Showcasing collaborative research from Prof. Yuichi Negishi’s laboratory, Tokyo University of Science, Prof. Tatsuya Tsukuda’s laboratory, The University of Tokyo, and Prof. Katsuyuki Nobusada’s laboratory, Institute for Molecular Science, Japan.

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Tuning the electronic structure of thiolate-protected 25-atom clusters by co-substitution with metals having different preferential sites†

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Trimetallic Au24−xAg,Pd and tetrametallic Au24−x−yAg,Cu,Pd clusters were synthesized by the subsequent metal exchange reactions of dodecanethiolate-protected Au25Pd clusters. EXAFS measurements revealed that Pd, Ag, and Cu dopants preferentially occupy the center and edge sites of the core, and staple sites, respectively. Spectroscopic and theoretical studies demonstrated that the synergistic effects of multiple substitutions on the electronic structures are additive in nature.

Small metal clusters have attracted substantial attention as new functional nanomaterials because they exhibit size-specific physical and chemical properties that are not found in the corresponding bulk metals.1 Substituting part of the atoms in these metal clusters with other elements enables us to generate still more varied functions.2

Recently, it has become possible to synthesize metal clusters substituted with other metals. For example, thiolate-protected gold clusters (Au13(SR)18)3,4 have been substituted to form Au25(SR)18,5,6 Au24Pd(SR)18,6 Au25−xAg13−x(SR)18,5,14,18 Au25−xCu13−x(SR)18,14,18,20 Au25−xHg13−x(SR)18,20,21 Au24Cd(SR)18,20,21 (R = C12H25, C2H4Ph, C6H11, or C6H13). Furthermore, it has been revealed that substitution of the clusters with Pt or Pd can improve their stability or reactivity.5,7 Meanwhile, continuous substitution with Ag or Cu allows fine adjustment of the gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of a cluster.12,13,18 If we simultaneously substitute some of the Au atoms in Au25(SR)18 with multiple elements, it might be possible to further modulate the electronic/geometrical structures and physical/chemical properties of the clusters. However, few 25-atom clusters containing three or more elements have been reported.23,24 Therefore, the effect of simultaneous substitution with multiple elements on the structure and properties of Au25(SR)18 still remains unclear.

Au25(SR)18 has a geometrical structure in which an Au13 core is covered by six -SR-[Au-SR-] staples (Fig. 1).25–31 It has been revealed that in Au25−xMx(SR)18, Pt and Pd substitute Au in the center (C site) of the Au13 core,5−7,10,11,12 and Ag preferentially replaces Au at the edge (E site) of the Au13 core.12,13,15,19,33 In contrast, Cu and Hg tend to substitute Au in the staples (S site) (Fig. 1).19,22 Cd has been reported to substitute both the C site20 and E site.21 These findings indicate that each element has a preferential site or sites. Therefore, it seems promising to combine elements with different preferential sites to effectively synthesize 25-atom clusters containing three or more elements without causing conflict among the substitution sites. In particular, only a single element should be selected for the C site because there is only one atom present in the C site (Fig. 1).

The purpose of this study is to elucidate the electronic/geometrical structures of thiolate-protected 25-atom clusters

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including three or more elements. To this end, we first synthesized these clusters. Pd, Ag, and Cu are selected as substitution elements because they substitute different sites. In the synthesis, dodecanethiolate (SC12)-protected Au$_{24}$Pd(SC12)$_{18}$ was first synthesized with atomic precision. Then a part of Au was substituted with Ag and subsequently with Cu. The mass analysis of the products confirmed the synthesis of the targeted tetrametallic Au$_{24-x-y}$Ag$_x$Pd$_y$(SC12)$_{18}$ and tetrametallic Au$_{24-x-y}$Ag$_x$Cu$_y$Pd$_y$(SC12)$_{18}$ clusters. The extended X-ray absorption fine structure (EXAFS) analysis demonstrated that the preferential site of each element does not change in these clusters even in the presence of an associated substituting element. The study of the electronic structure implied that this co-substitution at different positions enables superposition of the effect of each heteroatom substitution on the electronic structure of the cluster.

We used SC12 as the ligand in the clusters. Recent studies have shown that metal exchange via the reaction of a cluster (template cluster) with an M–SR complex (M = Ag or Cu) allows effective Ag and Cu substitutions. Therefore, we used this metal exchange reaction for Ag and Cu substitution in this work.

Au$_{24-x-y}$Ag$_x$Pd$_y$(SC12)$_{18}$ was synthesized by reacting highly pure Au$_{24}$Pd(SC12)$_{18}$ (top spectrum in Fig. 2(a)) with Ag-SC12. The middle spectrum in Fig. 2(a) shows the matrix-assisted laser desorption ionization (MALDI) mass spectrum of the product obtained after the reaction with Ag-SC12 for 48 h (Fig. S1 and S2†). The peaks attributed to Au$_{24-x-y}$Ag$_x$Pd$_y$(SC12)$_{18}$ (x = 1–5) are observed in the mass spectrum. Au$_{15}$Ag$_5$Pd (SC12)$_{18}$ was also observed after the reaction of 120 h (Fig. S1†). These results indicate that the Au atoms were successfully exchanged with Ag atoms. After a long reaction time, the peak of Au$_{20}$Ag$_6$Pd(SC12)$_{18}$ was usually observed with the highest ion intensity in the mass spectrum (Fig. 2(a) and S3†). This suggests that Au$_{20}$Ag$_6$Pd(SC12)$_{18}$ is the most stable cluster among Au$_{24-x-y}$Ag$_x$Pd$_y$(SC12)$_{18}$ under these experimental conditions (Fig. S4†).

Au$_{24-x-y}$Ag$_x$Cu$_y$Pd$_y$(SC12)$_{18}$ was synthesized by a reaction of the obtained Au$_{24-x-y}$Ag$_x$Pd$_y$(SC12)$_{18}$ (upper spectrum in Fig. 2(b)) with Cu-SC12. The lower spectrum in Fig. 2(b) is the MALD mass spectrum of the product obtained after reaction for 3 h. In addition to Au$_{24-x-y}$Cu$_y$Pd$_y$(SC12)$_{18}$, the spectrum exhibits new peaks assignable to tetrametallic Au$_{24-x-y}$Ag$_x$Cu$_y$Pd$_y$(SC12)$_{18}$. This means that the target tetrametallic clusters were formed by this reaction (Fig. S5†). The yield of the tetrametallic clusters could not be enhanced even by prolongation of the reaction time. Thus, we also attempted the synthesis of Au$_{24-x-y}$Ag$_x$Cu$_y$Pd$_y$(SC12)$_{18}$ using a different route. Au$_{24-x-y}$Cu$_y$Pd$_y$(SC12)$_{18}$ was allowed to react with Ag-SC12 to obtain Au$_{24-x-y}$Ag$_x$Cu$_y$Pd$_y$(SC12)$_{18}$. However, the peaks due to the Cu-containing clusters disappeared after the prolonged reaction (Fig. S6†). These results indicate that Cu substitution induces the degradation of the cluster in solution or destabilization in the reaction with an M–SR complex.

The substitution site of each element in Au$_{24-x-y}$Ag$_x$Pd$_y$(SC12)$_{18}$ and Au$_{24-x-y}$Ag$_x$Cu$_y$Pd$_y$(SC12)$_{18}$ was investigated by EXAFS analysis. As shown in Fig. 1, the substitution number of Ag varies with the reaction time. We measured the Pd K, Ag K, and Cu K-edge EXAFS spectra of Au$_{24-x-y}$Ag$_x$Pd$_y$(SC12)$_{18}$ (Fig. S7†) and Au$_{24-x-y}$Ag$_x$Cu$_y$Pd$_y$(SC12)$_{18}$ (Fig. S8†) prepared using a short reaction time to identify the preferential sites of Ag and Cu at the early stage of substitution. The spectra were measured at 10 K to obtain quantitative structure information by suppressing the thermal fluctuation of the metal–metal bonds. We found that the preferential sites of Pd, Ag, and Cu were maintained even in the presence of co-substituting elements.

We first monitored whether the location of Pd atoms initially doped was changed during the reaction. It is already known that the Pd dopant is located at the C site of the Au$_{113}$ core. Fig. 3(a) presents the Pd K-edge Fourier transform (FT)-EXAFS spectra of Au$_{24-x-y}$Ag$_x$Pd$_y$(SC12)$_{18}$ and Au$_{24-x-y}$Ag$_x$Cu$_y$Pd$_y$(SC12)$_{18}$ together with that of bimetallic Au$_{24}$Pd(SC12)$_{18}$ as a reference (Fig. S9(a)†). The results of curve fitting are summarized in Table S2. The spectra of Au$_{24-x-y}$Ag$_x$Pd$_y$(SC12)$_{18}$ and Au$_{24-x-y}$Ag$_x$Cu$_y$Pd$_y$(SC12)$_{18}$ exhibit a peak attributed to the Pd–M (M = Au and Ag) bonds in the vicinity of 2.7 Å. The total coordination numbers (CNs) of the Pd–M (M = Au and Ag) bonds were estimated to be 10.3 and 11.8, respectively (Table S2†). Although these CN values include the contribution from the precursors Au$_{24}$Pd(SC12)$_{18}$ (Fig. S7†) and by-products Au$_{24-x-y}$Cu$_y$Pd$_y$(SC12)$_{18}$ (Fig. S8†) contained in the samples used for the measurement, they indicate that the Pd atom remained at the C site during the synthesis of Au$_{24-x-y}$Ag$_x$Pd$_y$(SC12)$_{18}$ (Fig. S7†) and Au$_{24-x-y}$Ag$_x$Cu$_y$Pd$_y$(SC12)$_{18}$ (Fig. S8†). This interpretation was further confirmed by the observation of the fragment ions of Au$_x$Ag$_y$Cu$_z$Pd$_w$.
The CN value of the Cu–S bond\(^{19}\) of \(\text{Au}_{24}x\rightarrow_{x,y}^{x,y}\text{Ag}_{x}Pd_{x,y}y(\text{SC}12)_{18}\) was estimated to be 2.2 (Table S4\(^{\dagger}\)). Although the CN value includes the contribution from the precursors \(\text{Au}_{24}x\rightarrow_{x,y}^{x,y}\text{Cu}_{x,y}Pd_{x,y}y(\text{SC}12)_{18}\) contained in the sample, this indicates that Cu introduced into \(\text{Au}_{24}x\rightarrow_{x,y}^{x,y}\text{Ag}_{x}Pd_{x,y}y(\text{SC}12)_{18}\) (Fig. S8\(^{\dagger}\)) preferentially occupies the S site.

Fig. 4 illustrates the effect of Ag or Cu substitution (Fig. 2) on the optical properties of the clusters. Substitution with Ag leads to the splitting of the peak at \(\sim 1.9\) eV (Fig. 4(a)). In contrast, following Cu substitution (Fig. 4(b)), only a slight peak shift to the lower energy side was observed; the overall characteristics of the spectrum were maintained. A similar result was also obtained following the Cu substitution of \(\text{Au}_{24}x\rightarrow_{x,y}^{x,y}\text{Ag}_{x}Pd_{x,y}y(\text{SC}12)_{18}\) containing different numbers of Ag atoms (Fig. S11\(^{\dagger}\)).

To investigate the origin of these spectral changes in detail, density functional theory calculations were performed for \([\text{Au}_{24}x\rightarrow_{x,y}^{x,y}\text{Pd}y(\text{SCH}3)_{18}]^{0}\), \([\text{Au}_{23}x\rightarrow_{x,y}^{x,y}\text{AgPd}y(\text{SCH}3)_{18}]^{0}\), and \([\text{Au}_{22}x\rightarrow_{x,y}^{x,y}\text{AgCuPd}y(\text{SCH}3)_{18}]^{0}\) (Fig. S11\(^{\dagger}\)). In the calculations, the substitution sites of Pd, Ag, and Cu were fixed at the C, E, and S sites, respectively (Fig. S12\(^{\dagger}\)), as suggested by the experimental results.

Fig. 5(b) shows the calculated optical absorption spectra for \([\text{Au}_{24}x\rightarrow_{x,y}^{x,y}\text{Pd}y(\text{SR})_{18}]^{0}\), \([\text{Au}_{23}x\rightarrow_{x,y}^{x,y}\text{AgPd}y(\text{SR})_{18}]^{0}\), and \([\text{Au}_{22}x\rightarrow_{x,y}^{x,y}\text{AgCuPd}y(\text{SR})_{18}]^{0}\). Ag substitution caused remarkable splitting of the peaks around 2.0 eV (Fig. 5(b)), consistent with that observed in Fig. 4(a). In the calculated optical spectrum of \(\text{Au}_{24}x\rightarrow_{x,y}^{x,y}\text{Pd}y(\text{SR})_{18}\), the peaks around 2.0 eV are attributed to the transitions from HOMO and HOMO–1 composed mainly of the 5d orbital of the Pd atom to LUMO+1 and LUMO+2 composed mainly of the 6p orbitals of Au atoms (Fig. 5(a)).\(^{6,35}\) The marked splitting of the peaks at 2.0 eV could be attributed to the increase of splitting between HOMO and HOMO–1 and that between LUMO+1 and LUMO+2 induced by Ag substitution (Fig. 5(a)).

Cu substitution (Fig. 5(b)) had a smaller effect on the calculated absorption spectrum, similar to the experimental result (Fig. 4(b)). However, a slight peak shift to the lower energy side can be seen in the calculated spectrum. This spectral change is considered to be caused by a slight lowering of LUMO+1 and a slight rise of HOMO–2 (Fig. 5(a)). A similar spectral shift was also induced in \(\text{Au}_{24}x\rightarrow_{x,y}^{x,y}\text{Ag}y(\text{SR})_{18}\) following Cu substitution.\(^{18,36}\)

These results indicate that the effect of Cu substitution is

\(x + y + z = 19–22; \; w = 9, 10\) in the laser dissociation mass spectra of these clusters (Fig. S10\(^{\dagger}\)).

We then studied the location of Ag atoms doped in \(\text{Au}_{24}x\rightarrow_{x,y}^{x,y}\text{AgPd}y(\text{SC}12)_{18}\) and \(\text{Au}_{24}x\rightarrow_{x,y}^{x,y}\text{AgCuPd}y(\text{SC}12)_{18}\). Fig. 3(b) shows the Ag K-edge FT-EXAFS spectra of \(\text{Au}_{24}x\rightarrow_{x,y}^{x,y}\text{AgPd}y(\text{SC}12)_{18}\) and \(\text{Au}_{24}x\rightarrow_{x,y}^{x,y}\text{AgCuPd}y(\text{SC}12)_{18}\) (Fig. S9(b)\(^{\dagger}\)) together with that of bimetallic \(\text{Au}_{25}x\rightarrow_{x,y}^{x,y}\text{Ag}y(\text{SC}2H4Ph)_{18}\) (Fig. S8\(^{\dagger}\)). These comparisons are overall similar to that of bimetallic \(\text{Au}_{25}x\rightarrow_{x,y}^{x,y}\text{Ag}y(\text{SC}2H4Ph)_{18}\). In these spectra, the peaks in the vicinity of 1.8–2.5 Å and 2.5–3.0 Å are attributable to the Ag–S and Ag–M (M = Au and Pd) bonds, respectively.\(^{19}\) The CNs of the Ag–S bond of \(\text{Au}_{24}x\rightarrow_{x,y}^{x,y}\text{AgPd}y(\text{SC}12)_{18}\) and \(\text{Au}_{24}x\rightarrow_{x,y}^{x,y}\text{AgCuPd}y(\text{SC}12)_{18}\) were estimated to be 1.4 and 1.1, respectively (Table S3\(^{\dagger}\)). The total CNs of the Ag–M (M = Au and Pd) bonds are close to those (1.0 and 6.0, respectively) of \(\text{Au}_{25}x\rightarrow_{x,y}^{x,y}\text{Ag}y(\text{SR})_{18}\) in which a single Ag occupies the E site of \(\text{Au}_{25}x\rightarrow_{x,y}^{x,y}\text{Ag}y(\text{SR})_{18}\) (Fig. 1).\(^{19}\) These comparisons indicate that Ag atom[s] introduced occupy the E site of \(\text{Au}_{24}x\rightarrow_{x,y}^{x,y}\text{Ag}y(\text{SC}12)_{18}\) (Fig. S7\(^{\dagger}\)) and \(\text{Au}_{24}x\rightarrow_{x,y}^{x,y}\text{AgCuPd}y(\text{SC}12)_{18}\) (Fig. S8\(^{\dagger}\)) as in the case of \(\text{Au}_{25}x\rightarrow_{x,y}^{x,y}\text{Ag}y(\text{SC}2H4Ph)_{18}\) (x ~ 1).\(^{19}\)

We finally studied the location of Cu atoms doped in \(\text{Au}_{24}x\rightarrow_{x,y}^{x,y}\text{AgCuPd}y(\text{SC}12)_{18}\). Fig. 3(c) displays the Cu K-edge FT-EXAFS spectrum of \(\text{Au}_{24}x\rightarrow_{x,y}^{x,y}\text{AgCuPd}y(\text{SC}12)_{18}\) (Fig. S9(c)\(^{\dagger}\)) together with that of bimetallic \(\text{Au}_{25}x\rightarrow_{x,y}^{x,y}\text{Cu}y(\text{SC}2H4Ph)_{18}\) (y ~ 1).\(^{19}\) Both spectra exhibit a peak at \(\sim 1.9\) Å due to the Cu–S bond.\(^{19}\)
superposed on that of Ag substitution in the electronic structure of \( \text{Au}_{24-\alpha,\beta,\gamma}\text{Ag}_\alpha\text{Cu}_\beta\text{Pd}(\text{SC}12)_{18} \).

In conclusion, trimetallic \( \text{Au}_{24-\alpha,\beta,\gamma}\text{Ag}_\alpha\text{Pd}(\text{SC}12)_{18} \) and tetra-metallic \( \text{Au}_{24-\alpha,\beta,\gamma}\text{Ag}_\alpha\text{Cu}_\beta\text{Pd}(\text{SC}12)_{18} \) clusters were synthesized by metal exchange reactions. EXAFS analysis of the products demonstrated that each substituting element maintains a preferential site in these clusters. The comparison of optical spectra suggested that the effect of substitution with each metal on the electronic structure is additive in nature. The results of this study indicate that the electronic structure of 25-atom Au clusters can be modulated for a specific application in a predictable manner. We hope that, in the future, further studies will be performed on hetero metal clusters containing more than three elements.

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Notes and references


