Shape-Controlled Synthesis of Trimetallic Nanoclusters: Structure Elucidation and Properties Investigation


Abstract: The shape-controlled synthesis of metal nano-clusters (NCs) with precise atomic arrangement is crucial for tailoring the properties. In this work, we successfully control the shape of alloy NCs by altering the dopants in the alloying processes. The shape of the spherical \([Pt_1Ag_{24}(SPhMe_2)_{18}]\)_NC is maintained when \([AuISR]\) is used as dopant. By contrast, the shape of \(Pt_1Ag_{24}\) is changed to be rodlike by alloying with \([Au'(PPh_3)Br]\). The structures of the trimetallic NCs were determined by X-ray crystallography and further confirmed by both DFT and far-IR measurements. The shape-preserved \([Pt_1Au_{6.4}Ag_{17.6}(SPhMe_2)_{18}]\)_NC is in a tristratified arrangement—\([Pt(central)@Au/Ag(shell)@Ag(exterior)]\)—and is indeed the first X-ray crystal structure of thiolated trimetallic NCs. On the other hand, the resulting rodlike NC \([Pt_2Au_{10}Ag_{13}(PPh_3)_{10}Br_7]\) exhibits a high quantum yield (QY \(=14.7\%)\), which is in striking contrast to the weakly luminescent \(Pt_1Ag_{24}\) (QY \(=0.1\%)\), about 150-fold enhancement). In addition, the thermal stabilities of both trimetallic products are remarkably improved. This study presents a controllable strategy for synthesis of alloy NCs with different shapes (by alloying heteroatom complexes coordinated by different ligands), and may stimulate future work for a deeper understanding of the morphology (shape)–property correlation in NCs.

Mastery over the size, shape or composition of alloy nanoparticles (NPs) enables control of their properties and enhancement of their usefulness for various applications. [4–6] Therefore, the insights into structure–property correlations are of great importance for guiding the synthesis of NPs with specific functionalities. [4–6] However, a general issue lies in the uncertainty of the surface structure of NPs; this significantly limits a deeper understanding of the structure–property correlations.

On this basis, noble-metal nanoclusters (NCs) with ultra-small sizes (<2 nm in diameter of the metal core) have attracted considerable research interest for their precise structures. In addition, accurately characterized structures by X-ray crystallography provide exciting opportunities to investigate the mechanism of the structure-induced properties at the atomic level.

So far, much effort has been devoted to synthesis of alloy NCs. [14–25] For example, our group recently developed a metal-exchange strategy to prepare the atomically precise alloy NCs, providing an efficient method to study the composition–property correlations. [26] The atomically precise homometallic NCs are used as templates, and are doped with the heteroatom complexes to generate the target alloy NCs. Compared with monometallic NCs, the alloy NCs may show significantly enhanced optical, [14, 17, 18, 19a] catalytic, [16a, 17b, 23a, 27] and electrochemical [16b, 20, 28] properties. However, the previously reported alloy NCs only show changes in composition compared with the monometallic counterparts, and less effects on the properties of the NCs. We are motivated to pursue both composition and shape alterations; this would create new opportunities for tailoring the material properties. To achieve this goal, a major question is how to control the shape of the alloy NCs at the atomic level; this necessitates the development of new synthetic methods for alloy NCs.

In the previously described metal-exchange method, the shape of the templating NCs is maintained by alloying with heteroatom complexes coordinated by the same ligands (exclusively thiolates in previous work). [26] Therefore, it remains unknown whether the shape could be altered or not when the templating NCs are doped by heteroatom complexes with different ligands (such as, the very different M–SR and M–PR₃ complexes, M = Au/Ag/Pt). In addition, whether or not the altered shape could induce the qualitative leap in properties deserves exploration. These studies will not only help us better understand the ligand effect in alloying processes in a confined environment (in the NC range), but also provide a reliable method to synthesize alloy NCs in an unprecedented shape-changing manner.

Herein, we report an effective way to change the shape of NCs by alloying the same precursor—\(Pt_1Ag_{24}\) (protected by -SPhMe₂)—with heteroatom complexes bearing different li-
gands. Specifically, when alloying the Pt\textsubscript{1}Ag\textsubscript{24} NC with [Au(PPh\textsubscript{3})Br] we successfully obtained a rod-shaped trimetallic M\textsubscript{25} (M = Au/Ag/Pt) NC, whereas [AuSR] (SR = SPhMe\textsubscript{2}) the same thiolate ligand as in the precursor NC) generated a spherical trimetallic M\textsubscript{25} without any changes in shape. The crystal structures of these two trimetallic NCs are determined by X-ray crystallography, and further characterized by high-resolution ESI-TOF-MS, far IR (FIR) measurements, and DFT computations.

As to the spherical-shaped NC, the X-ray crystal structure indicates that the average formula is [Pt\textsubscript{1}Au\textsubscript{6.4}Ag\textsubscript{17.6}(SR)\textsubscript{18}]\textsuperscript{2–} (Pt\textsubscript{1}Au\textsubscript{24} for short). To the best of our knowledge, this is the first report of an X-ray crystal structure of thiolated trimetallic NCs. In addition, the rod-shaped NC is identified to be [Pt\textsubscript{1}Au\textsubscript{0.6}Ag\textsubscript{10.4}(PPh\textsubscript{3})\textsubscript{10}Br\textsubscript{7}] (Pt\textsubscript{2}Au\textsubscript{10}Ag\textsubscript{13} for short). Interestingly, the luminescent quantum yield (QY) of Pt\textsubscript{1}Au\textsubscript{0.6}Ag\textsubscript{10.4} is drastically increased from 0.1 to 14.7% (about 150 times that of the Pt\textsubscript{1}Ag\textsubscript{24} precursor NC), presumably owing to the changes in chemical composition (surface) as well as the transformation in morphology (shape). Furthermore, the thermal stability of both Pt\textsubscript{1}Au\textsubscript{0.6}Ag\textsubscript{10.4} and Pt\textsubscript{1}Au\textsubscript{0.6}Ag\textsubscript{10.4} NCs is remarkably improved compared with the Pt\textsubscript{1}Ag\textsubscript{24} precursor.

Briefly, the syntheses of either Pt\textsubscript{1}Au\textsubscript{24} or Pt\textsubscript{1}Au\textsubscript{0.6}Ag\textsubscript{10.4} involve two steps: the first step is the synthesis of the precursor (Pt\textsubscript{1}Au\textsubscript{0.6}Ag\textsubscript{10.4}), and the second step is the alloying of Pt\textsubscript{1}Ag\textsubscript{24} with [AuSR] or [Au(PPh\textsubscript{3})Br] (see the Supporting Information for details). An illustrative scheme of the synthetic method and the related X-ray crystal structures of the trimetallic NCs are given in Figure 1 (and Figures S1–S4 for more details). The structural representation of Pt\textsubscript{1}Ag\textsubscript{24} is altered to a biicosahedral configuration in Pt\textsubscript{2}Au\textsubscript{10}Ag\textsubscript{13}. The thiolates of the precursor are completely peeled away and none is left in the final product, and thus the final biicosahedral core is co-protected by PPh\textsubscript{3} and Br ligands. In addition, the partial occupancy analysis indicates that each position of Pt\textsubscript{1}Au\textsubscript{0.6}Ag\textsubscript{10.4} is essentially occupied by a single composition. In conclusion, the shape is altered from spherical to rodlike when doped with [Au(PPh\textsubscript{3})Br].

Nonetheless, given the difficulty in distinguishing Au from Pt in X-ray crystallographic analysis, both the FIR measurements and DFT computations further clarify the accurate site of the Pt atom (see below).

High-resolution ESI-TOF-MS was employed to characterize the chemical composition of the trimetallic and confirmed the trimetallic compositions of the NCs (Figure S6 in the Supporting Information). The mass spectrum of Pt\textsubscript{1}Au\textsubscript{24} suggests that the product is a mixture of [Pt\textsubscript{1}Au\textsubscript{6.4}Ag\textsubscript{17.6}(SR)\textsubscript{18}]\textsuperscript{2–} with \(x = 4–9\), and the percentages of these components are 2.3, 12.5, 33.0, 34.8, 14.9, and 2.5%, respectively. As a result, the average number of gold atoms is 6.5 (see Table S2 in the Supporting Information for the calculation details). Herein, the calculated component from ESI is consistent with the X-ray crystal structure [Pt\textsubscript{1}Au\textsubscript{6.4}Ag\textsubscript{17.6}(SR)\textsubscript{18}]\textsuperscript{2–} (counter ion: [PPh\textsubscript{4}]\textsuperscript{2–}). By contrast, the Pt\textsubscript{1}Au\textsubscript{0.6}Ag\textsubscript{10.4} NC is charge neutral, and it is difficult to observe the molecular ion peak, thus, the ESI mass spectrum of Pt\textsubscript{1}Au\textsubscript{0.6}Ag\textsubscript{10.4} was not obtained. To ensure the composition of these trimetallic NCs, the atom ratio was examined by both inductively coupled plasma (ICP) MS, X-ray photoelectron spectroscopy (XPS), and elemental analysis (EA) measurements (see Figures S8 and S9 and Tables S3 and S4, in the Supporting Information, for the detailed results), and the ratio of elements agrees well with that from the X-ray crystallographic analysis.

Although the composition and ratio of different metal atoms in Pt\textsubscript{1}Au\textsubscript{24} and Pt\textsubscript{1}Au\textsubscript{0.6}Ag\textsubscript{10.4} NCs have been successfully identified by ESI, ICP, XPS, and EA measurements, the accurate site of the Pt atom(s) remains to be ascertained. As X-ray crystallographic analysis can hardly distinguish Au from Pt (due to the close atomic numbers), we sought to examine the accurate location of the Pt atom in the core of Pt\textsubscript{1}Au\textsubscript{24} (i.e., the center or the icosahedral shell. Note: the occupancy analyses reveal that no Pt/Au atoms are located on the external staple motifs). Similarly, the possibility that the Pt atoms are placed at the center or at the neck sites in Pt\textsubscript{1}Au\textsubscript{0.6}Ag\textsubscript{10.4} was also examined. Considering that one primary distinction between these different positions is the absence/presence of the Pt–S (P–P) bond, we performed FIR measurements to address the chemical interactions between the surface structures of Ag\textsubscript{25}, PtAg\textsubscript{24}, and Pt\textsubscript{1}Au\textsubscript{0.6}Ag\textsubscript{10.4} (including the bond lengths, bond angles, as well as the π–π interactions) are given in the Supporting Information (Figure S5 and Table S1).

Unlike the case of [AuSR], in which the doped trimetallic NCs possess the same spherical shape, the use of [Au(PPh\textsubscript{3})Br] in the alloying process leads to a shape-changed trimetallic NC. As shown in Figure 1, the initial spherical core-shell structure of Pt\textsubscript{1}Ag\textsubscript{24} is altered to a biicosahedral configuration in Pt\textsubscript{1}Au\textsubscript{0.6}Ag\textsubscript{10.4}. The thiolates of the precursor are completely peeled away and none is left in the final product, and thus the final biicosahedral core is co-protected by PPh\textsubscript{3} and Br ligands. In addition, the partial occupancy analysis indicates that each position of Pt\textsubscript{1}Au\textsubscript{0.6}Ag\textsubscript{10.4} is essentially occupied by a single composition. In conclusion, the shape is altered from spherical to rodlike when doped with [Au(PPh\textsubscript{3})Br]. Similar structures of Pt\textsubscript{1}Au\textsubscript{0.6}Ag\textsubscript{10.4} have been reported by Teo and co-workers, as well as Steggerda and co-workers; these differ only by the halogen atom (i.e., Cl instead of Br).}

As the X-ray crystallography only gave an average electron-density map of the Pt\textsubscript{1}Au\textsubscript{24} alloy NCs, consisting of different numbers of Au atoms, we carried out further partial occupancy analysis to ascertain the average number of Au dopants (\(x = 6.4\)) in the total structure. Thus, the average molecular formula of the thiolated Pt\textsubscript{1}Au\textsubscript{24} is [Pt\textsubscript{1}Au\textsubscript{6.4}Ag\textsubscript{17.6}(SR-Ag-SR-Ag-SR)\textsubscript{18}]\textsuperscript{2–} with a tristarrified arrangement. The heteroatoms (Au atoms) are controllably doped in the icosahedral shell of Pt\textsubscript{1}Ag\textsubscript{24} with the spherical shape of Pt\textsubscript{1}Ag\textsubscript{24} maintained (Figure 1). More information and discussion on the comparison between the surface structures of Ag\textsubscript{25}, PtAg\textsubscript{24}, and Pt\textsubscript{1}Au\textsubscript{0.6}Ag\textsubscript{10.4} (including the bond lengths, bond angles, as well as the π–π interactions) are given in the Supporting Information (Figure S5 and Table S1).

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this issue (Figures S10–S12 in the Supporting Information). We first measured the FIR spectra of the reference samples, M–SPhMe$_2$ (M = Au, Ag, or Pt, see Figure S10a–c in the Supporting Information) and Br–M–PPh$_3$ (M = Au or Pt, see Figure S12a and b in the Supporting Information), for the M–S and M–P bond vibration energies. For Pt$_x$Au$_{1-x}$S, the FIR spectrum clearly shows the bands centered at 343 cm$^{-1}$ (i.e., an Au–S bond according to the FIR spectrum of Au–SPhMe$_2$) and 381 cm$^{-1}$ (i.e., Ag–S), whereas no band can be identified around 323 cm$^{-1}$ (i.e., Pt–S). The results indicate that Pt$_x$Au$_{24-x}$S consists of both Au–S and Ag–S bonds, but no Pt–S bonds. Hence, the absence of Pt–S bonds implies that the only plausible location for the Pt atom is the central position. On the other hand, the presence of Au–P bonds (436 cm$^{-1}$) and absence of Pt–P bonds (394 cm$^{-1}$) in Pt$_x$Au$_{12}$S$_{13}$ indicate that the two Pt atoms are exclusively located at the central positions of two icosahedrons. In other words, the central position for the Pt atom in the precursor nanocluster is retained, rather than displaced by Au dopant atoms, regardless if the shape changes or not.

The $^{31}$P NMR spectra of both Pt$_x$Au$_{x}$Ag$_{24}$- and the precursor ([PPh$_3$AuBr]) were measured. As shown in Figure S13 in the Supporting Information, the narrow $^{31}$P NMR signals of the NCs indicate high purity of the final product.

To further confirm the position of the Pt atoms in the trimetallic NCs, DFT calculations were performed. Three possible Pt positions were considered, that is, the center of the icosahedron (M1), the shell of the icosahedron (M2), and a staple motif (M3). For each scenario, the ten lowest-energy isomer structures were used as parent structures. To illustrate the favorable position of the Pt atom, the position of the Ag or Au atom is mutually exchanged for a Pt atom. According to the relative electronic energies of the different isomer structures (Figure 2), the Pt atom favors the central position. Moving the Pt atom to the shell of icosahedral core or to the staple motif significantly increases the electronic energy. This energy tendency agrees with the FIR spectral analysis and confirms the central position of the Pt atom in Pt$_x$Au$_{12}$Ag$_{24-x}$-.

Structurally, the central Pt atom in the M$_3$ core of the two synthesized trimetallic alloy NCs was unexceptionally retained compared to the positions in the Pt$_1$Ag$_{24}$ precursor. On the contrary, according to a recent study of Bakr and co-workers, the central Ag atom of Ag$_{25}$ would be replaced by a Au atom when alloying with [Au(PPh$_3$)Br].\[24\] Regarding the formation mechanism, Bakr et al. suggest that the Au atom first replaces one Ag atom on the icosahedral surface of the Ag$_{25}$ NC, and then immediately diffuses into the center due to the thermodynamic stability of the resultant configuration. In this context, the structural arrangements of the Pt$_x$Au$_{12}$Ag$_{24-x}$ and Pt$_x$Au$_{12}$Ag$_{13}$ NCs imply that the Pt atom in Pt$_x$Ag$_{24}$ is stable enough to hold the central position (compared to the Ag atom in Ag$_{25}$). Note that the stability of the central Pt atom is also supported by both DFT calculations and experiments on Pt$_x$Ag$_{14}$ and Pt$_x$Au$_{14}$ NCs.\[22a, 23a\] The difference in alloying process of the Ag$_{25}$ and Pt$_x$Ag$_{24}$ NCs is most likely controlled by the intrinsic electronic structure and the thermodynamic stability of the NCs. Applying this rule would provide a promising strategy to engineer the heteroatoms into the designated position.

Based on the well-defined structures of these NCs, we propose a plausible mechanisms of alloying Pt$_x$Ag$_{24}$ with [AuSR] or [Au(PPh$_3$)Br] complexes (Figure 3). In Figure 3a, the [AuSR] complexes diffuse to the surface of the icosahedral Pt$_{12}$Ag$_{13}$ core, and then replace the Ag atoms. These processes are similar to those reported in previous studies on alloying Au$_{25}$ with [AgSR]. The alloying processes occur and eventually stabilize in the thermodynamically favorable state with a tristratified arrangement, that is, [Pt(center)@AuAg(shell)@Ag(exterior)].

Regarding Pt$_x$Au$_{12}$Ag$_{13}$, Pt$_x$Ag$_{24}$ (Figure 3b), the Ag atoms on the icosahedral Pt$_{12}$Ag$_{13}$ core are exchanged by the Ag atoms of the [Au(PPh$_3$)Br] complexes (the thiolates binding to these Ag atoms are simultaneously peeled away), and the PPh$_3$ ligands keep in connection with Au atoms in this process. Meanwhile, the Br$^-$ ions link to the Ag atoms neighboring the Au atoms, and the Ag–S bond dissociates simultaneously (because of the stronger Ag–Br). As a consequence, the icosahedral Pt$_{12}$Ag$_{13}$ core is peeled away from the surrounding six [Ag$_{25}$SR$_x$]$_x$ motifs and the Pt@Au–Ag NCs, co-protected by PPh$_3$ and Br ligands, are generated. Finally, two icosahedral Pd@Pt–Au–Ag NCs, couple together by sharing the Ag atom in vertex and five Br atoms, are formed. The Pt atom maintain the central position in the final biicosahedral structure and the neck sites are completely occupied by Au atoms to form a symmetric structure.

To investigate the correlation between the composition/shape and the optical properties, the absorption spectra on the energy scale and photoluminescence (PL) of all samples were analyzed. The energy-scale UV/Vis spectra of the homosilver, Ag$_{25}$ bi-metallic, Pt$_2$Ag$_{24}$, and trimetallic, Pt$_x$Au$_{12}$Ag$_{24-x}$ as well as the Pt$_x$Au$_{12}$Ag$_{24-x}$ NCs are shown in Figure 4a. The optical energy gap of Ag$_{25}$ occurs at 1.57 eV and significantly blue-shifts to 1.72 and 1.93 eV in Pt$_x$Ag$_{14}$ and Pt$_x$Au$_{12}$Ag$_{13}$, respectively. On the other hand, a slight blue-shift by 0.05 eV (1.62–1.57 eV) is determined from the spectrum of Pt$_x$Au$_{12}$Ag$_{24-x}$. The results indicate an increase of energy gap in Pt$_x$Au$_{12}$Ag$_{24-x}$, Pt$_x$Ag$_{24}$, or Pt$_x$Au$_{10}$Ag$_{13}$ NCs. Meanwhile, the three NCs with the same framework (i.e., Pt$_x$Au$_{12}$Ag$_{24-x}$, Pt$_x$Ag$_{24}$, and Ag$_{25}$) vary in color from greenish yellow to green and orange, indicating that the doped heteroatoms significantly affect the electronic
structure of the NCs, and thus strongly perturb the optical properties.

With respect to the PL intensity of these NCs, the QY of Pt$_1$Ag$_{24}$ is about 20 times that of Ag$_{25}$. Nonetheless, the PL intensity of Pt$_1$Ag$_{24}$ (QY = 0.1%) is still too weak to be observed by the naked eye. Meanwhile, the PL intensity of the doped Pt$_{AuAg_{24-x}}$ was totally quenched and no PL was detected even by highly sensitive instruments. Considering that the alteration of shape is more likely to lead to a qualitative leap in properties, the PL measurement of shape-altered Pt$_{AuAg_{13}}$ was performed. Interestingly, Pt$_{AuAg_{13}}$ exhibits a strong emission centered at 648 nm with a QY of 14.7% (Figure 4b). In other words, the QY increases from 0.1 to 14.7% (150 times) and the fluorescence is strong enough to be perceived by the naked eye (Figure 4a, inset). With a view to the difference between Pt$_2$Au$_{10}$Ag$_{13}$ and its precursor, we speculated that the increase in QY of emission originated not only from the changes in the chemical composition, but also from the transformation in shape. The PL excitation spectrum of Pt$_2$Au$_{10}$Ag$_{13}$ is almost identical to the absorption spectrum (Figure S14 in the Supporting Information). From the PL spectra in Figure 4b, the emission peaks of Ag$_{25}$, Pt$_1$Ag$_{24}$, and Pt$_2$Au$_{10}$Ag$_{13}$ are determined to be 1.53, 1.70 and 1.91 eV, respectively; these are consistent with the energy gaps derived from the spectra on the energy scale. The almost identical energies imply that the fluorescence possibly corresponds to the gap transition.

To further explore the properties of the trimetallic NCs, we investigated the thermodynamic stability of the shape-altered and conserved trimetallic NCs (relative to Pt$_1$Ag$_{24}$). It should be noted that Ag$_{25}$ is far less stable than Pt$_1$Ag$_{24}$ at room temperature (Figure S15 in the Supporting Information). The stability of all three alloy NCs was tested at 50°C (dissolved in CHCl$_3$, exposed to air). The optical absorption spectra of the Pt$_{AuAg_{24-x}}$ and Pt$_{AuAg_{13}}$ NCs remained unchanged after 12 h, whereas that of Pt$_1$Ag$_{24}$ significantly decreased in intensity after 2 h, and completely disappeared in approximately 6 h (Figure S16 in the Supporting Information). In addition, the PL intensity of the Pt$_{AuAg_{13}}$ NCs did not decrease at all (Figure S17 in the Supporting Information). Therefore, the stability of Pt$_1$Ag$_{24}$ is drastically enhanced when doped with Au complexes, regardless if the shape is altered or conserved.

In summary, syntheses of alloy NCs of different shapes have been achieved by modulating the dopants. The spherical [Pt$_1$Ag$_{24}$(SR)$_{18}$]$_2$ NC could be controllably converted to spherical or rodlike trimetallic NCs by a metal-exchange method. Our results illustrate that alloying Pt$_1$Ag$_{24}$ with Au complexes coordinated by the same ligands maintains the spherical structure. On the contrary, alloying with [Au$_2$(PPh$_3$)$_2$Br] alters the shape to a rodlike one, owing to the different ligands. The crystal structures of the products were determined by X-ray crystallography and confirmed by ESI, XPS, ICP, and FIR measurements, as well as DFT calculations. The shape-maintained [Pt$_{2}$_Au$_{10}$Ag$_{13}$(SPhMe$_2$)$_{18}$(PPh$_4$)$_2$] NCs exhibit a tristratified arrangement—[Pt(center)@Au/Ag(shell)@Ag(exterior)]—that represents the first X-ray crystal structure of thiolated trimetallic NCs. The PL QY of the rodlike [Pt$_{2}$_Au$_{10}$Ag$_{13}$(PPh$_3$)$_{10}$Br$_7$] cluster is drastically increased from 0.1% for Pt$_1$Ag$_{24}$ to 14.7% (about

Figure 3. Proposed exchange mechanisms of alloying Pt$_1$Ag$_{24}$ with:

a) [Au(SR)] or b) [Au(PPh$_3$)$_2$Br] complexes; i/i is the site for Au/Ag replacement; ii is the site of Ag–Br bonding.

Figure 4. The optical properties of the trimetallic NCs; a) energy scale optical absorption spectra of the different NCs; b) PL of the Ag$_{25}$, Pt$_1$Ag$_{24}$, Pt$_{AuAg_{24-x}}$, and Pt$_{2}$_Au$_{10}$Ag$_{13}$ NCs. Insets: a) digital photo of each NC in CH$_2$Cl$_2$ under visible and UV light; b) the peak shift in normalized PL spectra.

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The dried NC was washed with methanol at least three times and collected by centrifugation (9 mg, 1.5 μmol, yield 83.3%).

**Synthesis of [Pt1Au4Ag13(SPhMe)18](PPh4)2**

For the NC synthesis, [Pt1Ag24(SPhMe2)18](PPh4)2 (10 mg, 1.8 μmol) was dissolved in CH2Cl2 (20 mL), and Au(PPh3)Br (powder; 10 mg, 18.6 μmol, ca. 10 equiv) was added to the solution. The reaction was allowed to proceed for 60 min at room temperature. The color of solvent transformed from bright green to orange. The reaction mixture was transferred to a centrifuge tube and centrifuged at about 9000 rpm. The organic layer was separated from the precipitate and evaporated to dryness. The [Pt1Au4Ag13(PPh3)Br]2 NC was obtained. The dried NC was washed with methanol at least three times and collected by centrifugation (11 mg, 1.6 μmol, yield 88.9% based on the Pt1Ag24 NC).

**Crystallization of [Pt2Au10Ag13(PPh3)10Br7] and [Pt2Au10Ag13(PPh3)10Br7]**

Single crystals of [Pt2Au10Ag13(SPhMe)18](PPh3)2 and [Pt2Au10Ag13(PPh3)10Br7] nanoclusters were grown for 2–3 days at 4 °C in CH2Cl2/hexane mixture solutions. Dark crystals were collected and the structures were determined by X-ray diffraction.

CCDC 1510048 ([Pt2Au10Ag13(SPhMe)18](PPh3)2) and 1510047 ([Pt2Au10Ag13(PPh3)10Br7]) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

### Acknowledgements

We acknowledge financial support by NSFC (21372006, U1532141, 21631001), the Ministry of Education, the Education Department of Anhui Province, 211 Project of Anhui University. Y.P. is supported by NSFC (21373176, 21422305), Hunan Provincial Natural Science Foundation of China (12JJ1003), and Scientific Research Fund of Hunan Provincial Education Department (13A100).

### Keywords:
crystallography · photoluminescence · shape control · surface chemistry · trimetallic nanoclusters

Shape-controlled synthesis of alloy metal nanoclusters (NCs) is achieved with atomic precision for the first time. The spherical \([\text{Pt}_1\text{Ag}_{24}(\text{SR})_{18}]\) was doped with \([\text{Au}^\text{SR}]\) or \([\text{Au}^\text{I}(\text{PPh}_3)\text{Br}]\), resulting in spherical or rodlike trimetallic products, respectively. The spherical \([\text{Pt}_1\text{Au}_{6.4}\text{Ag}_{17.6}(\text{SPhMe}_2)_{18}]\) NC represents the first X-ray crystal structure of a thiolated trimetallic NCs. The rodlike trimetallic \([\text{Pt}_2\text{Au}_{10}\text{Ag}_{13}(\text{PPh}_3)_8\text{Br}_7]\) exhibits strong emission with a quantum yield of 14.7%.
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