

# Manifestation of Geometric and Electronic Shell Structures of Metal Clusters in Intercluster Reactions

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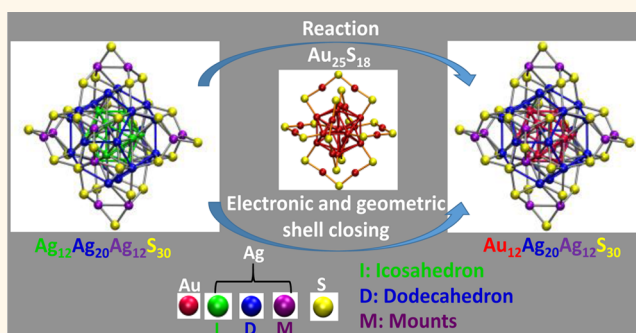
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**S** Supporting Information

**ABSTRACT:** Monolayer protected clusters exhibit rich diversity in geometric and electronic structures. However, structure–reactivity relationships in these clusters are rarely explored. In this context,  $[\text{Ag}_{44}(\text{SR})_{30}]^{4-}$ , where  $-\text{SR}$  is an alkyl/aryl thiolate, is an interesting system due to its geometrically and electronically closed-shell structures and distinct charge states. We demonstrate that these structural features of  $[\text{Ag}_{44}(\text{SR})_{30}]^{4-}$  are distinctly manifested in its solution-state reaction with another cluster,  $[\text{Au}_{25}(\text{SR})_{18}]^-$ . Through this reaction, an alloy cluster anion,  $[\text{Au}_{12}\text{Ag}_{32}(\text{SR})_{30}]^{4-}$ , evolves spontaneously as revealed by high-resolution electrospray ionization mass spectrometry.

Ultraviolet–visible absorption spectroscopy and density functional theory calculations indicate that  $[\text{Au}_{12}\text{Ag}_{32}(\text{SR})_{30}]^{4-}$  is formed by the substitution of all of the Ag atoms in the innermost icosahedral shell of  $[\text{Ag}_{44}(\text{SR})_{30}]^{4-}$  and the abundance is attributed to its higher stability due to closed geometric as well as electronic shell structure, similar to the reactant clusters. We further demonstrate that the substitution of metal atoms in the middle dodecahedral shell and the outermost mount sites are also possible, however such substitutions produce  $\text{Au}_x\text{Ag}_{44-x}(\text{SR})_{30}$  alloy clusters with geometrically and electronically open shells. Depending on specific sites of substitution, an unexpected superatom–nonsuperatom transition occurs in the distribution of  $\text{Au}_x\text{Ag}_{44-x}(\text{SR})_{30}$  alloy clusters formed in this reaction. Our results present a unique example of a structure–reactivity relationship in the metal atom substitution chemistry of monolayer protected clusters, wherein a systematic trend, reflecting the geometric and the electronic shell structures of the reactant as well as the product clusters, was observed.

**KEYWORDS:** monolayer protected clusters, shell closure, superatom, intercluster reactions, cluster science



Monolayer protected atomically precise noble metal clusters are a new class of nanomaterials exhibiting molecule-like characteristics in their size,<sup>1–5</sup> structure,<sup>6–8</sup> and properties.<sup>9–11</sup> A new fascinating aspect of these clusters is the intercluster reactions,<sup>12</sup> wherein their molecule-like chemical reactivity is demonstrated. In such reactions, the clusters exchange metal atoms, ligands, and metal–ligand fragments between them spontaneously in ambient conditions, conserving nuclearity.<sup>12</sup> Reactions between two structurally analogous clusters,  $\text{Au}_{25}(\text{SR})_{18}$  and  $\text{Ag}_{25}(\text{SR})_{18}$ , where  $-\text{SR}$  is alkyl/arylthiolate, shows that these exchange processes occur through an adduct formed between the two clusters.<sup>13</sup> Experiments by Bürgi *et al.*, also showed that intact clusters are the truly reacting species in such processes.<sup>14</sup> However, mechanistic aspects of these reactions are yet to be understood in detail. Another important aspect of these reactions is the correlations between structure of the clusters and the site selectivity and specificity of the metal, ligand, and metal–ligand

fragment substitutions occurring due to the exchange processes. Molecular structure is reflected in the reactivity and associated effects with implications to mechanisms. Often, the structure dictates the product formation and kinetics of reactions. Though the crystal structures of several monolayer protected clusters are known, their structure–reactivity relationships are rarely investigated, except in a few cases where ligand exchange reactions are explored.<sup>15–17</sup>

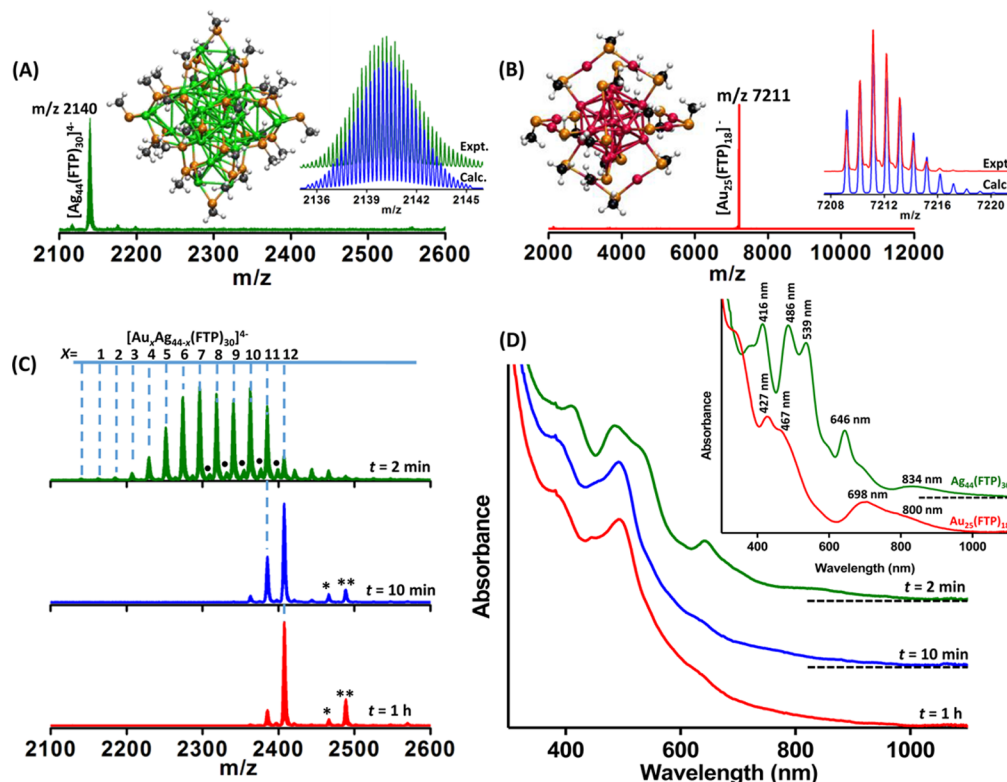
In this context,  $[\text{Ag}_{44}(\text{SR})_{30}]^{4-}$  is an interesting molecule<sup>6,18,19</sup> due to its multishell structure, distinct charge states, and unique sites<sup>12</sup> for metal, ligand, and metal–ligand fragment substitution reactions. The Ag atoms in  $[\text{Ag}_{44}(\text{SR})_{30}]^{4-}$  are located in three distinct, symmetry unique sites, namely, the

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**Figure 1.** ESI mass spectra of  $\text{Ag}_{44}(\text{FTP})_{30}$  (A) and  $\text{Au}_{25}(\text{FTP})_{18}$  (B). Experimental and calculated isotopic distributions of these clusters are also shown. Mass spectra (C) and absorption spectra (D) of a mixture of these clusters at a  $\text{Ag}_{44}(\text{FTP})_{30}:\text{Au}_{25}(\text{FTP})_{18}$  molar ratio of 2.8:1.0, measured at various time intervals,  $t = 2$  min, 10 min, and 1 h. UV-vis absorption spectra of pure  $\text{Ag}_{44}(\text{FTP})_{30}$  and  $\text{Au}_{25}(\text{FTP})_{18}$  are shown in the inset of (D) with characteristic peak positions marked. The peaks labeled as “•” in (C) are due to alloy clusters,  $\text{Au}_x\text{Ag}_{44-x}(\text{FTP})_{29}(\text{BuS})_1$ , containing butanethiol which comes from  $\text{Au}_{25}(\text{BuS})_{18}$  used for synthesis of  $\text{Au}_{25}(\text{FTP})_{18}$  (see [Materials and Methods](#) section). The peaks labeled as “\*” and “\*\*” in (C) are due to alloy clusters containing additional Ag-FTP and Au-FTP units, respectively (see [Figure S6](#)). Schematic structures of the clusters are also shown in (A) and (B). Color codes for the structures shown: green (Ag), red (Au), orange (S), black (C), and white (H).

innermost icosahedral, middle dodecahedral, and the outermost mount positions.<sup>6,12,20</sup> Further, this cluster has a closed valence electronic shell with 18 electrons and is, hence, considered as a superatom.<sup>6</sup> Here we demonstrate that the geometric and electronic shell structures of  $[\text{Ag}_{44}(\text{FTP})_{30}]^{4-}$ , where 4-fluorothiophenol is FTP, are manifested in the metal atom substitution reactions with another closed-shell cluster,  $[\text{Au}_{25}(\text{FTP})_{18}]^-$ . We show that at appropriate concentrations of reactant clusters, complete substitution of all of the icosahedral Ag atoms in  $[\text{Ag}_{44}(\text{FTP})_{30}]^{4-}$  by Au atoms is possible, producing  $[\text{Au}_{12}\text{Ag}_{32}(\text{SR})_{30}]^{4-}$  as an almost exclusive, geometrically, and electronically closed-shell alloy product. Our density functional theory (DFT) calculations suggest that the 12 Au atoms in  $[\text{Au}_{12}\text{Ag}_{32}(\text{SR})_{30}]^{4-}$  prefer to occupy the central icosahedral shell. Further, the absorption spectroscopic features of the  $[\text{Au}_{12}\text{Ag}_{32}(\text{SR})_{30}]^{4-}$  formed, which are distinctly different from those of  $[\text{Ag}_{44}(\text{FTP})_{30}]^{4-}$ , match perfectly with the features of the  $\text{Au}_{12}\text{Ag}_{32}(\text{SR})_{30}$  clusters synthesized by Zheng *et al.*, through co-reduction method, wherein the Au atoms in the  $[\text{Au}_{12}\text{Ag}_{32}(\text{SR})_{30}]^{4-}$  occupy the innermost icosahedral position.<sup>20</sup> Hence, we conclude that the structure of  $[\text{Au}_{12}\text{Ag}_{32}(\text{SR})_{30}]^{4-}$  formed in this reaction is the same as that of the cluster reported by Zheng *et al.*

Further, we show that Au atom incorporation in the middle dodecahedral or the outermost mount sites of  $[\text{Ag}_{44}(\text{SR})_{30}]^{4-}$  is indeed possible through intercluster reactions, however, only at the expense of a change in the overall charge state from  $4^-$  to

$3^-$ . Such substitutions always result in a mixture of alloys, in the  $3^-$  charge state, irrespective of the relative concentrations of the reactants, unlike the case of the exclusive formation of  $\text{Au}_{12}\text{Ag}_{32}(\text{SR})_{30}$  in the  $4^-$  charge state. In other words, it is impossible to incorporate more than 12 Au atoms in  $[\text{Ag}_{44}(\text{SR})_{30}]^{4-}$ , preserving the charge state of  $4^-$  through these reactions, *i.e.*,  $[\text{Au}_{12}\text{Ag}_{32}(\text{SR})_{30}]^{4-}$  is the upper limit of product clusters having the general formula,  $[\text{Au}_x\text{Ag}_{44-x}(\text{SR})_{30}]^{4-}$ . Such site dependence on the product distribution and charge state is rarely addressed in monolayer protected clusters. This method suggests a way to systematically investigate the substitution chemistry occurring in this cluster size regime. We hope that our results will initiate more activities in this area to explore the intercluster reactions of monolayer protected metal clusters in detail.

## RESULTS AND DISCUSSION

**Characterization of Clusters.** We used  $[\text{Ag}_{44}(\text{FTP})_{30}]^{4-}$  [ $\text{PPh}_4$ ]<sub>4</sub> and  $[\text{Au}_{25}(\text{FTP})_{18}]^-$  [ $\text{TOA}$ ]<sub>18</sub> clusters for this study, where FTP is the ligand protecting the  $\text{Ag}_{44}$  and the  $\text{Au}_{25}$  cores. Further,  $\text{Ag}_{44}(\text{FTP})_{30}$  and  $\text{Au}_{25}(\text{FTP})_{18}$  are anions with  $4^-$  and  $1^-$  charges, respectively, and tetraphenyl phosphonium ( $\text{PPh}_4$ ) and tetraoctyl ammonium (TOA), respectively, are the corresponding counter cations. For convenience,  $[\text{Ag}_{44}(\text{FTP})_{30}]^{4-}$  and  $[\text{Au}_{25}(\text{FTP})_{18}]^-$  are denoted as  $\text{Ag}_{44}(\text{FTP})_{30}$  and  $\text{Au}_{25}(\text{FTP})_{18}$ , respectively, in the following discussion. These clusters were synthesized by the reported

procedures as described in the [Materials and Methods](#) section and thoroughly characterized by ultraviolet–visible (UV–vis) absorption spectroscopy as well as mass spectrometry, as discussed below. Electrospray ionization (ESI) mass spectrometry (MS) of  $\text{Ag}_{44}(\text{FTP})_{30}$  is presented in [Figure 1A](#) which shows the expected feature due to  $[\text{Ag}_{44}(\text{FTP})_{30}]^{4-}$ , centered at  $m/z$  2140. Inset of [Figure 1A](#) shows the isotopic pattern of  $[\text{Ag}_{44}(\text{FTP})_{30}]^{4-}$  comprised of a series of peaks separated by 0.25 mass units, confirming the  $4^-$  charge state of the cluster. A full range mass spectrum of  $\text{Ag}_{44}(\text{FTP})_{30}$ , showing its  $3^-$  charge state, is presented in [Figure S1](#). ESI MS spectrum of  $\text{Au}_{25}(\text{FTP})_{18}$  is presented in [Figure 1B](#) which manifests its expected feature at  $m/z$  7211. Experimental and calculated isotopic patterns of these two clusters are matching, as shown in the corresponding insets, further confirming the identity of these clusters. UV–vis absorption spectra of  $\text{Ag}_{44}(\text{FTP})_{30}$  and  $\text{Au}_{25}(\text{FTP})_{18}$  are presented in the inset of [Figure 1D](#) with their characteristic features<sup>18,19,12</sup> marked. Thus, the mass spectrometric as well as the UV–vis absorption spectroscopic measurements presented above confirm the purity and the identity of these two clusters.

**Evolution of  $[\text{Au}_{12}\text{Ag}_{32}(\text{FTP})_{30}]^{4-}$  from  $\text{Ag}_{44}(\text{FTP})_{30}$  and  $\text{Au}_{25}(\text{FTP})_{18}$ .** For the substitution of Au atoms into  $\text{Ag}_{44}(\text{FTP})_{30}$ , we adopted an intercluster reaction route using  $\text{Au}_{25}(\text{FTP})_{18}$  as the source of Au. This method provides an easy route to synthesize alloy clusters<sup>12</sup> compared to the co-reduction method,<sup>21–23</sup> wherein the alloy clusters are derived from a mixture of individual metal salt precursors. Reactions were conducted by mixing the cluster solutions in DCM at  $\sim 30^\circ\text{C}$ .

[Figure 1C](#) shows the evolution of  $[\text{Au}_{12}\text{Ag}_{32}(\text{FTP})_{30}]^{4-}$  from a mixture of  $\text{Ag}_{44}(\text{FTP})_{30}$  and  $\text{Au}_{25}(\text{FTP})_{18}$ , where the  $\text{Ag}_{44}(\text{FTP})_{30}:\text{Au}_{25}(\text{FTP})_{18}$  molar ratio was 2.8:1.0. Mass spectra of this reaction mixture measured at various time intervals ( $t = 2$  min, 10 min, and 1 h) after the addition of  $\text{Au}_{25}(\text{FTP})_{18}$  into a solution of  $\text{Ag}_{44}(\text{FTP})_{30}$  (see [Materials and Methods](#) section for details) are presented in [Figure 1C](#). These measurements show that the feature due to the undoped  $[\text{Ag}_{44}(\text{FTP})_{30}]^{4-}$ , at  $m/z$  2140, disappeared almost completely, and a series of features separated by 22.25 mass units were observed (see [Figure 1A](#) and uppermost panel in [Figure 1C](#)). Isotopic patterns of any of these features ([Figures S2–S5](#)) consist of a bunch of peaks separated by 0.25 mass units. This mass separation confirms the  $4^-$  charge state of the species detected, as mentioned earlier in the case of undoped  $\text{Ag}_{44}(\text{FTP})_{30}$ . Mass separation of 22.25 mass units between the peaks in  $4^-$  charge state implies that the actual mass difference between their corresponding unit negative charge ( $z = 1$ ) species is 89 Da. This mass separation is the difference between the masses of an Au atom (197 amu) and an Ag atom (108 amu). From the information on the mass separation (22.25 mass units) and charge state ( $4^-$ ), the series of peaks in [Figure 1C](#) can be given a general formula,  $[\text{Au}_x\text{Ag}_{44-x}(\text{FTP})_{30}]^{4-}$ , where  $x$  is the number of Au atoms. Comparison of the theoretical and experimental isotope patterns of some of these alloy clusters, presented in [Figures S2–S5](#), further confirms the formation of  $[\text{Au}_x\text{Ag}_{44-x}(\text{FTP})_{30}]^{4-}$  clusters. Mass spectrum measured within 2 min (uppermost trace in [Figure 1C](#)) reveals that  $[\text{Au}_x\text{Ag}_{44-x}(\text{SR})_{30}]^{4-}$  clusters containing 1–12 Au atoms were formed immediately after mixing  $\text{Ag}_{44}(\text{FTP})_{30}$  and  $\text{Au}_{25}(\text{FTP})_{18}$ . However, the mass spectrum measured after 10 min (middle trace in [Figure 1C](#)) contains peaks due to  $[\text{Au}_{11}\text{Ag}_{33}(\text{FTP})_{30}]^{4-}$  and  $[\text{Au}_{12}\text{Ag}_{32}(\text{FTP})_{30}]^{4-}$  only, confirm-

ing that the  $[\text{Au}_x\text{Ag}_{44-x}(\text{SR})_{30}]^{4-}$  clusters with lesser numbers of Au atoms disappeared within this time interval. The mass spectrum measured after 1 h (bottom trace in [Figure 1C](#)) consists of only one prominent feature due to  $[\text{Au}_{12}\text{Ag}_{32}(\text{FTP})_{30}]^{4-}$ . Experimental and theoretical isotope patterns of  $[\text{Au}_{12}\text{Ag}_{32}(\text{FTP})_{30}]^{4-}$  are presented in [Figure S2](#), which further confirms the assignment. The peaks labeled as ‘\*’ and ‘\*\*’ at higher  $m/z$  region in [Figure 1C](#) are due to alloy clusters containing additional Ag-FTP or Au-FTP units (see [Figure S6](#)). However, these species do not belong to the general formula,  $[\text{Au}_x\text{Ag}_{44-x}(\text{FTP})_{30}]^{4-}$ . Note that no  $[\text{Au}_x\text{Ag}_{44-x}(\text{SR})_{30}]^{4-}$  clusters containing more than 12 Au atoms, *i.e.*, clusters such as  $[\text{Au}_{13}\text{Ag}_{31}(\text{FTP})_{30}]^{4-}$ ,  $[\text{Au}_{14}\text{Ag}_{30}(\text{SR})_{30}]^{4-}$ , *etc.*, were not observed from this set of measurements. However, alloy clusters containing more than 12 Au atoms were observed in the  $3^-$  charge state (not in the  $4^-$  state) for this reaction mixture, as shown in [Figure S7](#) (see later for a detailed discussion). Hence, this set of measurements indicates that a mixture of  $[\text{Au}_x\text{Ag}_{44-x}(\text{FTP})_{30}]^{4-}$  clusters, containing less than 12 Au atoms, transforms spontaneously in solution to a single entity,  $[\text{Au}_{12}\text{Ag}_{32}(\text{SR})_{30}]^{4-}$ .

[Figure 1D](#) shows temporal changes in the UV–vis absorption features of the same reaction mixture (2.8:1.0) studied above. The spectra measured within 2 min after mixing (uppermost trace in [Figure 1D](#)) show significant changes in features compared to those of  $\text{Ag}_{44}(\text{FTP})_{30}$ . Most of these features disappeared within 10 min, (see middle trace in [Figure 1D](#)), and two major features appeared around 493 and 385 nm. The absorption spectra measured after 10 min and after 1 h (middle and bottom traces in [Figure 1D](#)) were similar, indicating that the composition of the reaction mixture did not change within this time scale. Moreover, we note that these spectra resemble that of previously reported  $\text{Au}_{12}\text{Ag}_{32}(\text{FTP})_{30}$  (see [Figure S8](#)). Hence, UV–vis spectroscopic measurements also prove the formation of  $[\text{Au}_{12}\text{Ag}_{32}(\text{FTP})_{30}]^{4-}$  as an exclusive species from a mixture of  $[\text{Au}_x\text{Ag}_{44-x}(\text{SR})_{30}]^{4-}$  clusters.

In order to know whether the exclusive formation of  $[\text{Au}_{12}\text{Ag}_{32}(\text{FTP})_{30}]^{4-}$ , in the  $[\text{Au}_x\text{Ag}_{44-x}(\text{FTP})_{30}]^{4-}$  series, is dependent on the relative concentrations of the reactant clusters, reactions were carried out at various  $\text{Ag}_{44}(\text{FTP})_{30}:\text{Au}_{25}(\text{FTP})_{18}$  molar ratios. Mass spectra of these reaction mixtures at  $\text{Ag}_{44}(\text{FTP})_{30}:\text{Au}_{25}(\text{FTP})_{18}$  molar ratios of 35.0:1.0, 14.0:1.0 and 5.0:1.0, measured 1 h after mixing, are presented in [Figure 2A–C](#), respectively. These measurements indicate that the number of Au atoms in the  $[\text{Au}_x\text{Ag}_{44-x}(\text{FTP})_{30}]^{4-}$  clusters formed is dependent on the relative concentrations of  $\text{Au}_{25}(\text{FTP})_{18}$ . More importantly, these data show that only a mixture of  $[\text{Au}_x\text{Ag}_{44-x}(\text{FTP})_{30}]^{4-}$  clusters were formed at lower concentrations of  $\text{Au}_{25}(\text{FTP})_{18}$  in the reaction mixtures (*i.e.*, 35.0:1.0 and 14.0:1.0 samples, see [Figure 2A,B](#)). Furthermore, any of these mixtures did not transform to a single cluster even after 1 h, as shown in [Figures 2A,B](#) and [S9–S10](#). However, the relative intensities of the alloy clusters present in these samples changed slightly with time, as shown in [Figures S9–S10](#). At a higher concentration of  $\text{Au}_{25}(\text{FTP})_{18}$  (5.0:1.0 mixture),  $[\text{Au}_{12}\text{Ag}_{32}(\text{FTP})_{30}]^{4-}$  is formed almost exclusively, as shown in [Figures 2C](#) and [S11](#). Absorption spectra ([Figure S12](#)) of these reaction mixtures further confirm the above observations. Mass spectra of these reaction mixtures showing the formation of alloy clusters in  $3^-$  charge states, *i.e.*,  $[\text{Au}_x\text{Ag}_{44-x}(\text{FTP})_{30}]^{3-}$ , presented in [Figures S13–S15](#), show that no clusters were formed with notably enhanced abundance.

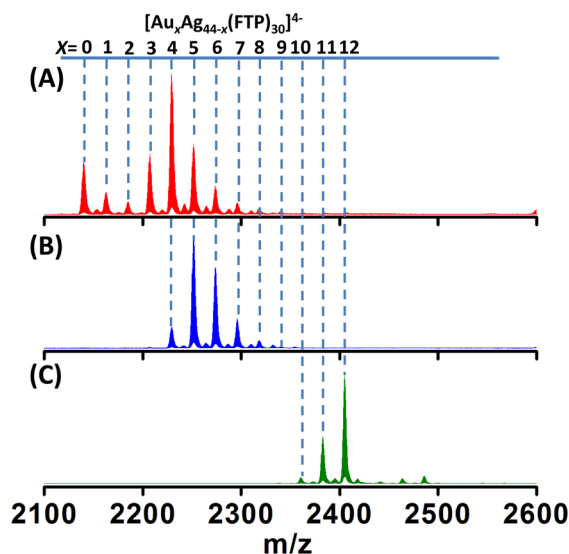


Figure 2. Mass spectra of the  $[\text{Au}_x\text{Ag}_{44-x}(\text{FTP})_{30}]^{4-}$  clusters formed from  $\text{Ag}_{44}(\text{FTP})_{30}$  and  $\text{Au}_{25}(\text{FTP})_{18}$  at  $\text{Ag}_{44}(\text{FTP})_{30}:\text{Au}_{25}(\text{FTP})_{18}$  molar ratios of 35.0:1.0 (A), 14.0:1.0 (B), and 5.0:1.0 (C).

**Substitution of More Than 12 Au Atoms in  $\text{Ag}_{44}(\text{FTP})_{30}$ .** In order to check whether excess of  $\text{Au}_{25}(\text{FTP})_{18}$  in the reaction mixture would result in the formation of  $[\text{Au}_x\text{Ag}_{44-x}(\text{FTP})_{30}]^{4-}$  with more than 12 Au atoms, a reaction was carried out at a  $\text{Ag}_{44}(\text{FTP})_{30}:\text{Au}_{25}(\text{FTP})_{18}$  molar ratio of 0.9:1.0. Time-dependent changes in the composition of this reaction mixture, presented in Figure 3, show that even though  $[\text{Au}_{12}\text{Ag}_{32}(\text{FTP})_{30}]^{4-}$  was formed abundantly within 10 min after mixing, no peaks due to this cluster were observed after 1 h (see Figure 3C). Expansion of the peaks in Figure 3C (see Figure S17) shows that these peaks are due to species with unit negative charge and, hence, not due to any  $\text{Au}_x\text{Ag}_{44-x}(\text{FTP})_{18}$  clusters. Though the positions of the peaks labeled as ‘\*\*’ (in B) and ‘#’ (in C) almost coincide, they are due to entirely different species, as shown in Figures S6 and S17. The peaks in Figure 3C are most probably due to metal thiolates containing Au and/or Ag; exact assignment of these peaks is difficult. Inset of Figure 3C shows that the undoped  $\text{Au}_{25}(\text{FTP})_{18}$  and Au-rich alloy clusters of the formula  $\text{Au}_{25-x}\text{Ag}_x(\text{FTP})_{18}$  were present in the solution even after 1 h. A comparison of the UV–vis spectrum of this reaction mixture (0.9:1.0) (see Figure S18) and that of the 2.8:1.0 mixture (see middle and bottom traces in Figure 1D) reveals that the features of the former are significantly changed compared to that of the latter. These data together suggest that the  $[\text{Au}_{12}\text{Ag}_{32}(\text{FTP})_{30}]^{4-}$  decompose in the presence of higher concentrations of Au source ( $\text{Au}_{25}(\text{FTP})_{18}$  or  $\text{Au}_{25-x}\text{Ag}_x(\text{FTP})_{18}$ ) in the reaction mixture. This is surprising, considering the high stability of  $\text{Au}_{12}\text{Ag}_{32}(\text{SR})_{30}$  reported previously.<sup>24</sup> However, the reason for this is not understood from the present study.

Hence, the mass spectrometric and absorption spectroscopic measurements presented above confirm unambiguously that (i) the exclusive formation of  $[\text{Au}_{12}\text{Ag}_{32}(\text{FTP})_{30}]^{4-}$  requires optimum relative concentrations of  $\text{Ag}_{44}(\text{FTP})_{30}$  and  $\text{Au}_{25}(\text{FTP})_{18}$  in the reaction mixture and (ii)  $[\text{Au}_x\text{Ag}_{44-x}(\text{FTP})_{30}]^{4-}$  with more than 12 Au atoms cannot be formed in the reaction between  $\text{Ag}_{44}(\text{FTP})_{30}$  and  $\text{Au}_{25}(\text{FTP})_{18}$ , irrespective of their relative concentrations. In other words,  $[\text{Au}_{12}\text{Ag}_{32}(\text{FTP})_{30}]^{4-}$  is the upper limit in the

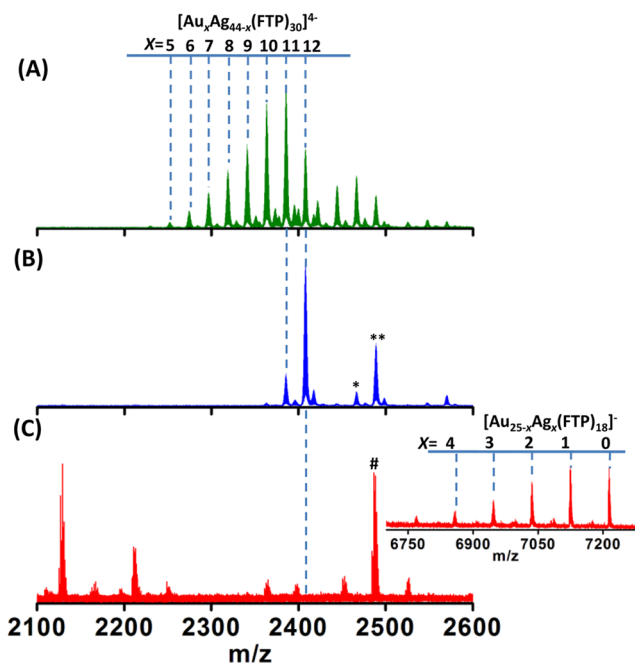
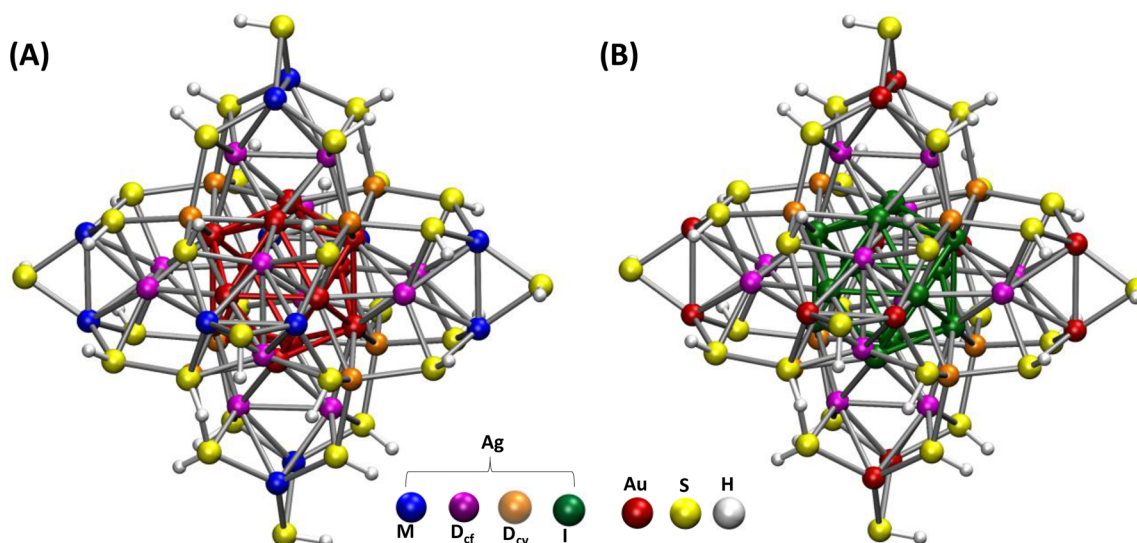


Figure 3. ESI MS spectra of a mixture of  $\text{Ag}_{44}(\text{FTP})_{30}$  and  $\text{Au}_{25}(\text{FTP})_{18}$  at a  $\text{Ag}_{44}(\text{FTP})_{30}:\text{Au}_{25}(\text{FTP})_{18}$  molar ratio of 0.9:1.0 measured within 2 min (A), 10 min (B), and 1 h (C) after mixing, showing the formation of  $[\text{Au}_{12}\text{Ag}_{32}(\text{FTP})_{30}]^{4-}$  and its decomposition to thiolates. The peaks labeled as ‘\*’ and ‘\*\*’ in (B) are due to alloy clusters containing additional Ag-FTP or Au-FTP units, as shown in Figure S6. The peak labeled as ‘#’ in (C) is due to one of the decomposition products, as shown in Figure S17. Inset of (C) shows the presence of  $\text{Au}_{25-x}\text{Ag}_x(\text{FTP})_{18}$  clusters in the reaction mixture even 1 h after mixing.

series  $[\text{Au}_x\text{Ag}_{44-x}(\text{FTP})_{30}]^{4-}$ . However, clusters containing more than 12 Au atoms in the  $3^-$  charge state were observed in the series  $[\text{Au}_x\text{Ag}_{44-x}(\text{FTP})_{30}]^{3-}$  at higher concentrations of  $\text{Au}_{25}(\text{FTP})_{18}$ , as shown in Figures S15 and S16. We note that no significant abundance was observed for any of the clusters in this series,  $[\text{Au}_x\text{Ag}_{44-x}(\text{FTP})_{30}]^{3-}$ , for any of the reaction mixtures studied (see Figures S13–S16). Hence, our results indicate that substitution of more than 12 Au atoms in  $\text{Ag}_{44}(\text{SR})_{30}$  clusters is indeed possible, however, resulting alloy clusters, such as  $\text{Au}_{13}\text{Ag}_{31}(\text{FTP})_{30}$ ,  $\text{Au}_{14}\text{Ag}_{30}(\text{FTP})_{30}$ , and so on, do not exist in the  $4^-$  charge state; they exist in only  $3^-$  or  $2^-$  states.

Mass spectrometric measurements presented above unambiguously confirm that (i) though  $[\text{Au}_x\text{Ag}_{44-x}(\text{FTP})_{30}]^{3-}$  clusters were formed in all of the reaction mixtures studied, they appeared only as a mixture; notably enhanced abundance was not observed for any one of these clusters in this series (see Figures S13–S16) and (ii) in the  $[\text{Au}_x\text{Ag}_{44-x}(\text{FTP})_{30}]^{4-}$  series,  $[\text{Au}_{12}\text{Ag}_{32}(\text{FTP})_{30}]^{4-}$  was formed as an exclusive entity at optimum relative concentrations of reactant clusters (see Figures 1C and 2–3). We think that the exclusive formation of  $[\text{Au}_{12}\text{Ag}_{32}(\text{FTP})_{30}]^{4-}$  could be due to its higher stability compared to that of the other clusters in the series  $[\text{Au}_x\text{Ag}_{44-x}(\text{SR})_{30}]^{4-}$ . The reasons behind these observations are discussed in the subsequent sections.

**Superatom–Nonsuperatom Transition in the formation of  $\text{Au}_x\text{Ag}_{44-x}(\text{SR})_{30}$  Clusters.** Bare metal clusters with certain nuclearities were found to be highly stable compared to the clusters with other nuclearities.<sup>25</sup> The number of valence electrons for such stable clusters were found to fall in a series of



**Figure 4.** DFT-optimized structures of the I isomer (A) and the M isomer (B) of  $\text{Au}_{12}\text{Ag}_{32}(\text{SH})_{30}$ . Color codes for the atoms in the structures: Red (Au), yellow (S), white (H), blue (Ag in M positions), magenta (Ag in  $D_{cf}$  positions), orange (Ag in  $D_{cv}$  positions), and green (Ag in I position).

numbers such as 2, 8, 18, 36, *etc.*, called magic numbers, which is equal to the electronic shell closing number, *i.e.*, the number of electrons required for the complete filling of the valence shell.<sup>25,26</sup> The attainment of such closed electronic shells is considered as one of the reasons behind the stability of metal clusters. This concept has been successful in understanding the stability of monolayer protected clusters also, and such clusters possessing magic numbers of valence electrons are referred to as superatoms.<sup>5–7,27</sup> For monolayer protected clusters, the magic number of electrons can be calculated using a simple formula:

$$n^* = N_A v_A - M - z$$

where  $n^*$  is the shell closing free electron count,  $N_A$  is the number of metal atoms of element A,  $v_A$  is the valency of metal atom A,  $M$  is the number of electron-localizing (or electron-withdrawing) ligands, and  $z$  is the overall charge of the cluster. According to this counting scheme, the number of shell closing free electrons for  $[\text{Ag}_{44}(\text{SR})_{30}]^{4-}$  can be calculated as  $n^* = (44 \times 1) - 30 - (-4) = 18$ , which is one of the magic numbers of electrons mentioned above, and, hence this cluster is a superatom. Similarly, all of the clusters in the series  $[\text{Au}_x\text{Ag}_{44-x}(\text{SR})_{30}]^{4-}$ , *i.e.*,  $[\text{Au}_1\text{Ag}_{43}(\text{FTP})_{30}]^{4-}$  to  $[\text{Au}_{12}\text{Ag}_{32}(\text{FTP})_{30}]^{4-}$  (shown in Figures 1–3) are superatomic with same number of shell closing free electrons since (i) they have the same number of metal atoms, ligands, and overall charge state of  $4^-$  and (ii) Ag and Au atoms possess the same number of valence electrons.

As noted before, mass spectrometric measurements (see Figures 1–3 and S13–S16) show that  $\text{Au}_x\text{Ag}_{44-x}(\text{SR})_{30}$  clusters containing more than 12 Au atoms do not exist in  $4^-$  charge state, *i.e.*, clusters such as  $[\text{Ag}_{13}\text{Au}_{31}(\text{FTP})_{30}]^{4-}$ ,  $[\text{Ag}_{14}\text{Au}_{30}(\text{FTP})_{30}]^{4-}$ , *etc.*, are not formed in the reaction, irrespective of the reactant concentrations. Instead, such clusters were observed in a  $3^-$  charge state (see Figures S13–S16). A counting of the shell closing free electrons for these clusters (containing more than 12 Au atoms) shows that they possess only 17 valence electrons [ $n^* = (44 \times 1) - 30 - (-3) = 17$ ]. Therefore, these clusters possess an open valence shell,

and hence they are nonsuperatoms. The decrease in the number of free electrons from 18 to 17 is due to the decrease in the overall charge state of these clusters from  $4^-$  to  $3^-$  when more than 12 Au atoms are incorporated in  $\text{Ag}_{44}(\text{SR})_{30}$ . This analysis, considering the number of Au atoms incorporated, overall charge state, and the number of shell closing free electrons, clearly shows that a superatom to nonsuperatom transition occurs in the distribution of  $\text{Au}_x\text{Ag}_{44-x}(\text{SR})_{30}$  clusters at  $x = 12$ . Such a transition has not been observed previously in metal atom substitution chemistry of well-known cluster systems, such as  $\text{Au}_{25}(\text{SR})_{18}$  (refs 28–30),  $\text{Ag}_{25}(\text{SR})_{18}$  (refs 31 and 32),  $\text{Ag}_{29}(\text{S}_2\text{R})_{12}$  (refs 33 and 34),  $\text{Au}_{38}(\text{SR})_{24}$  (refs 35 and 21),  $\text{Au}_{144}(\text{SR})_{60}$  (ref 36), *etc.*

Furthermore, if the attainment of the superatomic electron configuration was the only criterion determining the product distribution, we do not expect enhanced abundance for any particular cluster in the series  $[\text{Au}_x\text{Ag}_{44-x}(\text{SR})_{30}]^{4-}$  because all of these clusters in this series will be superatomic, as discussed above. However, Figures 1–3 show that  $[\text{Au}_{12}\text{Ag}_{32}(\text{FTP})_{30}]^{4-}$  is formed almost exclusively at appropriate conditions. Therefore, the exclusive formation of  $[\text{Au}_{12}\text{Ag}_{32}(\text{FTP})_{30}]^{4-}$  in the series  $[\text{Au}_x\text{Ag}_{44-x}(\text{SR})_{30}]^{4-}$  cannot be explained by electronic shell closing alone.

**DFT Calculations on the Structure and Stability of  $[\text{Au}_{12}\text{Ag}_{32}(\text{FTP})_{30}]^{4-}$ .** In order to know whether the exclusive formation of  $[\text{Au}_{12}\text{Ag}_{32}(\text{SR})_{30}]^{4-}$  is due to any geometrical factors, possible geometries of this cluster were analyzed. Crystal structure of  $\text{Ag}_{44}(\text{SR})_{30}$  shows that there are four symmetry unique positions for Ag atoms, as shown in Figure S19. They are (i) the innermost  $\text{Ag}_{12}$  icosahedron (I), (ii) the cube vertex positions in the middle dodecahedron ( $D_{cv}$ ), (iii) the cube face-capping positions of the middle dodecahedron ( $D_{cf}$ ), and (iv) the outermost  $\text{Ag}_2(\text{SR})_5$  mounts (M).

Since there are 12 atoms each in I,  $D_{cf}$ , and M positions, these sites can be the three distinct locations for  $\text{Au}_{12}$  in  $\text{Au}_{12}\text{Ag}_{32}(\text{SR})_{30}$ . We note that there are only eight  $D_{cv}$  positions, and hence it will not be possible to contain all the 12 Au atoms in these positions. Thus, there can be three structural isomers of high symmetry (I,  $D_{cf}$  and M) for  $\text{Au}_{12}\text{Ag}_{32}(\text{SR})_{30}$ , depending on where the substitution of all 12

atoms is made into the same type of symmetry unique positions. We did not consider mixed-shell isomers due to substitution into more than one type of symmetry unique positions, because alloy clusters resulting from such substitutions would be of lower symmetry, and hence they are less likely to be formed in the reaction, compared to those derived from substitutions in one type of shells. We do not expect this assumption to affect our conclusions.

In order to understand the stabilities of the isomers of  $[\text{Au}_{12}\text{Ag}_{32}(\text{FTP})_{30}]^{4-}$ , their energies were calculated using DFT. The calculations were performed using the methods described in Computational Details section. The reported crystal structure<sup>6</sup> of  $\text{Ag}_{44}(\text{SR})_{30}$  was used for the initial structures for the calculations. For efficient computations, we terminated each sulfur atom with a hydrogen atom in all the clusters. First, the structure of  $[\text{Ag}_{44}(\text{SH})_{30}]^{4-}$  was geometry optimized, and then 12 Ag atoms were replaced in symmetry nonequivalent positions by Au atoms, *i.e.*, first in the outermost mounts (M), second in the 12 cube-face capping positions ( $\text{D}_{\text{cf}}$ ) of the middle dodecahedron, and last in the inner icosahedron (I) (see Figure S19). Then, the geometries of these resulting configurations were optimized. The overall structural features, such as the innermost icosahedral  $\text{M}_{12}$  ( $\text{M} = \text{Au}/\text{Ag}$ ) shell, the middle dodecahedral  $\text{M}_{20}$  shell, and the outer  $\text{M}_2(\text{SR})_5$  mounts, bonding network, and atomic coordination of these isomers are preserved in comparison to those of the undoped  $[\text{Ag}_{44}(\text{SR})_{30}]^{4-}$  (see Figures 4 and S20). The conservation of the structure of the products is in agreement with our earlier study<sup>13</sup> on the reaction between  $\text{Au}_{25}(\text{SR})_{18}$  and  $\text{Ag}_{25}(\text{SR})_{18}$ .

Calculated energies of the isomers, listed in Table 1, show that the I isomer is most stable (−362.8 eV), followed by the

**Table 1. Energies of the DFT-Optimized Isomers of  $[\text{Au}_{12}\text{Ag}_{32}(\text{SR})_{30}]^{4-}$  Alloy Cluster**

| isomer of $[\text{Au}_{12}\text{Ag}_{32}(\text{SR})_{30}]^{4-}$ | energy (eV) |
|-----------------------------------------------------------------|-------------|
| icosahedron (I)                                                 | −362.8      |
| dodecahedral cube face ( $\text{D}_{\text{cf}}$ )               | −358.6      |
| mounts (M)                                                      | −356.7      |

$\text{D}_{\text{cf}}$  isomer (−358.6 eV), and finally the M isomer (−356.7 eV). Further, as mentioned earlier, the absorption spectra shown in middle and bottom traces of Figure 1D resemble that of previously reported  $\text{Au}_{12}\text{Ag}_{32}(\text{FTP})_{30}$ , wherein the  $\text{Au}_{12}$  occupies the I positions.<sup>20</sup> These observations suggest that the 12 Au atoms in  $[\text{Au}_{12}\text{Ag}_{32}(\text{FTP})_{30}]^{4-}$  formed in the reaction between  $\text{Ag}_{44}$  and  $\text{Au}_{25}$  are more likely to occupy the icosahedral (I) positions. However, crystal structure of the reaction product is required to confirm this unambiguously. Nevertheless, mass spectra, isotope patterns, optical absorption spectrum, and computations together suggest that the complete filling of the icosahedral shell by Au atoms in the reaction product,  $[\text{Au}_{12}\text{Ag}_{32}(\text{FTP})_{30}]^{4-}$ , is almost certain.

**Role of Geometrical and Electronic Shell Closing in the Substitution Chemistry of  $\text{Ag}_{44}(\text{FTP})_{30}$ .** The concept of electronic shell closing has been discussed in a previous section. Geometric shell closing refers to the existence of concentric polyhedral shells consisting of only one type of metal atoms.<sup>37</sup> Such effects have been observed in bare, gas-phase metal clusters,<sup>37–40</sup> and such closed-shell clusters were observed with higher abundance and stability. In the context of alloy clusters, the closure of the shell can be defined as the occupation of a

polyhedral shell with only one type of atom (*e.g.*, only Au or only Ag), and if there are two types of atoms in a polyhedral shell (*e.g.*, both Au and Ag), it is considered geometrically incomplete or open. Furthermore, if a shell contains atoms of different elements, there can be distortions in the shell geometry and the overall symmetry due to the differences in the bond lengths, and these factors might decrease the overall stability of the cluster. Hence, in the case of  $[\text{Au}_{12}\text{Ag}_{32}(\text{SR})_{30}]^{4-}$ , the metal atoms (Ag/Au) in the outermost M positions do not form a complete (polyhedral) shell since these atoms are the part of isolated  $\text{M}_2(\text{SR})_5$  mounts. Therefore, the M isomer of  $[\text{Au}_{12}\text{Ag}_{32}(\text{SR})_{30}]^{4-}$  cannot be considered as a geometrically closed-shell cluster. A similar situation exists in the case of the  $\text{D}_{\text{cf}}$  isomer also since 20 Au atoms are required to form a geometrically complete ( $\text{M}_{20}$ ) dodecahedral shell consisting of similar atoms, which we may not expect to be very stable since gold is not known to form a dodecahedral arrangement, unlike silver. Contrary to the M and the  $\text{D}_{\text{cf}}$  isomers, the substitution of all of the 12 Ag atoms in the icosahedral core of  $\text{Ag}_{44}(\text{SR})_{30}$  by Au atoms produces the I isomer of  $[\text{Au}_{12}\text{Ag}_{32}(\text{SR})_{30}]^{4-}$ , wherein a geometrically complete icosahedral shell consisting of only Au atoms is present. However, in  $[\text{Au}_x\text{Ag}_{44-x}(\text{SR})_{30}]^{4-}$  clusters containing <12 Au atoms, such geometrical shell closing is not possible because of the insufficient number (<12) of Au atoms in them. Hence, these clusters containing <12 Au atoms possess only a mixed-metal icosahedral shell, lacking the geometric shell closing and associated stability. Hence, the Au atoms in  $[\text{Au}_{12}\text{Ag}_{32}(\text{FTP})_{30}]^{4-}$  are more likely to occupy the innermost icosahedral shell, fulfilling the criterion of geometric as well as electronic shell closing. Therefore, we believe that exclusive formation of  $[\text{Au}_{12}\text{Ag}_{32}(\text{SR})_{30}]^{4-}$  is due to the high stability of this cluster gained by the combined effects of electronic as well as geometric shell closing. In order to understand the contributions of shell closing effects and other factors to the stability, theoretical calculations of  $\text{Au}_x\text{Ag}_{44-x}(\text{SH})_{30}$  in 3<sup>−</sup> and 4<sup>−</sup> charge states for each value of *x* and analyses of their bond lengths, bond angles, HOMO–LUMO gaps, electronic charge density distribution, *etc.*, have to be performed, probably with real ligands (instead of −SH), which are beyond the scope of the present work.

In the light of the experimental evidence and the DFT calculations presented above, we suggest that Au atom substitution into  $\text{Ag}_{44}(\text{SR})_{30}$ , *via* intercluster reactions, shows a systematic trend in terms of the sites of metal atom substitution, charge state, and overall structure. This trend can be summarized as follows: (i) When the concentrations of  $\text{Au}_{25}(\text{FTP})_{18}$  are low, the substitution reaction produces  $[\text{Au}_x\text{Ag}_{44-x}(\text{SR})_{30}]^{4-}$  containing <12 Au atoms (see Figure 2A,B) which are likely to be located in the I positions, as predicted from the calculations. These clusters possess a geometrically incomplete shell (of <12 Au atoms) though they have electronically closed shells. (ii) When the concentration of  $\text{Au}_{25}(\text{FTP})_{18}$  is higher, the reaction gradually progresses to substitute all of the Ag atoms in the I positions, forming  $[\text{Au}_{12}\text{Ag}_{32}(\text{SR})_{30}]^{4-}$  which is a geometrically as well as electronically closed-shell system. (iii) Further Au atom substitution could occur at the  $\text{D}_{\text{cf}}$ ,  $\text{D}_{\text{cv}}$ , or the M positions; however, the resulting  $\text{Au}_x\text{Ag}_{44-x}(\text{SR})_{30}$  alloy clusters do not have a closed geometric or electronic shell, as described earlier. Hence, our studies reveal that the geometrical as well as electronic shell structures of  $\text{Ag}_{44}(\text{SR})_{30}$  are reflected in its metal atom substitution chemistry.

## CONCLUSION

In conclusion, we demonstrated the manifestation of the shell structure of monolayer protected metal clusters in their intercluster reactivity in solution. We showed that two closed-shell clusters,  $[\text{Ag}_{44}(\text{SR})_{30}]^{4-}$  and  $[\text{Au}_{25}(\text{SR})_{18}]^{-}$ , produce another closed-shell alloy cluster,  $[\text{Au}_{12}\text{Ag}_{32}(\text{SR})_{30}]^{4-}$ , with its overall geometrical structure, electronic configuration, and charge states preserved. We observed a systematic trend in the Au atom substitution into  $\text{Ag}_{44}(\text{SR})_{30}$ , reflecting the geometric shell structure of the reactant and product clusters. We showed that the metal atom substitution chemistry of  $\text{Ag}_{44}(\text{SR})_{30}$  proceeds through an unexpected superatom–nonsuperatom transition, resulting from a change in the overall charge state of the  $\text{Au}_x\text{Ag}_{44-x}(\text{SR})_{30}$  alloy clusters formed. Our study also shows that structural factors play an important role in determining the sites of substitution as well as the overall charge states of the alloy clusters formed and further supports the molecular nature of such materials. We hope that our results will initiate more activities in this area of monolayer protected clusters to understand their substitution chemistry and associated structure–reactivity relationships in greater detail.

## MATERIALS AND METHODS

**Materials.** Chloroauric acid trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ), *n*-butanethiol (*n*-BuS), 4-fluorothiophenol (FTP), tetraoctylammonium bromide (TOAB), tetraphenyl phosphonium bromide ( $\text{PPh}_4\text{Br}$ ), and sodium borohydride ( $\text{NaBH}_4$ ) were purchased from Sigma-Aldrich. Silver nitrate ( $\text{AgNO}_3$ ) 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.**  $[\text{Au}_{25}(\text{FTP})_{18}][\text{TOAB}]$ . This cluster was synthesized through the ligand exchange of  $\text{Au}_{25}(\text{n-BuS})_{18}$  with FTP ligand. For the synthesis of  $\text{Au}_{25}(\text{n-BuS})_{18}$ , 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 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 BuS was added at a stretch while stirring at the same speed. The deep red color slowly turned to yellow and eventually became colorless after about 45 min. After stirring further for about 1.5 h, 2.5 mL of ice cold aqueous  $\text{NaBH}_4$  (0.2 M) was added in one shot. The solution turned black immediately and was then stirred for 5 h. The solution was then rotary evaporated, methanol was added, and the solution was washed repeatedly with the same and dried.

**Ligand Exchange of  $\text{Au}_{25}(\text{n-BuS})_{18}$ .** Five mg of dried  $\text{Au}_{25}(\text{n-BuS})_{18}$  was dissolved in 0.5 mL of toluene and then pure FTP, 150 times (by weight), was added to it. The solution was heated at 50 °C in an oil bath while stirring. After about 25 min, clusters were precipitated with hexane and collected by centrifugation. This precipitate was washed with hexane, dissolved in DCM, and centrifuged to remove thiolates. This cluster solution in DCM was dried using rotary evaporation and stored at 4 °C. The product was nearly pure, however, the presence of BuS was noticed in the alloy clusters,  $\text{Au}_x\text{Ag}_{44-x}(\text{FTP})_{29}(\text{BuS})_1$  (see uppermost panel in Figure 1C).

$[\text{Ag}_{44}(\text{FTP})_{30}][\text{PPh}_4]_4$ . This cluster was synthesized following a previously reported method.<sup>12</sup> 20 mg of  $\text{AgNO}_3$  and 12 mg of  $\text{PPh}_4\text{Br}$  were ground thoroughly in an agate mortar and pestle for 5 min. About 76  $\mu\text{L}$  of FTP was added to it at a stretch, and the mixture was ground further for about 3 min. About 45 mg of dry  $\text{NaBH}_4$  was added, and the mixture was ground until the pasty mass became brown in color. 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 UV–vis spectrum. The clusters were purified adopting the same protocol used for  $\text{Au}_{25}(\text{SR})_{18}$ .

**Reaction between  $\text{Ag}_{44}(\text{FTP})_{30}$  and  $\text{Au}_{25}(\text{FTP})_{18}$ .** Stock solutions of  $[\text{Ag}_{44}(\text{FTP})_{30}][\text{PPh}_4]_4$  (1.0 mg in 0.3 mL, 0.34 mM) and  $[\text{Au}_{25}(\text{FTP})_{18}][\text{TOA}]$  (3.7 mg in 1.0 mL, 0.48 mM) were prepared in DCM. Reactions were carried out as follows: 100  $\mu\text{L}$  of the stock solution of  $[\text{Ag}_{44}(\text{FTP})_{30}][\text{PPh}_4]_4$  was diluted to 0.5 mL using DCM. Then, various volumes (2, 5, 15, 25, 35, and 50  $\mu\text{L}$ ) of  $[\text{Au}_{25}(\text{FTP})_{18}][\text{TOA}]$  stock solution were added to the diluted  $[\text{Ag}_{44}(\text{FTP})_{30}][\text{PPh}_4]_4$  solution at a stretch using a micropipette. The  $\text{Ag}_{44}:\text{Au}_{25}$  molar ratios for the reaction mixtures prepared with 2, 5, 15, 25, 35, and 50  $\mu\text{L}$  of  $[\text{Au}_{25}(\text{FTP})_{18}][\text{TOA}]$  were 35.0:1.0, 14.0:1.0, 5.0:1.0, 2.8:1.0, 2.0:1.0, and 1.4:1.0, respectively. The mixture was stirred with a pipet, not magnetically. The reaction occurred immediately after mixing as observed from the color changes and time-dependent ESI MS measurements. All reactions were carried out at room temperature ( $\sim 30$  °C).

**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 are given in Supporting Information.

**Computational Details.** We used density functional theory (DFT) as implemented in the real-space grid-based projector augmented wave (GPAW) package.<sup>41</sup> For computational efficiency during the structural optimizations, rather than employing the finite-difference real-space grid method for the expansion of the pseudo-wave functions, we used instead the linear combination of atomic orbitals (LCAO) method<sup>42</sup> as implemented in GPAW by employing a double- $\zeta$  plus polarization (DZP) basis set. For greater precision in calculations, we then recalculated the total energies at this geometry minimum using the finite-difference method in GPAW. For the calculations, the  $\text{Ag}(4d^{10}5s^15p^0)$ ,  $\text{Au}(5d^{10}6s^1)$ , and  $\text{S}(3s^23p^4)$  electrons were treated as valence electrons, and the inner electrons were included in a frozen core. We included extra unoccupied 5p states on Ag atoms for improved accuracy. The GPAW setups for gold and silver included scalar-relativistic corrections. The exchange–correlation functional employed was the generalized gradient approximation of Perdew, Burke, and Ernzerhof (GGA-PBE).<sup>43</sup> Spin polarization was used for all the calculations. A grid spacing of 0.2 Å was used for electron density in all calculations, and a convergence criterion of 0.05 eV/Å for the residual forces on atoms was used in all structure optimizations, without any symmetry constraints. The structures of  $[\text{Au}_{25}(\text{SCH}_3)_{18}]^{-}$  and  $[\text{Ag}_{44}(\text{SCH}_3)_{30}]^{4-}$  (in Figure 1A,B) and the isomers of  $[\text{Au}_{12}\text{Ag}_{32}(\text{SR})_{30}]^{4-}$  (Figures 4 and S20) were built up with the help of the Avogadro software package,<sup>44</sup> and visualizations were created with Visual Molecular Dynamics (VMD) software.<sup>45</sup> The structures of  $[\text{Ag}_{44}(\text{SCH}_3)_{30}]^{4-}$  and  $[\text{Au}_{25}(\text{SCH}_3)_{18}]^{4-}$  have been modeled assuming coordinates from reported crystal structures.<sup>6,8</sup>

## ASSOCIATED CONTENT

## Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.7b01912.

Details of instrumentation and mass spectrometric measurements, additional ESI MS and UV–vis spectra, additional computational results, coordinates of the DFT-optimized geometries of the I,  $\text{D}_{\text{cf}}$ , and M isomers of  $\text{Au}_{12}\text{Ag}_{32}(\text{SH})_{30}$  (PDF)

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## Author Contributions

K.R.K. designed and carried out the reactions, A.B. carried out mass spectrometric measurements, A.G. synthesized the clusters, G.N. carried out DFT calculations and created the visualization of optimized structures, and T.P. supervised the whole project.

## Notes

The authors declare no competing financial interest.

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