

## Synthesis and Structural Analysis of a Gold Cluster $\text{Au}_{18}\text{S}_2(\text{SR})_{12}$ ( $\text{R} = 2,4,6\text{-C}_6\text{H}_2\text{Pr}_3\text{CH}_2$ ) Protected by Bulky Thiolate Ligands

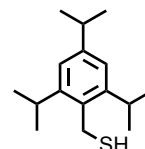
(<sup>1</sup>Graduate School of Science, The University of Tokyo, <sup>2</sup>ESICB, Kyoto University)

○Taro Shigeta,<sup>1</sup> Shinjiro Takano,<sup>1</sup> Tatsuya Tsukuda<sup>1,2</sup>

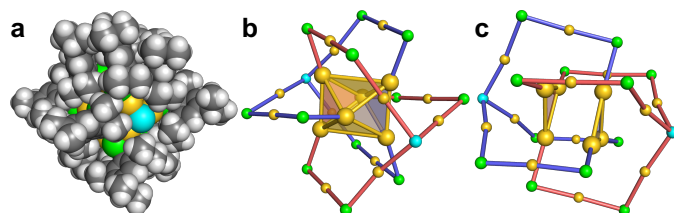
**Keywords:** Ligand-Protected Gold Cluster; Superatom; Interlocked Cage Structure; Single-Crystal X-Ray Diffraction; Density Functional Theory Calculation

The structure of the organic ligands and their binding interactions with the gold clusters have a significant impact on the geometric structure and physicochemical properties of the gold clusters.<sup>1)</sup> For example, associative interaction between the adjacent ligands enhances the photoluminescence quantum yields by rigidification of the Au cores,<sup>2)</sup> whereas repulsive interaction between the adjacent ligands results in direct coordination of thiolates to the Au core<sup>3,4)</sup> and formation of  $\text{S}^{2-}$  ligands on the Au core.<sup>5)</sup> In this study, a new gold cluster,  $\text{Au}_{18}\text{S}_2(\text{STipb})_{12}$ , was obtained using a bulky thiol, interaction between the adjacent ligands 2,4,6-triisopropylbenzyl mercaptan (TipbSH, Fig. 1).

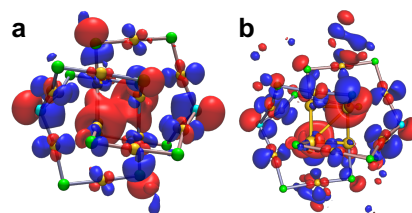
$\text{Au}_{18}\text{S}_2(\text{STipb})_{12}$  was isolated via the following steps: (i) reduction of  $\text{AuClS}(\text{CH}_3)_2$  with  $\text{NaBH}_4$  in the presence of TipbSH; (ii) incubation at  $80^\circ\text{C}$  in the presence of an excess amount of TipbSH; (iii) purification by gel permeation chromatography; (iv) fractional precipitation. Single-crystal X-ray diffraction analysis revealed that  $\text{Au}_{18}\text{S}_2(\text{STipb})_{12}$  has a deformed octahedral  $\text{Au}_6$  core clutched by two tridentate  $\text{S}[\text{Au}_2(\text{STipb})_2]_3$  units in an interlocked manner (Fig. 2). The electronic structures of  $\text{Au}_{18}\text{S}_2(\text{STipb})_{12}$  and a simplified model  $\text{Au}_{18}\text{S}_2(\text{SCH}_3)_{12}$  were investigated by density functional theory calculations. Comparison of the HOMO-1 in Fig. 3 indicates that the electron density in the region between the two  $\text{Au}_3$  units in  $\text{Au}_{18}\text{S}_2(\text{STipb})_{12}$  is much smaller than that in  $\text{Au}_{18}\text{S}_2(\text{SCH}_3)_{12}$ . Therefore, we propose that the  $\text{Au}_6$  core is better viewed as a face-to-face dimer of  $\text{Au}_3$  superatoms rather than a  $\text{Au}_6$  superatom and that the interaction between the two  $\text{Au}_3$  superatoms is weakened by the steric repulsion owing to the bulky TipbS ligands.



**Fig. 1.** Structure of TipbSH



**Fig. 2.** X-ray structure of  $\text{Au}_{18}\text{S}_2(\text{STipb})_{12}$ . (yellow: Au, green: S of STipb, cyan: S, gray: C, white: H)



**Fig. 3.** Shape of Kohn-Sham orbital of HOMO-1 of (a)  $\text{Au}_{18}\text{S}_2(\text{SCH}_3)_{12}$  and (b)  $\text{Au}_{18}\text{S}_2(\text{STipb})_{12}$ .

1) S. Takano *et al.*, *J. Am. Chem. Soc.* **2021**, *143*, 1683. 2) K. Pyo *et al.*, *J. Am. Chem. Soc.* **2015**, *137*, 8244. 3) J. Nishigaki *et al.*, *J. Am. Chem. Soc.* **2012**, *134*, 14295. 4) J. Nishigaki *et al.*, *Chem. Commun.* **2014**, *50*, 839. 5) R. Jin *et al.*, *Chem. Rev.* **2016**, *116*, 10346.