

# SYNTHESIS OF NOVEL ALLOY CLUSTERS USING LIGAND EXCHANGE REACTION

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## INTRODUCTION

Thiolate protected gold clusters ( $Au_n(SR)_m$ ) exhibit high stability against degradation and show various size-specific function unlike bulk gold. In these gold clusters, gold 25-atom clusters research has been most-actively conducted (Figure 1). Other group reported that when gold 25 clusters ( $Au_{25}(SC_2H_4Ph)_{18}$ ) and *tert*-butylbenzenthioi ( $HSPh^tBu$ ) are reacted, the different core size cluster (gold 28 clusters) could be synthesized.<sup>[1]</sup> These gold 28 clusters are known that it's formed by the fusion of icosahedron cores which gold 25 clusters have (Figure 2). Also, research in alloy clusters has recently become hot topic. Alloy clusters ( $Au_{24}M(SR)_{18}$ ) exhibit functionalities unlike those of single metal clusters (Figure 3). In this research, we applied this reaction to alloy clusters which exhibit functionalities unlike those of single metal clusters.<sup>[2]</sup> We used Pd doped alloy cluster to synthesis new alloy clusters.

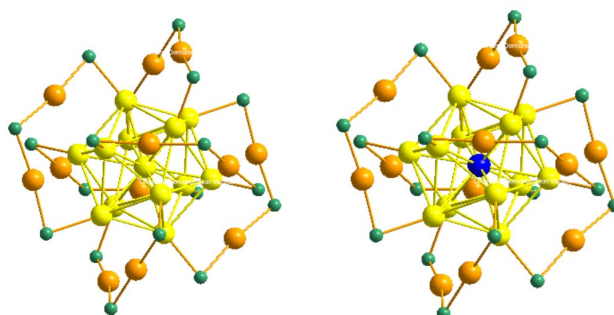


Figure 1.  $Au_{25}(SR)_{18}$

Figure 3.  $Au_{24}M(SR)_{18}$

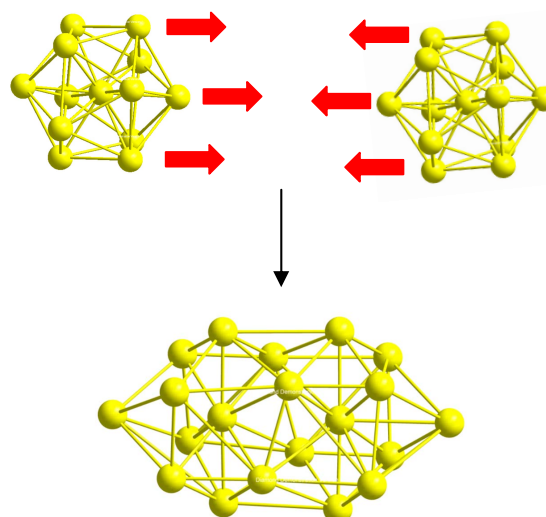


Figure 2. Fusion of icosahedron cores

## EXPERIMENTS

The precursor cluster  $Au_{24}Pd(SC_2H_4Ph)_{18}$  was synthesized by the method we reported in the past.<sup>[3]</sup> The  $Au_{24}Pd(SC_2H_4Ph)_{18}$  was mixed with  $HSPh^tBu$  in toluene at room temperature. Reaction solutions of 0 h, 2 h, 4 h, 6 h, 8 h, and 16 h were collected and the product was evaluated using reverse phase high performance liquid chromatography (RP-HPLC).<sup>[4]</sup> In addition, reaction products at each time were evaluated by ultraviolet-visible absorption spectroscopy and electrospray ionization mass spectrometry (ESI-MS).

## RESULTS AND DISCUSSION

Figure 4 shows the UV chromatogram of the product at each reaction time. Multiple peaks appear in each UV chromatogram. As time passes, the retention times are getting longer than those of  $Au_{24}(SC_2H_4Ph)_{18}$  which is a precursor cluster. Since  $SPH^tBu$  is less polar than  $SC_2H_4$ , it is interpreted that such a peak shift occurred with ligand exchange. Figure 5(a) and 5(b) show ultraviolet-visible absorption spectra of clusters before reaction (0 h) and after 16 h reaction, respectively. The absorption spectrum of the cluster after 16 h reaction is largely different from that

before the reaction. These results strongly suggest that a new metal cluster was formed by the ligand exchange reaction. Indeed, several peaks attributed to clusters of chemical composition which are not reported in the past were observed in the ESI mass spectrum of the cluster after 16 h reaction. (Figure 6)

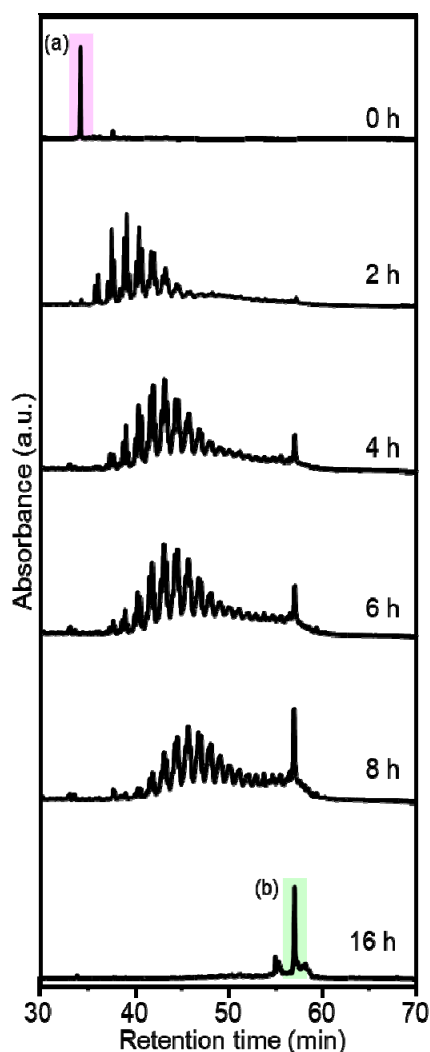


Figure 4. The UV chromatogram of the cluster of each reaction time

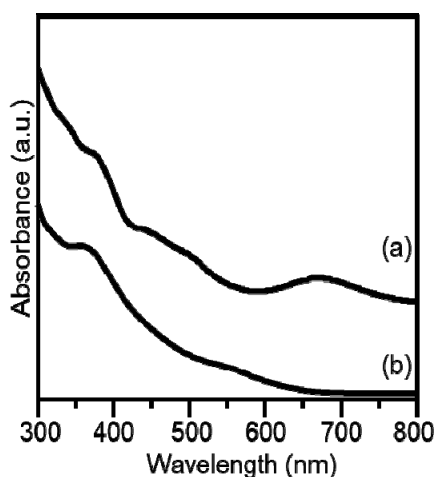


Figure 5. Ultraviolet-visible absorption spectrum of cluster (a) before reaction (0 h) (b) after 16 h reaction

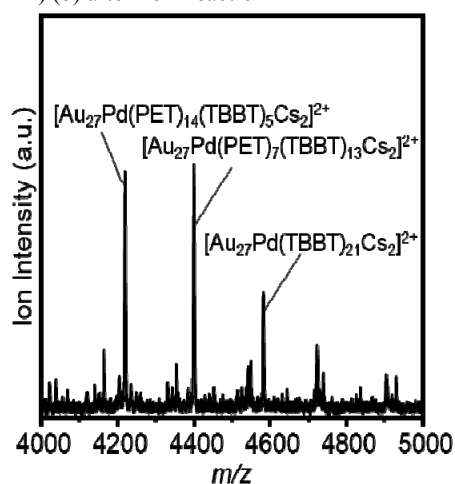


Figure 6. ESI mass spectra of clusters after 16 h reaction

## CONCLUSION

This work implied that we succeeded in synthesizing a new alloy cluster. In future, we will work on isolation and single crystal X-ray structural analysis in order to determine the geometry of new alloy clusters.

## REFERENCES

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