Doping Silver Increases the Au38(SR)24 Cluster Surface Flexibility

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ABSTRACT: Multiple Ag atoms were doped inside Au38-(SCH2CH2Ph)24 nanoclusters using the metal exchange method for the first time for the synthesis of AgAu38-x(SCH2CH2Ph)24. MALDI-TOF mass spectrometry revealed the time dependence of the synthesis. Cluster species with different numbers of Ag atoms (different x values) migrate differently on a chromatography (HPLC) column, which allows one to isolate cluster samples with a narrowed distribution of exchanged metal atoms. The enantiomers of selected AgAu38-x(SCH2CH2Ph)24 samples (average x = 6.5 and 7.9) have been separated by HPLC. Doping changes the electronic structure, as is evidenced by the significantly different CD spectra. UV-vis spectra of the doped sample also show diminished features. The temperature required for complete racemization follows Au38 > AgAu38-x (x = 6.5) > Au38Ag(SR)24, suggesting no complete metal–S bond breaking in the process.

INTRODUCTION

Thiolate-protected gold nanoclusters with a size range of <3 nm have attracted extensive attention over the recent decades due to their atomic precise composition. Structure determination revealed their core–shell structure with typically a symmetric metal core and multiple –SR–(Au–SR)ₙ (n = 1, 2, 3, 4, 5) staple motifs. These clusters exhibit unique size-dependent properties such as photoluminescence, optical activity, and catalytic activity. Particular attention has been paid to the intrinsic chirality along with the discovery of the chiral structure of Au28, Au38, Au40, Au102, Au133, etc. Gold cluster surface. The results therefore show an increased flexibility of the cluster with increasing silver content. The weaker Ag–S bonds compared to Au–S are proposed to be at the origin of this observation. The experimentally determined activation energy for the racemization is ca. 21.5 kcal/mol (x = 6.5) and 19.5 kcal/mol (x = 7.9), compared to 29.5 kcal/mol for Au38(SCH2CH2Ph)24, suggesting no complete metal–S bond breaking in the process.

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study, Ag$_{Au_{38-x}}$(SCH$_2$CH$_2$Ph)$_{24}$ was synthesized by the Brust method, using a mixture of both silver and gold salt as the precursor. In this study, we investigated the time dependence in the synthesis of Ag$_{Au_{38-x}}$, using metal exchange between the Ag salt and Au$_{38}$ nanocluster. This is the first time that the metal exchange method has been applied for the synthesis of a doped Au$_{Au_{38-x}}$(SCH$_2$CH$_2$Ph)$_{24}$ nanocluster. The composition of the as-synthesized clusters was monitored by MALDI. Isolation and enantioseparation of selected samples were performed by HPLC. Ag$_{Au_{38-x}}$(SCH$_2$CH$_2$Ph)$_{24}$ (x = 6.5 and 7.9) enantiomers were characterized by UV–vis spectroscopy and CD, showing a significant change of characteristic features with silver doping. We also performed a racemization study on Ag$_{Au_{38-x}}$ enantiomers to compare the activation barrier with that of Au$_{38}$. Doping Ag significantly increases the flexibility of the ligand shell, and this increase is sensitive to the dopant number. For a high Ag content, the cluster undergoes racemization already at room temperature.

**METHODS**

All chemicals were purchased from standard suppliers and used as received. Nanopure water (>18 MΩ) was used.

**Synthesis and Separation of Ag$_{Au_{38-x}}$(SCH$_2$CH$_2$Ph)$_{24}$** Ag$_{Au_{38-x}}$(SCH$_2$CH$_2$Ph)$_{24}$ was synthesized by metal exchange of AgSCH$_2$CH$_2$Ph and Au$_{Au_{38}}$(SCH$_2$CH$_2$Ph)$_{24}$. The synthesis was performed according to a recent protocol. A 0.04 mmol portion of AgSCH$_2$CH$_2$Ph was added to the solution of Au$_{Au_{38}}$(SCH$_2$CH$_2$Ph)$_{24}$ (1 mg, dissolved in 1 mL). A 0.2 mL volume of the reaction suspension was taken at 0, 3, 8, 24, and 48 h, respectively, filtered, dried, washed with methanol, and characterized by UV and MALDI. Synthesis b: A 1 mg portion of AgSCH$_2$CH$_2$Ph was added to the solution of Au$_{Au_{38}}$(SCH$_2$CH$_2$Ph)$_{24}$ (1 mg, dissolved in 0.8 mL) for 24 h. The second sample (sample B) was obtained by adding 2.0 mg of AgSCH$_2$CH$_2$Ph to the Au$_{Au_{38}}$(SCH$_2$CH$_2$Ph)$_{24}$ solution (2 mg, dissolved in 2 mL of toluene) and stirring for 20 h. A 0.2 mL portion of Au$_{Au_{38}}$(SCH$_2$CH$_2$Ph)$_{24}$ (1 mg, dissolved in 0.8 mL) for 24 h. Two racemic Ag$_{Au_{38-x}}$(SCH$_2$CH$_2$Ph)$_{24}$ samples were synthesized. The first sample (sample A) was obtained by adding 2 mg of AgSCH$_2$CH$_2$Ph to the Au$_{Au_{38}}$(SCH$_2$CH$_2$Ph)$_{24}$ solution (2 mg, dissolved in 2 mL of toluene) and stirring for 20 h. A 0.2 mL portion of AgSCH$_2$CH$_2$Ph was added to the solution of Au$_{Au_{38}}$(SCH$_2$CH$_2$Ph)$_{24}$ (1 mg, dissolved in 0.8 mL) for 24 h. Two racemic Ag$_{Au_{38-x}}$(SCH$_2$CH$_2$Ph)$_{24}$ samples were synthesized. The first sample (sample A) was obtained by adding 2 mg of AgSCH$_2$CH$_2$Ph to the Au$_{Au_{38}}$(SCH$_2$CH$_2$Ph)$_{24}$ solution (2 mg, dissolved in 2 mL of toluene) and stirring for 22 h. After cleaning, 1.8 mg of sample A and 1.7 mg of sample B were collected.

**Step 4.** Isolation of Ag$_{Au_{38-x}}$(SCH$_2$CH$_2$Ph)$_{24}$ was tested via HPLC. The sample from synthesis b was used directly for separation. Two fractions were collected and characterized by MALDI.

**Step 5.** Ag$_{Au_{38-x}}$(SCH$_2$CH$_2$Ph)$_{24}$ samples A and B from synthesis c were used directly for HPLC enantioseparation. Two fractions were collected, dried immediately, and stored in a refrigerator to reduce racemization. The distribution of doped clusters with different Ag numbers was determined by MALDI.

**Characterization.** UV–vis spectra were recorded on a Varian Cary 50 spectrometer. A quartz cuvette of 10 mm path length was used (the solvents were methylene chloride and toluene). CD spectra were recorded on a JASCO J-815 CD spectrometer. Full spectra were recorded in toluene or dichloromethane. For time-course measurements, the chiroptical responses at 303 nm (sample A) and 355 nm (sample B) were followed in 10 s intervals at different temperatures (20, 30, 40, 50, and 60 °C for sample A, 20, 30, 35, 40, and 50 °C for sample B, JASCO Peltier element, toluene, 5 mm path length), and the average signal of toluene at the corresponding temperature over 5 min was subtracted.

**HPLC.** Chiral HPLC was performed on a JASCO 20XX HPLC system equipped with a Phenomenex Lux Cellulose-1 column (100 Å, 250 mm × 4.6 mm), and the eluting analytes were detected with a JASCO 207 plus UV detector (485 nm). The analytes were dissolved in toluene and eluted with n-hexane/2-propanol (80:20) at a flow rate of 2.5 mL/min. The separation temperature was set at 20 °C for sample A and 18 °C for sample B and the sample for the HPLC isolation test. The collected fractions were dried and injected into the HPLC instrument to determine the enantiomeric excess (ee).

**Racemization.** A stock solution in toluene was made and stored in a refrigerator for the first enantiomer collected in HPLC (0.77 mg/mL, ee 83.70%, for sample A; 1.06 mg/mL, ee 46.36%, for sample B) and split for racemization at different temperatures. Prior to and after heating, CD and UV–vis spectra were recorded for comparison. The samples were heated to 20, 30, 40, 50, and 60 °C (sample A) and 20, 30, 35, 40, and 50 °C (sample B) for 30 min. The CD response was monitored in situ at the wavelength which showed the highest intensity (303 nm for sample A and 355 nm for sample B). The signal of the solvent at the corresponding temperature was subtracted for the plots of ln(ee) versus time.
RESULTS AND DISCUSSION

Time-Dependent Synthesis. Metal exchange between AgSCH2CH2Ph and Au38(SCH2CH2Ph)24 was applied to synthesize AgAu38−x(SCH2CH2Ph)x nanoclusters. MALDI-TOF mass spectrometry was used to follow the composition of the reaction mixture at reaction times of 0, 3, 8, 24, and 48 h (Figure 1). AgAu38−x alloy was obtained by metal exchange. A clear shift to lower masses of the MALDI peak can be observed due to the low laser intensity applied in the measurements. The fragmentation peaks at 24 and 48 h were not observed due to the large mass differences between Ag and Au (∆m/z = 89.1). The peaks below 9500 (m/z) are due to the AgAu38−x(SCH2CH2Ph)24 species over the spectral range and scaled with the ee determined by HPLC (Figure S3). The maximum anisotropy factor found is about 7 × 10−4 (433 nm) and 5.7 × 10−4 (356 nm) for sample A and sample B, respectively.

Enantioseparation and Chirality. In the HPLC chromatogram of the parent nanocluster, two bands were observed, which correspond to the two enantiomers of Au38(SCH2CH2Ph)24. The two bands of AgAu38−x(SCH2CH2Ph)24 were therefore separated for further study. To investigate the sensitivity of the Au38(SCH2CH2Ph)24 properties to the Ag dopant number, two AgAu38−x(SCH2CH2Ph)24 samples (sample A and sample B) with close reaction times were synthesized. The two fractions of both AgAu38−x(SCH2CH2Ph)24 samples were collected repeatedly over several HPLC runs (Figure 2). A narrow retention time range was chosen for the collection due to the slight overlap between the two peaks. The average silver number of the first fraction was determined from MALDI spectra (Figure 2), which is 6.5 for sample A and 7.9 for sample B. The second fractions showed similar silver numbers; however, the average number deviates slightly from the first fraction (5.4 for sample A and 5.8 for sample B), which can be ascribed to the narrow collection range in HPLC separation. UV–vis spectra of the two fractions were similar in both samples, respectively, with the main absorption bands at 445, 512, and 610 nm (Figure 2).

HPLC Separation. As is shown in Figure 1, the sample contains species with different numbers of silver dopant atoms. The diversity of AgAu38−x(SCH2CH2Ph)24 species increases if we consider the isomers of each doped cluster (with silver atoms doped at different positions). Isolation of AgAu38−x(SCH2CH2Ph)24 with different dopant numbers was studied in the first place. A AgAu38−x(SCH2CH2Ph)24 sample with a silver dopant number from 5 to 15 was synthesized (Figure S2a). HPLC separation of the sample gave two broad bands corresponding to clusters with different handedness (see below). Two fractions were taken from the second band (Figure S2b), with retention times of 70–90 and 90–110 min, respectively. A clear difference of the cluster composition is shown in the MALDI spectra of the two fractions (Figure S2a). AgAu38−x(SCH2CH2Ph)24 with a smaller dopant number were eluted faster in the method applied (first sample with a dopant number of 5–9 and second sample with a dopant number from 6 to 14). However, it remains a challenge to isolate the individual AgAu38−x(SCH2CH2Ph)24 with the current method.

Racemization. A stock toluene solution of sample A, fraction 1, was prepared and split into five aliquots which were then subjected to thermal treatment at 20, 30, 40, 50, and 60 °C for 30 min, respectively. The CD response at 303 nm was followed during the time course (Figure 3). At a first glance, after 30 min, complete racemization of sample A was achieved.
at 60 °C (also shown in the CD spectra after heating, Figure S4), which is much lower than the 80 °C required for Au$_{38}$(SCH$_2$CH$_2$Ph)$_{24}$. A considerable decrease of the CD response had already occurred in the heating process at 30 °C. The UV–vis spectra of the solution after heating resemble those of the starting Ag$_x$Au$_{38}$−(SCH$_2$CH$_2$Ph)$_{24}$ nanoclusters (Figure S4), which confirmed the stability of the clusters against decomposition under the conditions of racemization. It can be concluded that silver doping lowered the racemization temperature of Au$_{38}$(SCH$_2$CH$_2$Ph)$_{24}$. Since the racemization

Figure 2. Characterization of the two Ag$_x$Au$_{38}$−(SCH$_2$CH$_2$Ph)$_{24}$ nanoclusters (sample A and sample B): top left, HPLC chromatogram of the enantioseparation of both samples (the two fractions collected for each cluster are denoted as AF1, AF2, BF1, and BF2); top right, MALDI spectra of the collected fractions (the maximum and minimum dopant numbers are marked with lines); bottom left, UV–vis spectra of the collected fractions; bottom right, comparison of the doped and parent Au$_{38}$ CD spectra.

Figure 3. Racemization experiment with Ag$_x$Au$_{38}$−(SCH$_2$CH$_2$Ph)$_{24}$ nanoclusters: left, CD response of AF1 at 303 nm as a function of time at different temperatures; right, CD response of BF1 at 355 nm as a function of time at different temperatures.
process involves a rearrangement of the staples on the cluster surface, it can be concluded that silver doping increases the flexibility of the metal–sulfur interface. To investigate the racemization behavior of nanoclusters with higher silver dopant numbers, a similar experiment was carried out for the toluene solution of sample B, fraction 1, at 20, 30, 35, 40, and 50 °C, and the detection wavelength was set at 355 nm. The racemization is surprisingly fast, with more than 10% inversion at 20 °C after 30 min. This suggests that the racemization of the sample took place during the HPLC separation at 18 °C. This explains the intensity observed in the chromatogram between the two main peaks (Figure 2). This intensity arises from clusters undergoing racemization within the column. Complete racemization of sample B, fraction 1, requires heating at 50 °C for around 20 min (Figure S4). The Ag$_{38}$ sample nanoclusters survived temperature treatment without decomposition, as is evident by the conserved UV–vis spectra after heating (Figure S4). This indicates the high sensitivity of the Au$_{38}$(SCH$_2$CH$_2$Ph)$_{24}$ surface flexibility to the Ag dopant number.

The linearity of the plot of ln(εε)$'$ vs time shows that the reaction is of first-order kinetics. Rate constants were determined from a linear fit of the initial slope (Figure 4).

In the Ag$_n$Au$_{38-}$-(SCH$_2$CH$_2$Ph)$_{24}$ (x ≤ S) obtained from the Brust method, Ag atoms were reported to be at the bis-capped Au$_{23}$ core surface of the cluster. In the present study, we used a different method for the doping. Therefore, in principle, the silver atoms might also exchange within the staple. To obtain a hint on this, we analyzed the fragmentation patterns in the MALDI spectra. The loss of the Au$_{38}$(SR)$_{24}$ unit was suggested by the fragmentation peak of Au$_{34}$(SR)$_{20}$ (9342 Da) and Au$_{34}$(SR)$_{16}$ (6055 Da) in the MALDI spectra of Au$_{38}$(SR)$_{24}$ and Au$_{34}$(SR)$_{24}$. Zeng et al. proposed a stepwise fragmentation mechanism of the staple motifs for the MALDI fragmentation in Au$_{32}$(SR)$_{18}$. MALDI spectra of sample A and sample B resemble that of the Au$_{38}$(SCH$_2$CH$_2$Ph)$_{24}$ cluster, with no coexistence of Ag$_n$Au$_{38-}$ (x = 1, 2, 3, and 4) species observed (Figure S5). This indicates that, by the metal exchange method, Ag atoms are also incorporated into the core surface. In sample A and sample B, we can speculate the coexistence of Au–S and Ag–S bonds on the surface. The weaker Ag–S bond contributes to the higher flexibility. The activation energy of Ag$_n$Au$_{38-}$-(SCH$_2$CH$_2$Ph)$_{24}$ nanoclusters is lower than the typical binding energy of Au–S (50 kcal/mol) and Ag–S (40 kcal/mol). It can be assumed that the complete metal–sulfur breaking is not involved in the racemization of Ag$_n$Au$_{38-}$-(SCH$_2$CH$_2$Ph)$_{24}$ nanoclusters.

In summary, we have presented an efficient metal exchange method for the incorporation of Ag into a Au$_{38}$ nanocluster, which showed time dependence and improved efficiency. Using HPLC separation, we were able to isolate Ag$_n$Au$_{38-}$ samples with a narrower distribution of the dopant number. This is based on the observation that species with different x values migrate slightly differently on the HPLC column. Both enantiomers of the Ag$_n$Au$_{38-}$ nanocluster were obtained by HPLC separation. Ag doping gives rise to significant changes in the UV–vis and CD spectra in comparison with those of Au$_{38}$, which can be related to the change in electronic structure. Silver doping lowers the racemization temperature required for Ag$_n$Au$_{38-}$. Clusters with a higher Ag content show racemization already at room temperature, which reflects the high flexibility of the metal–sulfur interface. The sensitivity of the racemization temperature to the Ag dopant number can be ascribed to the number of weak Ag–S bonds.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b12690.

MALDI, UV–vis, and CD measurement results described in the text (PDF)

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Notes

The authors declare no competing financial interest.

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**Table 1. Activation Parameters for the Thermal Inversion of Au$_{38}$(SCH$_2$CH$_2$Ph)$_{24}$ Nanoclusters and Ag$_n$Au$_{38-}$-(SCH$_2$CH$_2$Ph)$_{24}$ Nanoclusters AF1 and BF1**

<table>
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<th>$\Delta S^\circ$ (cal K$^{-1}$ mol$^{-1}$)</th>
<th>$\Delta G^\circ$ (kcal mol$^{-1}$)</th>
<th>$E_r$ (kcal mol$^{-1}$)</th>
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MALDI-TOF, matrix-assisted laser desorption time-of-flight; CD, circular dichroism; HPLC, high-performance liquid chromatography

REFERENCES


