Thiol Ligand-Induced Transformation of $\text{Au}_{38}(\text{SC}_2\text{H}_4\text{Ph})_{24}$ to $\text{Au}_{36}(\text{SPh-t-Bu})_{24}$

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$[\text{Au}_{38}(\text{SC}_2\text{H}_4\text{Ph})_{24}]^0 \xrightarrow{TBBT, 80 \, ^\circ\text{C}} [\text{Au}_{36}(\text{SPh-t-Bu})_{24}]^0$
INTRODUCTION

- The synthesis of thiolate-protected gold nanoclusters and studies of their properties have achieved significant advances in recent years.

- Size-focusing methodology has been successfully established giving rise to molecularly pure $\text{Au}_{25}(\text{SR})_{18}$, $\text{Au}_{38}(\text{SR})_{24}$, and $\text{Au}_{144}(\text{SR})_{60}$ nanoclusters and bimetal ones as well as some larger nanoclusters.

- In addition to the size-focusing method, another useful approach pertains to ligand exchange, such as phosphine-to-thiol exchange processes.

- However, in many cases molecular purity product could not be obtained except in the case of phosphine-capped $\text{Au}_{11}$ to thiolate-capped $\text{Au}_{25}$.
IN THIS PAPER

- An interesting disproportionation mechanism identified in the transformation of $\text{Au}_{38}\text{(PET)}_{24}$ to $\text{Au}_{36}\text{(TBBT)}_{24}$ is discussed.
- The ligand exchange reaction of $\text{Au}_{38}\text{(PET)}_{24}$ with bulkier TBBT induces structural distortion of the initial rod-like biicosahedral $\text{Au}_{38}\text{(PET)}_{24}$ structure.
- This process is evidenced by detailed mass spectrometric and optical spectroscopic analyses.
- The optical spectrum of $\text{Au}_{36}\text{(TBBT)}_{24}$ was further interpreted by theoretical simulations on a $\text{Au}_{36}\text{(SCH}_3\text{)}_{24}$ model cluster.
Scheme 1: Conversion of $\text{Au}_{38}(\text{PET})_{24}$ to $\text{Au}_{36}(\text{TBBT})_{24}$ nanoclusters (the carbon tails are not shown for clarity; S atoms, yellow; kernel Au atoms, magenta; surface Au atoms, green or cyan).
RESULTS AND DISCUSSION

- **Stage I:** In the first stage (0-5 min), ligand exchange reaction occurs.

- **Stage II:** In this stage (10-15 min), the ligand exchange reaction continues, but it starts to induce structural distortion of the original $\text{Au}_{38}(\text{SR})_{24}$ cluster, as manifested in the optical spectra.

- **Stage III:** It is in this critical stage (20-60 min) that the size and structural conversions take place.

- **Stage IV:** During the fourth stage (120-300 min), during which a size focusing conversion occurs together with further ligand exchange toward completion.
(A) Time-dependent ESI-MS of the transformation reaction. The doubly charged region is shown. The three gray shadows indicate three groups of peaks: (left) \( \text{Au}_{36}(\text{TBBT})_m(\text{PET})_{24-m} \), (middle) \( \text{Au}_{38}(\text{TBBT})_m(\text{PET})_{24-m} \), (right) \( \text{Au}_{40}(\text{TBBT})_{m+2}(\text{PET})_{24-m} \). The numbers on the top of the mass peaks indicate the number of TBBT ligands \((m)\) exchanged onto the cluster.

(B) Corresponding UV–vis spectra of different times in parallel with ESI-MS.
Scheme 2: Reaction pathway for conversion of $\text{Au}_{38}(\text{PET})_{24}$ to $\text{Au}_{36}(\text{TBBT})_{24}$. Stage I, ligand exchange; II, structure distortion; III, disproportionation; IV, size focusing.
A) Full range ESI-MS spectrum for the 5-min product:

B) Full range ESI-MS spectrum for the 20-min product:
Kinetic curve (monitored by absorbance at 550 nm) for the conversion of \( \text{Au}_{38}(\text{PET})_{24} \) to \( \text{Au}_{36}(\text{TBBT})_{24} \) at 80 °C.

\[ E_{a,\text{II}} = 107 \text{ kJ/mol} \]
\[ E_{a,\text{III}} = 152 \text{ kJ/mol} \]
Time-dependent UV–vis spectral evolution of 4-\textit{tert}-butylbenzenethiol with Au_{38}(PET)_{24}.

Time-dependent UV–vis spectral evolution of cyclohexanethiol reaction with Au_{38}(PET)_{24}.
(A) Comparison of simulated UV–vis absorption spectrum of \( \text{Au}_{36}(\text{SR})_{24} \) with the experimental spectrum. (B) Estimation of contributions of \( \text{Au}(6\text{sp}), \text{Au}(5\text{d}), \) and \( \text{S}(3\text{p}) \) to KS orbitals.
Comparison of the MALDI-MS and ESI-MS spectra of $\text{Au}_{36}(\text{TBBT})_{23}$. The asterisks indicate the fragments due to MALDI.
CONCLUSION

- The detailed mechanism of the ligand-induced conversion from $\text{Au}_{38}(\text{PET})_{24}$ to $\text{Au}_{36}(\text{TBBT})_{24}$ is discussed.

- The reaction pathway can be roughly divided into four stages.

- This process gave rise to $\text{Au}_{36}$ nanoclusters in $\sim90\%$ yield (Au atom basis), approaching the theoretical yield of $\sim94\%$ according to the disproportionation mechanism.

- The conversion of biicosahedral $\text{Au}_{38}$ structure to fcc $\text{Au}_{36}$ structure is remarkable; it provides an unprecedented example of ligand bulkiness induced size and structural transformation in thiolate-protected nanoclusters.
The role of ligand in the formation and crystallization of clusters!

Chiral Structure of Thiolate-Protected 28-Gold-Atom Nanocluster Determined by X-ray Crystallography

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