

VERTEX-SHARING POLYICOSAHEDRAL GOLD CLUSTERS: A FIRST STEP TOWARD CLUSTER-ASSEMBLED MATERIALS

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Extensive studies of nanometer-sized metal clusters have shown their novel physicochemical properties that are significantly different from those of the corresponding bulk metals. These metal nanoclusters are also expected to have potential for their application to development of new materials functioning as molecular-sized quantum devices. In contrast to the rapidly growing understanding of fundamental properties of each individual metal nanocluster, relatively little is known about whether these clusters are assembled retaining their individual properties while producing new collective features due to the aggregation. The most direct approach to this issue might be to specify a unit cluster that serves as a *building block* of cluster-assembled compounds and then reveal how the assembled compounds are constructed from the units. Very recently, Tsukuda and coworkers made significant progress toward realizing the cluster-assembled compounds in a bottom-up approach [1]. They synthesized a gold cluster compound $[\text{Au}_{25}(\text{PPh}_3)_{10}(\text{SC}_2\text{H}_5)_5\text{Cl}_2]^{2+}$ (**1**) and characterized its geometric structure through single X-ray crystal analysis. The cluster has a unique structure in the sense that the Au_{25} core is constructed by bridging two icosahedral Au_{13} clusters with thiolates sharing a vertex gold atom and is terminated by two chlorine atoms.

In this study, we theoretically characterize geometric and electronic structures of a dimer cluster $[\text{Au}_{25}(\text{PH}_3)_{10}(\text{SCH}_3)_5\text{Cl}_2]^{2+}$ (**2**) mimicking the cluster **1** by carrying out density-functional-theory calculations, and reveal the mechanism of the dimerization [2]. We further discuss polymerization, as an example, the trimerized gold cluster $[\text{Au}_{37}(\text{PH}_3)_{10}(\text{SCH}_3)_{10}\text{Cl}_2]^+$ (**3**). All the calculations were carried out by utilizing the TURBOMOLE package of ab initio quantum chemistry programs [3]

Fig. 1(a) shows side and top views of the optimized structure of **2** with C_s molecular symmetry. For convenience, we indicate the four layers (I-IV denoted in Fig. 1) of the gold pentagonal rings. It is clearly seen that the two icosahedral Au_{13} clusters are bridged (between II and III layers) by the methanethiolates sharing a vertex gold atom and terminated by the chlorine atoms. In other words, this gold cluster is considered to be a dimer with the biicosahedral structure. This structure reasonably agrees with the experimental X-ray data of **1**. A natural question then arises whether polymerization more than the dimerization is achieved. To answer this question, we have further carried out geometry optimization of a trimer structure within C_i molecular symmetry in the same way as in the dimer one. We succeeded in obtaining the trimer structure of **3** as shown in Fig. 1(b). At the present level of calculation, the 1+ cationic state was preferred. As is similar to the structure of the dimer, the three icosahedral Au_{13} clusters are bridged by the methanethiolates sharing vertex gold atoms at two different sites and terminated by the chlorine atoms. Furthermore, comparison between the absorption spectra of the two structures has revealed that new electronic structures due to the polymerization come into being one after another, whereas the electronic properties of the individual Au_{13} units almost remain unchanged.

It is expected that the scheme of the present polymerization is utilized to achieve cluster-assembled compounds starting from a building block of the icosahedral Au_{13} cluster incorporating with thiolate molecules.

References:

- [1] Y. Shichibu, Y. Negishi, T. Watanabe, N. K. Chaki, H. Kawaguchi, T. Tsukuda, *J. Phys. Chem. C*, **111** (2007) 7845.
[2] K. Nobusada, T. Iwasa, submitted to *J. Phys. Chem. C*.
[3] TURBOMOLE Version 5.7, Quantum Chemistry Group, University of Karlsruhe, Germany.

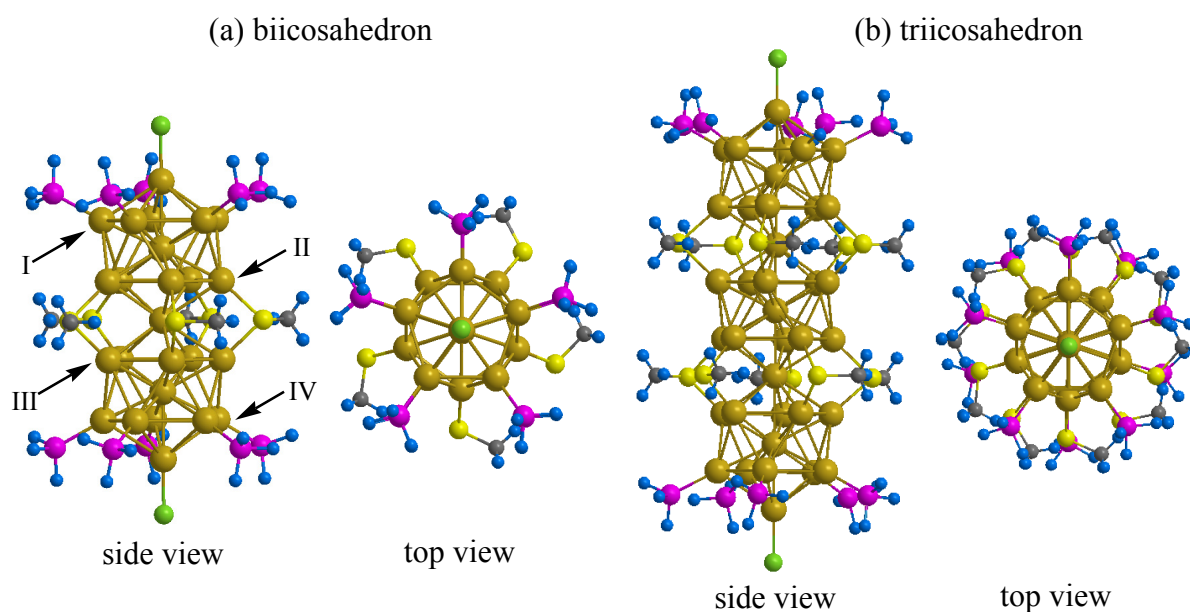
Figures:

Fig.1 Optimized structures of (a) bi- and (b) triicosahedral gold clusters