

## 論文の内容の要旨

### 論文題目 Development of Gold Superatoms and Superatomic Molecules with Novel Structures (特異な幾何・電子構造を持つ金超原子及び金超原子分子の開発)

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#### 1. Introduction

Ultra-small metal particles, which are called as metal clusters, exhibit unique geometric and electronic structures that are significantly different from those of bulk metal. Metal clusters tend to take icosahedral-based structure rather than the bulk metal structure in order to minimize the surface energy. The electronic structures of metal clusters are quantized due to quantum size effect. The magic stability of clusters of simple metals such as Na and Au has been explained by Jellium model [1]. Superatom concept was introduced to describe the electronic shell structure. According to the superatomic model, the clusters gained high stability when the superatomic orbitals 1S, 1P, 1D, 2S, 1F, 2P, 1G... are closed by accommodating the following numbers of valence electrons: 2, 8, 18, 20, 34, 40, 58...

Ligand-protected gold clusters are ideal systems to deepen our understanding on fundamental properties of metal clusters and to develop new functional materials based on their structural features [2]. A variety of icosahedral-based Au clusters with 8 valence electrons such as  $[\text{Au}_{11}(\text{PR}_3)_7\text{X}_3]$ ,  $[\text{Au}_{11}(\text{PR}_3)_8\text{X}_2]^+$ ,  $[\text{Au}_{11}(\text{PR}_3)_{10}]^{3+}$ ,  $[\text{Au}_{13}(\text{dppe})_5\text{Cl}_2]^{3+}$ , and  $[\text{Au}_{13}(\text{Au}_2(\text{SR})_3)_6]^-$  ( $\text{PR}_3$  = phosphine; X = halogen; dppe = 1,2-bis(diphenylphosphino)ethane; RS = thiolate) have been reported. In addition, new class of assembled materials made of superatoms (superatomic molecules), such as dimer, trimer, and pentamer of  $\text{Au}_{13}$  building units, have been synthesized. These superatomic molecules exhibit unique physicochemical properties depending on the number and bonding scheme of the superatomic units. However, the synthesis of superatoms has been mainly limited to systems with closed electronic shell and the synthesis of superatomic molecules has been based on try-and-error approach. In order to expand the potential of the ligand-protected Au clusters as the building unit for nanoscale functional materials, it is strongly desired to establish an aimed synthesis of superatoms and superatomic molecules with new electronic and geometric structures. Aim of my study is to develop synthetic methods of gold superatoms and superatomic molecules with novel structures and to reveal their fundamental properties.

## 2. Phosphine/thiolate-protected Au<sub>11</sub> superatom with 10 electrons

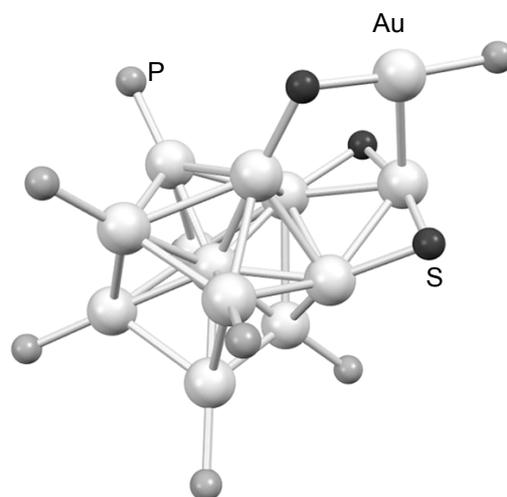
High stability of the ligand-protected Au clusters originates from the complete protection of the core surface by the ligands and closure of the electronic structures. Free counter ions, originated from the synthetic precursors, play an important role to compensate their excess charge on the clusters. These previous results hint the possibility that Au superatoms with unclosed electronic structures can be synthesized in the absence of counter ions. To test this hypothesis, neutral gold(I) complex Au(PPh<sub>3</sub>)(*p*-MBA) (*p*-MBA = *p*-mercaptobenzoic acid) was reduced by NaBH<sub>4</sub> in EtOH at 0 °C. After stirring the reaction mixture for 2 h and removing the solvent and by-product, the cluster was purified by crystallization. After 1 month, dark-red platelet crystals were obtained.

Single-crystal X-ray crystallography revealed that the product is formulated as Au<sub>13</sub>(PPh<sub>3</sub>)<sub>8</sub>(*p*-MBA)<sub>3</sub> (**1**). Figure 1 shows X-ray crystal structure of **1**. Thirteen gold atoms unexpectedly do not form a cuboctahedral nor icosahedral Au<sub>13</sub> core, but are divided into two parts of Au<sub>11</sub> and Au<sub>2</sub>. The formal number of valence electrons is calculated to be 10. Thus, one can assume that **1** can be viewed as heterodimer made of Au<sub>2</sub> and Au<sub>11</sub><sup>3+</sup> units with closed electronic configurations of (1S)<sup>2</sup> and (1S)<sup>2</sup>(1P)<sup>6</sup>, respectively. However, a preliminary density functional theory calculation showed that the frontier orbitals appear to be 1D orbitals that are distributed exclusively to the Au<sub>11</sub> moiety. This suggests that **1** has a Au<sub>11</sub><sup>+</sup> core with 10 valence electrons. The formation of open electronic shell is supported by the fact that the optical absorption spectrum of **1** (black curve in Figure 2) has a significantly different profile from that of Au<sub>11</sub>(PPh<sub>3</sub>)<sub>7</sub>(*p*-MBA)<sub>3</sub> having 8 electrons (gray curve in Figure 2).

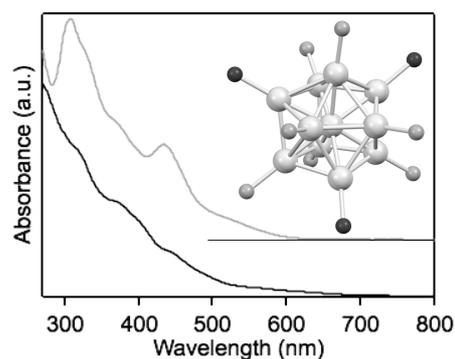
Two excess Au atoms in **1** bundle three thiolates. The construction of this unique motif is associated with the spatial distribution of the three thiolates. Three thiolates are bonded separately on an equatorial region of the Au<sub>11</sub> core in Au<sub>11</sub>(PPh<sub>3</sub>)<sub>7</sub>(*p*-MBA)<sub>3</sub>, whereas they are concentrated on one facet of the Au<sub>11</sub> core in **1**. Because of these additional Au atoms, the three thiolates can withdraw formally only one electron from the Au<sub>11</sub> core. Electronic structure, photophysical and electrochemical properties of the new superatom **1** are under investigation.

## 3. Toward controlled-assembly of protected Au superatom

Fundamental properties of protected Au superatoms have been studied extensively in the solution phase. These studies have revealed that individual protected Au superatoms show unique optical, electrochemical, and catalytic properties. In contrast, the tuning of collective properties is the main target in modern materials chemistry. In this work, I aimed to develop suitable building units for ordered solid structure to investigate



**Figure 1.** Single-crystal X-ray structure of **1**. The organic parts are omitted for clarity. White, gray, and black balls represent gold, phosphorus, and sulfur atoms, respectively.



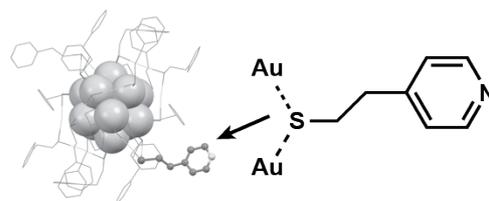
**Figure 2.** UV-vis absorption spectra of **1** (black) and Au<sub>11</sub>(PPh<sub>3</sub>)<sub>7</sub>(*p*-MBA)<sub>3</sub> (gray). Inset shows single-crystal X-ray structure of Au<sub>11</sub>(PPh<sub>3</sub>)<sub>7</sub>(*p*-MBA)<sub>3</sub> cluster with the same drawing scheme as Figure 1.

the collective properties of the solid of protected superatom.

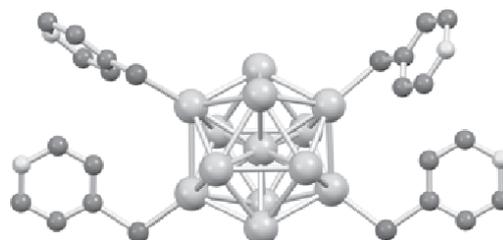
First, I synthesized  $\text{Au}_{25}(\text{SR})_{18}$  cluster covered by a pyridineethane thiolate as its monolayer (Figure 3). The cluster formed precipitates in a MeOH solution containing various metal salts such as  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pd}^{2+}$ , and  $\text{Ag}^{+}$  ions. Optical absorption spectroscopy revealed that the  $\text{Au}_{25}$  cluster was partially decomposed in the case of  $\text{Cu}^{2+}$ ,  $\text{Pd}^{2+}$ , and  $\text{Ag}^{+}$  ions. The further investigation about the precipitates formed with  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  was conducted by X-ray absorption and powder X-ray diffraction techniques. Au-L<sub>3</sub> edge extended X-ray absorption fine structure spectra of the precipitates indicated that the  $\text{Au}_{25}$  cluster remained as intact form. However, Ni and Zn K-edge X-ray absorption near edge structure spectra suggested that the coordination environment around those metal ions is randomly occupied by pyridyl nitrogens and water molecules. This observation was confirmed by powder XRD patterns of the precipitates. Based on these result, I found that the more sophisticated building unit is strongly necessary to obtain an well ordered structure. In order to obtain such ideal precursor, I synthesized a novel diphosphine protected Au superatom using the method I described in the section 2. Figure 4 shows the single crystal X-ray structure of  $\text{Au}_{13}(\text{dppe})_4(\text{SPy})_4$  ( $\text{SPy}$  = 4-mercaptopyridine) which I obtained. The surface pyridine sites of the cluster was X-shaped geometry. This high symmetry is useful to build up a two-dimensional ordered structure. The assembly of the cluster is a future subject.

#### 4. Thiolate-protected pentamer of $\text{Au}_{13}$ superatoms

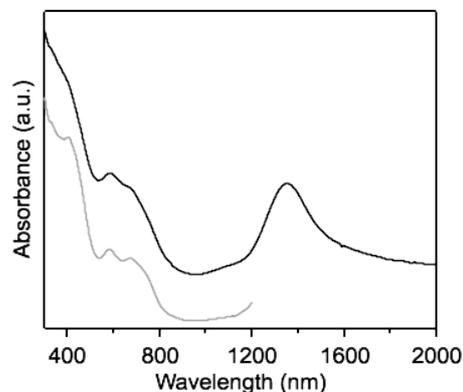
The synthesis of superatomic molecules is conventionally based on try-and-error approach and a synthesis of aimed structures has not yet been established. Template method is a promising approach to synthesize gold clusters with anisotropic morphology. In this work, I attempted to synthesize a one-dimensional oligomer of Au superatoms by slow reduction of a  $[-\text{Au}(\text{I})-\text{SR}-]_n$  polymer which has a chain structure. First, the  $\text{Au}(\text{I})$ -(4-MEBA) polymer was produced by mixing ethanolic solution of 4-mercaptoethylbenzoic acid (4-MEBA) and aqueous solution of  $\text{HAuCl}_4$ . Then the  $\text{Au}(\text{I})$ -(4-MEBA) polymer was reduced by adding aqueous solution of  $\text{NaBH}_4$  at 20 °C. This reduction was conducted after adjusting pH value to >12 by the addition of  $\text{NaOH}$  in order to reduce the reduction rate. The optical spectra during the reduction indicate that the reduction proceeded much slower as compared to the rapid reduction in the conventional synthesis (not shown). The products obtained after 96 h were purified by size exclusion chromatography using Superdex-20pg column. The first elution band colored in green was collected for further characterization. Chemical formula of the clusters contained in the fraction was determined to be  $\text{Au}_{76}(\text{SR})_{44}$  (**2**) by the combination of mass spectrometry and thermogravimetry. UV-vis-NIR absorption spectrum of **2** in water shows several humps and peaks in the UV-vis region (gray curve in Figure 5). More surprisingly, a distinct NIR absorption band was observed in the spectrum of a film form (black curve in



**Figure 3.** A schematic structure of pyridineethane thiolate modified  $\text{Au}_{25}(\text{SR})_{18}$  cluster.



**Figure 4.** X-ray structure of  $\text{Au}_{13}(\text{dppe})_4(\text{SPy})_4$  cluster. Hydrogen atoms and dppe ligands are omitted for clarity.

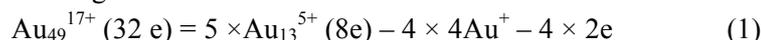


**Figure 5.** UV-vis-NIR absorption spectra of **2**. Gray and black lines correspond to solution form and film form of **2**, respectively.

Figure 5) and the molar absorption coefficient of the cluster is  $3 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$  at 1340 nm.

Geometric structure of **2** was examined by powder X-ray diffraction (XRD) technique since a single crystal of **2** has not been obtained so far. Powder XRD pattern of **2** is shown in a black curve in Figure 6. The XRD pattern is similar with that of the bulk having fcc structure (bottom gray peaks in Figure 6). The most notable feature of Figure 6 is that the diffraction peak at  $s \sim 4 \text{ nm}^{-1}$  for (200) reflection is much sharper than the other peaks, which are broadened as a result of the small crystalline size. This indicates that the Au core has a one-dimensional structure that is elongated along the {100} direction. Highly anisotropic structure of **2** was also confirmed by a pair-distribution function analysis of high-energy XRD data. In the analysis of powder XRD data, I limit myself to mainly considering model structures

that have an elongated fcc structure and axial symmetry along the {100} direction. From the comparison of XRD patterns simulated for several model structures using the Debye formula revealed that the most plausible structure is polycuboctahedral  $\text{Au}_{49}$  model (inset in Figure 6) whose distance of between (100) planes is longer by 5 % than that in the bulk Au. The  $\text{Au}_{49}$  core can be constructed by connecting five cuboctahedral  $\text{Au}_{13}$  while sharing two electrons and four Au atoms as described as follows.



The formation of a one-dimensional structure is ascribed to the slow reduction of the Au precursor ions in the highly basic condition ( $\text{pH} > 12$ ). A rapid reduction without adjusting pH value to  $> 12$  gave spherical clusters that showed an exponential-like optical absorption spectrum and a brownish color.

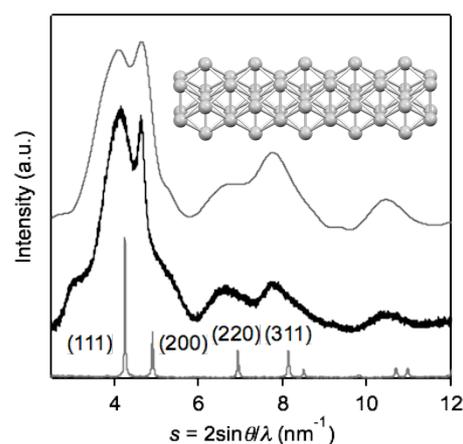
The strong absorption in NIR region can be explained within either the framework of an electronic transition with large electronic-transition moment or a longitudinal mode of localized surface plasmon resonance. Further work is necessary to unravel the nature of the NIR band of **2**.

## 5. Conclusion

In this study, ligand-protected gold clusters with novel structures were synthesized using original approaches. The reduction of gold(I) precursors in the absence of counter ions produced for the first time the  $\text{Au}_{11}$  superatom with open electronic structure which will exhibit unique redox and magnetic properties. Pyridine modified  $\text{Au}_{25}(\text{SR})_{18}$  superatom with metal ions formed a coordination polymer with amorphous structure. Based on this result, I developed a novel superatom with controlled surface functionalization. This superatom will give a highly ordered assembly of superatoms. The slow reduction of gold(I)-thiolate polymers yielded one-dimensional Au superatomic molecules which exhibited a strong NIR absorption band. Optical spectroscopy during the synthesis suggested that the number of constituent superatoms could be tuned by the reaction period. A series of Au superatomic molecules with different lengths will provide us an opportunity to study the optical transition behavior from a single electron excitation to collective excitation of electrons. This study not only deepened our understanding on the structure-property correlation of superatoms, but also will open up a new possibility towards aimed synthesis of superatomic-based materials.

## 5. References

[1] de Heer, W. A. *Rev. Mod. Phys.* **1993**, *65*, 611. [2] *Protected Metal Clusters: From Fundamentals to Applications* (edited by T. Tsukuda and H. Häkkinen), Elsevier, Amsterdam, **2015**.



**Figure 6.** Powder XRD patterns of **2** (middle), bulk gold (bottom), and simulated pattern of  $\text{Au}_{49}$  core model (top). Inset shows the structure of  $\text{Au}_{49}$  core model.