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ARTICLE

The Pivotal Radical Intermediate $[Au_{21}(SR)_{15}]^+$ in the Ligand-Exchange-Induced Size-Reduction of $[Au_{23}(SR)_{16}]^-$ to $Au_{16}(SR)_{12}$

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Swetashree Acharya
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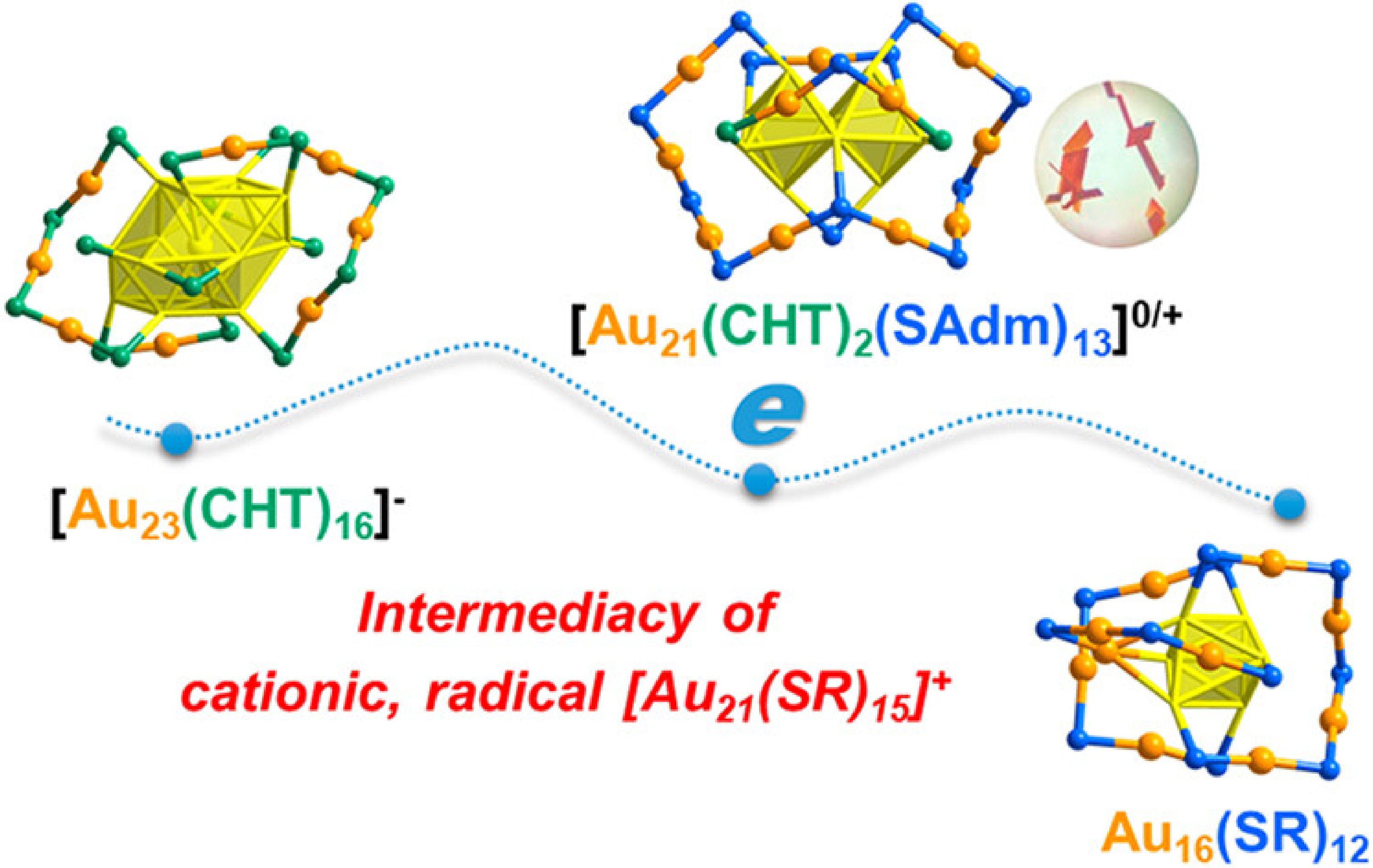
Abstract


$[Au_{23}(CHT)_{16}]^-$
$[Au_{21}(CHT)_2(SAdm)_{13}]^{0/+}$
e
Intermediacy of
cationic, radical $[Au_{21}(SR)_{15}]^+$
$Au_{16}(SR)_{12}$

Background

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Communication

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Total Structure Determination of $Au_{21}(S\text{-}Adm)_{15}$ and Geometrical/Electronic Structure Evolution of Thiolated Gold Nanoclusters

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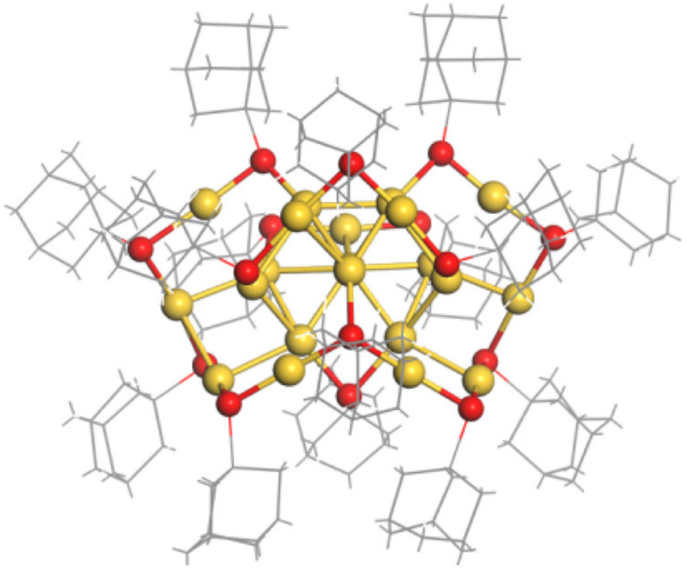

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Structure determination of a metastable $Au_{22}(SAdm)_{16}$ nanocluster and its spontaneous transformation into $Au_{21}(SAdm)_{15}$†

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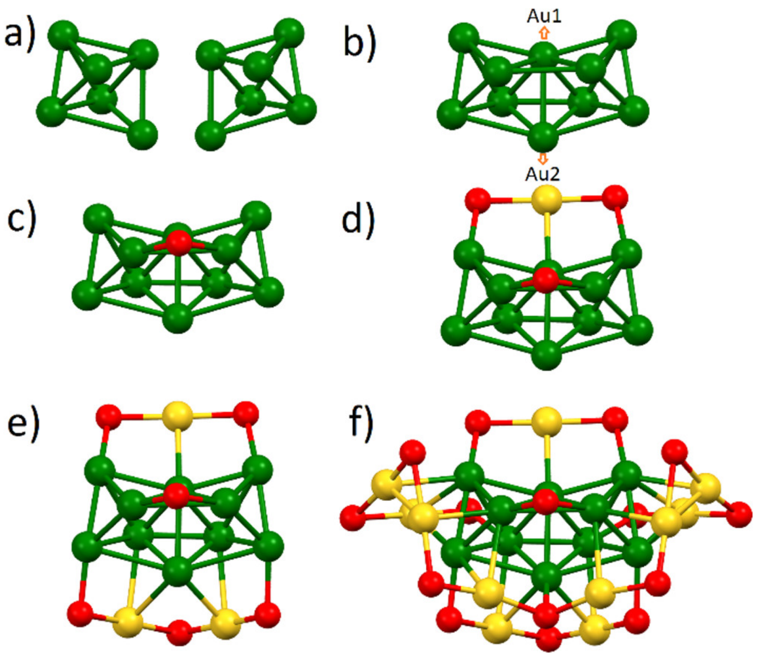

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Total Structure Determination of $Au_{16}(S\text{-}Adm)_{12}$ and $Cd_1Au_{14}(StBu)_{12}$ and Implications for the Structure of $Au_{15}(SR)_{13}$

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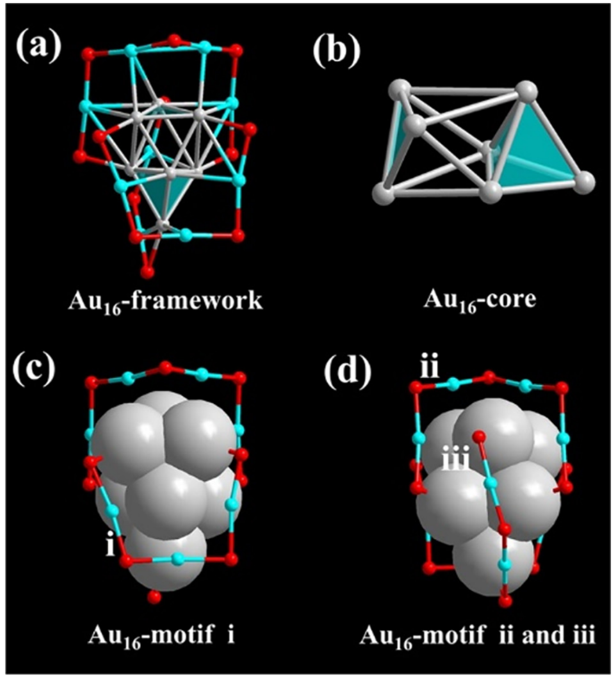
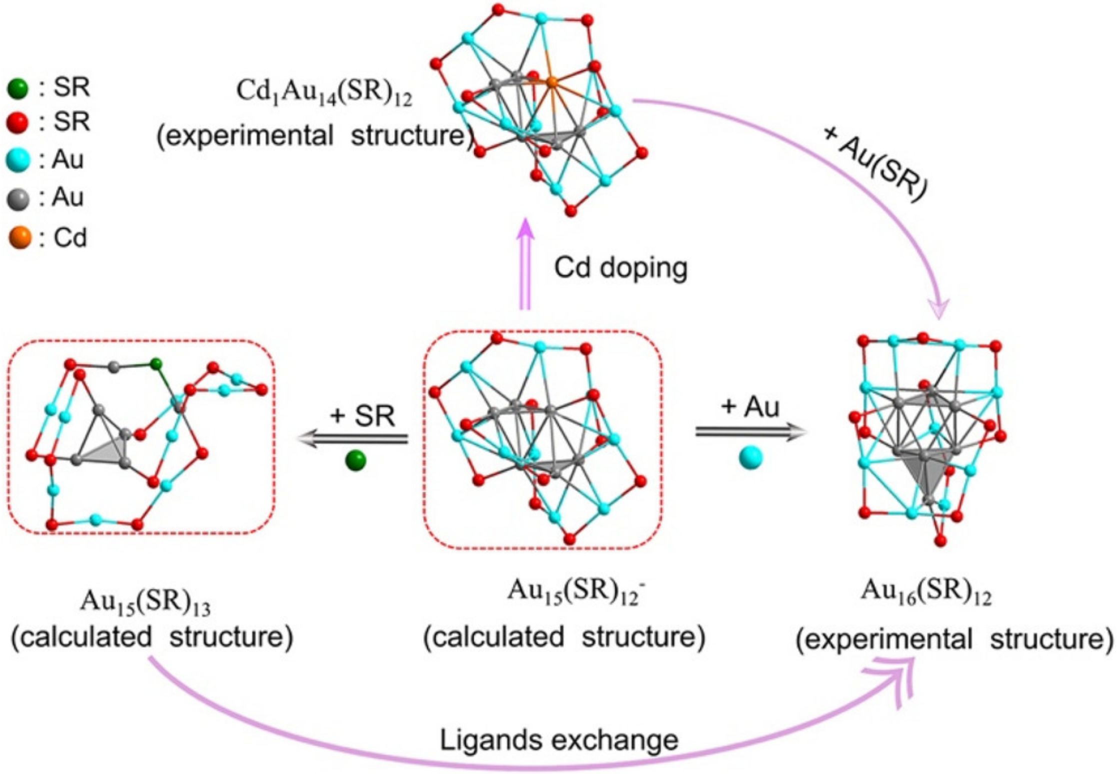




Motivation

- In recent years, ligand-exchange-induced enhancement in photoemission, chirality, or solubility has greatly expanded the practical applications of these ultrasmall nanoclusters in bioclinics, catalysis, and interfacial assembly.
- Structural characterization on the key intermediate, and ideally with single crystal strategies, becomes a highly demanding and rewarding issue.

Importance

- Explored the reaction and especially the kinetic profiles of the reaction of $[Au_{23}(CHT)_{16}]^-$ with HSAdm.
- Showed that, the neutral, 6e $Au_{21}(SR)_{15}$ is a resting state, and its 1e-reduction state, i.e., the 5e, cationic radical, $[Au_{21}(SR)_{15}]^+$, is an active intermediate to mainly account to the formation of thermodynamic stable Au_{16} products. The oxidation of 8e → 6e → 4e occurs associated with the core size-reduction (via preferentially removing the corner Au atoms on the core surface and the longer Au_nS_{n+1} staples)

Introduction

- The atomic precision of sub-nanometer-sized metal nanoclusters makes it possible to elucidate the kinetics of metal nanomaterials from the molecular level.

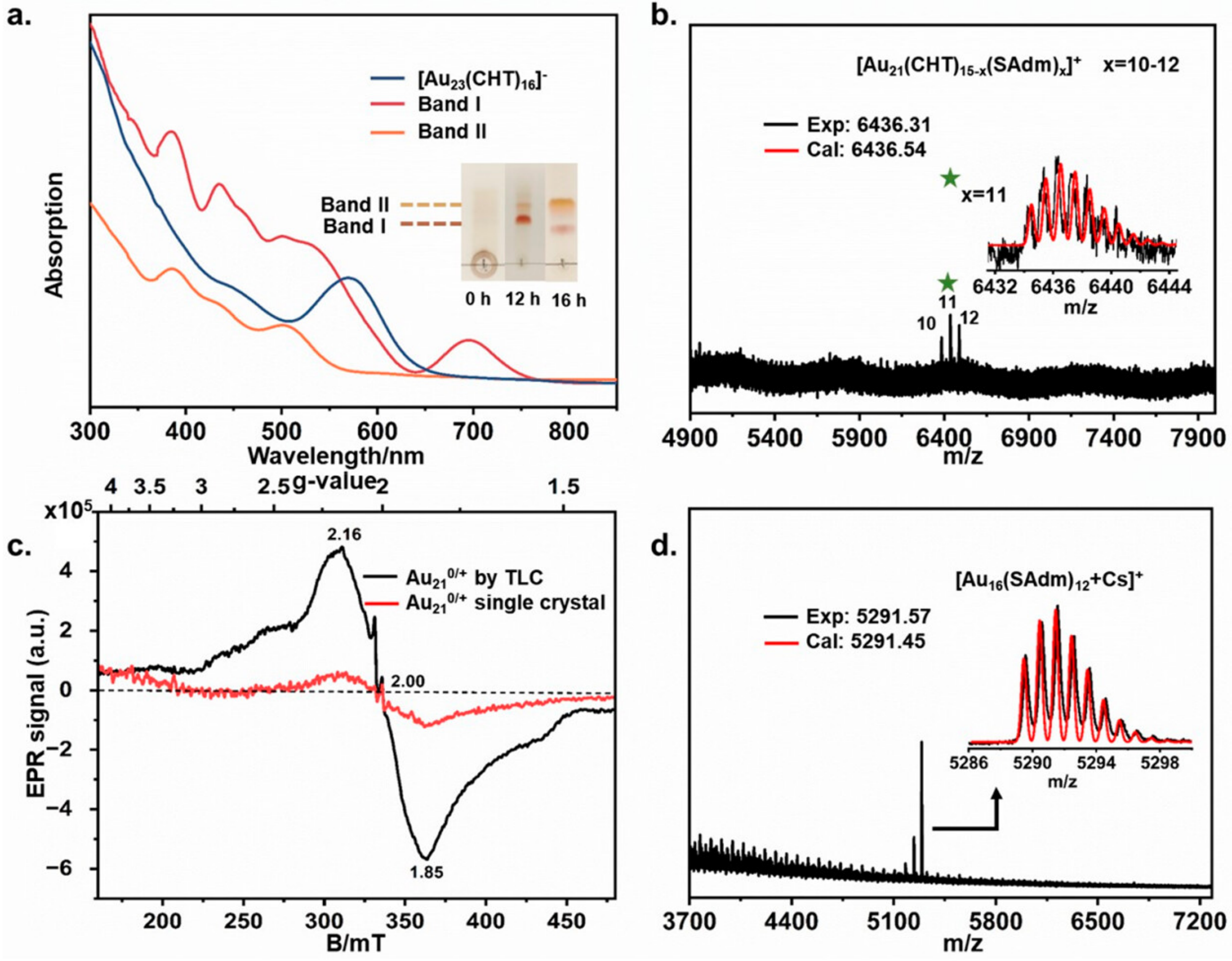
- Herein, the size reduction of an atomically precise $[Au_{23}(CHT)_{16}]^-$ (HCHT = cyclohexanethiol) cluster upon ligand exchange with HSAdm (1-adamantanethiol) has been reported.

- During the 16 h conversion of $[Au_{23}(CHT)_{16}]^-$ to $Au_{16}(SR)_{12}$, the neutral 6e $Au_{21}(SR)_{15}$, and its 1e-reduction state, i.e. the 5e, cationic radical, $[Au_{21}(SR)_{15}]^+$, are active intermediates to account for the formation of thermodynamically stable Au_{16} products.

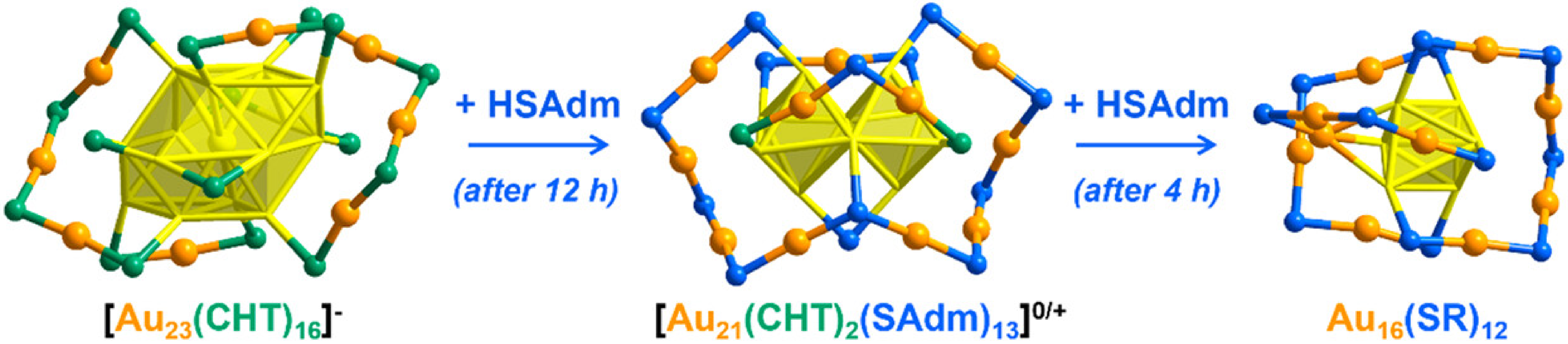
- The combination of spectroscopic monitoring by UV−vis with ESI-MS and DFT calculations indicates the preferential size-reduction on the corner Au atoms on the core surface and the terminal Au atoms on longer Au_nS_{n+1} staples.

- This study provides a reassessment on the electronic state of the Au_{21} structure and highlights the single electron transfer processes in cluster systems and thus the importance of the EPR analysis on the mechanistic issues.

Results and discussion

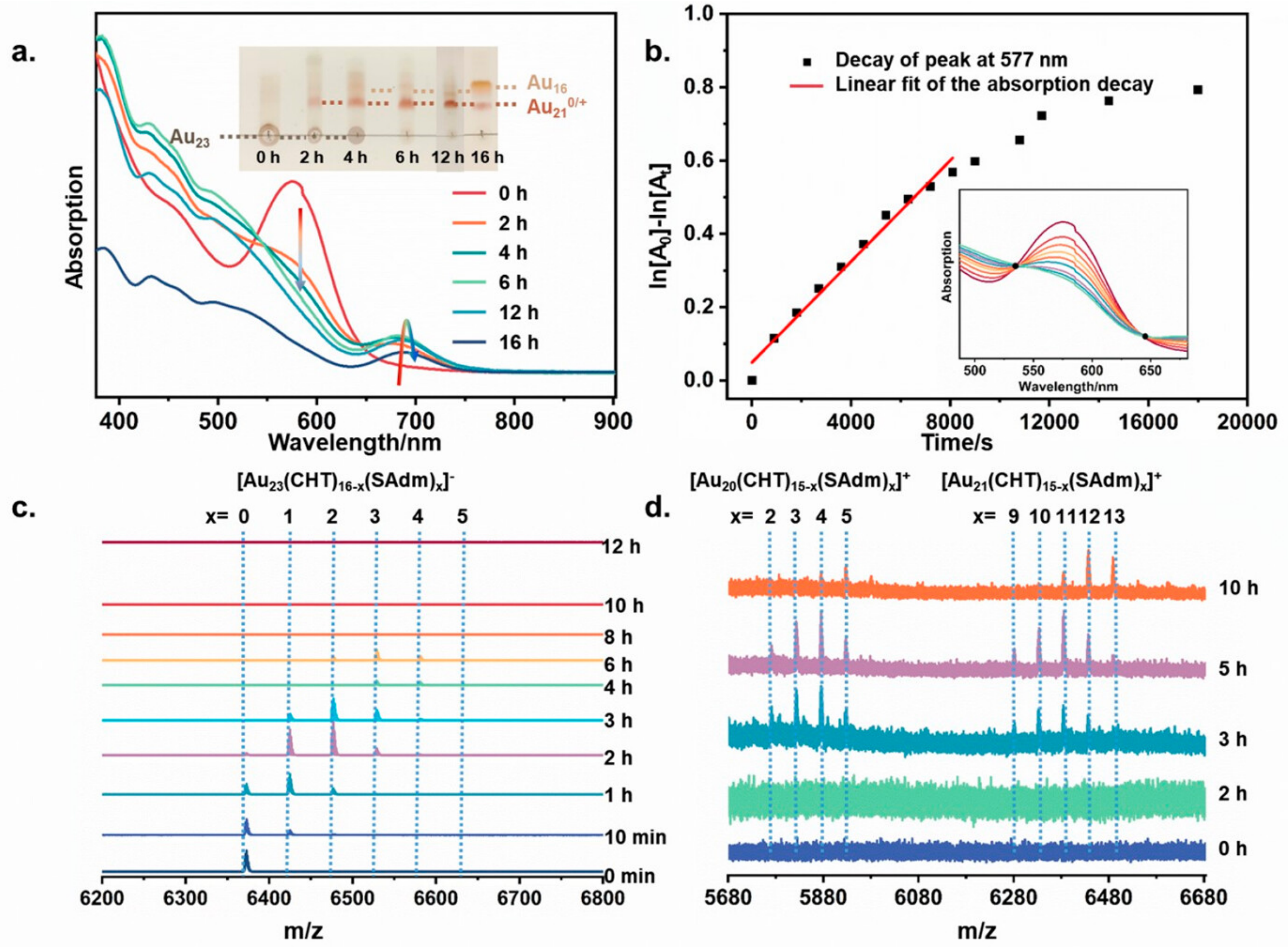


Scheme 1

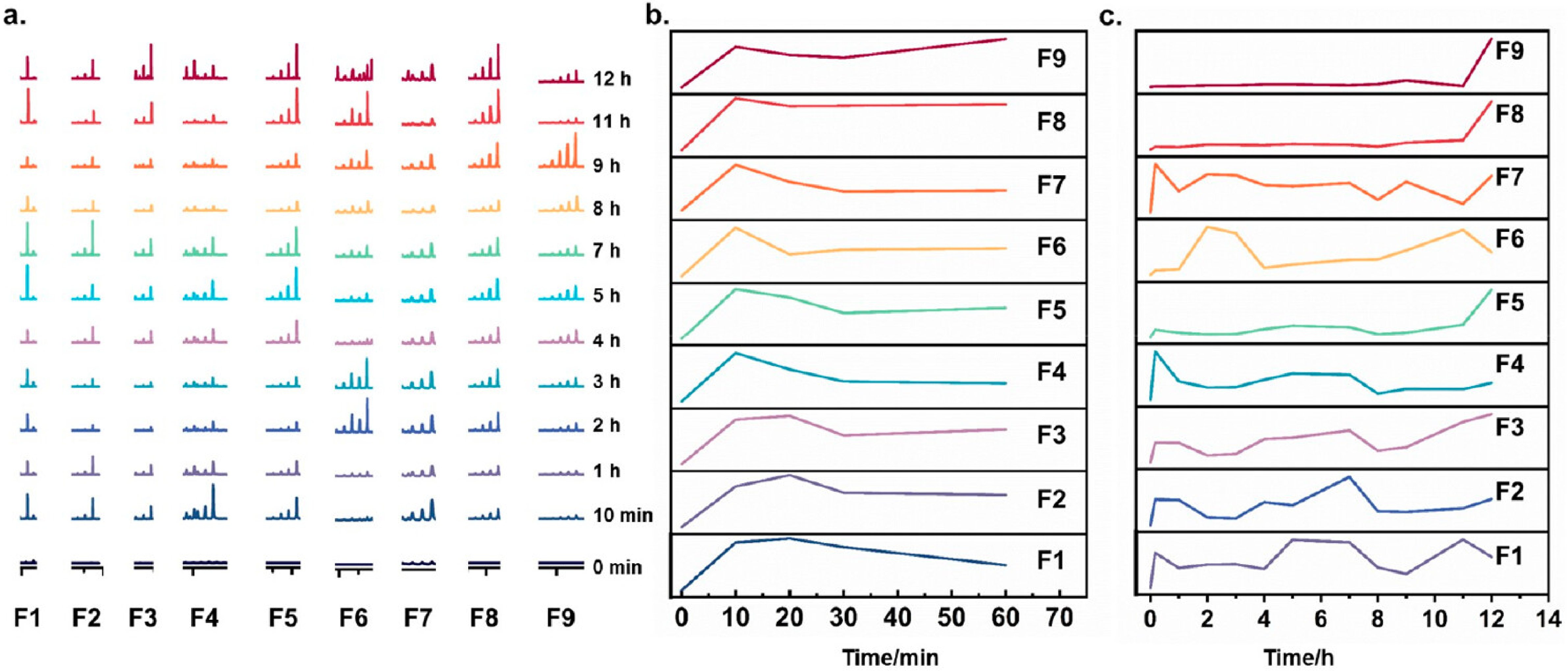


In DCM at RT

Reaction progress

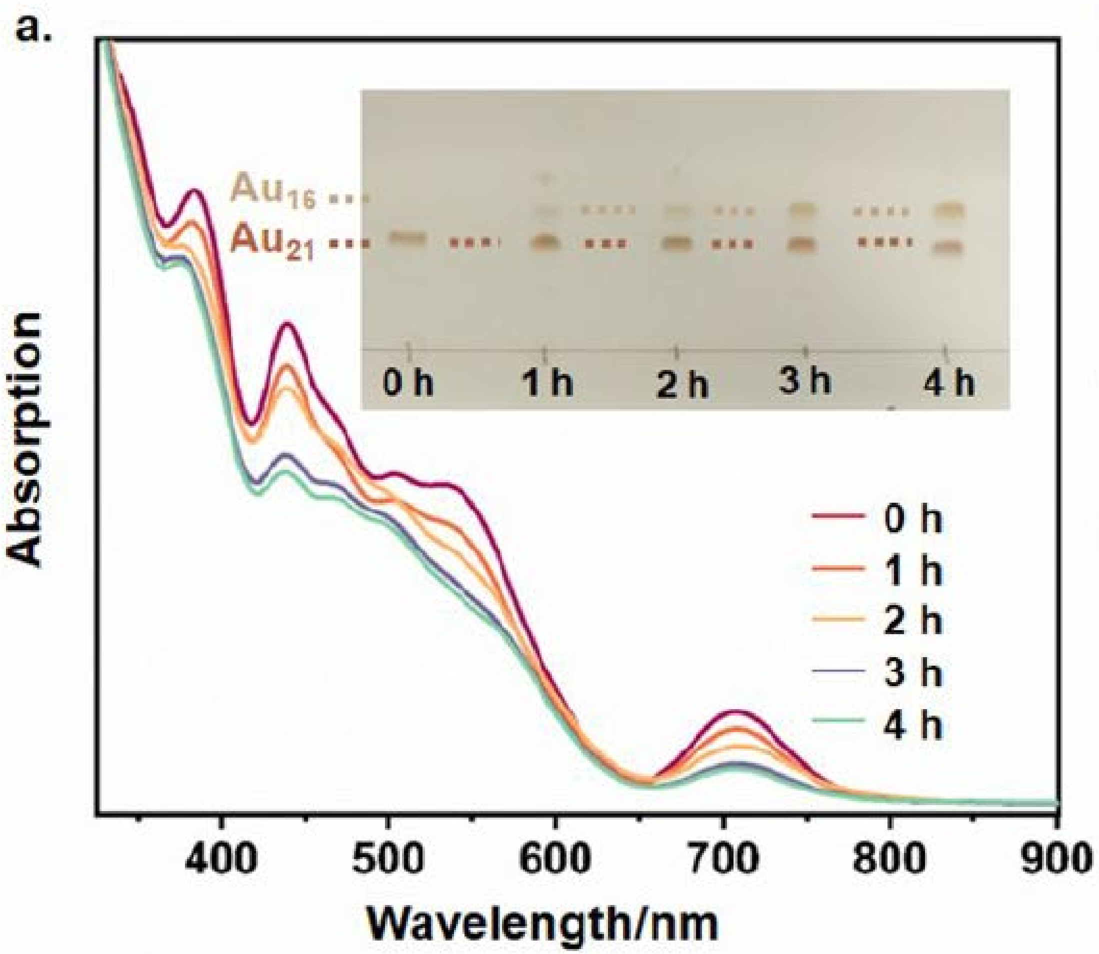


Au-SR complexes

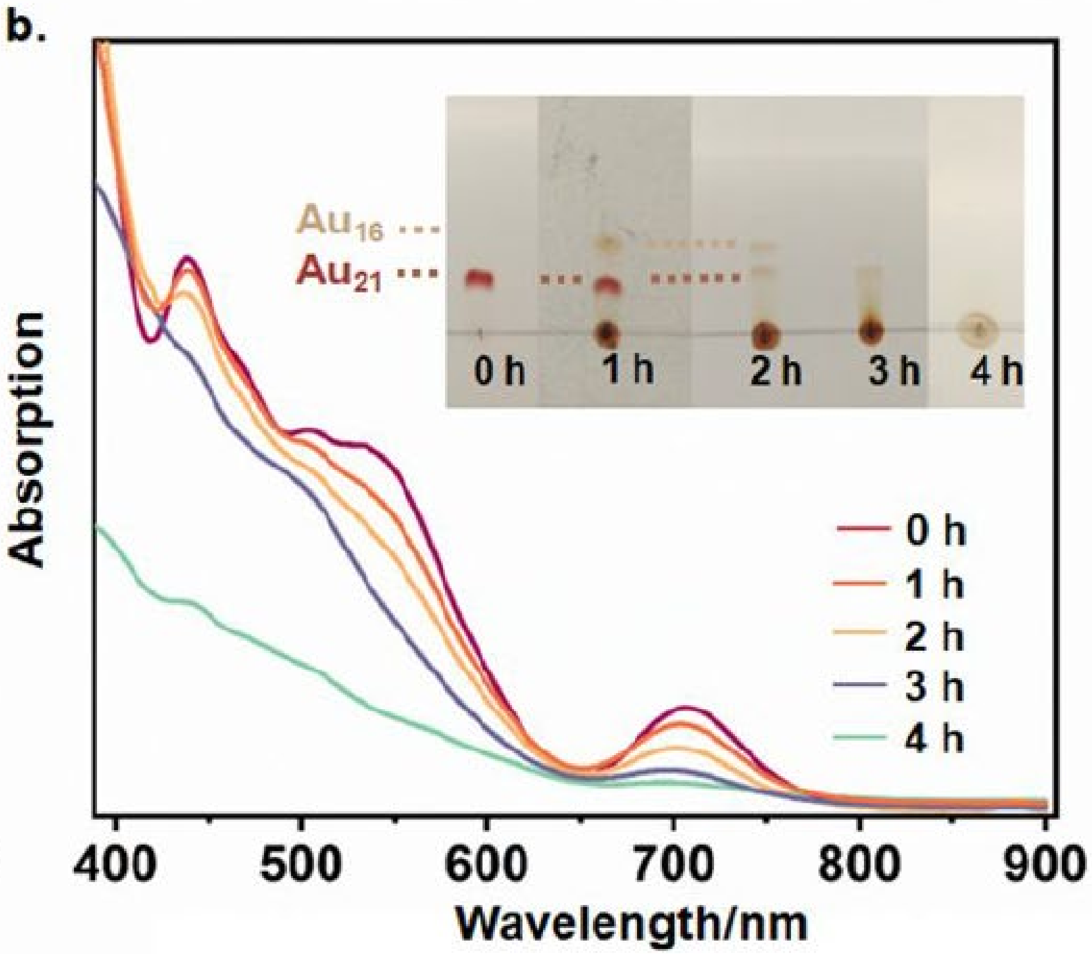


F1: $[Au_1SAdm_1Cl_1]^-$; F2: $[Au_1SAdm_2]^-$; F3: $[Au_2SAdm_3]^-$; F4: $[Au_3SAdm_3CHT_1]^-$; F5: $[Au_3SAdm_4]^-$; F6: $[Au_4SAdm_4Cl_1]^-$; F7: $[Au_4SAdm_4CHT_1]^-$; F8: $[Au_4SAdm_5]^-$; F9: $[Au_5SAdm_6]^-$.

Control experiment

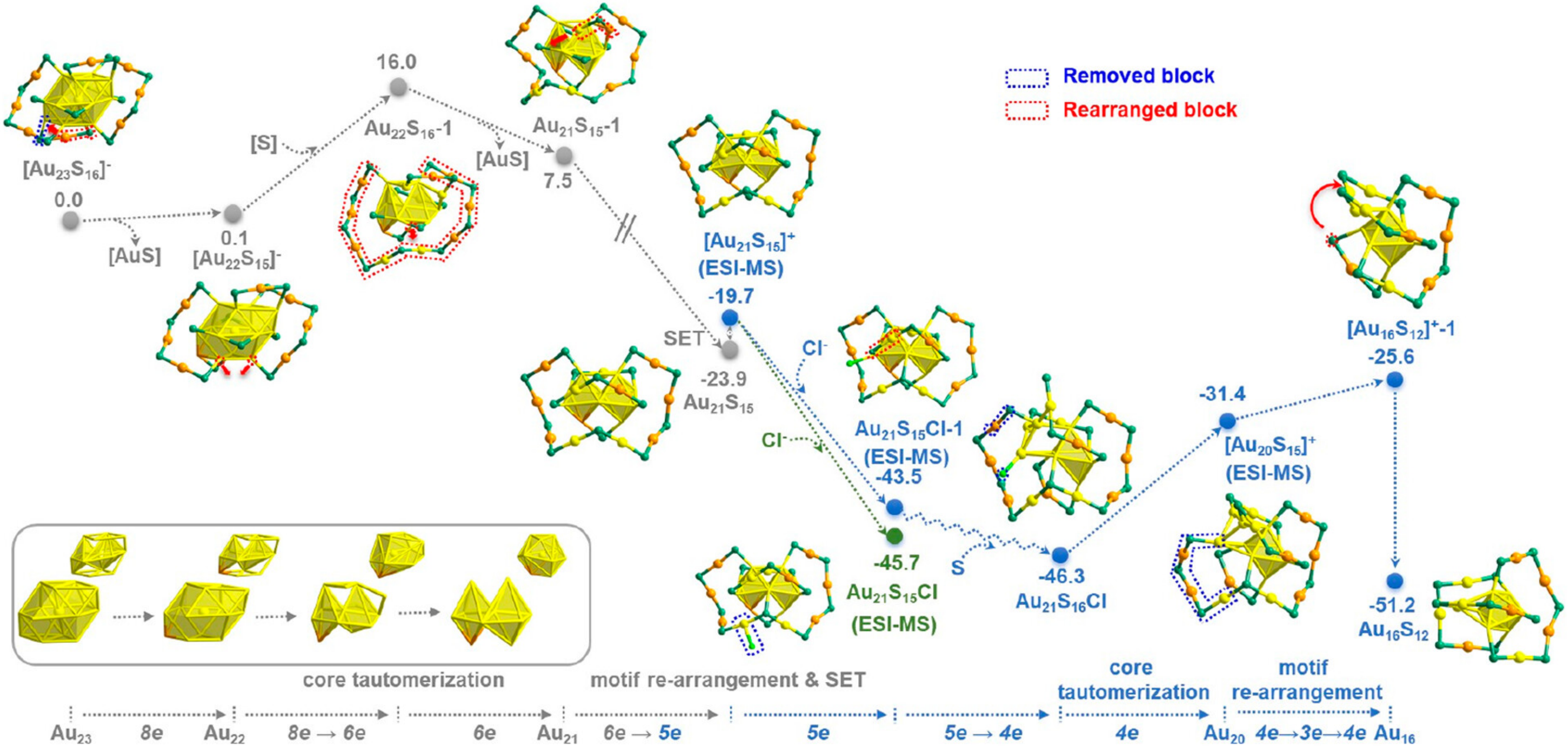


Presence of excess HSAdm



Absence of excess HSAdm

Energy profile



Conclusions

- This study reported a ligand-exchange-induced size-reduction of $[Au_{23}(SR)_{16}]^-$ to $Au_{16}(SR)_{12}$ and elucidates the intermediacy of one redox pair of $[Au_{21}(SR)_{15}]^{0/+}$ by means of X-ray single crystal diffraction, UV−vis, ESI-MS, and EPR, etc.

- The radical type $[Au_{21}(SR)15]^+$ intermediate was identified, and its coexistence with the neutral charge states indicate the flexible electronic state of the $Au_{21}(SR)_{15}$ framework.

- Herein, the single electron transfer processes in cluster systems and thus the importance of the EPR analysis on the mechanistic issues was emphasized.

- With the combination of in situ UV−vis, ESI-MS, and DFT calculations, the conversion mechanism was proposed, the Au atoms on the corner of the metallic core structure were found to be liable to be removed, and the $Au_{16}(SR)_{12}$ was finally formed as the thermodynamic product.

- The size-reduction occurs preferentially on the corner Au atoms on the core surface or the terminal Au atoms on longer Au_nS_{n+1} staples.