

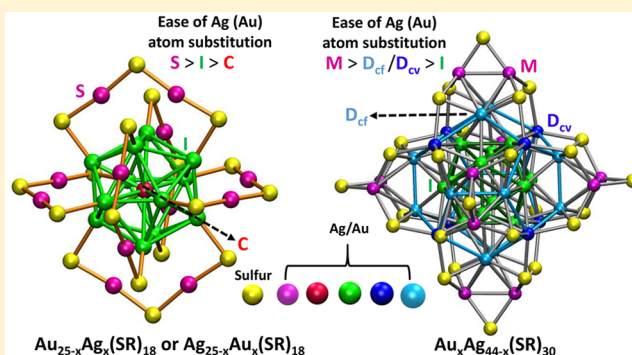
Structure–Reactivity Correlations in Metal Atom Substitutions of Monolayer-Protected Noble Metal Alloy Clusters

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Supporting Information

ABSTRACT: Structure–reactivity correlations in metal atom substitution reactions of three model monolayer-protected alloy clusters, $\text{Ag}_{25-x}\text{Au}_x(\text{SR})_{18}$ (I), $\text{Au}_{25-x}\text{Ag}_x(\text{SR})_{18}$ (II), and $\text{Au}_x\text{Ag}_{44-x}(\text{SR})_{30}$ (III) where $(-\text{SR} = \text{alkyl/arylthiolate})$, are demonstrated. We show that the Au atoms of I and III and Ag atoms of II can be substituted by their reactions with the parent clusters $\text{Ag}_{25}(\text{SR})_{18}$, $\text{Ag}_{44}(\text{SR})_{30}$, and $\text{Au}_{25}(\text{SR})_{18}$, respectively. Though these alloy clusters possess certain common structural features, they exhibit distinctly different reactivities in these substitution reactions. The Au of I and III and Ag of II at the outermost sites, i.e., $\text{M}_2(\text{SR})_3$ staples of I and II and $\text{M}_2(\text{SR})_5$ mounts of III, were substituted more easily compared to those at the inner, icosahedral sites. Au atoms at the icosahedral shell of I were completely substituted while Ag atoms of II at similar positions were not labile for substitution. This shows that the icosahedral shell of II is more rigid compared to that in I. We show that the Au atom in $\text{Ag}_{24}\text{Au}_1(\text{SR})_{18}$ cannot be substituted, which indicates that this Au atom is located at the center of the icosahedral shell. Similarly, when $x \leq 12$, the Au atoms of III cannot be substituted, indicating that these atoms are located in the innermost icosahedral shell. In summary, our results demonstrate that metal atom substitution reactions correlate with the geometric structures of these clusters.



INTRODUCTION

Structure–reactivity correlations are some of the central aspects of chemistry. Chemistry of ligand-protected, atomically precise noble metal clusters^{1–4} is an emerging area in nanomaterials science. The molecule-like nature of these clusters has been well-established by their discrete optical absorption features,⁵ luminescence,⁶ atomically precise compositions,^{7–14} and well-defined geometric structures. Typically, these clusters consist of a core containing a precise number of metal atoms protected by a specific number of ligands; $\text{Au}_{102}(\text{SR})_{40}$,⁹ $\text{Au}_{25}(\text{SR})_{18}$,^{14,15} $\text{Ag}_{25}(\text{SR})_{18}$,¹⁶ $\text{Au}_{38}(\text{SR})_{24}$,¹⁷ $\text{Ag}_{44}(\text{SR})_{30}$,^{10,12} etc., where $-\text{SR}$ is an alkyl/aryl thiolate, are some of the better known examples. Crystallographic studies^{7,11,12,14,18} show that metal atoms and the ligands of these clusters occupy distinct, symmetry-unique sites. For example, $\text{M}_{25}(\text{SR})_{18}$ ($\text{M} = \text{Ag/Au}$)^{14,18,16} clusters constitute an M_{13} icosahedron which is protected by six $\text{M}_2(\text{SR})_3$ staple motifs. Therefore, metal atoms of these clusters can be classified into three symmetry-unique sites, namely, center of the icosahedron (C), surface of the M_{13} icosahedron (I), and $\text{M}_2(\text{SR})_3$ staples (S). The ligands on $\text{M}_{25}(\text{SR})_{18}$ clusters can be classified into two groups, namely, terminal and bridging ligands.^{19,20} Recent spectroscopic investigations revealed conformations and stereochemistry of protecting ligands of such clusters.^{21,22} Structural models have been evolved to understand the growth mechanisms, structural

diversity, and reactivity of ligand-protected clusters.^{23–25} In spite of significant advances in understanding the structural details of these clusters, their structure–reactivity relationships are rarely addressed, except for a few studies on ligand-exchange reactions.^{19,20}

Substitution or exchange of the ligands^{26–30} is one of the earliest of their reactions. Ligand substitution reactions is the only type of their reactions explored to date to understand the structure–reactivity relations in these clusters, and such studies indicated that the ligands on $\text{M}_{25}(\text{SR})_{18}$ ($\text{M} = \text{Ag/Au}$) clusters occupy two distinct sites, terminal and bridging, as mentioned earlier. However, because the ligands are connected to the outermost sites, ligand substitution cannot provide overall structural information on these clusters. Structural framework of these clusters is largely determined by the arrangements of metal atoms in the form of polyhedral shells, such as icosahedra, dodecahedra, etc., and metal–ligand staples ($\text{M}_2(\text{SR})_3$, for example)¹⁴ and mounts ($\text{M}_2(\text{SR})_5$, for example).¹² Hence, the metal atom substitution reaction is expected to provide useful structural information about these clusters. Metal atoms in these clusters can be substituted by

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reactions with metal ions, metal–ligand complexes,^{31–34} or with other clusters.^{35–39} Recently we have shown that metal atoms, ligands, and metal–ligand fragments of these clusters can be substituted through intercluster reactions.^{35–38,40,41}

Here we demonstrate that metal atom substitution reactions of three well-known classes of alloy clusters, namely, $\text{Ag}_{25-x}\text{Au}_x(\text{SR})_{18}$ (**I**), $\text{Au}_{25-x}\text{Ag}_x(\text{SR})_{18}$ (**II**), and $\text{Au}_x\text{Ag}_{44-x}(\text{SR})_{30}$ (**III**) can be used to establish structure–reactivity correlations in them. These alloy clusters were chosen because the positions of metal atoms in them are precisely known either from crystallography or from accurate computations.^{11,34,42–44} Though these clusters possess certain common structural features, we demonstrate that they exhibit distinct reactivities in substitution of their metal atoms. The metal atoms at the outermost shells, i.e., $\text{M}_2(\text{SR})_3$ staples for **I** and **II** and $\text{M}_2(\text{SR})_5$ mounts for **III**, were substituted more easily compared to those at the inner shells. Metal atoms at the middle icosahedral shell of **I** could be completely substituted while those of **II** were not labile for substitution. This shows that the icosahedral shell of **II** is more strongly bound than that in **I**. The Au atom in $\text{Ag}_{24}\text{Au}_1(\text{SR})_{18}$ cannot be substituted, which indicates that this Au atom is located at a unique position, namely the center of the icosahedral shell. Similarly, when $x \leq 12$, the Au atoms of **III** cannot be substituted, indicating that these atoms are located in the innermost shell. In summary, we show that the metal atoms belonging to various sites could be distinguished using these substitution reactions.

EXPERIMENTAL SECTION

Materials. Chloroauric acid trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), *n*-butanethiol (BT), 4-fluorothiophenol (FTP), 2-phenylethanethiol (PET), 2,4-dimethylbenzenethiol (DMBT), tetraoctylammonium bromide (TOAB), tetraphenyl phosphonium bromide (PPh_4Br), and sodium borohydride (NaBH_4) were purchased from Sigma-Aldrich. Silver nitrate (AgNO_3) was purchased from Rankem India. All the solvents used, tetrahydrofuran (THF), methanol, and dichloromethane (DCM), were of analytical grade and used without further purification.

Synthesis of Clusters. $[\text{Ag}_{25}(\text{DMBT})_{18}][\text{PPh}_4]$ was synthesized by adopting a method reported by Bakr et al.¹⁶ $[\text{Au}_{25}(\text{PET})_{18}][\text{TOAB}]$ was synthesized using a reported method.³⁷

$[\text{Au}_{25}(\text{FTP})_{18}][\text{TOAB}]$ was synthesized through the ligand exchange of $\text{Au}_{25}(\text{BT})_{18}$ with FTP. For the synthesis of $\text{Au}_{25}(\text{BT})_{18}$, 2 mL of 50 mM $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ in THF was diluted to 7.5 mL using THF. About 65 mg of TOAB was added to this solution, and the mixture was stirred at 1500 rpm for 30 min at room temperature. The initial yellow color of the solution turned deep red during stirring. About 0.5 mmol of pure BT was added at a stretch while stirring at the same speed. The deep red color slowly turned to yellow, and the solution eventually became colorless after about 45 min. After the solution was stirred further for about 1.5 h, 2.5 mL of ice cold aqueous NaBH_4 (0.2 M) was added in one shot. The solution turned black immediately, and the mixture was stirred for 5 h. The solution was then rotary evaporated; methanol was added, and the precipitate was washed repeatedly with the same and dried.

The $[\text{Ag}_{44}(\text{FTP})_{30}][\text{PPh}_4]_4$ cluster was synthesized following a previously reported method. A 20 mg sample of AgNO_3 and 12 mg of PPh_4Br were thoroughly ground using an agate mortar and pestle for 5 min. About 76 μL of FTP was added to

it at a stretch, and the mixture was ground further for about 3 min. About 45 mg of dry NaBH_4 was added, and the mixture was ground until the pasty mass became brown. This paste was extracted with about 7 mL of DCM and kept undisturbed at room temperature until all the characteristic features of the cluster appeared in the ultraviolet/visible (UV/vis) spectrum. The clusters were purified adopting the same protocol used for $\text{Au}_{25}(\text{SR})_{18}$.

Synthesis of **I and its Reactions with $\text{Ag}_{25}(\text{DMBT})_{18}$.** $\text{Ag}_{25-x}\text{Au}_x(\text{SR})_{18}$ clusters containing 1–6 Au atoms, i.e., $x = 1$ –6 (denoted as **Ia**), were prepared by adding 50 μL of $\text{Ag}_{25}(\text{DMBT})_{18}$ solution (0.63 mM, in DCM) to 700 μL of DCM followed by the addition of 15 μL of $\text{Au}_{25}(\text{PET})_{18}$ (1.25 mM, in DCM). Because the concentration of $\text{Ag}_{25}(\text{DMBT})_{18}$ in this reaction mixture was higher than that of $\text{Au}_{25}(\text{PET})_{18}$, the latter was consumed completely. Due to this, $\text{Ag}_{25-x}\text{Au}_x(\text{SR})_{18}$ alloy clusters formed were rich in Ag, and no Au-rich alloy clusters, i.e., clusters such as $\text{Au}_{25-x}\text{Ag}_x(\text{SR})_{18}$, were observed. The solution of **Ia** thus formed was kept at room temperature for about 1 h for equilibration. This solution of alloy clusters was used for further reactions without any purification. In order to substitute Au atoms in **Ia** by Ag atoms, 120 μL of a solution of $\text{Ag}_{25}(\text{DMBT})_{18}$ (0.63 mM) was added to the above **Ia** solution at a stretch. The extent of metal atom substitution was monitored by measuring the mass spectra of this reaction mixture at various time intervals.

The Au-rich $\text{Ag}_{25-x}\text{Au}_x(\text{SR})_{30}$, containing 15–22 Au atoms (denoted as **Ib**) were prepared by adding 25 μL of $\text{Ag}_{25}(\text{DMBT})_{18}$ solution (0.63 mM, in DCM) to 475 μL of DCM followed by the addition of 40 μL of $\text{Au}_{25}(\text{PET})_{18}$ (1.25 mM, in DCM). The concentration of $\text{Ag}_{25}(\text{DMBT})_{18}$ in this reaction mixture was less than that in the previous synthesis (where 1–6 Au atoms were substituted); therefore, the **Ib** clusters formed in this synthesis contained higher number of Au atoms. In order to substitute the Au atoms of these alloy clusters with Ag atoms, 40 μL of a solution of $\text{Ag}_{25}(\text{DMBT})_{18}$ (0.63 mM, in DCM) was added to it. The extent of metal atom substitution was monitored by measuring the mass spectra of this reaction mixture at various time intervals.

Synthesis of **II and Its Reactions with $\text{Au}_{25}(\text{PET})_{18}$.** $\text{Au}_{25-x}\text{Ag}_x(\text{SR})_{18}$ clusters containing 1–7 Ag atoms, i.e., $x = 1$ –7 (denoted as **IIa**) were prepared by adding 25 μL of $\text{Au}_{25}(\text{PET})_{18}$ solution (1.25 mM, in DCM) to 475 μL of DCM followed by the addition of 5 μL of $\text{Ag}_{25}(\text{DMBT})_{18}$ (0.63 mM, in DCM). Because the concentration of $\text{Ag}_{25}(\text{DMBT})_{18}$ in this reaction mixture was lesser than that of $\text{Au}_{25}(\text{PET})_{18}$, all of the $\text{Ag}_{25}(\text{DMBT})_{18}$ was consumed by $\text{Au}_{25}(\text{PET})_{18}$. Therefore, the **IIa** clusters formed were rich in Au and no Ag-rich alloy clusters, i.e., clusters such as $\text{Ag}_{25-x}\text{Au}_x(\text{SR})_{18}$, were observed. The solution of **IIa** thus formed was kept at room temperature for about 1 h for equilibration. We used this solution of alloy clusters for further reactions without any purification. In order to substitute the Ag atoms of these alloy clusters with Au atoms, 20 μL of a solution of $\text{Au}_{25}(\text{PET})_{18}$ (1.25 mM) was added to the above **IIa** solution at a stretch and mass spectra of this reaction mixture were measured at various time intervals to monitor the substitution of the Ag atoms in **IIa** by Au atoms from the added $\text{Au}_{25}(\text{PET})_{18}$. The extent of metal atom substitution was monitored by measuring the mass spectra of this reaction mixture at various time intervals.

$\text{Au}_{25-x}\text{Ag}_x(\text{SR})_{18}$ clusters containing 9–16 Ag atoms (denoted as **IIb**) were prepared by adding 25 μL of $\text{Au}_{25}(\text{PET})_{18}$ solution (1.25 mM, in DCM) to 475 μL of

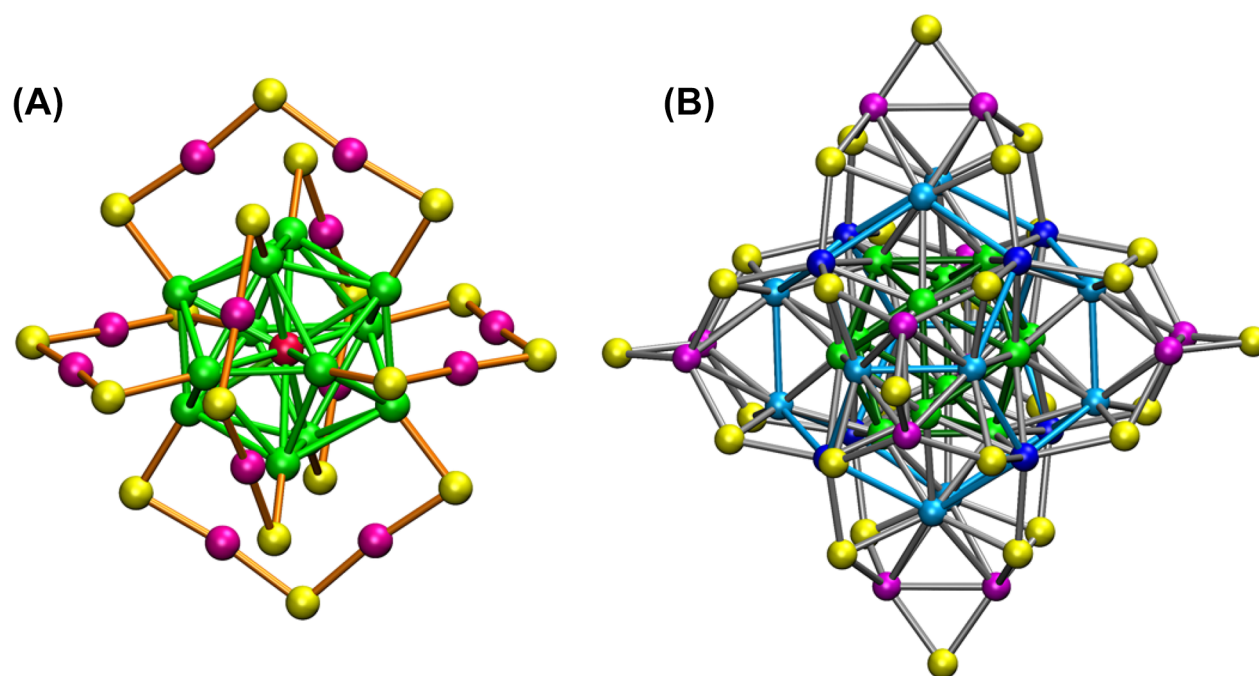


Figure 1. Schematic of the crystal structures of $M_{25}(SR)_{18}$ ($M = Ag/Au$) (A) and $Ag_{44}(SR)_{30}$ (B) showing various symmetry-unique sites of metal atoms and sulfur atoms of the thiolate ligands. The $-R$ groups are omitted for clarity. Color codes of atoms: red, Ag/Au at the center (C) of icosahedron; green, Ag/Au at the surface of icosahedron (I); magenta, Ag/Au at the staple (S) and the mount (M) positions; blue, Ag/Au at the dodecahedral cube vertex (D_{cv}) positions; cyan, Ag/Au at the dodecahedral cube face (D_{cf}) positions; yellow, sulfur.

DCM followed by the addition of 80 μ L of $Ag_{25}(DMBT)_{18}$ (0.63 mM, in DCM). In order to substitute the Ag atoms of **IIb** with Au atoms, 60 μ L of a solution of $Au_{25}(PET)_{18}$ (1.25 mM, in DCM) was added to it. The extent of metal atom substitution was monitored by measuring the mass spectra of this reaction mixture at various time intervals.

Synthesis of **III and Its Reactions with $Ag_{44}(FTP)_{30}$.** $Au_xAg_{44-x}(FTP)_{30}$ clusters containing 4–9 Au atoms (denoted as **IIIa**) were prepared by adding 25 μ L of $Ag_{44}(FTP)_{30}$ solution (0.67 mM, in DCM) into 225 μ L of DCM followed by the addition of 10 μ L of $Au_{25}(FTP)_{18}$ (0.48 mM, in DCM). Because the concentration of $Ag_{44}(FTP)_{30}$ in this reaction mixture was higher than that of $Au_{25}(FTP)_{18}$, all of the $Au_{25}(FTP)_{18}$ were consumed by $Ag_{44}(FTP)_{30}$. Therefore, the **IIIa** clusters formed were rich in Ag and no Au-rich alloy clusters derived from $Au_{25}(FTP)_{18}$, i.e. clusters such as $Au_{25-x}Ag_x(FTP)_{18}$, were observed. The solution of **IIIa** thus formed was kept at room temperature for about 1 h for equilibration. We used this solution of alloy clusters for further reactions without any purification. In order to substitute the Au atoms of **IIIa** with Ag atoms, 20 μ L of a solution of $Ag_{44}(FTP)_{30}$ (0.67 mM) was added to the above **IIIa** solution at a stretch. The extent of metal atom substitution was monitored by measuring the mass spectra of this reaction mixture at various time intervals.

$Au_xAg_{44-x}(FTP)_{30}$ containing more than 12 ($x > 12$) Au atoms (denoted as **IIIb**) were prepared by adding 50 μ L of $Ag_{44}(FTP)_{30}$ solution (0.67 mM, in DCM) to 450 μ L of DCM followed by the addition of 105 μ L of $Au_{25}(FTP)_{18}$ (0.48 mM, in DCM). In order to substitute the Au atoms of **IIIb** with Ag atoms, 40 μ L of a solution of $Ag_{44}(FTP)_{30}$ (0.67 mM, in DCM) was added to it. The extent of metal atom substitution was monitored by measuring the mass spectra of this reaction mixture at various time intervals.

Mass Spectrometric Measurements. Electrospray ionization (ESI) mass spectrometry (MS) measurements were performed using a Waters Synapt G2-Si mass spectrometer which had a maximum resolution of 50 000 in the mass range of interest. More details about the measurements and exact instrumental parameters are given in the [Supporting Information](#).

Ultraviolet–Visible Absorption Spectroscopic Measurements. The UV/vis spectra were recorded using a PerkinElmer Lambda 25 UV/vis spectrometer. Absorption spectra were typically measured in the range of 200–1100 nm.

Visualization of Crystal Structures. The structures of $M_{25}(SR)_{18}$ ($M = Ag/Au$) and $Ag_{44}(SR)_{30}$ ($-R$ groups not shown for clarity) in [Figure 1A,B](#) were built up with the help of Avogadro software package.⁴⁵ We used the coordinates from the crystal structure of $Au_{25}(SR)_{18}$,¹⁸ without any structural relaxation, for building the structures of $M_{25}(SR)_{18}$ ($M = Ag/Au$) because the overall structure of $Au_{25}(SR)_{18}$ and $Ag_{25}(SR)_{18}$ are the same. The actual structures of these two clusters are not exactly the same because of differences in the bond angles in the ligand shell. The structure shown in [Figure 1B](#) is built up using the coordinates from the crystal structure of $Ag_{44}(FTP)_{30}$.¹² All visualizations were created with visual molecular dynamics (VMD) software.⁴⁶

RESULTS AND DISCUSSION

Structures of $M_{25}(SR)_{18}$ ($M = Ag/Au$), $Ag_{44}(SR)_{30}$, and Alloy Clusters Derived from them. The clusters $Ag_{25}(DMBT)_{18}$, $Au_{25}(PET)_{18}$, $Ag_{44}(FTP)_{30}$, and $Au_{25}(FTP)_{18}$ were synthesized as described in the [Experimental Section](#). Mass spectra and the UV/vis absorption spectra of these clusters, presented in the [Supporting Information](#) (see Figures S1–S4), confirm the purity and the identity of these clusters. Schematics of their crystal structures showing various

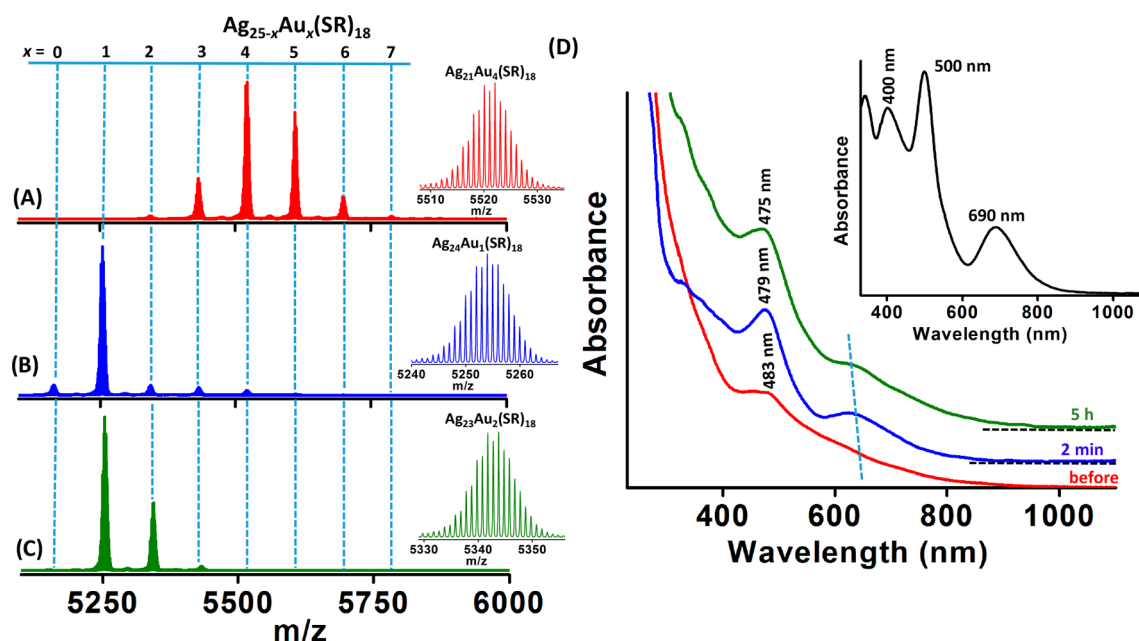


Figure 2. ESI mass spectra (A–C) and UV/vis absorption spectra (D) of **Ia** before and after the addition of $\text{Ag}_{25}(\text{DMBT})_{18}$. Traces A–C are the mass spectra of **Ia** before, 2 min, and 5 h after the addition of $\text{Ag}_{25}(\text{DMBT})_{18}$, respectively. All the features are with isotopic resolution, as illustrated in the respective insets. Red, blue, and green traces in panel D are the UV/vis absorption spectra of **Ia** before, 2 min, and 5 h after the addition of $\text{Ag}_{25}(\text{DMBT})_{18}$, respectively. UV/vis spectrum of pure $\text{Ag}_{25}(\text{DMBT})_{18}$ is shown in the inset of panel D. The exact numbers of PET and DMBT ligands in **Ia** are not known; hence, –SR is used in their formulas instead of PET and DMBT. Because the total number of ligands is the same as that of parent clusters and the masses of these ligands are equal, peak positions are not affected by any difference in the exact numbers of PET and DMBT in their formulas.

symmetry-unique sites of metal atoms and sulfur atoms of the thiolate ligands are shown in Figure 1. $\text{Au}_{25}(\text{SR})_{18}$ and $\text{Ag}_{25}(\text{SR})_{18}$ possess identical structural framework,^{18,16} consisting of three symmetry-unique metal atom sites, namely, center (C) of the icosahedron, surface of icosahedron (I), and the staple (S) positions, as shown in Figure 1A. $\text{Ag}_{44}(\text{SR})_{30}$ has an innermost, hollow Ag_{12} icosahedron, middle Ag_{20} dodecahedron, and six outermost $\text{Ag}_2(\text{SR})_5$ mounts (see Figure 1B).¹² The Ag_{20} dodecahedron can be considered as made up of an Ag_8 cube whose faces are capped by a pair of Ag atoms. Therefore, there are four symmetry-unique metal atom sites in $\text{Ag}_{44}(\text{SR})_{30}$, namely the icosahedral (I), cube vertices and faces of dodecahedron (D_{cv} and D_{cf} , respectively), and the mount (M) positions (see Figure 1B).

The alloy clusters $\text{Ag}_{25-x}\text{Au}_x(\text{SR})_{18}$ (I), $\text{Au}_{25-x}\text{Ag}_x(\text{SR})_{18}$ (II), and $\text{Au}_x\text{Ag}_{44-x}(\text{SR})_{30}$ (III) were synthesized by inter-cluster reactions between the suitably chosen undoped clusters as described in the Experimental Section. It has been shown that I and II possess overall structural frameworks which are similar to that of $\text{M}_{25}(\text{SR})_{18}$ ($\text{M} = \text{Ag}/\text{Au}$).^{34,42} $\text{Au}_x\text{Ag}_{44-x}(\text{SR})_{30}$ (III) alloy clusters were also reported recently.^{11,47,36} In the following sections, we show that the Au atoms of I and III and Ag atoms of II can be substituted by their reactions with undoped $\text{Ag}_{25}(\text{SR})_{18}$, $\text{Ag}_{44}(\text{SR})_{30}$, and $\text{Au}_{25}(\text{SR})_{18}$, respectively. We also show that these reactions can be correlated with the positions of the metal atoms and the rigidity of the icosahedral shells of these alloy clusters.

Substitution of Au of I with Ag Using $\text{Ag}_{25}(\text{DMBT})_{18}$. The mass spectrum of $\text{Ag}_{25-x}\text{Au}_x(\text{SR})_{18}$ alloy clusters containing 1–6 Au atoms (denoted as **Ia**) is presented in Figure 2A. These alloys were formed by the substitution of Ag atoms of $\text{Ag}_{25}(\text{DMBT})_{18}$ by Au atoms of $\text{Au}_{25}(\text{PET})_{18}$ (see Experimental Section for details). Apart from Ag–Au

substitution, DMBT can also be substituted by PET.³⁵ Because the masses of these ligands are equal (137 Da), the substitution of DMBT with PET cannot be detected from standard mass spectrometric measurements. Hence, we do not know the exact numbers of these ligands in **Ia**. Therefore, we use –SR in their formulas instead of PET and DMBT in the discussion about the reactions of **Ia**.

In order to substitute the Au atoms in **Ia** with Ag atoms, a solution of $\text{Ag}_{25}(\text{DMBT})_{18}$ was added to the as-prepared solution of **Ia** (see Experimental Section for details). The mass spectra of this reaction mixture, measured within 2 min after the addition of excess $\text{Ag}_{25}(\text{DMBT})_{18}$ (see Figure 1B), reveals that (i) the intensity of the features due to **Ia** with $x > 1$ decreased significantly and (ii) $\text{Ag}_{24}\text{Au}_1(\text{SR})_{18}$ was the most prominent alloy cluster present in the reaction mixture. The mass spectrum of the same reaction mixture measured after about 5 h is presented in Figure 2C which showed that (i) the only prominent clusters remaining in the solution were $\text{Ag}_{24}\text{Au}_1(\text{SR})_{18}$ and $\text{Ag}_{23}\text{Au}_2(\text{SR})_{18}$ and (ii) features due to **Ia** with $x > 2$ disappeared. These observations show that Au atoms of **Ia** were substituted by the Ag atoms of $\text{Ag}_{25}(\text{DMBT})_{18}$ to form $\text{Ag}_{24}\text{Au}_1(\text{SR})_{18}$ and $\text{Ag}_{23}\text{Au}_2(\text{SR})_{18}$. Furthermore, note that $\text{Ag}_{24}\text{Au}_1(\text{SR})_{18}$ is present in solution even after 5 h without any significant decrease in the intensity. This could be due to the higher stability of $\text{Ag}_{24}\text{Au}_1(\text{SR})_{18}$ over alloy clusters containing larger numbers of Au atoms. In order to confirm this, $\text{Ag}_{25}(\text{DMBT})_{18}$ was added to the solution, the mass spectrum of which is shown in Figure 2C, containing $\text{Ag}_{24}\text{Au}_1(\text{SR})_{18}$ and $\text{Ag}_{23}\text{Au}_2(\text{SR})_{18}$. Within 1 h, $\text{Ag}_{25}(\text{DMBT})_{18}$ disappeared (see Figure 3C), and $\text{Ag}_{24}\text{Au}_1(\text{SR})_{18}$ was still present as the most prominent cluster in solution even after 12 h (see Figure 3D). The above set of experiments confirm that (i) $\text{Ag}_{24}\text{Au}_1(\text{SR})_{18}$ is more stable compared to $\text{Ag}_{25}(\text{DMBT})_{18}$

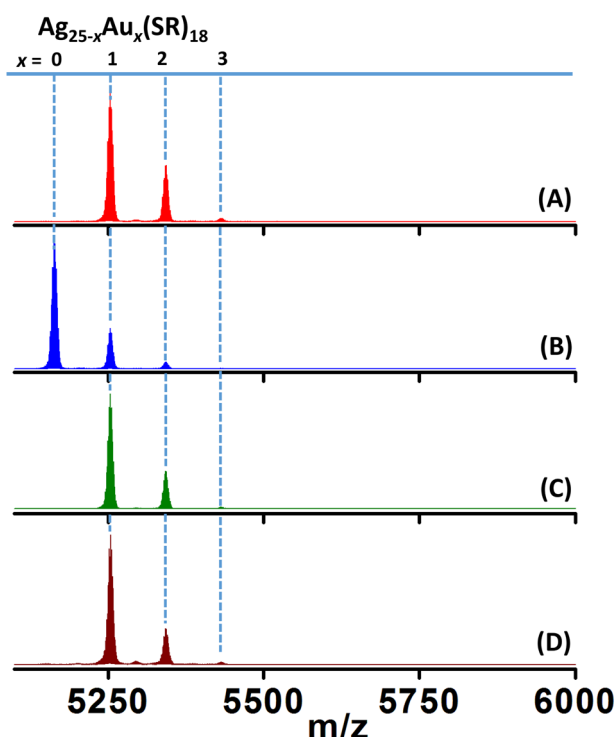


Figure 3. ESI mass spectra of a mixture of $\text{Ag}_{24}\text{Au}_1(\text{SR})_{18}$ and $\text{Ag}_{23}\text{Au}_2(\text{SR})_{18}$ before (A), 2 min (B), 1 h (C), and 12 h (D) after the addition of $\text{Ag}_{25}(\text{DMBT})_{18}$ into it. The exact numbers of PET and DMBT ligands in these clusters are not known; hence, –SR is used in their formulas instead of PET and DMBT. Because the total number of ligands is the same as that of parent clusters and the masses of these ligands are equal, peak positions are not affected by any difference in the exact numbers of PET and DMBT in their formulas.

and (ii) Au atom in $\text{Ag}_{24}\text{Au}_1(\text{SR})_{18}$ cannot be substituted by reaction with $\text{Ag}_{25}(\text{DMBT})_{18}$. A possible reason for this will be described later.

Changes in the UV/vis absorption spectrum of **Ia**, before and after the addition of $\text{Ag}_{25}(\text{DMBT})_{18}$, are presented in Figure 2D. Absorption spectrum of the as-prepared solution of **Ia** (red trace in Figure 2D) changed significantly compared to those after the addition of $\text{Ag}_{25}(\text{DMBT})_{18}$ into it (blue and green traces in Figure 2D). The addition of $\text{Ag}_{25}(\text{DMBT})_{18}$ resulted in the appearance of new features in the absorption spectra at ~ 630 and ~ 475 nm (see green and blue traces in Figure 2D). Note that the UV/vis spectrum after 2 min (see blue trace in Figure 2D) resembles that of undoped $\text{Ag}_{25}(\text{DMBT})_{18}$. This resemblance is not due to the presence of excess $\text{Ag}_{25}(\text{DMBT})_{18}$ in the reaction mixture because the mass spectra of **Ia** before the addition of $\text{Ag}_{25}(\text{DMBT})_{18}$ (see Figure 2A) does not contain any features due to $\text{Ag}_{25}(\text{DMBT})_{18}$. We note that the absorption spectrum of $\text{Ag}_{24}\text{Au}_1(\text{SR})_{18}$ and that of $\text{Ag}_{25}(\text{DMBT})_{18}$ are almost similar³⁴ except for a slight blue shift in their peak maxima. Hence, our UV/vis spectroscopic measurements further confirm that Au atoms of **Ia** were substituted by the Ag atoms of $\text{Ag}_{25}(\text{DMBT})_{18}$ to form largely $\text{Ag}_{24}\text{Au}_1(\text{SR})_{18}$ along with some $\text{Ag}_{23}\text{Au}_2(\text{SR})_{18}$.

Crystal structure of $\text{Ag}_{25}(\text{SR})_{18}$ (see Figure 1A) shows that Ag atoms can occupy three symmetry-unique sites, namely, center of the icosahedron (C), surface of the icosahedron (I) and the staple (S).¹⁶ Crystal structure of $\text{Ag}_{24}\text{Au}_1(\text{SR})_{18}$ shows that the Au atom occupies the C position.³⁴ In the case of $\text{Ag}_{25-x}\text{Au}_x(\text{SR})_{18}$, it has been theoretically predicted that when

$x = 2-12$, Au atoms prefer to occupy the I positions,³⁵ however, this has not yet been verified experimentally. Therefore, we think that the Au atom in $\text{Ag}_{24}\text{Au}_1(\text{SR})_{18}$, formed in this reaction, is located at the C position and that this atom will not be accessible for substitution because it is well-protected by the compact Ag_{12} icosahedron and six outer $\text{Ag}_2(\text{SR})_3$ staples. In comparison to the Au atom at the C position, those at the I positions would be more accessible because (i) they are at the surface of the M_{12} ($\text{M} = \text{Ag}/\text{Au}$) icosahedron and (ii) they can be considered as part of the dynamic $\text{Ag}_8(\text{SR})_6$ rings.³⁵

In order to check whether the Au atoms present at the I and the S positions of **I** can be distinguished by metal atom substitution reactions, we carried out a reaction between $\text{Ag}_{25-x}\text{Au}_x(\text{SR})_{18}$ alloy clusters containing 15–22 Au atoms (denoted as **Ib**) with $\text{Ag}_{25}(\text{DMBT})_{18}$ (see Figure S5). Because there are only 12 positions for I and S sites, at least 3–7 Au atoms in **Ib** can occupy the S positions. Panels B and C of Figure S5 show that number of Au atoms in **Ib** has decreased from 15 to 22 to 11–19 and 11–17 within 2 min and within 20 min, respectively, after the addition of $\text{Ag}_{25}(\text{DMBT})_{18}$. These observations clearly show that some of the Au atoms at the S positions of **Ib** were substituted by Ag atoms of $\text{Ag}_{25}(\text{DMBT})_{18}$ within 2 min after its addition. Therefore, our experiments show that Au atoms at the S positions of **Ib** were substituted faster compared to those at the I positions. The experiments on **Ia** and **Ib** presented above clearly demonstrate that the Au atoms at the C, I, and S positions of $\text{Ag}_{25-x}\text{Au}_x(\text{SR})_{18}$ can be distinguished using metal atom substitution reactions.

Substitution of Ag of **II with Au Using $\text{Au}_{25}(\text{PET})_{18}$.** The mass spectrum of $\text{Au}_{25-x}\text{Ag}_x(\text{SR})_{18}$ alloy clusters containing 1–7 Ag atoms (denoted as **IIa**) is presented in Figure 4A. The alloys were formed by the substitution of Au atoms of $\text{Au}_{25}(\text{PET})_{18}$ by Ag atoms of $\text{Ag}_{25}(\text{DMBT})_{18}$ (see Experimental Section for details). As mentioned earlier in the case of **I**, the substitution of PET with DMBT cannot be detected by standard mass spectrometric measurements. Hence, we do not know the exact numbers of these different ligands in **IIa**. Therefore, we use –SR in their formulas instead of PET and DMBT in the discussion about the reactions of **IIa**.

In order to substitute the Ag atoms of **IIa** with Au atoms, a solution of $\text{Au}_{25}(\text{PET})_{18}$ was added to the as-prepared solution of **IIa** (see Experimental Section for details). The mass spectra of the resulting mixture, measured within 2 min after the addition of undoped $\text{Au}_{25}(\text{PET})_{18}$ (Figure 4B), shows an intense feature due to $\text{Au}_{25}(\text{PET})_{18}$ itself and features due to the alloy clusters. Figure 4C shows that (i) the intensity of the feature due to undoped $\text{Au}_{25}(\text{PET})_{18}$ decreased and (ii) most of the alloy clusters which were originally present in **IIa** (see Figure 4A) remain in solution even after 5 h. From Figure 4A,C, we see that $\text{Au}_{21}\text{Ag}_4(\text{SR})_{18}$ was the most abundant cluster in the parent solution of **IIa** (see the peak corresponding to $x = 4$ in Figure 4A) while $\text{Au}_{24}\text{Ag}_1(\text{SR})_{18}$, $\text{Au}_{23}\text{Ag}_2(\text{SR})_{18}$, and $\text{Au}_{22}\text{Ag}_3(\text{SR})_{18}$ (see the peaks corresponding to $x = 1-3$ in Figure 4C) emerged with highest abundance after 5 h. This small shift in the centroid of the mass spectra before and after the addition of $\text{Au}_{25}(\text{PET})_{18}$ shows that Ag atoms in **IIa** were substituted by the Au atoms of $\text{Au}_{25}(\text{PET})_{18}$. However, alloy clusters of **IIa** with $x > 1$, i.e., $\text{Au}_{21}\text{Ag}_4(\text{SR})_{18}$ and $\text{Au}_{20}\text{Ag}_5(\text{SR})_{18}$, were still present in the reaction mixture along with $\text{Au}_{25}(\text{PET})_{18}$ (see Figure 4C). This is in contrast to the case of **Ia** wherein substitution proceeded up to the formation of $\text{Ag}_{24}\text{Au}_1(\text{SR})_{18}$ as an almost exclusive product (i.e.,

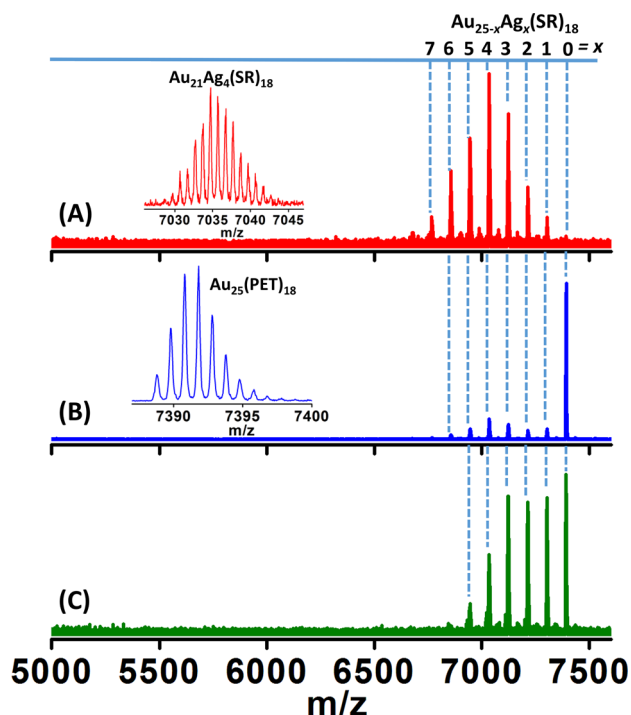


Figure 4. ESI mass spectra of **IIa** before the addition of $\text{Ag}_{25}(\text{DMBT})_{18}$ (A), 2 min after the addition (B), and after 5 h (C). The exact numbers of PET and DMBT ligands in **IIa** are not known; hence, $-\text{SR}$ is used in their formulas instead of PET and DMBT. Because the total number of ligands is the same as that of parent clusters and the masses of these ligands are equal, peak positions are not affected by any difference in the exact numbers of PET and DMBT in their formulas. Isotopic patterns of some of the peaks are shown in the insets.

$\text{Au}_{25-x}\text{Ag}_x(\text{SR})_{18}$ clusters with $x > 2$ disappeared; see Figure 2B,C), while in the case of **IIa**, product distribution remained almost the same even after several hours after the addition of $\text{Au}_{25}(\text{PET})_{18}$. These observations clearly demonstrate that metal atom substitution of **IIa** is less facile compared to that of **Ia**. A possible reason for this will be described later.

$\text{Au}_{25}(\text{SR})_{18}$ has three symmetry-unique metal atom sites (see Figure 1A) as in the case of $\text{Ag}_{25}(\text{SR})_{18}$.^{14,18} Single-crystal X-ray diffraction and theoretical calculations suggest that when $x < 12$, the Ag atoms in $\text{Au}_{25-x}\text{Ag}_x(\text{SR})_{18}$ prefer to occupy the icosahedral surface (I) positions, compared to the C and the S positions.^{42,43,48} Furthermore, in $\text{Au}_{25-x}\text{Ag}_x(\text{SR})_{18}$, the C position is the least preferred site for an Ag atom.^{42,43,48} Therefore, we think that the Ag atoms of **IIa** (shown in Figure 4A) also occupy the I positions. Therefore, as explained earlier in the case of **Ia**, Ag atoms in **IIa** are less accessible for substitution. The Ag atoms present in the S position are expected to be more accessible for substitution. In order to confirm this, we carried out a reaction between $\text{Au}_{25-x}\text{Ag}_x(\text{SR})_{18}$ clusters containing 9–16 Au atoms i.e., $x = 9$ –16 (denoted as **IIb**) with $\text{Au}_{25}(\text{PET})_{18}$ (see Figure S6). Assuming that the 12 Au atoms occupy all of the 12 I positions, the remaining four Ag atoms in **IIb** occupy the S positions. We observed that the number of Au atoms in it has decreased from 9–16 to 0–11 and 4–9 within 2 min and within 5 h, respectively, after the addition of $\text{Au}_{25}(\text{PET})_{18}$ (see Figure S6B,C). These observations clearly show that the Ag atoms at the S positions of **IIb** can be substituted more easily compared to those at the I positions. Furthermore, these results confirm

that the Au atoms in the $\text{Au}_{25-x}\text{Ag}_x(\text{SR})_{18}$ when $x < 12$ are present at the I positions. This is in accordance with the previously reported crystal structures and theoretical calculations.^{42,48} The experiments on **IIa** and **IIb** presented above clearly demonstrate that the Ag atoms at the I and S positions of $\text{Au}_{25-x}\text{Ag}_x(\text{SR})_{18}$ can be distinguished using metal atom substitution reactions. However, the crystal structures of the reactants and the products are needed to unambiguously confirm these observations.

The experiments described above indicate that the substitution of Ag atoms of **IIa** is sluggish. However, as mentioned earlier, substitution of ligands and metal–ligand fragments of $\text{Au}_{25-x}\text{Ag}_x(\text{SR})_{18}$ also might occur which cannot be detected by routine mass spectrometry because masses of the PET and DMBT are equal. Therefore, we carried out a reaction of $\text{Au}_{25-x}\text{Ag}_x(\text{SR})_{18}$ clusters containing 1–10 Au atoms (denoted as **IIc**) with $\text{Au}_{25}(\text{BT})_{18}$ in order to test whether the substitution of ligands and metal–ligand fragments occurs or not. Furthermore, we thought that the use of another ligand, BT, may enhance the metal atom substitution. Figure S7A shows the mass spectrum of **IIc**. We see that within 2 min after the addition of $\text{Au}_{25}(\text{BT})_{18}$ (see Figures S7B and S8), the number of Au atoms in **IIc** decreased from 1–9 to 1–4. Furthermore, peaks due to the substitution of Ag–SR fragment ($-\text{SR} = \text{PET/DMBT}$) of **IIc** with Au–BT fragment are also observed in this mass spectrum (see Figure S8). These sets of experiments clearly indicate that substitution of metal–ligand fragments also contribute to the reduction in the number of dopant metal atoms. However, even though fragment substitution occurs, the reaction mixture still contains $\text{Au}_{25-x}\text{Ag}_x(\text{SR})_{18}$ clusters with $x = 1$ –4. This observation further confirms that the substitution of Ag atoms of $\text{Au}_{25-x}\text{Ag}_x(\text{SR})_{18}$ is less facile.

The reactions of **Ia**, **Ib**, **IIa**, **IIb**, and **IIc** presented above unambiguously prove that $\text{M}_2(\text{SR})_3$ staples or $\text{M}_8(\text{SR})_6$ rings are more rigid, and hence less labile for metal atom substitution, when they are rich in Au (in the case of $\text{Au}_{25-x}\text{Ag}_x(\text{SR})_{18}$) compared to the situation when they are rich in Ag (in the case of $\text{Ag}_{25-x}\text{Au}_x(\text{SR})_{18}$). Note that even although the alloy clusters **Ia** and **IIa** possess identical structural frameworks, wherein the icosahedral sites can be considered to be equally accessible, metal atom substitution of **Ia** was much more facile compared to that of **IIa**. This shows that the steric factors alone cannot explain the feasibility of intercluster reactions. Bürgi et al. showed that Ag doping increases the flexibility of metal–thiolate interface in $\text{Au}_{38-x}\text{Ag}_x(\text{SR})_{24}$ clusters^{49,50} which was attributed to the fact that the Au–Au bond is stronger and less polar compared to that of Ag–Ag and Ag–Au bonds. Therefore, we conclude that (i) the rigidity of the structural framework plays an important role in dictating intercluster reactions and (ii) irrespective of the similarity in the structural framework of $\text{M}_{25}(\text{SR})_{18}$ ($\text{M} = \text{Ag/Au}$) they differ in their metal atom substitution reactions.

Substitution of Au of III with Ag Using $\text{Ag}_{44}(\text{FTP})_{30}$. The mass spectrum of $\text{Au}_x\text{Ag}_{44-x}(\text{FTP})_{30}$ in the 4^- charge state, containing 4–9 Au atoms (denoted as **IIIa**) is presented in Figure 5A (see Experimental Section for details). In order to substitute Au atoms in **IIIa** with Ag atoms, a solution of $\text{Ag}_{44}(\text{FTP})_{30}$ (0.67 mM) was added to the as-prepared solution of **IIIa** (see Experimental Section for details). The mass spectra of the resulting mixture, measured within 2 min and 1 h after the addition of $\text{Ag}_{44}(\text{FTP})_{30}$ presented in panels B and C of Figure 5, respectively, reveal that the intensities of the features

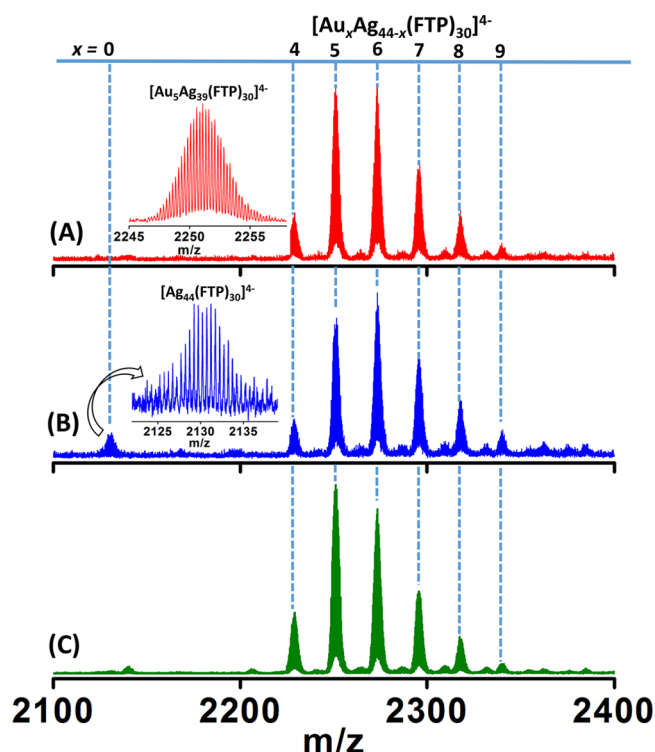


Figure 5. ESI mass spectra of **IIIa** before the addition of $\text{Ag}_{44}(\text{FTP})_{30}$ (A), after 2 min (B), and after 1 h (C) of addition. Isotopic patterns of $[\text{Au}_5\text{Ag}_{39}(\text{FTP})_{30}]^{4-}$ and $[\text{Ag}_{44}(\text{FTP})_{30}]^{4-}$ are shown in the insets.

due to alloy clusters in **IIIa** remain almost unchanged even upon the addition of excess $\text{Ag}_{44}(\text{FTP})_{30}$. Note that the features due to $\text{Ag}_{44}(\text{FTP})_{30}$ are present in the spectra measured within 2 min (see Figure 5B). Mass spectra of this reaction mixture showing the 3[−] charge state of the alloy clusters, presented in Figure S9, further confirm these observations. Hence, this set of experiments shows that the substitution of Au atoms of **IIIa** by $\text{Ag}_{44}(\text{FTP})_{30}$ is not possible. A possible reason for this will be described later.

Crystal structure of $\text{Ag}_{44}(\text{FTP})_{30}$ shows (see Figure 1B) that Ag atoms occupy four symmetry-unique sites, namely, surface of the icosahedron (I), dodecahedral positions (D_{cv} and D_{cf}), and the mounts (M).^{12,35–37} Single-crystal X-ray crystallography of $\text{Au}_{12}\text{Ag}_{32}(\text{FTP})_{30}$, reported by Zheng et al., shows that the 12 Au atoms in this cluster occupy the I position.¹¹ In the case of $\text{Au}_x\text{Ag}_{44-x}(\text{FTP})_{30}$, it has been predicted theoretically that when $x < 12$, Au atoms prefer to occupy the I positions compared to the D_{cf} , D_{cv} , and the M positions.³⁵ Therefore, we think that the Au atoms of **IIIa** are also present at the I positions; hence, these Au atoms will not be accessible for substitution because the innermost icosahedron is well-protected by the compact M_{20} ($\text{M} = \text{Ag}/\text{Au}$) dodecahedron and the six outermost $\text{Ag}_2(\text{FTP})_5$ mounts.

In order to test whether Au atoms present at the outer sites (D_{cf} , D_{cv} , and M) can be substituted, we carried out a reaction between $\text{Au}_x\text{Ag}_{44-x}(\text{FTP})_{30}$ containing more than 12 Au atoms (denoted as **IIIb**) with $\text{Au}_{25}(\text{FTP})_{18}$ (see Figures S10 and S11). This reaction shows that Au atoms in **IIIb** can be substituted by Ag atoms from $\text{Ag}_{44}(\text{FTP})_{30}$. Mass spectra of this reaction mixture showing the 3[−] charge state of the clusters, presented in Figure S10, also confirm these observations. Furthermore, reactions of **IIIa** and **IIIb** presented above (see Figures 5 and S9–S11) confirm that the Au atoms of **III** present in the outer

sites (M, D_{cf} , and D_{cv}) of $\text{Au}_x\text{Ag}_{44-x}(\text{FTP})_{30}$ can be substituted while those at the I positions cannot be substituted. Au atoms located at the D_{cv} , D_{cf} , or the M positions are more accessible and hence more labile for substitution. The experiments on **IIIa** and **IIIb** presented above clearly demonstrate that the Au atoms at the I and outer positions of $\text{Au}_x\text{Ag}_{44-x}(\text{SR})_{30}$ can be distinguished using metal atom substitution reactions. However, it has not been possible to distinguish between the metal atoms at the D_{cf} and the D_{cv} positions.

From the mass spectrometric and the UV/vis absorption spectroscopic measurements presented above, we conclude the following: (i) The Au atoms present in the I and the S positions of **I** can be substituted almost completely by reactions with $\text{Ag}_{25}(\text{DMBT})_{18}$; however, the Au atom at its C position cannot be substituted. (ii) The Ag atoms present in the S positions of **II** can be substituted more easily compared to those at its I positions, by reactions with $\text{Au}_{25}(\text{PET})_{18}$. (iii) The Au atoms present in the I positions of **III** cannot be substituted by reactions with $\text{Ag}_{44}(\text{FTP})_{30}$; however, those Au atoms at the other sites (D_{cf} , D_{cv} , and M) can be substituted. However, the dynamics of these metal atom exchanges, i.e., which of the metal atom sites (inner or outer) are involved in the initial steps of these reactions, whether metals atoms exchange their positions within the cluster,⁵¹ etc., are not understood in detail. Note that we detected only the metal atom substitution reactions. Other processes such as exchange of ligands and metal–ligand fragments, decomposition of clusters, etc., also could occur in solution, and details of such processes are beyond the scope of the present study.

CONCLUSION

In summary, we presented metal atom substitution reactions of three model, ligand-protected noble metal alloy clusters, $\text{Ag}_{25-x}\text{Au}_x(\text{SR})_{18}$, $\text{Au}_{25-x}\text{Ag}_x(\text{SR})_{18}$, and $\text{Au}_x\text{Ag}_{44-x}(\text{SR})_{30}$. We show that although these clusters possess a few common structural features, they show distinctly different reactivities in metal atom substitution reactions. The positions of the metal atoms in these clusters could be distinguished using these reactions which demonstrate that metal atom substitution reaction correlates with the geometric structures (and consequently thermodynamic stabilities) of these clusters. Furthermore, our work demonstrates that the steric factors as well as the structural rigidity of the clusters determine the feasibility of intercluster reactions. We believe that our work will initiate more activities to establish structure–reactivity relations in the chemistry of monolayer-protected clusters.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b07605.

Details of instrumentation and mass spectrometric measurements; mass spectra and UV/vis spectra of $\text{Ag}_{25}(\text{DMBT})_{18}$, $\text{Au}_{25}(\text{PET})_{18}$, $\text{Ag}_{44}(\text{FTP})_{30}$, and $\text{Au}_{25}(\text{FTP})_{18}$; additional ESI MS spectra (PDF)

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Author Contributions

K.R.K. designed and carried out the reactions; D.G. carried out mass spectrometric measurements; A.G. synthesized the clusters; T.P. supervised the whole project. The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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