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Dynamic Behavior of Thiolate-Protected Gold−Silver 38-Atom Alloy Clusters in Solution

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Intercluster Reactions between $Au_{25}(SR)_{18}$ and $Ag_{44}(SR)_{30}$

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Manifestation of Geometric and Electronic Shell Structures of Metal Clusters in Intercluster Reactions

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INTRODUCTION

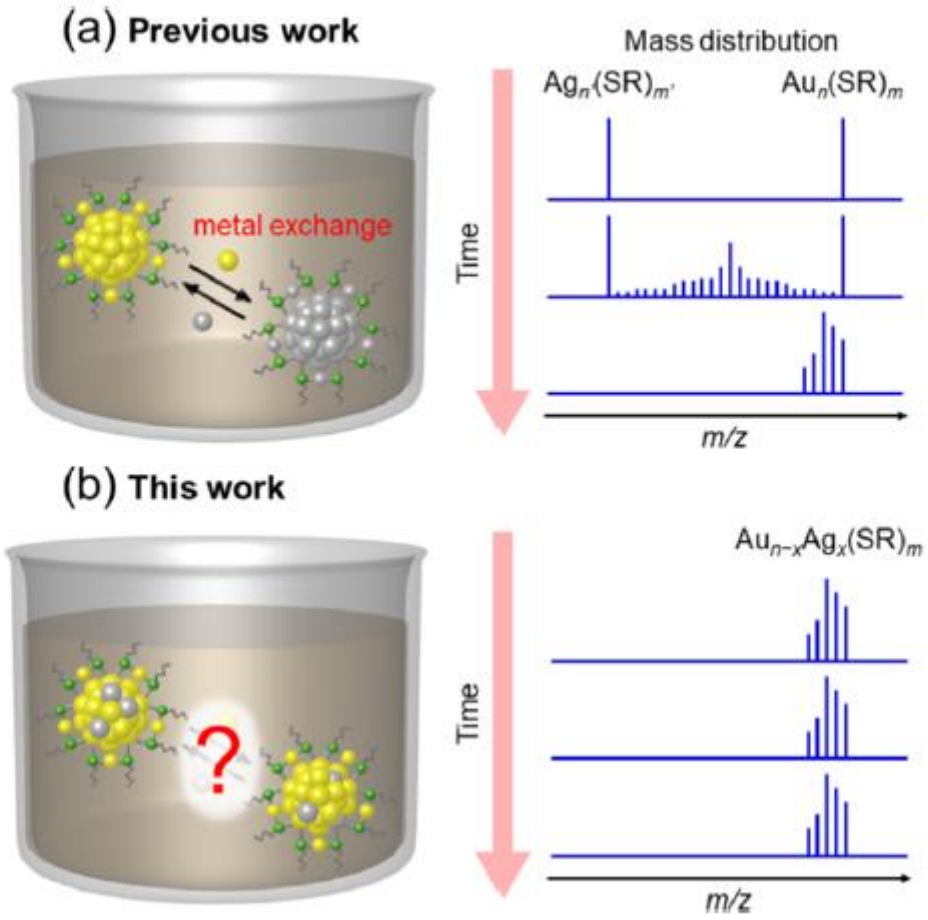

Figure 1. Comparison between (a) previous work and (b) this work.

EXPERIMENTAL SECTION

Synthesis of $[Au_{38-x}Ag_x(SC_4H_9)_{24}]^0$

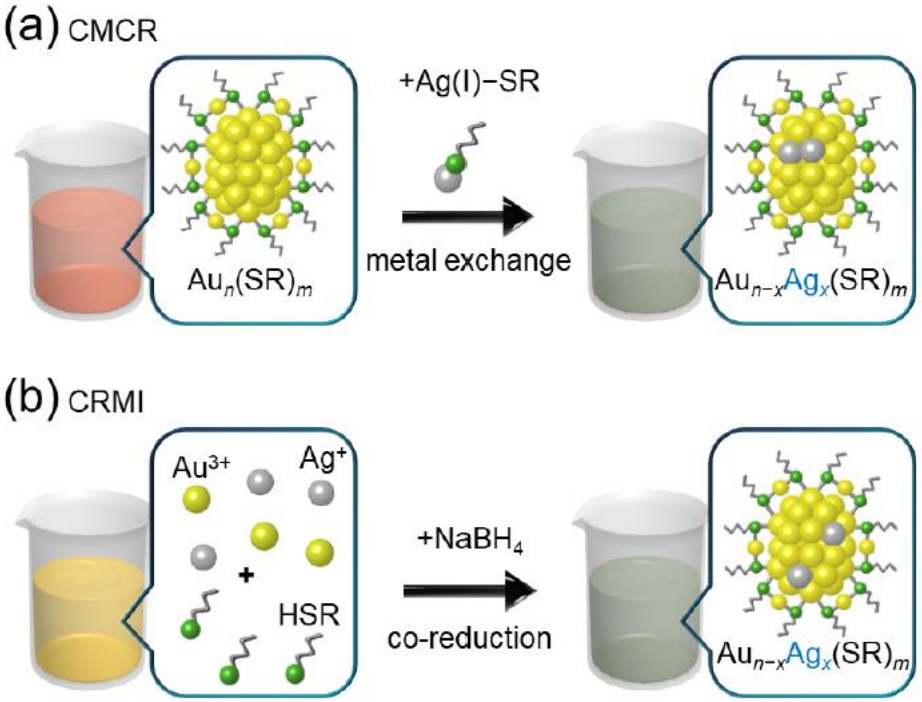

Figure S1. Comparison of the synthesis methods used in this work; (a) cluster−metal complex reaction (CMCR) and (b) co-reduction of two kinds of metal ions (CRMI).

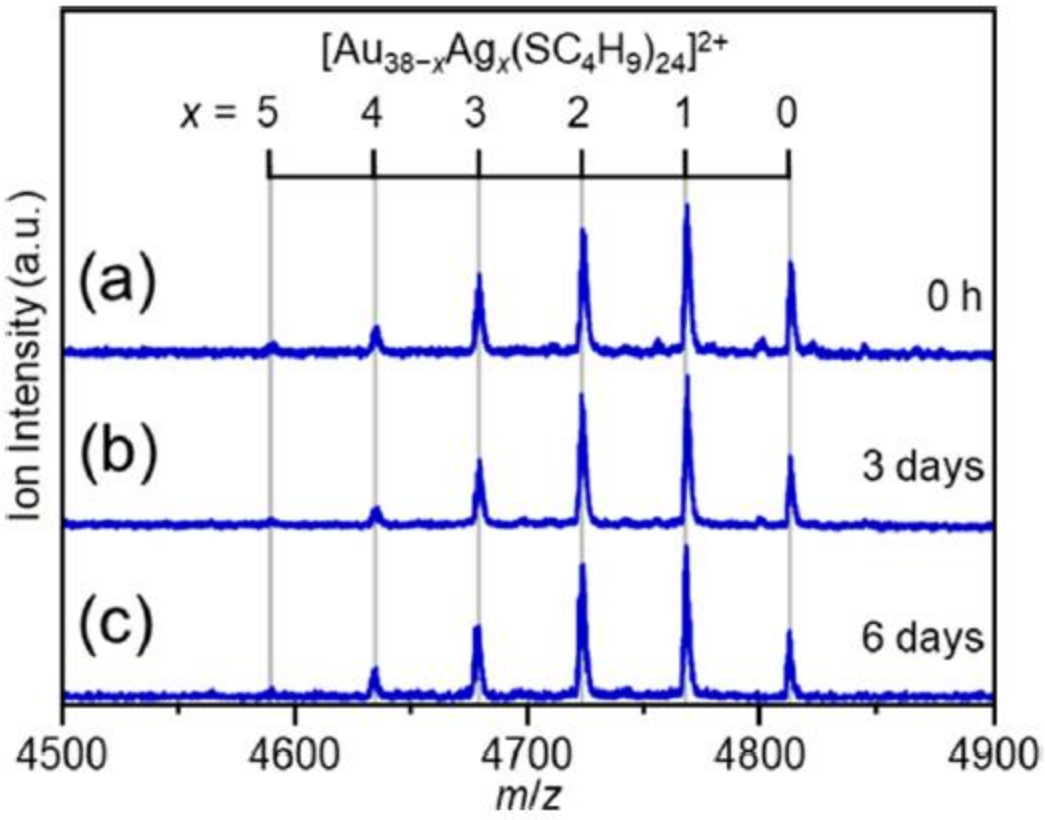

Figure 2. Time dependence of positive-ion ESI mass spectra (+2 region) of $[Au_{38-x}Ag_x(SC_4H_9)_{24}]^0$ synthesized by CMCR; (a) 0 h, (b) 3 days, and (c) 6 days. Each cluster is observed as a cation because it ionized during the ESI process.

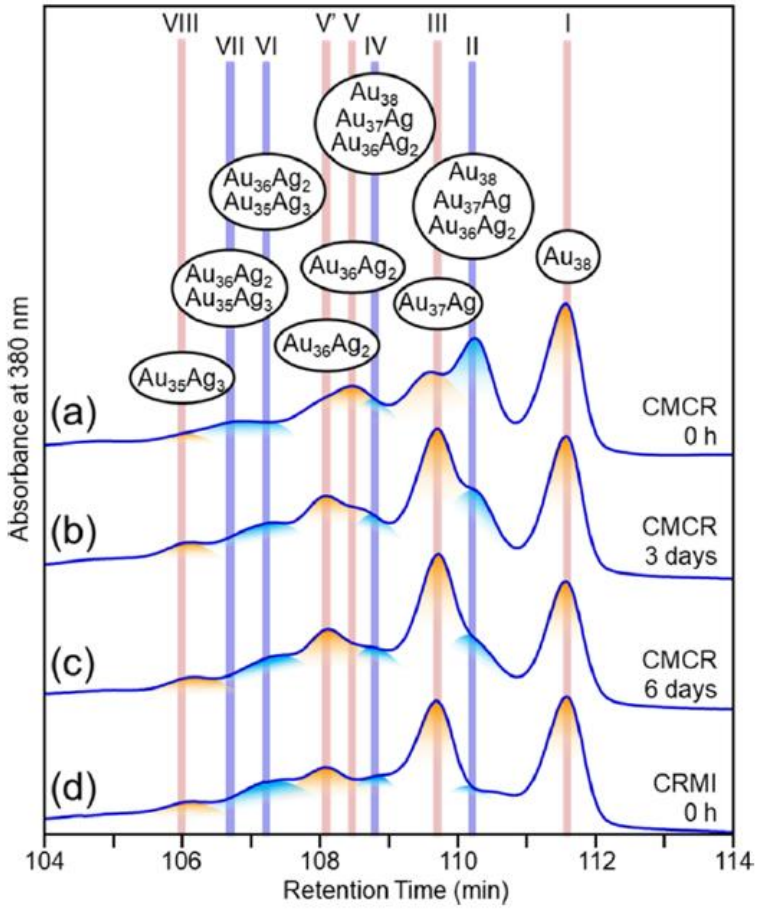

Figure 3. Time dependence of chromatograms of $[Au_{38-x}Ag_x(SC_4H_9)_{24}]^0$ synthesized by CMCR; (a) 0 h, (b) 3 days, and (c) 6 days. (d) Chromatogram showing $[Au_{38-x}Ag_x(SC_4H_9)_{24}]^0$ synthesized by CRMI (0 h).

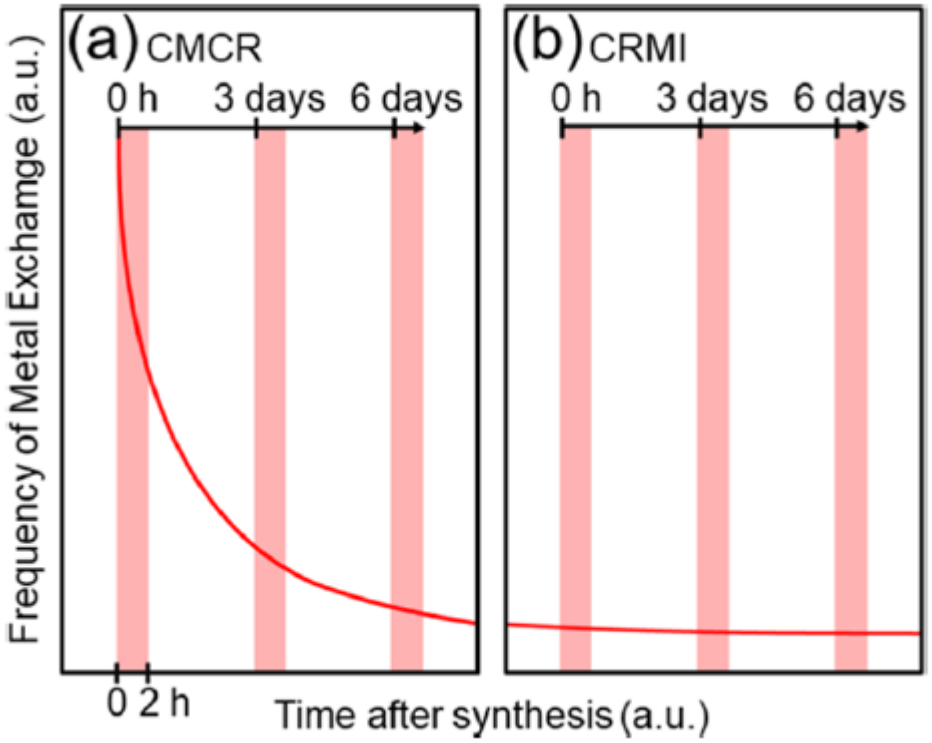

Figure 4. Relationship between standing time and the frequency of metal exchange for (a) CMCR and (b) CRMI.

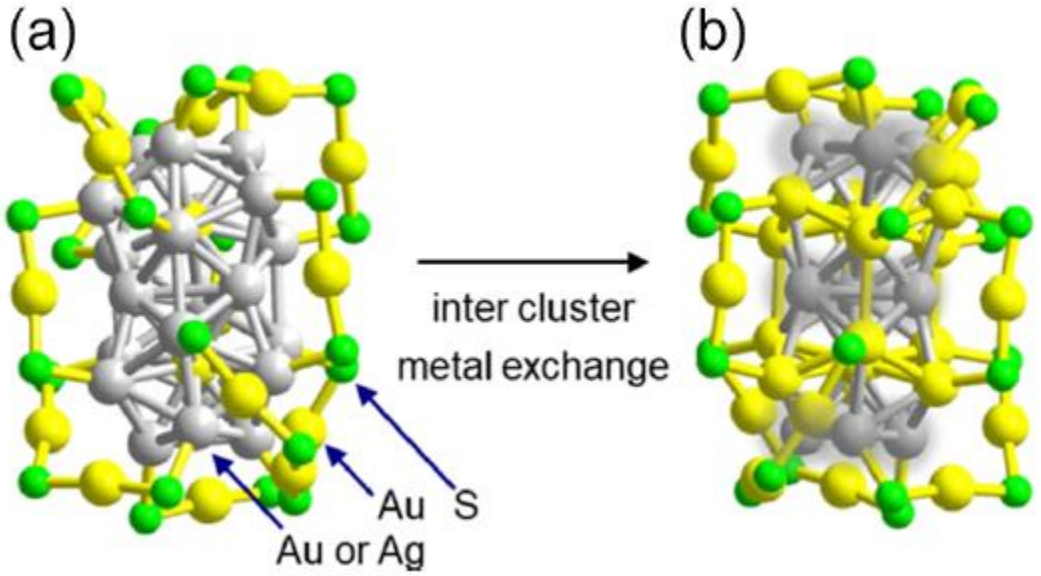

Figure 5. Structural change caused by metal exchange between $[Au_{38-x}Ag_x(SC_4H_9)_{24}]^0$ clusters.

CONCLUSIONS

- Dynamic behaviour of $[Au_{38-x}Ag_x(SC_4H_9)_{24}]^0$ in solution was studied combining RP-HPLC and ESI-MS.

- Findings :

1. Clusters synthesized by **CMCR method**, metastable species are also generated that undergo inter-cluster metal exchange (and intra-cluster metal exchange) in solution to transform the geometrical structure into the thermodynamically stable one.

2. In **CMRI synthesis method**, thermodynamically stable products are formed predominantly.

- The study is specific to the experimental conditions.