu_{24}$ clusters having mixed ligands using various HPLC-based methods.

The high-resolution separation of $PdAu_{24}(SC_{12}H_{25})_{18-n}(SBB)_n$ (n = 6−16) is described below, with the distribution shown in Figure 1a. The separation was accomplished in two steps (Figure S2). First, all clusters were adsorbed onto the stationary phase (the column). Methanol, a solvent in which the clusters were insoluble, was specifically chosen as the mobile phase. Upon injection of a suspension of the clusters, they were adsorbed onto the stationary phase. Next, the adsorbed clusters were eluted slowly from the stationary phase. To accomplish this, the mobile phase was gradually adjusted from pure methanol to tetrahydrofuran (THF) using a linear gradient program (Figure S3). Since $PdAu_{24}(SC_{12}H_{25})_{18-n}(SBB)_n$ dissolves in THF, as the concentration ratio of $[THF]/[CH_3OH]$ was increased, $PdAu_{24}(SC_{12}H_{25})_{18-n}(SBB)_n$ gradually eluted into the mobile phase. Because -SBB (which incorporates a benzene ring) possesses greater polarity than the alkyl chain $-SC_{12}H_{25}$, the $PdAu_{24}(SC_{12}H_{25})_{18-n}(SBB)_n$ containing a greater amount of -SBB eluted into the mobile phase faster (i.e., had a shorter retention time). The two steps described above were the key points to achieving high-resolution separation of $PdAu_{24}(SC_{12}H_{25})_{18-n}(SBB)_n$ (Figure S4).

Figure 1b shows the dependence of $PdAu_{24}(SC_{12}H_{25})_{18-n}(SBB)_n$ chromatograms on the time required to fully replace the mobile phase with THF; the label (e.g., [10]) in the figure indicates that time (in minutes) (also see Figure S3). When the replacement time was 10 min, a set of peaks was observed around a retention time of 11.5 min. In this experiment, only a small gap exists between each peak in a set of peaks, with each peak displaying a large overlap. Taking a longer time to replace the mobile phase resulted in slower elution of the clusters into the mobile phase (i.e., retention time increased). Therefore, greater peak-to-peak separation was obtained, and peak overlap gradually diminished (Figure S5). When the replacement time was set at 40 min or longer, the peaks separated more completely, and peak distribution looked similar to that of the corresponding matrix-assisted laser desorption/ionization (MALDI) mass spectrum (Figures 1a and S6). The fractionation of each peak followed by mass spectrometry analysis revealed that each peak contained clusters with only one chemical composition (Figure S7). Thus, using this method, $PdAu_{24}(SC_{12}H_{25})_{18-n}(SBB)_n$ clusters with ligands of different chemical compositions were separated with high resolution (Figure S8). Similar separation/fractionation experiments were conducted on $PdAu_{24}(SC_{12}H_{25})_{18-n}(SBB)_n$ with various ligand distributions (Figure S9a). Results demonstrated that each distribution was separated into clusters with individual compositions with high resolution (Figure S9b), and all ligand combinations of $PdAu_{24}(SC_{12}H_{25})_{18-n}(SBB)_n$ (n = 0−18) were isolated with high purity (Figure 2); the purity of each separated cluster, estimated from the mass spectrum (Figure 2), was >95%. In this way, the precise and systematic synthesis and separation of $PdAu_{24}(SC_{12}H_{25})_{18-n}(SBB)_n$ (n = 0, 1, 2, ..., 18) protected by two types of thiolate ligands was achieved for the first time (Figure S10).

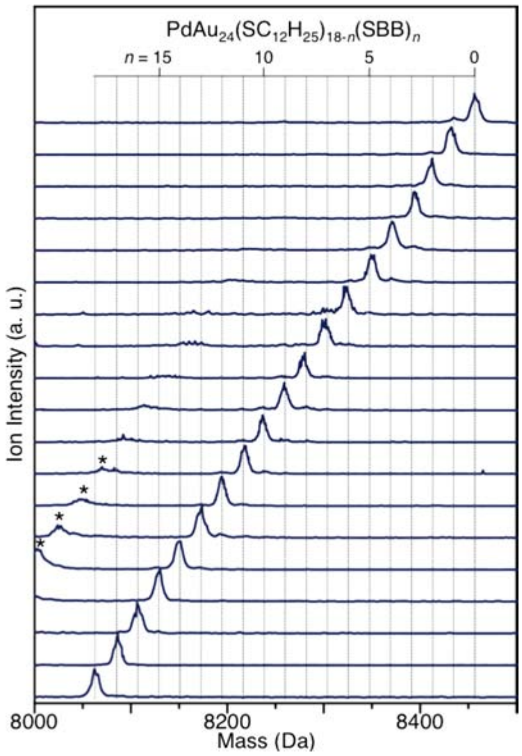

Figure 2. Negative-ion MALDI mass spectra of each cluster of composition $PdAu_{24}(SC_{12}H_{25})_{18-n}(SBB)_n$ (n = 0−18), isolated in this work. The asterisks indicate laser-induced fragments.

To investigate the versatility of this separation method, similar experiments were conducted using $PdAu_{24}$ clusters with combinations of other ligands. $PdAu_{24}(SC_{12}H_{25})_{18-n}(SC_2H_4Ph)_n$ (Figures 3a,b and S11) and $PdAu_{24}(SC_{12}H_{25})_{18-n}(SC_6H_{13})_n$ (Figure S12) underwent similar high-resolution

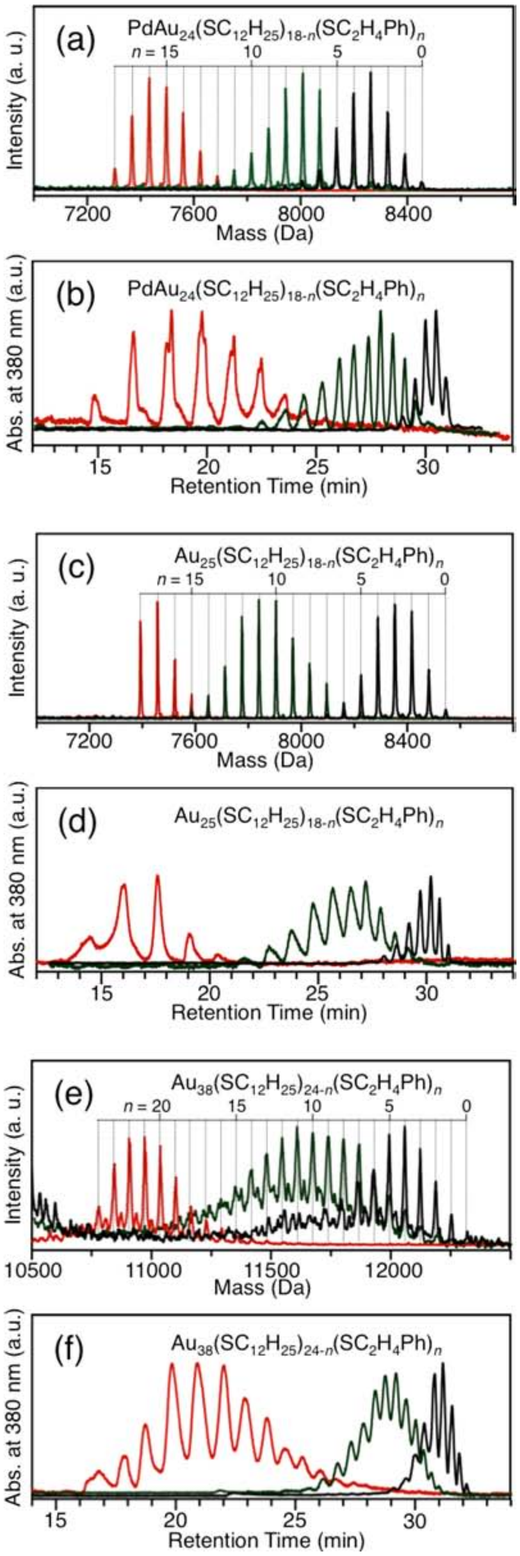

Figure 3. Comparison between the MALDI mass spectrum and chromatogram for (a,b) $PdAu_{24}(SC_{12}H_{25})_{18-n}(SC_2H_4Ph)_n$, (c,d) $Au_{25}(SC_{12}H_{25})_{18-n}(SC_2H_4Ph)_n$, and (e,f) $Au_{38}(SC_{12}H_{25})_{24-n}(SC_2H_4Ph)_n$. MALDI mass spectra (a), (c), and (e) were observed in negative, negative, and positive ion modes, respectively. In (a,b), (c,d), and (e,f), the same color indicates the same sample. The fine structures appearing in the chromatograms (especially (b)) are presumed to be due to the coordination isomers.[51] In (e), peaks which are not assigned to $Au_{38}(SC_{12}H_{25})_{24-n}(SC_2H_4Ph)_n$ are due to laser-induced fragments.

separations.[51] This indicates that the procedure used in the present study is applicable to systems with other ligand combinations also. By using $-SC_{12}H_{25}$ with $-SC_2H_4Ph$ and $-SC_{12}H_{25}$ with $-SC_6H_{13}$, which possess significant differences in relative polarity between them, we ensured that the composition of the ligands affected the solubility of the cluster in the solvent of choice (i.e., mobile phase). Because of this effect, high-resolution separation of $PdAu_{24}$ clusters with combinations of these ligands occurred under the conditions examined in this study. In contrast, for clusters with ligand combinations having smaller polarity differences, $PdAu_{24}(SC_{12}H_{25})_{18-n}(SC_{10}H_{21})_n$ and $PdAu_{24}(SC_{12}H_{25})_{18-n}(SC_{16}H_{33})_n$, the chromatograms did not show clear separation (Figures S13 and S14). This suggests that the precise separation of metal clusters protected by two types of thiolates requires a moderate polarity difference between the two ligand types.

When appropriate ligands were combined, similar high-resolution separation also was achieved for Au_{25} clusters as well as Au_{38} clusters (Figures 3c–f, S15, and S16; samples were prepared as given in Supporting Information I). Thus, the procedure described in this report is effective regardless of the size or composition of the metal core, indicating its broad applicability. The peak resolution and separation of $Au_{25}(SC_{12}H_{25})_{18-n}(SC_2H_4Ph)_n$ were not as sharp as for $PdAu_{24}(SC_{12}H_{25})_{18-n}(SC_2H_4Ph)_n$. $Au_{25}(SR)_{18}$ was synthesized in its negative-ion form $[Au_{25}(SR)_{18}]^-$, but reports have indicated that $[Au_{25}(SR)_{18}]^-$ is oxidized when left in solution, becoming the neutral species $[Au_{25}(SR)_{18}]^0$.[52] For $Au_{25}(SC_{12}H_{25})_{18-n}(SC_2H_4Ph)_n$, this type of distribution of charge states occurs, so an unclear separation of peaks is predicted. In addition, a slight difference in structure exists between $Au_{25}(SR)_{18}$ and $PdAu_{24}(SR)_{18}$; the latter is slightly skewed compared to the former.[23] It is possible that this difference in structure is also associated with the difference in the number of coordination isomers.[51] This could be the reason for the broadness and unclear separation of peaks of $Au_{25}(SC_{12}H_{25})_{18-n}(SC_2H_4Ph)_n$. For $Au_{38}(SC_{12}H_{25})_{24-n}(SC_2H_4Ph)_n$, the broadness and unclear separation are likely to be due to the difference in the number of the coordination isomers in addition to the existence of optical isomers.[15,41]

Finally, although a linear gradient program (Figure S3) was chosen for the experiments described here, the gradient need not necessarily be linear for conducting this type of high-resolution separation. A program that allows each cluster to elute at equivalent intervals will produce a chromatogram that has a shape very similar to the mass spectrum (Figure S17), thus confirming separation of the clusters and making an investigation of the conditions required for separation easier.

In conclusion, the precise and systematic synthesis of metal clusters with two types of thiolate ligands was achieved for the first time. This method has broad applicability and shows potential for use as a basic technology for the study of metal clusters. This study demonstrated the ability to precisely control the chemical compositions of metal clusters with two types of ligands. The results imply that control of the physical/chemical properties of thiolate-protected metal clusters could be achieved at a higher level than previously possible. In addition, information about ligand-exchange effects on the electronic structure of a cluster could be obtained (Figure S10), leading to a deeper understanding of the interactions between the metal core and the ligands[53] and those between the ligands themselves. The results presented imply that structural isomers of clusters with mixed ligands are possible, and investigations of their structure and properties pose challenges for the future.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of experimental procedures and characterization of the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(51) Even when the chemical composition of metal clusters with two types of thiolate protective ligands is the same, there may be coordination isomers with ligands having different configurational arrangements. The configurational differences between these isomers are expected to affect the polarity slightly on the cluster surfaces. Therefore, in principle, these coordination isomers should be separable using the method described here. Thus, we predict that the detailed peak structure observed in the chromatogram of $PdAu_{24}(SC_{12}H_{25})_{18-n}(SC_2H_4Ph)_n$ (Figure 3b) could be due to coordination isomers. When the peaks of $PdAu_{24}(SC_{12}H_{25})_2(SC_2H_4Ph)_{16}$ were actually fractionated and a mass-spectral analysis was conducted, the mass spectrum of each fraction showed only peaks attributable to $PdAu_{24}(SC_{12}H_{25})_2(SC_2H_4Ph)_{16}$. This strongly supports the above interpretation.

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