Thiol Ligand-Induced Transformation of $Au_{38}(SC_2H_4Ph)_{24}$ to $Au_{36}(SPh\text{-}t\text{-}Bu)_{24}$

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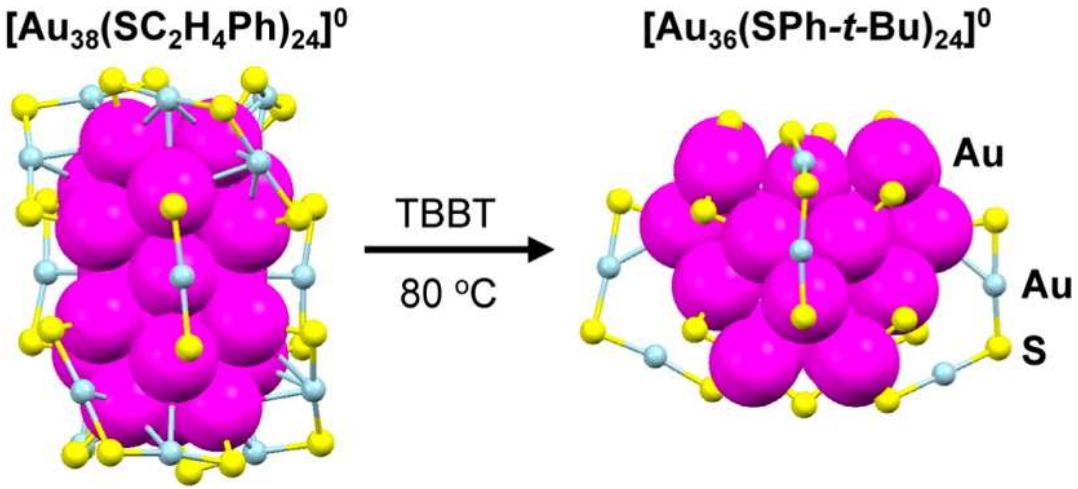

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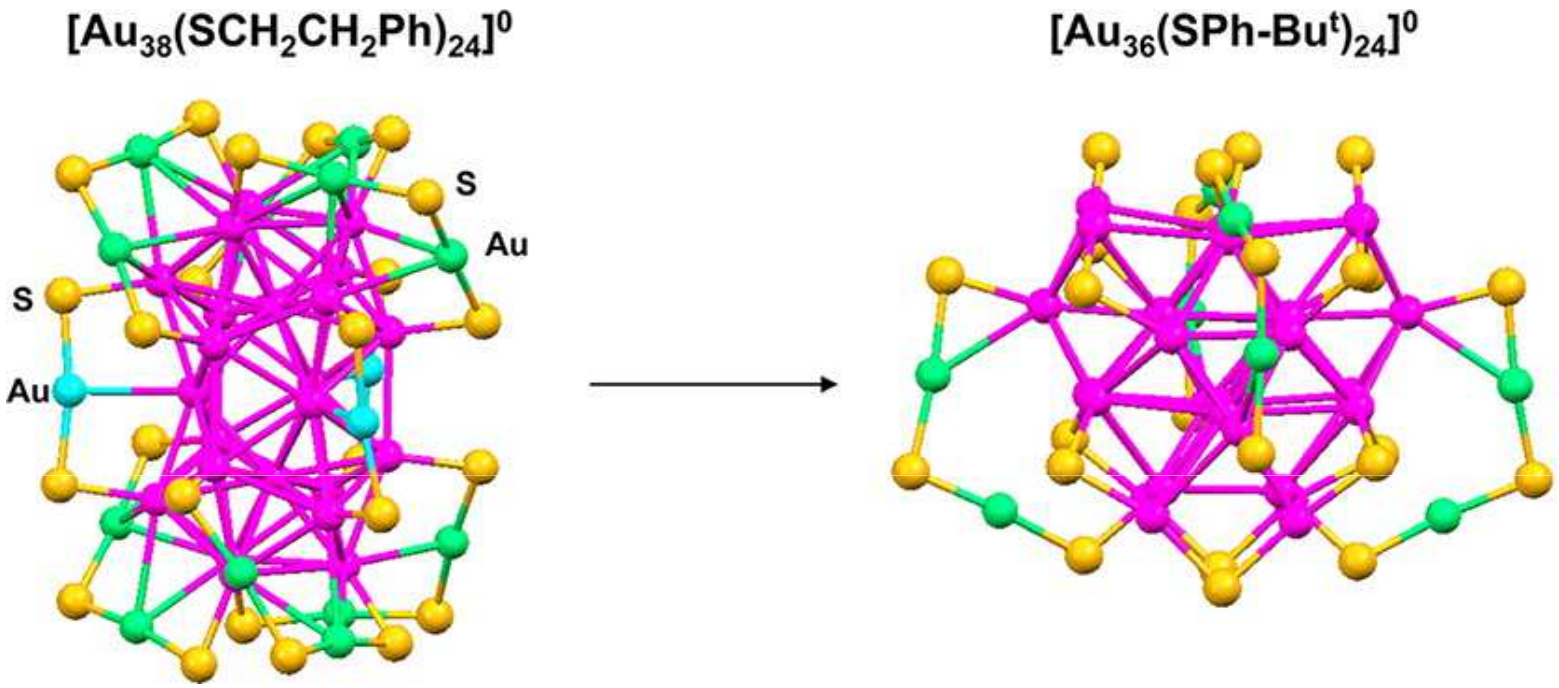
INTRODUCTION

- 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 $Au_{25}(SR)_{18}$, $Au_{38}(SR)_{24}$, and $Au_{144}(SR)_{60}$ 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 Au_{11} to thiolate-capped Au_{25}.

IN THIS PAPER

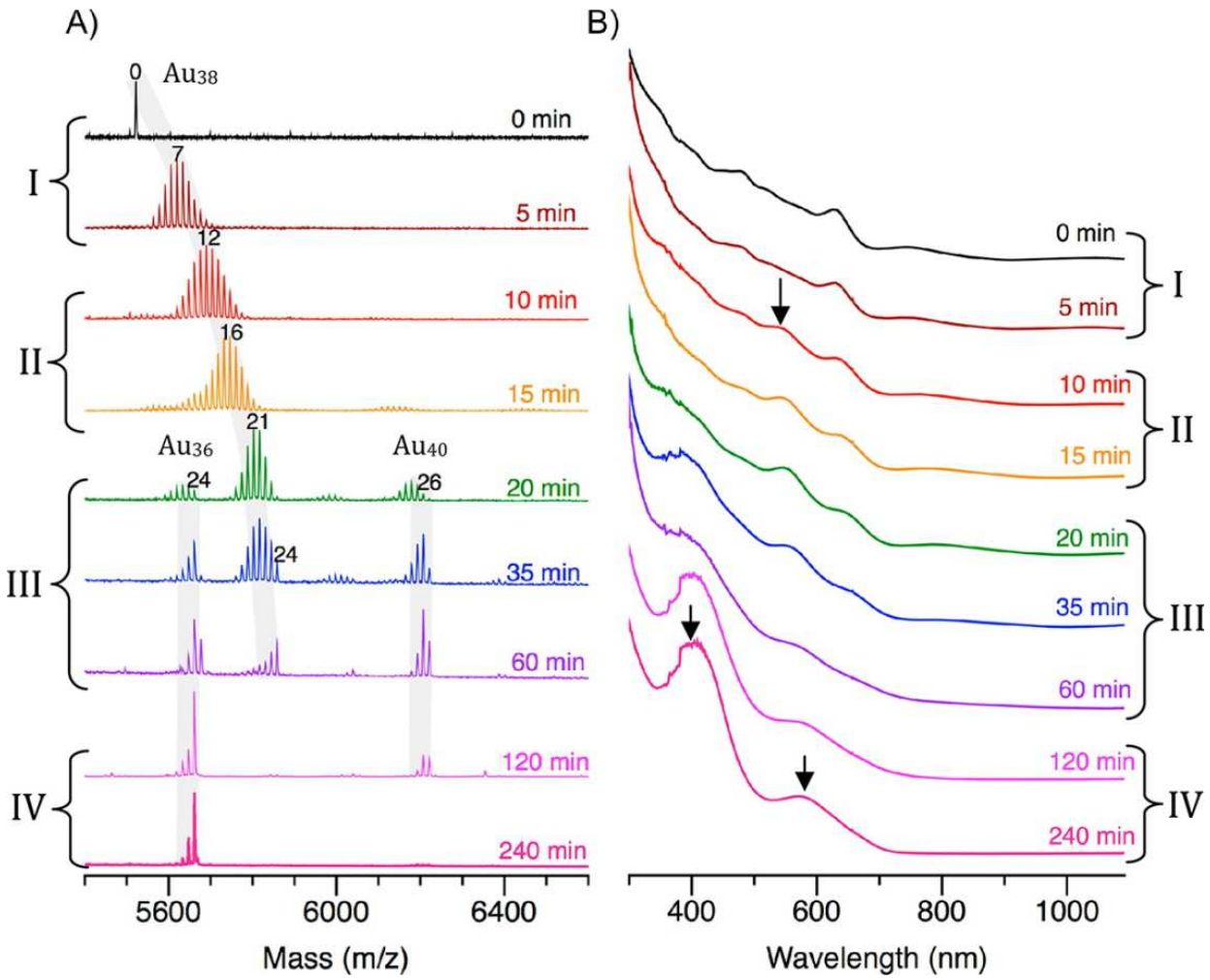
- An interesting disproportionation mechanism identified in the transformation of $Au_{38}(PET)_{24}$ to $Au_{36}(TBBT)_{24}$ is discussed.
- The ligand exchange reaction of $Au_{38}(PET)_{24}$ with bulkier TBBT induces structural distortion of the initial rod-like biicosahedral $Au_{38}(PET)_{24}$ structure.
- This process is evidenced by detailed mass spectrometric and optical spectroscopic analyses.
- The optical spectrum of $Au_{36}(TBBT)_{24}$ was further interpreted by theoretical simulations on a $Au_{36}(SCH_3)_{24}$ model cluster.



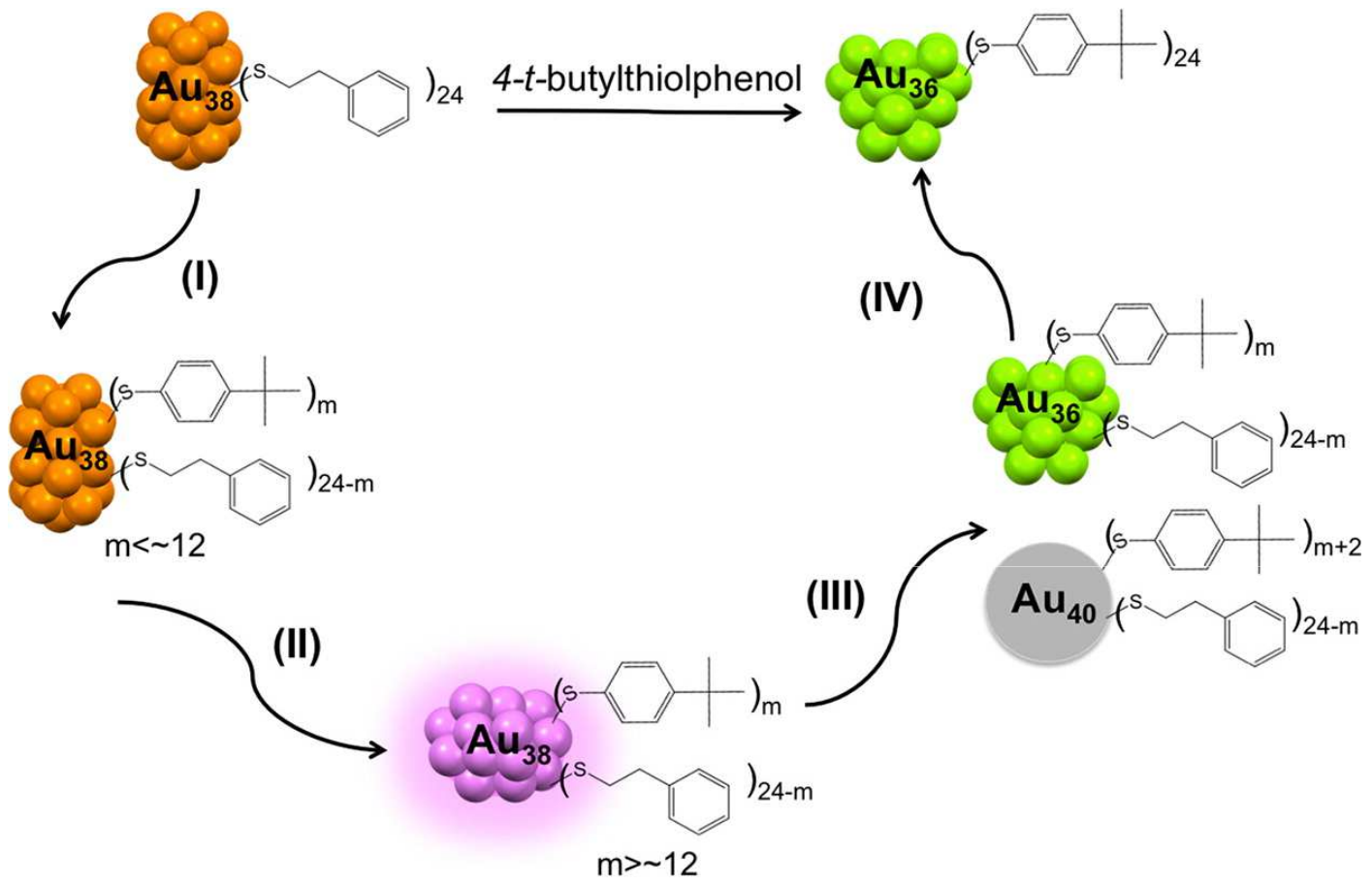
Scheme 1: Conversion of $Au_{38}(PET)_{24}$ to $Au_{36}(TBBT)_{24}$ nanoclusters (the carbon tails are not shown for clarity; S atoms, yellow; kernel Au atoms, magenta; surface Au atoms, green or cyan).

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 $Au_{38}(SR)_{24}$ 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.

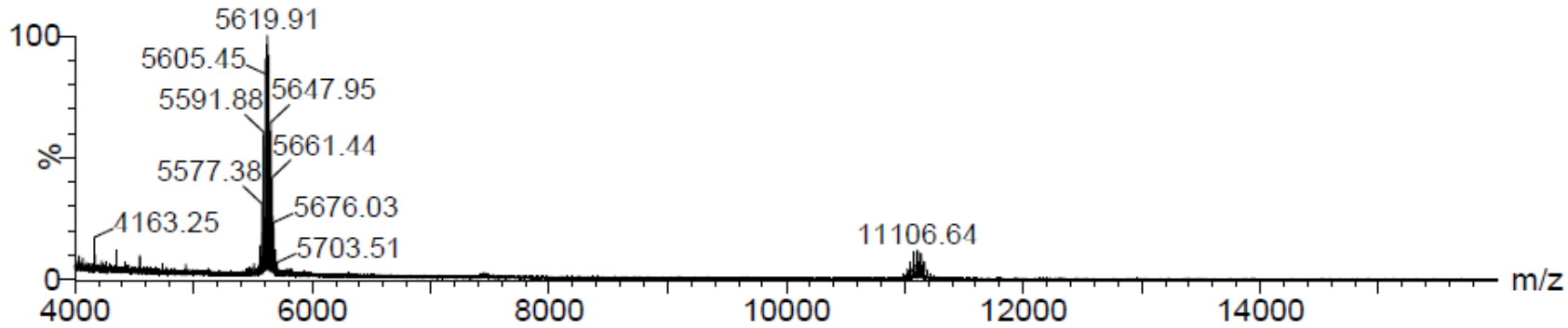


(A) Time-dependent ESI-MS of the transformation reaction. The doubly charged region is shown. The three gray shadows indicate three groups of peaks: (left) $Au_{36}(TBBT)_m(PET)_{24-m}$, (middle) $Au_{38}(TBBT)_m(PET)_{24-m}$, (right) $Au_{40}(TBBT)_{m+2}(PET)_{24-m}$. The numbers on the top of the mass 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.

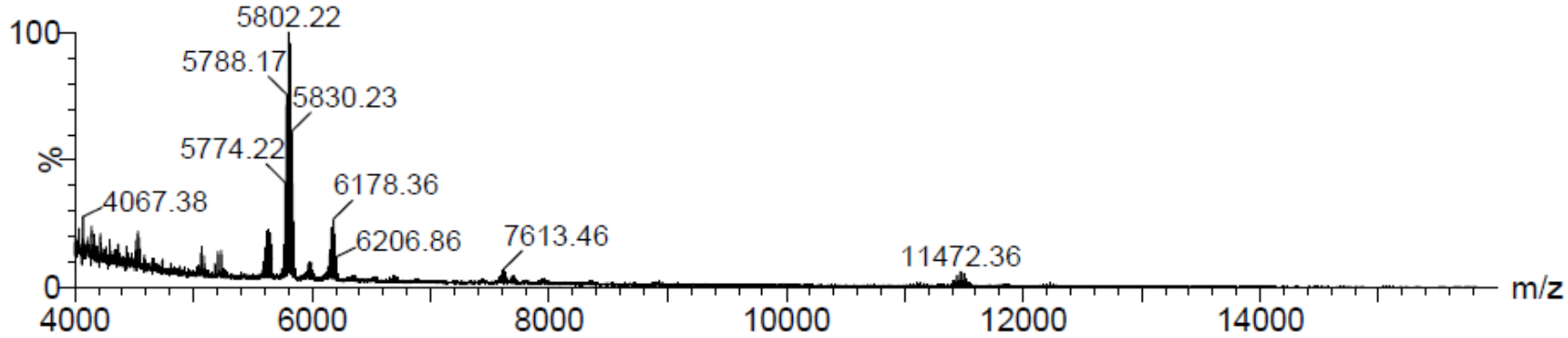


Scheme 2: Reaction pathway for conversion of $Au_{38}(PET)_{24}$ to $Au_{36}(TBBT)_{24}$. Stage I, ligand exchange; II, structure distortion; III, disproportionation; IV, size focusing.

A) Full range ESI-MS spectrum for the 5-min product:



B) Full range ESI-MS spectrum for the 20-min product:



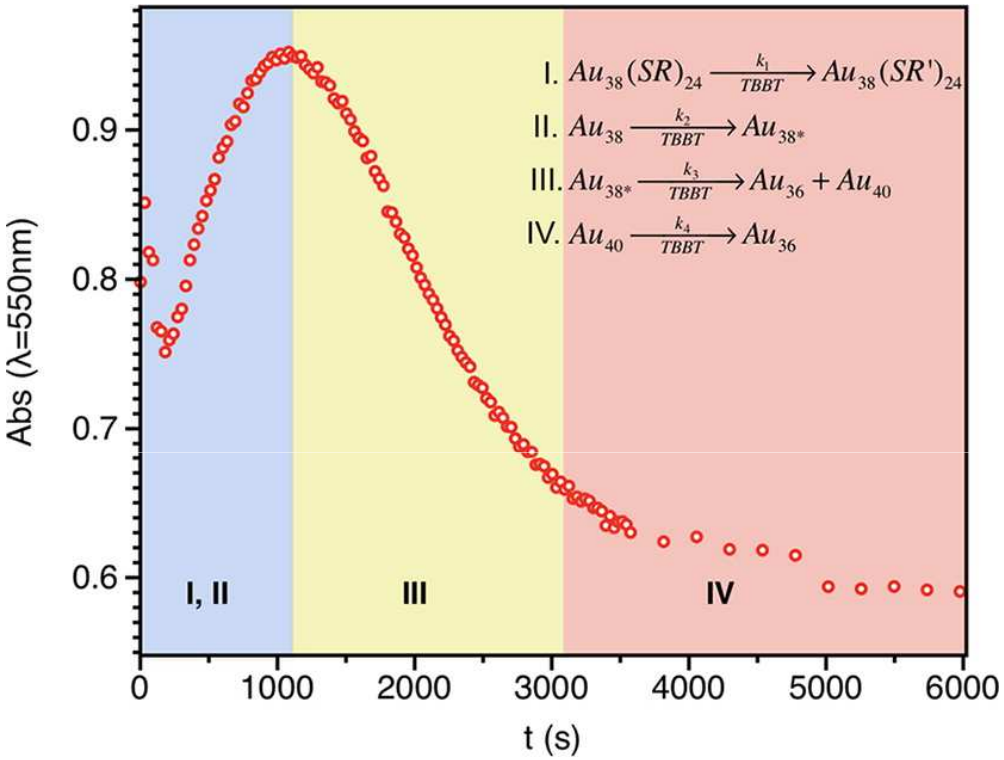
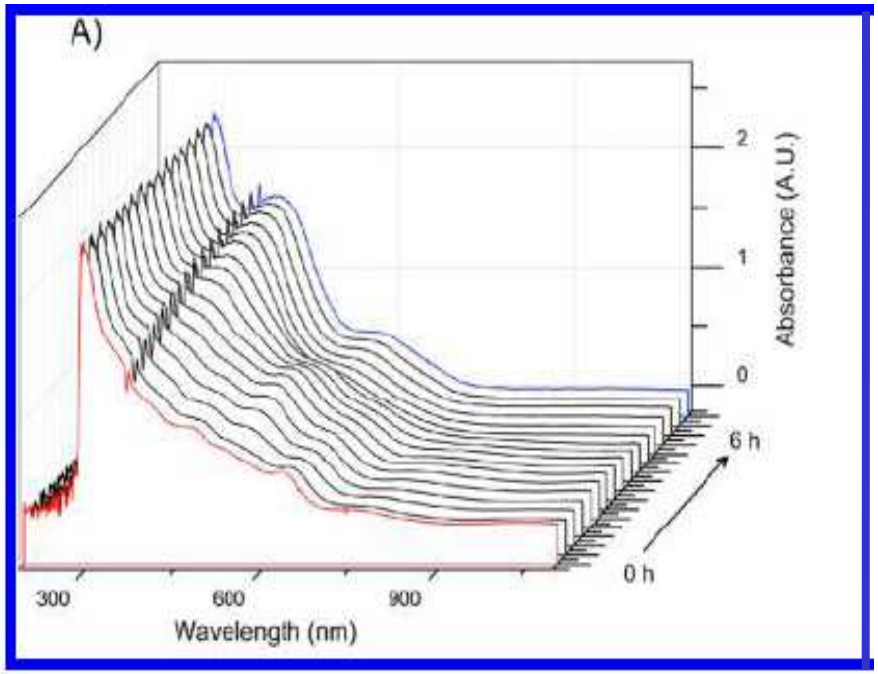


TABLE 1. Rate Constants for Stages II and III at Different Reaction Temperatures

	60 °C	70 °C	80 °C
$k_{2,obs}$ (s^{-1})	4.0×10^{-4}	1.4×10^{-3}	3.5×10^{-3}
$k_{3,obs}$ (s^{-1})	4.8×10^{-5}	1.8×10^{-4}	1.1×10^{-3}

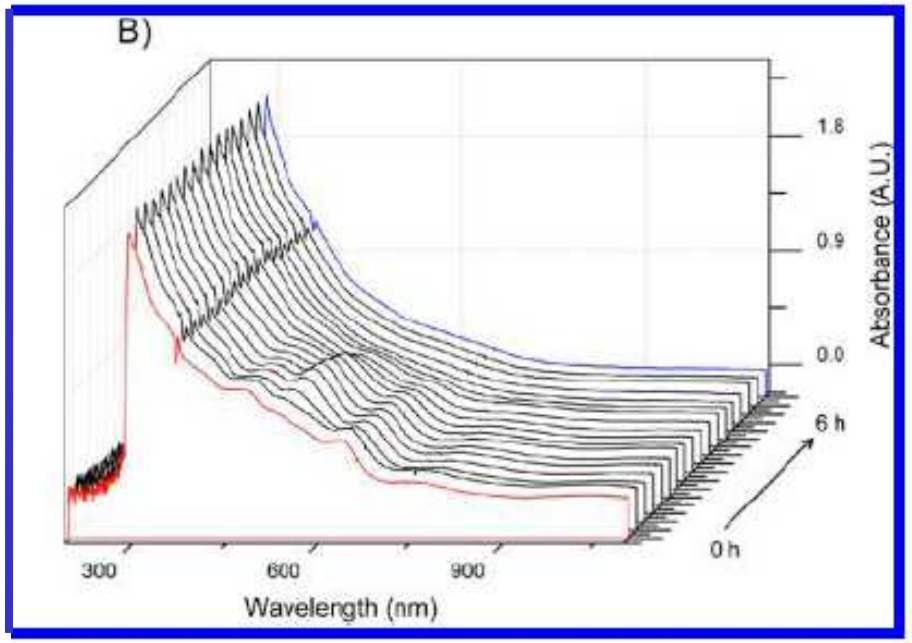
$E_{a,II}$ = 107 kJ/mol
$E_{a,III}$ = 152 kJ/mol

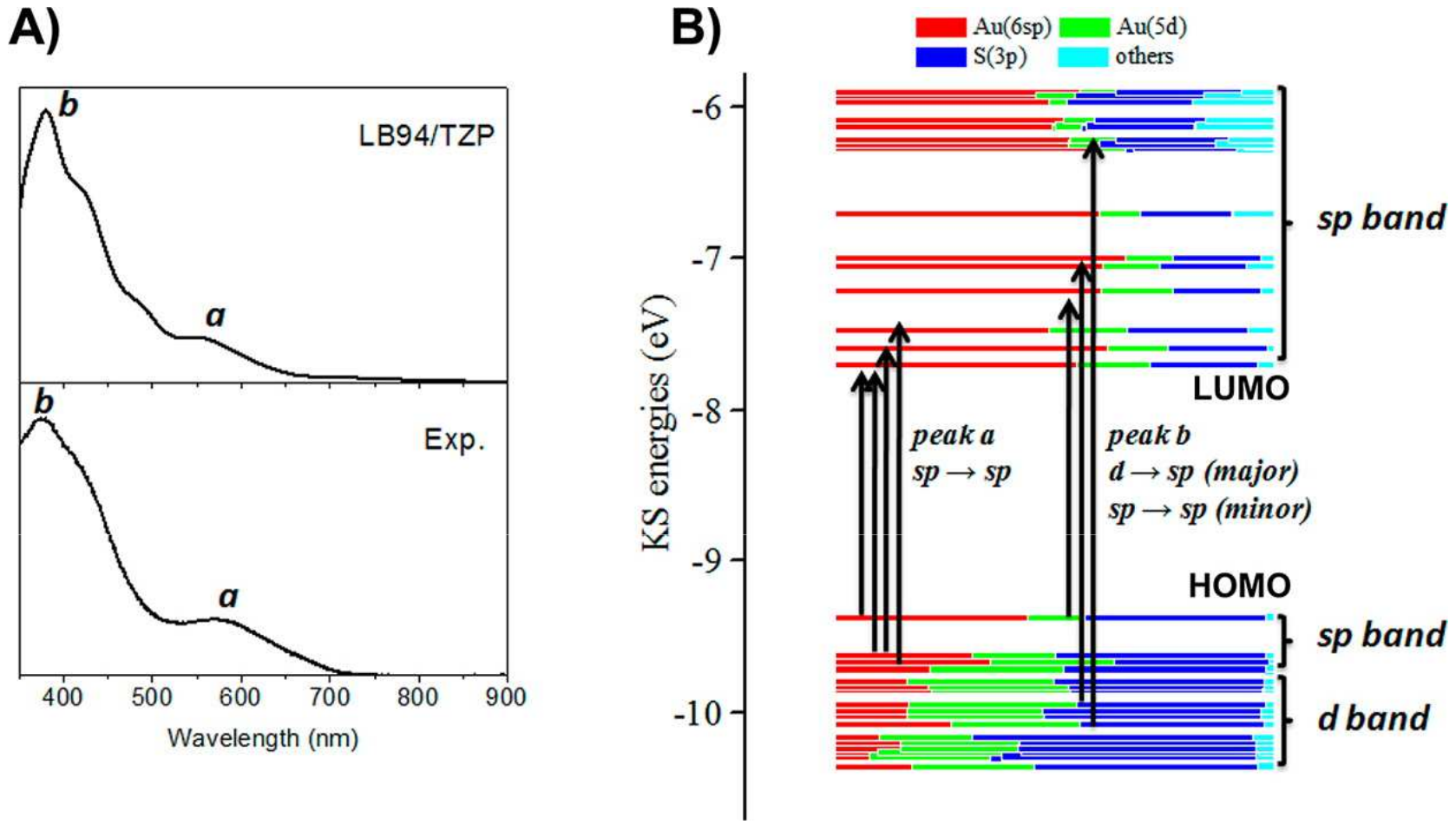
Kinetic curve (monitored by absorbance at 550 nm) for the conversion of $Au_{38}(PET)_{24}$ to $Au_{36}(TBBT)_{24}$ at 80 ° C.



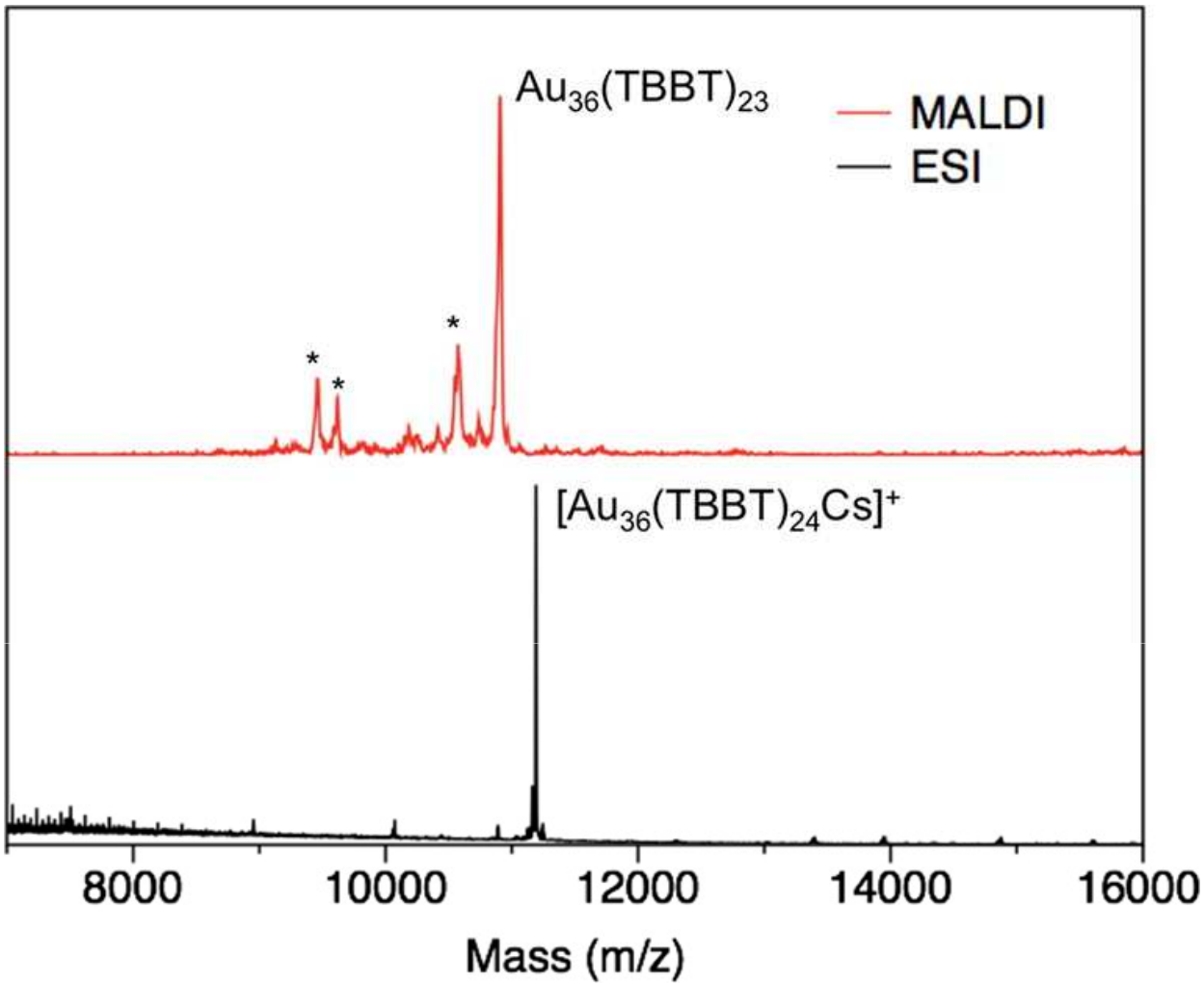
Time-dependent UV–vis spectral evolution of 4-*tert*-butylbenzenethiol with $Au_{38}(PET)_{24}$.

Time-dependent UV–vis spectral evolution of cyclohexanethiol reaction with $Au_{38}(PET)_{24}$.





(A) Comparison of simulated UV–vis absorption spectrum of $Au_{36}(SR)_{24}$ with the experimental spectrum. (B) Estimation of contributions of Au(6sp), Au(5d), and S(3p) to KS orbitals.



Comparison of the MALDI-MS and ESI-MS spectra of $Au_{36}(TBBT)_{24}$. The asterisks indicate the fragments due to MALDI.

CONCLUSION

- The detailed mechanism of the ligand-induced conversion from $Au_{38}(PET)_{24}$ to $Au_{36}(TBBT)_{24}$ is discussed .
- The reaction pathway can be roughly divided into four stages.
- This process gave rise to Au_{36} nanoclusters in ~90% yield (Au atom basis), approaching the theoretical yield of ~94% according to the disproportionation mechanism.
- The conversion of biicosahedral Au_{38} structure to fcc Au_{36} structure is remarkable; it provides an unprecedented example of ligand bulkiness induced size and structural transformation in thiolate-protected nanoclusters.

SIGNIFICANCE

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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