学位論文

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)

平成27年12月博士 (理学) 申請

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Abstract

Metal clusters composed of simple metals such as Na, Al, Cu, Ag, and Au have unique geometric and electronic structures that are significantly different from those of bulk metals. Superatom concept has succeeded to describe their electronic shell structures and reactivity. Since bare superatoms are unstable towards aggregation, surface protection of superatoms gained much attention to stabilize those superatoms under the ambient condition. Ligand protected Au superatom is the most stable protected superatom and recent studies have unraveled their size evolutional properties with atomic precision. However, we have to overcome certain problems to broaden the chemistry of protected superatoms.

First, the library of protected Au superatoms is almost limited to the rare-gas like property, thus it must be expanded to metal element like superatoms. Second, there is no principle to construct a superatom based hierarchical structure, thus a general guide must be established. Finally, the synthesis of quasi molecule composed of Au superatom is only based on the try-and-error approach, thus an aimed synthesis method must be developed to establish the bond theory of the Au superatomic molecules. In this thesis, I described the development of novel synthetic method of protected Au superatoms to overcome those problems.

In chapter 1, I described the general introduction of metal clusters and protected superatoms. I also mentioned about the aim of this thesis.

In chapter 2, I investigated an aimed synthesis method to obtain protected Au superatom with unclosed electronic shell structure. The obtained cluster had 10 valence electrons with a novel surface protecting motif. Theoretical calculation suggested that the cluster has triplet electronic structure.

In chapter 3, I examined one method to construct the ordered superatom based structure. The attempts did not afford positive result, however certain important findings were obtained. Based on the result, I synthesized a novel superatom, that can overcome the problems using the method developed in chapter 2.

In chapter 4, I described the development of an aimed synthesis of one-dimensional superatomic molecules. The one-dimensional superatomic molecule exhibited an intense near-infrared absorption band. I investigated the origin of the band from the view point of its anisotropic geometric and electronic structure.

In chapter 5, I presented the conclusion of this thesis and future prospects as concluding remarks.

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Chapter 1.

General introduction

1.1. Introduction

1.1.1. Size specific properties of metal clusters

Metal nanoparticles whose diameters are larger than few nm have gained much attention in a variety of fields of research and application because their properties deviate from those of corresponding bulk metal due to small size and evolve with their diameters in a scalable manner (Figure 1).

Figure 1. A schematic of size evolutional property of cluster and nanoparticle.

In contrast, clusters composed of less than a few hundreds of metal atoms are newly emerging materials in the field of chemistry and physics. They are attractive targets in the field of nanoscience because of potential application in a variety of fields such as catalysis, optics, electronics, and bio applications.[1, 2] For example, development of novel catalysis based on clusters will contribute to overcome the current concerns on environment and energy for sustainable society. The most notable feature of the clusters is that they exhibit specific physicochemical properties that are absent in the corresponding bulk metal. Previous studies of "bare" metal clusters with a control size have provided us insight into the fundamental question how the metallic properties evolve with the number of atoms. Metal clusters smaller than a certain critical size show

Figure 2. Metal-insulator transition of mercury clusters. (a) A plot of ionization potential of neutral mercury clusters as a function of size.[3] (b) Photoelectron spectra of a series of anionic mercury clusters.[4] (c) A schematic of photoemission from negatively charged small clusters. Reprinted from ref 3 with permission for (a). 1987 American Physical Society. Reprinted from ref 4 with permission for (b). 1998 American Physical Society.

not metallic, but insulator-like electronic structures. In case of mercury clusters, for example, size-dependent evolution of ionization potentials and HOMO-LUMO gaps indicates metal-to-insulator transition occurs at the size range of 400 ± 30 (Figure 2).[3-5] Thermodynamical propertie of clusters are significantly different from the bulk counterpart. Melting points of clusters are much lower than those of bulk metal as experimentally demonstrated for alkaline metal clusters.[6]

Another attractive feature of metal clusters is that their properties are altered dramatically by addition or removal of a single constituent, but in a nonscalable manner (Figure 1). In other words, every atom counts for the properties of clusters.[7] Since the discovery of catalysis of gold (Au) nanoparticles for low-temperature CO oxidation by

Haruta,[8] the catalysis of Au has been extensively studie.[9] Recently, Tsukuda and coworkers have synthesized size-controlled Au clusters on hydroxyapatite (HAP) and unraveled a volcano type size dependency in the cyclohexane oxidation catalysis (Figure 3a).[10] They also succeeded in demonstrating the effect of single palladium (Pd) atom doping into Au clusters (Figure 3b).[11] The Pd atom doping dramatically improved the catalytic activity. The other atomically precise catalysis was investigated with platinum (Pt) clusters towards the oxygen reduction reaction.[12, 13] These results indicate that catalysis of metal clusters can be optimized or improved by controlling the size and compositions precisely.

Figure 3. (a) A plot of turnover frequency of Au/HAP catalyst over the cyclohexane oxidation as a function of size.[10] (HAP = hydroxyapatite) (b) A result of one atom doping effect of Au_{25}/CNT catalyst over the benzyl alcohol oxidation.[11] (CNT = carbon nanotube) Reprinted from ref 10 with permission for (a). 2011 American Chemical Society. Reprinted from ref 11 with permission for (b). 2012 American Chemical Society.

1.1.2. Magic numbers of metal clusters

When one considers the synthesis of metal clusters, information on size-dependent stability or especially stable clusters with magic numbers is indispensable. There are two origins for magic stability of metallic clusters; electronic and geometric shell

closure.

Magic numbers of simple metals such as alkaline metals and coinage metals have been explained in terms of electronic shell closure. Figure 4a shows an abundance spectrum of sodium (Na) clusters.[14, 15] Apparently, clusters with 8, 20, 40, and 58 atoms were abundant than the neighbors. The similar magic numbers have been found in the coinage metal clusters (Cu, Ag, Au) since those metals have similar electronic configuration with the alkaline metals having s valence electrons. Figure 5 shows abundance spectra of cationic Cu, Ag, and Au clusters.[16] Copper and silver showed same electronic magic numbers of 8, 20, 40, and 58, whereas gold showed slightly different numbers from 8, 20, 34, and 58.

Figure 4. (a) An abundance spectrum of sodium clusters. (b) Calculated energy difference of electronic states using two models.[14, 15] Reprinted from ref 15 with permission for (a) and (b). 1993 American Physical Society.

Figure 5. Abundance spectra of cation clusters of Cu (left top), Ag (right top), and Au (bottom).[16] Reprinted from ref 16 with permission. 1985 Elsevier B. V.

These metal atoms have a similar electron configuration of [RG](ns)^1 (RG = rare gas configuration). Because of the spherical nature of s orbital, the valence electrons behave like free electrons.[17] Thus, those metals are thought to be good examples to explain the electronic properties of metals in general. We can simplify the electronic contribution of those clusters in the framework of the jellium model, in which valence electrons feel a constant positive background.

The high abundance of these clusters was successfully explained using the energy diagram obtained from the jellium model (Figure 4b). In the framework of the jellium model, we can assume three types of potential shapes such as harmonic, intermediate (Woods-Saxon type), and square wells. The calculated electronic shells of those potentials are shown in Figure 6.[15] The electronic magic number can be explained by using the energy diagram as follows. In the case of the intermediate potential, the

energy gaps between 8 and 18, 20 and 34, and 40 and 58 are large, whereas those between 18 and 20, and 34 and 40 are relatively small. Hence, the shell closure at 8, 20, 40, and 58 are energetically favorable. These magic numbers agree with those observed for clusters of the Na, Cu, and Ag. In contrast, in the case of square well potential, the energy splitting between 34 and 40 becomes large. The successful explanation of those magic numbers by electronic shell model means that the stability of small metal clusters (n < ~100) can be explained by a major electronic contribution of valence electrons.

Figure 6. Shapes of the jellium potentials and their electronic shell structures. Harmonic, intermediate, and square well potentials (From left to right).[15] Reprinted from ref 15 with permission. 1993 American Physical Society.

The other origin of magic stability is a geometric shell closure. Typical examples are perfect cuboctahedron and icosahedrons composed of 13, 55, 147, 309,… atoms (Figure 7). These structures are highly symmetrical. For example, the abundance of large Na clusters was measured by Bjøenholm, Martin, and coworkers.[18-20] The oscillatory abundance pattern of Na_n has been explained in such a manner that electronic shell closure is important for n < ~ 2000 and geometric shell closure such as

the formation of perfect Mackay icosahedron becomes important for n > ~2000. In some specific cases, both electronic and geometric shell closure contribute to the extraordinarily high stability. For example, Al_{13}^- cluster has closed shell closure with 40 valence electrons. *Ab initio* calculation suggested the geometric structure of the cluster is an icosahedron. The remarkable stability of Al_{13}^- against oxygen[21, 22] is explained by those electronic and geometric shell closures.[23-25]

Figure 7. Examples of geometric shell closure of (a) cuboctahedron and (b) icosahedron. Each structure corresponds to 13, 55, 147, 309-mers (from left to right).

1.1.3. Superatomic concept

The electronic shells of clusters are characterized by their angular momentum quantum numbers since the clusters have a central force potential. Also, the clusters tend to form a compact geometry such as a spherical structure in order to minimize their surface energy. These electronic shell structure and spherical geometric structure of the clusters make us to develop a superatomic concept as an analog of the conventional atom. A good example of the superatom is Al_{13} cluster. Al_{13} anion has 40 valence

electrons and electronic configuration of the cluster is described as $(1S)^2(1P)^6(1D)^{10}(2S)^2(1F)^{14}(2P)^6$. Here, capital letters such as S, P, D, F,…, denote the number of nodes of the superatomic orbitals. The HOMO is P shell, thus the neutral cluster, Al_{13}, can be viewed as a halogen-like superatom in terms of its electronic configuration. Pseudohalogen nature of Al_{13} cluster has been demonstrated by Castleman, Khanna, and coworkers.[26] They used HI molecule as a reactant and they observed $Al_{13}I^-$ anion. From the theoretical calculation, the anionic charge localizes on Al_{13} unit suggesting that electron affinity of Al_{13} is higher than that of iodine. They also succeeded in observing polyhlide-like $Al_{13}I_x^-$ clusters and alkaline earth metal salt such as $Al_{14}I_y^-$ clusters by the reaction with I_2 molecule.[27] Bare Au clusters are also viewed from the superatomic concept.[28] For example, Figure 8 shows a theoretical calculation of bare Au superatoms.[29] Certain 6sp states form localized shells and diffuse 6sp+5d hybridized band. The localized shells show molecular orbitals with superatomic nature (Figure 8).

Figure 8. A theoretical calculation of gold superatoms.[29] Reprinted from ref 29 with permission. 2007 Wiley-VCH.

1.1.4. Protected superatoms

Since the free metal clusters generated in vacuum have highly active surfaces, we have to overcome various difficulties for their usage under ambient conditions. The major challenge is to avoid their aggregation, since their characteristic features will be lost by aggregation. The surface passivation by ligands or polymer is a promising way to stabilize the metal clusters, whereas immobilization of clusters on a solid support is an ideal approach for catalytic application (Figure 9).[30]

Figure 9. The stabilization schemes of metal clusters.[30] Reprinted from ref 30 with permission. 2012 Royal Society of Chemistry.

The ligand-protected Au clusters have been studied extensively because the current synthetic efforts enable us to synthesize the clusters as a stable compounds with atomic precision.[2] Typical protecting ligands used include thiolates, phosphines, and terminal alkynes. Especially, there are many examples of the Au clusters protected by the former two ligands because of their high affinity to gold.[2, 31] Figure 10 shows the examples of X-ray structures of ligand protected gold clusters having icosahedral cores.[32-34] At first glance, we find that the surfaces of icosahedral Au_{13} core are fully protected by ligands. The formal number of valence electrons N^* of these clusters are calculated to be 8 based on the following formula,[30, 35]

Figure 10. X-ray structures of (a) $[Au_{13}(dppe)_5Cl_2]^{3+}$ and (b) $[Au_{25}(SC_2Ph)_{18}]^-$ (dppe = 1,2-Bis(diphenylphosphino)ethane; SC_2Ph = 2-phenylethane thiolate).[32, 34] Yellow, blue, pink, and green balls represent gold, phosphorus, chlorine, and sulfur atoms, respectively. The core gold is depicted by CPK model and the organic parts are depicted by gray sticks.

Figure 11. A conceptual view of protected superatoms. Au_{13}^{5+} and Au_{79}^{21+} clusters correspond to the cores of $[Au_{25}(SR)_{18}]^-$ and $Au_{102}(SR)_{44}$.[32, 36]

$$N^* = n \times V_A - m - z \qquad (1)$$

where n, V_A, m, and z correspond to the number of atoms, the number of valence electrons, the total charge removed by ligands, and the net charge of the cluster, respectively. This result suggests that the core of the ligand-protected Au clusters shows

same shell closing number to the bare Au clusters. Namely, the ligand-protected magic Au clusters can be viewed as protected Au superatoms with closed electronic shells (Figure 11).[32, 36]

Figure 12. (a) Frontier orbitals of $[Au_{25}(SR)_{18}]^{-1}$ and (b) LUMO state of $Au_{102}(p\text{-MBA})_{44}$ clusters.[35, 37] (*p*-MBA = 4-thiobenzoic acid) Reprinted from ref 37 with permission for (a). 2008 American Chemical Society. Reprinted from ref 35 with permission for (b). 2008 The National Academy of Science.

The electronic structure of those superatoms has been studied by *ab initio* calculations (Figure 12).[35, 37] The HOMO of $[Au_{25}(SR)_{18}]^{-}$ cluster is predicted as 1P state by a consideration of simple superatomic shell structure (Figure 11). The theoretical calculation clearly indicated that HOMO of the Au_{25} cluster has 1P character and the LUMO and LUMO+1 have 1D character localized on the core (Figure 11a).[37] A calculation for $Au_{102}(SR)_{44}$ cluster also clearly indicated that LUMO had a 1H character as predicted in the simple consideration (Figures 11 and 12b).[35] The superaomic natures are also found in thiolate-protected Ag cluster, $[Ag_{44}(SR)_{30}]^{4-}$, and heteroatom doped $[MAu_{24}(SR)_{18}]^{0/2-}$ (M = Pd, Pt).[38-40]

1.1.5. Current stage and challenges

There are many studies of the protected Au superatoms in the last two decades. However, major challenges in the field are still remained as listed below.

•Aimed and facile synthesis of desired superatom.

•Unraveling novel properties of protected superatom dependent on the size and structure.

•Developing superatom based materials by using superatoms as atom equivalent.

The first challenge has been partially achieved. For example, many thiolate-protected Au clusters have been reported to date. Figure 13 shows the chemical

Figure 13. Plots of chemical compositions of thiolate-protected Au clusters reported by the ends of 2014. Red circles, blue squares, aqua diamonds, purple triangles, and open circles represent the type of ligands such as PET = 2-phenylethane thiolate, alkanethiolate, other thiolates, bulky thiolate, and totals, respectively. Gray solid line is guide for the eye. Reprinted from ref 2 with permission. 2015 Elsevier Ltd.

compositions of such clusters identified by mass spectrometry and the range is from Au_{10} to $Au_{\sim 920}$ by the end of 2014.[2] This rich library unravels the magic stability of certain superatoms.[2, 41-43] For example, $Au_{25}(SR)_{18}$ cluster exhibits a markedly high stability in chemically harsh condition and is converted from an unstable superatom by chemical etching by thiol.[44] This chemical etching procedure is commonly used for the synthesis of thiolate-protected superatoms.[2] Based on these efforts, the magic clusters such as $[Au_{25}(SR)_{18}]^{-}$ and $[Au_{13}(dppe)_5Cl_2]^{3+}$ can be synthesized in a large scale. However, it is still difficult to control the atomicity, the number of valence electrons, and the structure of superatom, on demand.

The second challenge is also partially achieved in the early and currant stages of the study. For example, Whetten, Murray and coworkers found the size evolutional optical and electrochemical properties of thiolate-protected Au clusters almost 20 years ago.[45-47] However, exact chemical compositions of the clusters were not identified in those days. Recently, the size evolutional properties are studied using well-identified clusters.[48] The result indicates that bulk like electronic and geometric structures are emerged on going from $Au_{144}(SR)_{60}$ to $Au_{187}(SR)_{68}$.[48] Regardless of these reports, several properties of superatoms still remain unknown. For example, the relationship between the properties and the shape of superatom is not clear. Size evolutional behaviors such as the birth of surface plasmon resonance in the superatom with anisotropic shape are also unclear.

The third challenge is undeveloped field in the chemistry of superatoms. Some X-ray crystallographic and theoretical studies revealed that the protected superatoms in the solid state have some interactions between the components.[49, 50] However, crystal engineering such as the formation of the ordered polymer of the protected superatom

with desired structure has not been reported so far.

1.2. Aim of the thesis

As I described in the previous section, the protected Au superatoms are the potential building units of cluster-based materials due to their high stability and controllability of their structural parameters. However, a variation in electronic structure is limited at present. Since electronic shell closure is a major origin for the stability of small clusters, only superatoms with "rare-gas" like electronic configuration, such as Au_{13}^{5+}, Au_{11}^{3+}, $Au_{12}Pd^{4+}$, and $Au_{11}Pd^{3+}$ are available (Figure 14).[31-33, 51-53] The assembled materials made of these superatoms (Figure 14) will correspond to a solid of "rare-gas" and will not exhibit any attractive functionality. The first aim of this thesis is to expand the superatomic library beyond the shell closure because Au superatom with

Figure 14. Aim of the thesis.

open electronic structure will give an additional functionality to a resultant superatom based material. In chapter 2, I will report synthesis of a novel phosphine/thiolate protected supertoms with 10 valence electrons using a counter-ion free synthetic method.

One of the attractive superatom based materials is the assembled superatom into well-ordered structure (distance and symmetry) (Figure 14). The current studies of superatom mainly focus on the individual properties prepared in solution. Thus, there is no general method established to construct the ordered assembly. The second aim of this thesis is the development of suitable building units for the ordered assembly and elucidation of the key to the construction of novel superatom assembly. In chapter 3, I will report the synthesis of the pyridine modified Au superatoms and preliminary results of the assembly experiment.

Some superatom-based materials such as quasi-molecule composed of Au superatoms have been reported so far.[54] The Au superatomic molecule is interesting research target because they will exhibit new electronic states depending on their bonding motif and the atomicity. Although the structure-dependent properties of new-type of molecules are fascinating, their synthesis mostly relies on a try-and-error approach. Thus, the correlation between the structure and properties of those molecules has not been established. The last aim of this thesis is to develop an aimed synthesis method of superatomic molecule to unravel an evolution of the structure correlated properties of gold superatomic molecules. In chapter 4, I will report a synthesis of one-dimensional pentamer of Au_{13} superatoms using a slow reduction method.

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Chapter 2.

Phosphine/thiolate-protected Au_{11} superatom with 10 valence electrons

2.1. Introduction

Stable protected Au clusters with spherical morphology have valence electrons with the numbers of 2, 8, 20, 34, and 58 in order to close their electronic shells. For example, the formal number of valence electrons are 2 for $[Au_4(P(t\text{-}Bu)_3)]^{2+}$ and $[Au_4(PPh_3)_4I_2]$ (t-Bu = tertiary butyl), 8 for $[Au_{10}(PPh_3)_8Cl]^+$, $Au_{11}(PPh_3)_7Cl_3$, $[Au_{11}(PPh_3)_8Cl_2]^+$, $[Au_{11}(PMePh_2)_{10}]^{3+}$, $[Au_{13}(PMe_2Ph)_{10}Cl_2]^{3+}$, $[Au_{13}(dppe)_5Cl_2]^{3+}$, $Au_{24}(SR)_{16}$, and $[Au_{25}(SR)_{18}]^-$ (dppe = 1,2-bis(diphenylphosphino)ethane), and 58 for $Au_{102}(SR)_{44}$.[1-7] Protected Au clusters having valence electrons of non magic numbers such as 4, 6, 12, have also been reported.[7-11] High stability of these Au clusters has been explained by considering an electronic structure of a non-spherical deformed superatom (Figure 1a). For example, 4 electrons are confined in a prorate Au_8 core of $[Au_8(dppp)_4Cl_2]^{2+}$ (dppp = 1,3-bis(diphenylphosphino)propane) (Figure 1b).[9] Six electrons are accommodated in

Figure 1. (a) Predicted cluster shapes under ellipsoidal shell model.[12] (b) X-ray structures of $[Au_8(dppp)_4Cl_2]^{2+}$ and (c) $[Au_9(dpph)_4]^{3+}$.[8-9] In (b) and (c), yellow, blue, and purple balls represent gold, phosphorus, and chlorine atoms, respectively. Organic residues are depicted as gray sticks. Reprinted from ref 12 with permission for (a). 1993 American Physical Society.

an oblate Au_9 core of $[Au_9(dpph)_4]^{3+}$ (dpph = 1,6-bis(diphenylphosphino)hexane) (Figure 1c).[8] Electronic shell closure in anisotropic cores has been explained by an ellipsoidal jellium model called as Clemenger-Nilsson potential; degenerated electronic levels in spherical potentials are split in such anisotropic potentials.[12] This suggests that the superatom having valence electrons without the spherical magic number may change its shape to satisfy a closed electronic shell structure. Indeed, structural isomerization of phosphine-protected Au_8 cluster upon redox has been reported.[13]

A superatom with open electronic structure is an attractive building unit for functional materials. For example, spherical superatom with open electronic structure is a potential candidate of a mediator of redox reaction. In addition, the open-shell superatom will exhibit magnetic behavior such as paramagnetism due to existence of the unpaired electrons. These features enable us to view the suepratom as an analogue of the conventional transition metal ions or metal atoms. Higher hierarchical structure of such superatoms will show cooperative phenomena such as catalysis, redox-mediated transport property, and magnetism. However, an example of stable spherical superatom

Figure 2. Examples of protected 8 electrons superatoms.[4, 5, 17, 18] The organic residues are depicted as gray sticks.

with open electronic structure reported so far has been limited to $[Au_{25}(SR)_{18}]^0$.[14-16] The $[Au_{25}(SR)_{18}]^0$ cluster shows a paramagnetic behavior, indicating that an unpaired electron (S = 1/2) is located at the core.[14-16]

In order to enrich the library of superatom having quasi transition metal element nature, the mechanism for the closure of electronic shell of the suepratoms (Figure 2) is considered.[4, 5, 17, 18] In the case of $Au_{11}(PPh_3)_7Cl_3$, the coordinated Cl ligands adjust the number of valence electrons to be 8. In contrast, the electronic shells of $[Au_{13}(dppe)_4Cl_2]^{3+}$ and $[Au_{25}(SR)_{18}]^-$ are closed by adjusting the net charge. The excess charges of the "ionic" clusters are compensated by counter ions, such as Cl^-, Br^-, I^-, SCN^-, NO_3^-, BF_4^-, PF_6^-, SbF_6^-, TOA^+, and PPh_4^+, originating from the precursor compounds and/or the phase transfer reagent used in the synthesis. Therefore, we can expect that superatom with open electronic structure can be synthesized in the neutral charge state without using counter ions.

Au(I) ions coordinated by thiolate and phosphine are promising precursors of neutral Au clusters for the above purpose. Thiolate will not act as a free counter anion but as an electron withdrawing ligand as already demonstrated by phosphine/thiolate-protected Au clusters.[19-21] In addition, the usage of both thiolates and phosphines will have additional benefits. For example, we can expect that two ligands are coordinated in a highly symmetric manner because of the difference in the sterical structures of the ligands. This allows us to introduced designed functionality into well-controlled Au clusters (Figure 3). The controlled surface functionalization will help us to arrange the superatom into desired and designed configuration using the self-assembly approach by the coordination of metal ions. In this chapter, I report the synthesis of a novel phosphine/thiolate protected Au superatom with open electronic

shell and symmetrical surface functionalization.

Figure 3. Synthetic concept in this work.

2.2. Experiment

2.2.1. Chemicals

Tetrachloroauric acid tetrahydrate ($HAuCl_4 \cdot 4H_2O$) was purchased from Tanaka Kikinzoku Kogyo. Sodium borohydride ($NaBH_4$), sodium methoxide, triphenylphosphine (TPP), chloroform-d_3, dichloromethane (DCM), *n*-hexane, ethanol (EtOH), *N,N*-dimethylformamide (DMF), methanol (MeOH), acetone, acetonitrile, and *n*-pentane were purchased from Wako Pure Chemical Industries. *p*-Mercaptobenzoic acid (MBA) was purchased from Tokyo Chemical Industry. Chloro(triphenylphosphine)gold(I) complex (Au(TPP)Cl) was prepared according to the literature procedure from $HAuCl_4 \cdot 4H_2O$.[22] Water of Milli-Q grade ($\rho > 18$ MΩ·cm) was used. All commercially available reagents were used as received.

2.2.2. General

Ultraviolet-visible (UV-vis) spectra were measured by V-670 spectrophotometer (JASCO, Japan). ^{1}H (400 MHz) NMR spectra were recorded by ECX-400 spectrometer

(JEOL, Japan) using chloroform-d_3 as a solvent. Chemical shifts of the NMR spectra were referenced to the internal standard of tetramethylsilane (TMS) peak (δ = 0 ppm). Positive-ion electrospray ionization mass spectra (ESI-MS) were measured by JMS-T100LP AccuTOF (JEOL, Japan). For the mass analysis, the cluster sample was dissolved in ethanol with the concentration of 1 mg/mL. The solution was diluted with acetonitrile to set the final concentration of 0.1 mg/mL. The solution was directly infused at a bias voltage of 3 kV. The mass spectra were calibrated by reference to $Cs(CsI)_n^+$ cluster ions generated from a 50 % aqueous methanol solution of CsI. Thermogravimetric (TG) measurement was conducted by SII TG-DTA 7200 instrument under N_2 gas flow (50 mL/min). The sample (~2 mg) was placed in Al crucible.

2.2.3. Synthesis

2.2.3.1. *p*-Carboxyphenylthio(triphenylphosphine)gold(I) complex [Au(TPP)(MBA)]

Scheme 1.

The title complex was prepared according to the literature procedure with slight modification.[23] Au(TPP)Cl (4.94 g; 10 mmol) was dissolved in DCM (100 mL). To this solution, a MeOH solution (50 mL) of MBA (1.54 g; 10 mmol) and NaOMe (590 mg; 11 mmol) was added dropwise under stirring. After 2 hours, the solvent was evaporated to dryness. The residue was triturated in 40 mL of DCM and the dispersion was filtered.

The filtrate was poured into 120 mL of *n*-hexane. The precipitate formed was filtered and washed with *n*-hexane and dried *in vacuo*. The title complex was obtained as a pale yellow powder with a yield of 81 % (4.96 g). ^{1}H NMR ($CDCl_3$): δ 7.81, 7.67 (AB system, 4H, J = 8.5 Hz), 7.58-7.48 (m, 15H). The NMR data is consistent with the literature data.[23]

2.2.3.2. $Au_{13}(TPP)_8(MBA)_3$ (1)

Scheme 2.

A dispersion of Au(TPP)(MBA) complex (306 mg; 0.5 mmol) in EtOH (95 mL) was cooled in an ice bath for at least 30 minutes with stirring. To the dispersion, a fleshly prepared solution of $NaBH_4$ (9.4 mg; 0.25 mmol) in EtOH (5 mL) was added at once under stirring. The color changed immediately and the gas was evolved. The reaction mixture was left stirring for 2 hours at room temperature and then the solution was filtered. The solvent was removed by rotary evaporator to dryness. The orange residue was triturated in DCM and the dispersion was filtered with a membrane filter (0.2 μm pore). After successively washing of the residue with acetone and water on the filter, the residue was dissolved in EtOH. The extract was concentrated to ~5 mL and DMF was added to the solution to set the final ratio between EtOH and DMF to be ~2:1. Then, the solution was transferred to a 30 mL vial and the open vial was placed in a 100 mL bottle. *n*-Pentane (30 mL) was added in the bottle and the pentane vapor was

allowed to diffuse into the inner vial. The bottle was kept at ~20 °C. After 1 month, dark-red platelet crystals that are suitable for X-ray crystallography experiment were obtained in the inner vial. The solution and crystals were filtered and the crystals were washed with *n*-hexane. Finally, the crystals were dried *in vacuo* giving ~10 mg of the title compound.

Ruby-red prism crystals were found occasionally in the crystallization batch when the diffusion process was fast. SCXRD revealed that the crystal was composed of $Au_{11}(TPP)_7(MBA)_3$ cluster (**2**) which were contained in the original dispersion as minor species. Since only small amount of **2** was isolated in the form of crystal, the detailed study of **2** was limited only to X-ray crystallography and UV-vis spectral measurement.

2.2.4. X-ray crystallography

Single-crystal X-ray diffraction (SCXRD) studies were conducted by VariMax dual with Saturn (Rigaku, Japan). The crystals were mounted on MicroMounts (MiTeGen, USA) covered with Paratone-N oil (Hampton research, USA) to avoid the evaporation of solvents. The mounts were placed on a goniometer head of AFC 11 partial-chi four-axis goniometer (Rigaku, Japan). The temperature of the sample was controlled by cooled N_2 gas flow with a resistive heater. The incident X-ray was generated by a rotating anode type generator with Mo target. The monochromatic X-ray (Mo Kα; λ = 0.71075 Å) was obtained by a confocal X-ray mirror and 0.3 mm collimator was used in all the experiment. Saturn 724+ CCD area detector (Rigaku, Japan) was used for a detection of diffracted X-ray. The crystal data were collected and processed by CrystalClear SM expert (Rigaku, Japan). All the collected data were corrected for Lorentz polarization factors and absorption correction was done by numerically using

NUMABS software (Rigaku, Japan). Direct method (SHELXS 2014)[24] was used for the initial phase trial and the trial structure was refined by full-matrix least-square methods on F^2 (SHELXL 2014) with Shelxle software. The diffused electron density was treated by SQUEEZE[25] on the PLATON platform.[26] All non-hydrogen atoms except for solvent molecules were refined anisotropically and hydrogen atoms were located at calculated positions and treated as riding models. Phenyl rings of the ligands were treated as rigid constrains to reduce the free parameters of the least squares. Solvent water molecules were treated as simple oxygen atoms. Crystallographic information files of **1** and **2** have been deposited at the Cambridge Crystallographic Data Centre (CCDC) with the deposition numbers of CCDC-1444409 and 1444410.

2.2.5. Computational details

Quantum chemical calculation of **1** was performed using Gaussian 09 package.[27] The single point calculation was conducted for the crystal structure with modification of the TPP and MBA ligands to PH_3 and SCH_3, respecively, to minimize the calculation cost. LANL2DZ basis set was used for gold and 6-31G+ basis set was used for other elements. Unrestricted Hartree-Fock, pure DFT, and B3LYP methods with assuming singlet or triplet spin state were used.

2.3. Results and discussion

2.3.1. Optimization of synthetic condition

Basically, cluster **1** can be synthesized by reduction of the precursor complex Au(TPP)(MBA) in a solvent as in the case of other phosphine-protected Au clusters.[7] In order to optimize the synthetic conditions, I have tested a variety of conditions. The

Table 1. Results of optimization of the synthetic conditions.[a]

Entry	Solvent	T (ºC)	Amounts of $NaBH_4$[b]	Reaction time (h)	Results
1	EtOH[c]	r.t.[d]	0.5	2	Formation of **1**[e]
2	EtOH[c]	0	0.5	2	Formation of **1**[e]
3	EtOH[c]	r.t.[d]	0.5	24	Decomposition[f]
4	EtOH[c]	0	0.25	1	Formation of **1**[e]
5	EtOH[c]	0	0.25	24	Formation of **1**[e]
6	EtOH-DCM[g]	0	0.25	2	Formation of **1**[e]
7	DMF[h]	r.t.[d]	1	2	Plasmonic particles[f]
8	DMF[h]	0	0.25	2	Plasmonic particles[f]
9	IPA[i]	r.t.[d]	0.25	2	Plasmonic particles[f]
10	DCM[h]	r.t.[d]	0.25	2	Plasmonic particles[f]
11	THF[k]	r.t.[d]	0.25	2	Plasmonic particles[f]

[a] 0.5 mmol of precursor complex was used for all the conditions. [b] Molar equivalents. [c] Room temperature. [d] 95 mL [e] Confirmed by the crystallization. [f] Checked by UV-vis spectrum. [g] 80 mL EtOH and 20 mL DCM. [h] 40 mL [i] 40 mL of 2-propanol. [j] 40 mL [k] 40 mL of tetrahydrofuran.

synthetic results under various conditions are summarized in Table 1. In EtOH, the formation of **1** was confirmed after the crystallization process. However, the amounts of the crude samples obtained before the crystallization were large in the case of entry 2 as compared to those of entries 1, 4, and 5 (Table 1). Since the precursor complex is insoluble in EtOH, DCM was added to improve the solubility in entry 6 (Table 1). In this case, the formation of **1** was confirmed after the crystallization, but the amounts of the crystals were too small (~1 mg). In other polar solvents such as DMF and IPA, large Au particles showing plasmon resonance absorption were observed after the reduction. The plasmonic particles were also observed in less polar solvents such as DCM and THF (entries 10 and 11 in Table 1). Because **1** has both hydrophobic TPP and hydrophilic MBA ligands as protecting monolayer, it shows a unique solubility to

organic solvents. For example, **1** is not dissolved in IPA, DCM and THF. Synthesis of **1** in such solvents may lead decomposition and growth to large plasmanic particles. On the other hand, **1** is dissolved in DMF, but plasmonic particles were observed using DMF as a reaction solvent. In order to explain these phenomena, I assume the following formation process.

$$13\mathrm{Au(TPP)(MBA)} + 13\mathrm{H}^{-} \rightarrow$$

$$\mathrm{Au_{13}(TPP)_8(MBA)_3}(\mathbf{1}) + 5\mathrm{TPP} + 10\mathrm{MBA} + 13/2\mathrm{H_2} \qquad (1)$$

Since the precursor complex contains stoichiometric amounts of TPP and MBA, excess amount of free ligands are formed after the formation of **1**. Thiol and/or thiolates have a strong binding affinity to Au and can etch the gold clusters. DMF can dissolve the ligands so that formation of plasmonic particles via growth or decomposition of **1** may proceed in DMF. Decomposition of **1** was observed after dissolving in the reaction mixture for long time (entry 3 of Table 1). Thus, the synthesis of **1** needs a low temperature and short reaction period.

The formation of **1** was confirmed by SCXRD experiment (as shown later). To check the existence of **1**, I performed positive mode ESI-MS measurement and TG analysis. Figure 4 shows the ESI-MS spectrum of **1**. Since the cluster is neutral, the ionization of **1** requires harsh ESI condition. As a result, some unassigned fragmentation peaks were also observed with weak intensities. However, the observed isotope pattern was reproduced by the calculated one for the composition of $\mathrm{Au_{13}(TPP)_8(MBA)_3}$. The weight loss of **1** determined by TG analysis was in good agreement with the calculated value (Figure 5). From these results, I concluded that **1** was successfully synthesized.

Figure 4. Positive-ion mode ESI-MS spectrum of **1**. The inset shows enlarged view of $\mathbf{1}^{2+}$ peak and the calculated isotope pattern of **1**.

Figure 5. TG chart of **1**.

2.3.2. X-ray crystallography

2.3.2.1. Crystal structure of 1

Figure 6 shows the photograph of the crystals of **1**. The crystal structure of **1** was unambiguously determined by

Figure 6. A photograph of the crystals of **1**.

Table 2. Crystal data of **1**.

Formula[a]	$C_{173}H_{159}Au_{13}O_{12}P_8S_3$
FW[a] (g mol^{-1})	5334.50
Crystal color and habit	Dark-red plate
Crystal size (mm)	0.090 × 0.080 × 0.040
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	21.6748(16)
b (Å)	28.443(2)
c (Å)	27.3187(19)
α (º)	90
β (º)	93.7190(10)
γ (º)	90
V (Å^3)	16806(2)
Z	4
T (K)	90(2)
Completeness to theta = 27.878º	99.9 %
ρ_{calc} (g cm^{-3})	2.108
μ (mm^{-1})	11.468
Max. and min. transmission	0.631 and 0.430
F(000)	9952
θ range (º)	1.857–27.878
Index ranges	$-28 \leq h \leq 28$, $-37 \leq k \leq 37$, $-35 \leq l \leq 35$
Collected reflections	291228
Independent reflections	40058 (R_{int} = 0.0574)
Data/restrains/parameters	40058/714/1633
Goodness-of-fit on F^2	1.195
Final $R^{b,c}$ indices [$I > 2\sigma(I)$]	R_1 = 0.0529, wR_2 = 0.0989
Final $R^{b,c}$ indices [all data]	R_1 = 0.0572, wR_2 = 0.1008
$(\Delta\rho)_{max,min}$ (e Å^{-3})	2.847, -2.261

[a]Including solvent molecules. [b] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [c] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$, where $p = [\max(F_o^2, 0) + 2F_c^2]/3$.

SCXRD experiment. The crystal data obtained from SCXRD experiment is summarized in Table 2. **1** was crystalized in the monoclinic crystal system with the space group of $P2_1/n$.

The chemical formula $Au_{13}(TPP)_8(MBA)_3$ of **1** suggests that **1** has icosahedral Au_{13} core. However, on the contrary to such initial guess, the Au core of cluster **1** has an unexpected structure. Figure 7 shows the total and core structures of **1**. Notably, the Au_{13} core is composed of two moieties. The larger moiety is Au_{11} which is similar to the core of conventional phosphine-protected Au_{11} clusters.[7, 18] The smaller moiety made of two Au atoms are attached to the Au_{11} moiety (Figure 7). The analysis of Au–Au bonds of the Au_{13} moiety (Figure 7) revealed that the Au–Au bond lengths within

Figure 7. X-ray structure of **1**. (a) Total structure of **1**. Yellow, green, blue, gray, and red balls represent gold, sulfur, phosphorus, carbon, and oxygen atoms, respectively. Phenyl rings of TPP ligands are depicted as gray sticks. Hydrogen atoms, solvent molecules, and disordered parts are omitted for clarity. (b) Core structure of **1**. Selected bond lengths in Å: Au12-Au13 2.9945(8); Au3-Au12 2.9306(7); Au4-Au12 2.9667(7); Au8-Au9 2.9678(7); Au9-Au10 3.0090(7).

the Au dimer and between Au dimer and Au_{11} moiety are comparable to those within the Au_{11} moiety. Three MBA ligands are coordinated to three Au atoms on a facet of the Au_{11} moiety. Two of them are also bonded to one of the Au atom and form the –SR-Au-SR- "staple" motif,[3] while the remaining thiolate is bonded to the staple via the bridging Au atom (Figure 8). The $Au_2(SR)_3$ moiety observed in **1** has totally different structure as compared to those found in small thiolate-protected Au clusters such as $Au_{25}(SR)_{18}$ and $Au_{38}(SR)_{24}$.[4, 5, 28] The growth mechanism of $Au_{25}(SR)_{18}$ has been studied by mass spectrometry.[29] The results indicated that the precursors of $Au_n(SR)_m$ are Au(I)-SR oligomeric complexes with closed chain structure. Thus, the formation of the $Au_2(SR)_3$ moiety with the chain structure is reasonable. In contrast, the precursor complex of **1** is a monodentate Au-SR complex. Thus, the formation of long Au-SR chain structure may not be favorable after the reduction and, as a result, the new surface protecting motif may be formed on the Au_{11} core.

Figure 8. Binding motif of three thiolates. Selected bond lengths in Å: Au3-S1 2.396(2); Au12-S1 2.334(2); Au4-S2 2.409(3); Au12-S2 2.325(3); Au2-S3 2.371(2); Au13-S3 2.344(2).

2.3.2.2. Crystal structure of 2

As mentioned above, a single crystal of cluster **2** was sometime obtained as a minor product. The photograph of the crystal of **2** is shown in Figure 9. The

Figure 9. A photograph of the crystals of **2**.

Table 3. Crystal data of **2**.

Formula	$C_{147}H_{120}Au_{11}O_6P_7S_3$
FW (g mol^{-1})	4462.02
Crystal color and habit	Red block
Crystal size (mm)	0.16 × 0.11 × 0.09
Crystal system	Orthorhombic
Space group	*Fdd*2
a (Å)	40.998(12)
b (Å)	42.851(13)
c (Å)	34.532(10)
α (º)	90
β (º)	90
γ (º)	90
V (Å^3)	60666(31)
Z	16
T (K)	93(2)
Completeness to theta = 27.515º	99.5 %
ρ_{calc} (g cm^{-3})	1.954
μ (mm^{-1})	10.759
Max. and min. transmission	0.465 and 0.332
F(000)	33152
θ range (º)	2.993–27.515
Index ranges	$-53 \leq h \leq 52$, $-55 \leq k \leq 55$, $-44 \leq l \leq 44$
Collected reflections	180036
Independent reflections	34685 (R_{int} = 0.0478)
Data/restrains/parameters	34685/934/1373
Goodness-of-fit on F^2	1.195
Final $R^{a,b}$ indices [$I > 2\sigma(I)$]	R_1 = 0.0406, wR_2 = 0.0889
Final $R^{a,b}$ indices [all data]	R_1 = 0.0436, wR_2 = 0.0909
Flack parameter	0.036(3)
$(\Delta\rho)_{max,min}$ (e Å^{-3})	2.847, -2.261

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$, where $p = [\max(F_o^2, 0) + 2F_c^2]/3$.

crystal habit of **2** was prismatic and the color was scarlet. These features are different from those of **1**. **2** was crystalized in the orthorhombic system with the space group of *Fdd*2. I could analyze the data using a lower symmetry system such as monoclinic. In this case, the analysis of the systematic absence suggested that the crystal belonged the space group of *Cc*. Although the least square analysis of Laue symmetry gave slightly better result in the case of 2/*m*, I adopted the highest symmetry *mmm* because almost the same structure was obtained in both cases. The crystal data obtained from SCXRD experiment is summarized in Table 3. The structure of **2** is analogous to that of $Au_{11}(TPP)_7(SC_5H_4N)_3$ reported previously.[19] Figure 10 shows the total and core structure of **2**. The protecting scheme of Au_{11} moiety of **2** is different from that of **1**. Three thiolates are independently bonded to Au atoms located at equatorial positions of the Au_{11} core. The lengths of Au-S bonds on the Au_{11} moiety in **2** are in the range of

Figure 10. X-ray structure of **2**. (a) Total structure of **1**. Drawing scheme is same to that of Figure 7. (b) Core and thiolate bonding structure of **2**. Selected bond lengths in Å: Au8-S1 2.340(4); Au4-S2 2.324(3); Au6-S3A 2.340(7).

2.324–2.340 Å and are significantly shorter than those in **1** (2.371–2.409 Å). This result suggests that the thiolates in **2** are more strongly bound and withdraw more electronic charge from the core than those in **1**. The reduction of the electron withdrawing ability by three MBAs in **1** is associated with the formation of the novel $Au_2(MBA)_3$ protecting motif as discussed later.

2.3.3. Electronic structure of 1

The formal number of the valence electrons of **1** is calculated to be 10. The 10 valence electrons system is rare and only one example, $Au_{14}(TPP)_8(NO_3)_4$, has been reported.[30] Although the formal number of valence electrons of $Au_{14}(TPP)_8(NO_3)_4$ was 10, SCXRD and computational studies revealed that the actual number of valence electrons in the core was 6. In this case, the actual electron withdrawing group was not NO_3 unit, but $Au(NO_3)$ moieties. This consideration was confirmed by the 2-dimensional shape of HOMO and LUMO of the cluster and the charge distribution analysis.[30]

In the framework of superatomic concept, the electron configuration of a superatom with 10 electrons can be described as $(1S)^2(1P)^6(1D)^2$.[31] In this case, the 1D orbitals are partially occupied, thus we can consider the two possible spin states, singlet and triplet, for the ground spin state of the superatom. To identify the ground spin state, I compared

Table 4. Results of quantum chemical calculations.

Entry	Method	Relative energy between singlet and triplet (E_{sin}^{a}–E_{tri}^{b}) (eV)
1	UHF	–0.37543
2	UBPV86	–0.02446
3	UB3LYP	–0.07061

[a] Total energy of singlet state. [b] Total energy of triplet state.

the total energies of the two spin states. It is well known that the calculation methods such as HF, pure DFT and hybrid DFT have some method-specific overestimation or underestimation of the energy of a spin state. Therefore, I have checked the energy difference of **1** using three different types of methods and the results are summarized in Table 4. The total energies of the triplet state are smaller than those of the singlet state in all the cases. The stability test of wavefunction after self-consistent-field calculation also indicated that the resultant wavefunctions of triplet are stable, but those of singlet are not stable. These results imply that the ground spin state of **1** is triplet.

To examine the nature of unpaired electrons, Kohn-Sham (KS) orbitals are analyzed. Figure 11 shows the energy diagram and KS orbitals obtained from the calculation using B3LYP functional assuming the triplet state as the ground state. The HOMO for α spin is localized on the Au_{11} moiety. Roughly speaking, the orbital has two nodal planes on the moiety and seems to correspond to a d-type orbital. The HOMO-1 orbital has two nodal planes and the direction of the orbital is orthogonal to that of HOMO. The HOMO-2, HOMO-3, and HOMO-4 have one nodal plane on Au_{11} moiety and those orbitals clearly show 1P natures. The HOMO, HOMO-1, and HOMO-2 for β spin state also show 1P-like nature of superatom. These results indicated that the superatomic electronic configuration of **1** is expressed as $(1S)^2(1P)^6(1D)^2$. On the contrary to the structural point of view, the valence electrons are mostly localized on Au_{11} moiety. How is the electronic contribution of the dimer unit? The LUMO for α spin has a large contribution of the Au dimer. The shape of the orbital is similar to a σ bond between two p atomic orbitals. The non-superatomic bonding nature is confirmed by the orbital coefficients analysis. In fact, the orbital mainly consists of two 6p orbitals of Au atoms. This result implies that the valence electrons, 6s electrons of Au, of the

Figure 11. Energy and selected Kohn-Sham orbitals of the simplified molecule model of **1** obtained from a single point energy calculation using B3LYP functional. The isosurfaces of the KS orbitals are depicted with 0.015 e levels. The drawing scheme of the structure models is same to that of Figure 7.

dimer have deep energy level and they strongly interact with coordinating ligands.

The calculation result suggests that **1** is the first example of spherical superatom

with 10 electrons. In order to confirm this by experimentally, I compared the optical absorption spectrum of **1** with that of Au clusters with 8 electrons. Figure 12 shows UV-vis absorption spectra of **1**, **2** and $Au_{11}(TPP)_7(SC_5H_4N_1)_3$. The absorption structure of **1** is totally different from those of **2** and $Au_{11}(TPP)_7(SC_5H_4N_1)_3$. In the cases of 8 electrons system, the peaked structure at around 430 nm and 300 nm was prominent. On the other hand, **1** did not show peaked structure. In addition, the absorption onset of **1** is located at around 700 nm whereas those of the 8 electrons systems are located at around 600 nm as clearly seen by the spectra represented in the energy scale (inset of Figure 12). The theoretical and experimental results led me conclude that the 10 valence electrons of **1** are confined in the Au_{11} moiety and the Au_{11} core can be viewed as superatom with 10 electrons. Namely, a spherical Au superatom with open electronic structure was successfully synthesized for the first time.

Figure 12. UV-vis absorption spectra of **1** in EtOH (red), **2** in DMF (green), and $Au_{11}(TPP)_7(SC_5H_4N)_3$ (blue) in DCM. The absorbance of those was normalized at 270 nm. Inset shows same spectra in energy scale corrected with Jacobian factor. Top two spectra are sifted vertically for clarity.

2.3.4. Formation of 10 electrons superatom

How can I explain the formation of 10 electrons superatom? The formation of **1** and **2** in the same synthesis batch suggests that a $Au_{11}(SR)_3$ moiety is the versatile unit in the absence of suitable counter anions since it has the electronic shell is closed with 8 electrons. The three thiolates in **2** is located separately each other and thus each thiolate withdraws one electron from the Au_{11} core (Figure 14). On the other hand, three thiolates in **1** are concentrated on one facet of Au_{11} and also bound by Au dimer unit. The 1S superatomic orbital of Au_2 is located deeper in energy than 1D orbitals of Au_{11}. Since thiolates also have a deep frontier energy level, the interaction between the frontier orbitals of Au dimer and thiolates is stronger than that of Au_{11} moiety. This expectation is clearly confirmed from the viewpoint of the bond length because the bond length reflects the interaction of each orbital. As shown in Figure 8, the bond lengths of Au-S are not symmetrical. All bond lengths between the dimer and thiolates

Figure 13. Schematic illustration of the electron withdrawing of the thiolates. (a) In the case of **2** and (b) the case of **1**.

are shorter than those of Au_{11} moiety. From this result, the thiolate is not actual electron withdrawing group, but the $Au_2(SR)_3$ moiety is actual one in **1**. Three thiolates in $Au_2(SR)_3$ already withdraw two electrons from the dimer, thus only one valence electron is removed from the Au_{11} moiety leaving 10 valence electrons. This explanation implies that the dimer is electronically insulated from the Au_{11} moiety like oligomeric $Au_2(SR)_3$ motif observed in thiolate protected Au clusters.

2.4. Summary

In this chapter, I described a synthesis of Au_{11} superatom with 10 valence electrons. The cluster **1** had a unique surface protecting motif and the formation of the motif was a key to realize the 10 electrons superatom. And the formation of **2** implied that the synthesis in the absence of suitable counter ions regulated the possible cluster species during the reaction. **1** has two 1D electrons and the *ab initio* calculation suggests that the triplet state is the ground state. Thus, the further work of magnetic measurement and electrochemical measurement will be done to investigate the electronic property of **1**, more precisely.

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Chapter 3.

Toward controlled-assembly of protected Au superatom

3.1. Introduction

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.[1] In most cases, they do not show any collective properties in the solid state because individual clusters are isolated by thick monolayers and, as a result, their interaction is negligible small. However, engineering of the solid state structure of the protected superatoms is an attractive approach to utilize them in practical application. Early attempts for packing the clusters into well-ordered structure have been made by Schmid and coworkers.[2] They assembled $Au_{55}(PPh_3)_{12}Cl_6$ clusters, also called as "Nanogold®" or "Schmid-gold", into ordered structures and studied their transport properties. After those pioneering works, a few works have been reported for cluster assembly into one- and three-dimensional structures.[3-5]

In the genuine crystal of protected clusters, the individual clusters are arranged regularly, with well-defined orientation. Such crystalline assemblies provide an ideal opportunity to study how new collective properties are emerged.[6, 7] For example, Figure 1 shows a packing structures of $[Au_{25}(SBu)_{18}]^0$ and $[Ag_{44}(MBA)_{30}]^{4-}$ (SEt = buthanethiolate; MBA = thiobenzoic acid). In the former case, individual $[Au_{25}(SBu)_{18}]^0$ clusters interact each other via aurophillic interaction between cationic Au atoms in the surface oligomer (Figure 1a).[7] The paramagnetic properties of $[Au_{25}(SBu)_{18}]^0$ due to one unpaired electron are affected significantly by the magnetic interaction from the neighbors.[7] In the latter case, individual $[Ag_{44}(MBA)_{30}]^{4-}$ clusters form flexible network via hydrogen boning between carboxylic groups of the protecting monolayer (Figure 1b).[6] Theoretical calculation suggested that the crystal is responsive

to mechanical stress due to their flexible hydrogen bonding.

Figure 1. Examples of the protected superatoms in the solid state. (a) Packing structure of $Au_{25}(SBu)_{18}$ (SBu = buthanethiolate) in the crystal.[7] Yellow and red balls represent gold and sulfur atoms, respectively. The organic residue is omitted for clarity. (b) Packing structure of $[Ag_{44}(MBA)_{30}]^{4-}$ (MBA = thiobenzoic acid) in the crystal.[6] Hydrogen bonded ordered packing are observed. Reprinted from ref 7 with permission for (a). 2014 American Chemical Society. Reprinted from ref 6 with permission for (b). 2014 Macmillan Publishers Ltd.

In less ordered structures, the individual clusters are arranged regularly, but with random orientation or they just form amorphous-like assembly. What kind of application is possible for such less ordered assembled solid of clusters? Catalytic application is promising because ligand-protected Au clusters have been used as precursors of size-selected Au catalysts supported on solid mateials.[8-10] If we can construct an assembly of protected Au clusters with pored structure, the solid can be used as a catalyst after proper activation of cluster surface, such as removal of ligands by thermal treatment. Such a solid, in which catalytically active clusters form highly-dense assembly with certain pore or channel (Figure 2) has a practical benefit in catalytic usage; robustness and easy recollection. If regularity of the assembled structure

Figure 2. An example of the usage of assembled superatom. In this figure, a concept of assembled superatom catalyst is presented.

can be further improved, one can expect high selectivity and new catalytic reactions due to unique assembled structures.

As an initial step toward such goal, I aimed to develop suitable building units for ordered assemble structures. Among a huge library of protected Au superatom, I focused on $Au_{25}(SR)_{18}$ as an initial choice because of the following reasons: (1) octahedral symmetry of the ligand position, (2) markedly high stability, and (3) wide tunability of the functional group in the ligand. In order to self-assemble a highly ordered structure of the clusters, I decided to introduce ligands having functional groups such as pyridyl or calboxyl groups. In this chapter, I report synthesis of protected Au clusters as building units of the assembly and attempts to construct a highly ordered superatom assembly by the coordination chemistry.

3.2. Experiment

3.2.1. Chemicals

Tetrachloroauric acid tetrahydrate ($HAuCl_4 \cdot 4H_2O$), Sodium borohydride ($NaBH_4$), sodium methoxide, triphenylphosphine (TPP), chloroform-d_3, dichloromethane (DCM), *n*-hexane, diethyl ether, methanol (MeOH), *n*-tetrabuthylammonium bromide (TBABr), barium sulfate ($BaSO_4$), zinc nitrate hexahydrate, copper tetrafluoroborate hexahydrate, and *n*-pentane were purchased from Wako Pure Chemical Industries. 4-Mercaptopyridine (4-PySH), 4-pyridineethanethiol hydrochloride (4-PyET·HCl), silver tetrafloroborate, and 1,2-bis(diphenylphosphino)ethane (dppe) were purchased from Tokyo Chemical Industry. Nickel tetrafluorobrate hexahydrate and palladium acetate were purchased from Aldrich. The preparation of Au(TPP)Cl complex was described in chapter 2. Water of Milli-Q grade (ρ > 18 MΩ·cm) was used. All commercially available reagents were used as received.

3.2.2. General

Ultraviolet-visible (UV-vis) spectra were measured by V-670 spectrophotometer (JASCO, Japan) and diffuse reflectance spectra were measured by an integrate sphere option. The sample was mixed and diluted with $BaSO_4$. IR spectra were measured by FT/IR-4200 (JASCO, Japan). Samples are grounded with KBr and made pellets for the measurement. ^1H (400 MHz) NMR spectra were recorded by ECX-400 spectrometer (JEOL, Japan) using chloroform-d_3 as a solvent. Chemical shifts of the NMR spectra were referenced to the internal standard of tetramethylsilane (TMS) peak (δ = 0 ppm). Matrix-assisted laser desorption ionization mass spectra (MALDI-MS) were measured by AXIMA-CFRs (Shimadzu, Japan). In MALDI-MS,

trans-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) was used as the matrix and the ratio between matrix and cluster was 1:100.[11] Powder X-ray diffraction (PXRD) patterns were measured by Miniflex X-ray diffractmeter (Rigaku, Japan). Transmission electron microscope (TEM) images were acquired by HF-2000 (Hitachi, Japan) with the working voltage of 200 kV.

3.2.3. Synthesis

3.2.3.1. 4-Pyridinethio(triphenylphosphine)gold(I) complex [Au(TPP)(SPy)]

Scheme 1.

The title complex was prepared according to the literature procedure with slight modification.[12] Au(TPP)Cl (2.48 g; 5 mmol) was suspended in MeOH (180 mL) and the solution was heated at reflux temperature. To this solution, a MeOH solution (20 mL) of 4-PySH (556 mg; 5 mmol; 1 eq.) and NaOMe (297 mg; 5.5 mmol; 1.1 eq.) was added under stirring and the reflux was continued. Upon the addition, the solution became clear. After 30 minutes, water was added to the reaction mixture until the solution became slightly cloudy. The resultant aqueous MeOH solution was slowly cooled to r.t. to form crystals. After the solution was kept at -20 °C for several hours, the solid crystals were filtered and washed with MeOH and diethyl ether. Finally, the crystals were dried *in vacuo*. The title complex was obtained as pale yellow plates or needles

with 2.06 g (70 %) yield. No further purification was conducted. ^{1}H NMR: δ 8.17 (d, 2H, J = 6.3 Hz), 7.58-7.47 (m, 17H). The NMR data is consistent with the literature data.[11]

3.2.3.2. $[Au_{25}(4\text{-PyET})_{18}]^{-}TBA^{+}$ (1)

Scheme 2.

To a stirring aqueous solution of $HAuCl_4$ (10 mM; 100 mL), TBABr (355 mg; 1.1 mmol; 1.1 eq.) was added. The clear yellow solution became cloudy orange dispersion by the addition of TBABr. Then, 4-PyET·HCl (527 mg; 3 mmol; 3 eq.) was added to the dispersion under stirring. The solution became gradually transparent and colorless. After the stirring for 1 hour, a fleshly prepared aqueous cold solution of $NaBH_4$ (0.5 M; 20 mL) was added at once under vigorously stirring. An immediately color change was observed. The reaction mixture was stirred for 3 hours and the black solution was transferred to a centrifugation tube. The solution was centrifuged for 30 minutes at 3500 rpm and the supernatant was removed. The black precipitate was washed three times with water by the centrifugation. Then, the crude sample was dried *in vacuo* and was purified by GPC (Sephadex LH-20; MeOH). The orange band eluted at the end was collected. The solvent of the collected fraction was removed by rotary evaporator and then the residue was dried *in vacuo*. Black sticky powder of ~70 mg (~25 % yield based

on Au) was obtained.

3.2.3.3. $Au_{13}(dppe)_4(SPy)_4$ (2)

Scheme 3.

Au(TPP)(Spy) (285 mg; 0.5 mmol) was dissolved in DCM (30 mL) under stirring. To this solution, dppe (200 mg; 0.5 mmol) was added and the solution was kept stirring for 1 h at r.t. To this solution, 10 mL of a freshly prepared ethanolic solution of $NaBH_4$ (20 mg; 0.5 mmol) at once. The color of the solution became red at the beginning and then gradually turned black. The reaction was kept for 12 hours at r.t. and the reaction mixture was poured into *n*-hexane (300 mL) to precipitate the product. After the overnight standing, the precipitate was filtered and then washed by 50 mL of *n*-hexane, 40 mL of *n*-hexane-DCM (1:1. v/v), and 30 mL of *n*-hexane-DCM (1:2), successively. The product was extracted from the residue by 90 mL of *n*-hexane-DCM (1:5) and the solvent was removed by rotary evaporator. The residue was crystallized by the vapor diffusion of *n*-pentane into the solution (DCM-EtOH; 1:1). Crimson-red platelet crystals were obtained after 3 days.

3.2.3.4. Assembly experiment

The assembly of cluster **1** was tested by adding the solution containing metal salts such as Ni^{2+}, Cu^{2+}, Zn^{2+}, Pd^{2+}, and Ag^{+} ions. The MeOH solutions containing equimolar amounts of **1** and metal ions were slowly mixed. The precipitates formed were collected by centrifugation or filtration by a membrane filter (pore diameter; 0.2 μm) and washed with MeOH. Then, the precipitate was dried *in vacuo*.

3.2.4. X-ray crystallography

Single-crystal X-ray diffraction (SCXRD) studies were conducted in the same way with those described in Chapter 2. The crystallographic information file of **2** has been deposited at the CCDC with the deposition number of CCDC-1444411.

3.2.5. X-ray absorption fine structure (XAFS)

XAFS experiment was conducted at beamline BL01B1 of SPring-8 facility with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (proposal no. 2014A1680). The incident X-ray was monochromated by a Si(311) double crystal monochrometer. For the transmission measurement of Au L_3-edge XAFS, the difference of X-ray intensities was monitored by two ionization chambers. For the fluorescence measurement of 3d metal K-edge XAFS, the intensity of incident X-ray was monitored by ionization chamber and the fluorescence X-ray was monitored by the Lytle detector. The energy calibration was conducted using a Cu foil. The analysis of the X-ray absorption near edge structure (XANES) spectra and the extended X-ray absorption fine structure (EXAFS) was according to the literature.[13]

3.3. Results and discussion

3.3.1. Synthesis of cluster 1

$Au_{25}(SR)_{18}$ is one of the most well-known stable clusters and various synthetic methods have been reported so far. However, cluster **1** could not be obtained by the conventional methods (Table 1). Conventionally, hydrophobic Au_{25} clusters have been obtained with high purity and yield by one phase reduction of Au precursor in THF.[14] However, large, plasmonic Au particles were obtained when using 4-PyET as the ligands (Entry 2 in Table 1). Unsuccessful synthesis of small Au clusters protected by 4-PyET by this method may be due to poor solubility of 4-PyET·HCl. Next, I tried to

Table 1. Results of optimization of the synthetic conditions of **1**.

Entry	Solvent	Method	Results
1[a]	Water	One-phase reduction	Formation of **1**
2[b]	THF	One-phase reduction	Formation of plasmonic particles
3[a]	MeOH	One-phase reduction	Formation of plasmanic particles
4[a]	EtOH	One-phase reduction	Formation of plasmonic particles
5	Toluene/water	Brust method[c]	Formation of plasmonic particles

[a] The amounts of the reagents are almost same. [b] 30 mL of solvent. [c] Tetraocthylammonium bromide was used instead of TBABr.

synthesize small Au clusters protected by 4-PyET using alcohol as solvent, since the Au_{25} cluster has been obtained as byproducts in the synthesis of $Au_{144}(SR)_{60}$. Synthesis in MeOH or EtOH both afforded plasmonic particles (Entries 3 and 4 in Table 1). Hydrophobic Au:SR clusters are usually insoluble in alcohol solvents and thus are precipitated in such synthetic condition. This precipitation prevents the overgrowth of the clusters. In contrast, Au:4-PyET clusters can be grown to larger Plasmonic particles because they are dissolved well in alcohol. Brust method, the most well-known method to synthesize small Au:SR clusters,[15] yielded only plasmanic particles (Entry 5 in Table

1). Based on these results, I tried to synthesize **1** in water with TBA cation and **1** was obtained successfully. There are three key points. The first one is that 4-PyET·HCl and the Au-(4-PyET) polymer formed are soluble in water. Monodisperse Au clusters were formed by homogeneous nucleation in this condition. The second point is that **1** was precipitated out after the formation. Thus, overgrowth can be suppressed. The third point is the usage of bulky counter cation, TBA. $Au_{25}(SR)_{18}$ cluster is easily oxidized in the absence of bulky counter cation in the synthesis.[16]

Cluster **1** was characterized by UV-vis spectroscopy and MALDI-MS. Figure 3 shows UV-vis spectrum of **1** in MeOH. UV-vis spectrum of small Au:SR clusters exhibit characteristic profiles due to their discontinuous nature of electronic states of the Au cores. Therefore, the spectrum can be used as a fingerprint of specific cluster. The spectrum shape is in good agreement with the reported $[Au_{25}(SR)_{18}]^-$ cluster.[16] Figure 4 shows negative-mode MALDI-MS spectrum of **1**. The spectrum exhibited only one peak in wide mass range and the mass number agrees well with the calculated value for $[Au_{25}(4\text{-PyET})_{18}]^-$. Based on these experimental results, I concluded that cluster **1** was

Figure 3. UV-vis spectrum of **1**.

Figure 4. Negative-ion mode MALDI-MS spectrum of **1**. Inset shows magnified view of the peak and the calculated isotope patterns (blue bars).

identified as $[Au_{25}(4\text{-PyET})_{18}]^{-}$.

3.3.2. Assembly experiment of 1

3.3.2.1. Preliminary results

The outer most shell of **1** is covered by pyridyl groups to which metal ions can be coordinated. Here, I tested 5 metals ions, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pd^{2+}, and Ag^{+}. Those metal ions form precipitates with **1** almost quantitatively. Figure 5 shows the diffuse reflectance UV-vis-NIR spectra of the precipitates. In Figures 5a and 5c, the spectrum shapes were almost retained. In Figure 5b, the peak at 450 nm was not prominent and the band at 680 nm was broadened. In Figures 5d and 5e, the spectral profiles changed dramatically. Substitution reactions of $Au_{25}(SR)_{18}$ with some hetero ions have been reported.[17, 18] Those studies demonstrated that the hetero-atom such as Cd^{2+} and Hg^{2+} can be doped into $Au_{25}(SR)_{18}$ by mixing.[17, 18] Based on these reports, the spectra of the product of reactions of **1** and metal ions can be explained as follows. In the case of Ni^{2+}

Figure 5. Diffuse reflectance UV-vis-NIR spectra of the precipitates of **1** with (a) Ni^{2+}, (b) Cu^{2+}, (c) Zn^{2+}, (d) Pd^{2+}, and (e) Ag^{+}.

and Zn^{2+}, the ions were not incorporated into the Au_{13} core of **1**, but were coordinated by pyridyl nitrogen atoms. In contrast, in the case of Cu^{2+}, Pd^{2+}, and Ag^{+}, the ions partially reacted with **1** and the remained ions were coordinated by the ligands.

3.3.2.2. Precipitations with Ni^{2+} and Zn^{2+}

The precipitate formed by the mixing with Ni^{2+} or Zn^{2+} and **1** were further investigated. Hereafter, the precipitates were abbreviated as **1**-Ni and **1**-Zn. Figure 6 shows Au-L_3 edge EXAFS spectra of **1**, **1**-Ni, and **1**-Zn. The patterns are similar each other. This result clearly indicated that the total structure of **1** did not change in **1**-Ni and **1**-Zn as suggested by reflectance spectra (Figures 5a and 5c). Next, I performed the K-edge XANES measurement for the metal ions in order to examine the coordination environment. Figure 7 shows the Ni-K edge XANES spectra of **1**-Ni and reference samples $[Ni(en)_3](NO_3)_2$ and NiO. The overall spectrum shape is similar to that of $[Ni(en)_3]^{2+}$ in which Ni^{2+} is coordinated by six nitrogens in octahedral symmetry. However, the white line shape is similar to that of NiO in which Ni^{2+} is coordinated by six oxygens in octahedral symmetry. These results suggested that the Ni in **1**-Ni is coordinated by both N and O atoms. Furthermore, a pre-edge peak observed at ~8328

Figure 6. Au-L_3 edge EXAFS spectra of **1** (black), **1**-Ni (red), and **1**-Zn (blue).

Figure 7. Ni-K edge XANES spectra of **1**-Ni (red), $[Ni(en)_3](NO_3)_2$ (green; NiN6), and NiO (blue; NiO6). The spectra of NiN6 (N-coordinated octahedron) and NiO6 (O-coordinated octahedron) are shown for comparison.

Figure 8. Zn-K edge XANES spectra of **1**-Zn (red), $[Zn(en)_3](NO_3)_2$ (green; ZnN6), $Zn(NO_3)_2 \cdot 6H_2O$ (blue; ZnO6), and $Zn(pyridine)_2(NCS)_2$ (orange; ZnN4). The spectra of ZnN6 (N-coordinated octahedron), ZnO6 (O-coordinated octahedron), and ZnN4 (N-coordinated tetrahedron) are for comparison.

eV indicates that the Ni has hole at 3d energy level and that the oxidation sate of Ni is +2. The same analysis was conducted for **1**-Zn. Figure 8 shows Zn-K edge XANES spectra of **1**-Zn and reference samples $[Zn(en)_3](NO_3)_2$, $Zn(NO_3)_2 \cdot 6H_2O$, and $Zn(pyridine)_2(NCS)_2$. The shape of the spectrum of **1**-Zn was complicated. The shape at higher energy region was similar to those of $[Zn(en)_3](NO_3)_2$ and $Zn(NO_3)_2 \cdot 6H_2O$ in which Zn^{2+} is coordinated by N or O atoms in octahedral symmetry, respectively. In contrast, the shape at near white line region appears to be superposition of $[Zn(en)_3](NO_3)_2$ and $Zn(pyridine)_2(NCS)_2$ in which Zn^{2+} is coordinated by N in octahedral and tetrahedral symmetry, respectively. These comparisons suggested that the local structure around Zn ions is occupied by water and pyridyl nitrogen atoms, randomly.

XAFS analysis of **1**-Ni and **1**-Zn indicated that the Ni and Zn ions were coordinated randomly by pyridyl nitrogens of precursor Au_{25} cluster and waters. This suggests that the Au_{25} clusters do not form ordered structures. In order to confirm this, I measured PXRD patterns of those samples. Figure 9 shows PXRD patterns of **1**-Ni and **1**-Zn.

Figure 9. PXRD patterns of (a) **1**-Ni and (b) **1**-Zn.

Characteristic peaks of icosahedral Au cluster were observed at $2\theta \sim 40^{\circ}$ indicating that the Au_{25} clusters retained their structures as suggested by the Au-L_3 edge EXAFS. In addition, I observed only one broad peak at low 2θ region due to superlattice reflections. Based on these X-ray structural studies, I concluded that the **1**-Ni and **1**-Zn formed disordered assemblies by the coordination between **1** and metal ions. Quality of crystallinity could not be improved by changing temperature and concentration of the solution for the assembly.

Figure 10. (a) TEM image of a film of **1** and Zn^{2+}. Fourier transformations of the (a) top left, (b) top right, (c) bottom left, and (d) bottom right regions in (a).

I also studied the local arrangement of the clusters in the assembly by TEM observation. Figure 10 shows TEM image of an assembled monolayer of **1** and Zn^{2+} and its Fourier transformation images. It is clearly seen from Figure 10a that the Au_{25} clusters form highly-dense monolayer film. They are located at similar distances, but are in random directions. Fourier transformation images in Figures 10b–e showed only halo rings, indicating that there is no symmetrical structure even in short distance.

On the basis of the assembly experiments of **1**, I propose that two parameters of the constituent clusters must be controlled to improve the crystallinity of superatomic assembly; (1) the number and symmetry of coordination sites and (2) charge state. As

shown in Figure 2, **1** has 18 thiolates. The amorphous assembly is formed probably because all these ligands are involved randomly for the cluster linkage. Therefore, the number of linking sites should be limited to small numbers and should be located at symmetry. As is evident from Figure 3, **1** has negative charge. Thus, kinetics of coordination of metal cations to the surface ligands will be affected by electrostatic interaction due to the net charge of the clusters. The presence of large counter ion also affects sterical packing of the clusters. Assembling process will be controlled better by using neutral clusters as building units.

3.3.3. Synthesis of Au cluster suitable for ordered assembly

Figure 11. A photograph of the crystals of **2** under polarized light.

As discussed in Chapter 2, neutral Au superatom whose surface is functionalized can be synthesized in the absence of counter ions. Thus, the problems discussed above will be overcome by this approach. In this work, I focused on diphosphine-protected icosahedral Au_{13} cluster.[19] Cluster **2** was synthesized by a modified procedure described in Chapter 2. The Au(TPP)(SPy) complex was mixed with dppe to exchange the ligands *in situ*. And then the Au ion was reduced by $NaBH_4$. After the purification steps, I obtained a single crystal of **2** (Figure 11). Figure 12 shows the X-ray structure of **2** and Table 2 summarizes the crystal data obtained from SCXRD experiment. The existence of the cluster determined from SCXRD was confirmed by MALDI-MS measurement (Figure 13). The structure of **2** was composed of icosahedral Au_{13} unit and 4-mercaptopyridine molecules. The mercaptopyridine ligands are arranged in X-shaped geometry. This geometry is useful to build up a

Table 2. Crystal data of **2**.

Formula	$C_{124}H_{112}Au_{13}N_4P_8S_4$
FW (g mol^{-1})	4594.73
Crystal color and habit	Red plate
Crystal size (mm)	0.11 × 0.11 × 0.08
Crystal system	Monoclinic
Space group	*P*-1
a (Å)	15.862(2)
b (Å)	19.834(3)
c (Å)	24.667(3)
α (º)	98.754(2)
β (º)	96.0033(13)
γ (º)	109.864(2)
V (Å^3)	7110.9(16)
Z	2
T (K)	100(2)
Completeness to theta = 27.515º	99.5 %
ρ_{calc} (g cm^{-3})	2.146
μ (mm^{-1})	13.542
Max. and min. transmission	0.203 and 0.337
F(000)	4190
θ range (º)	1.832–25.242
Index ranges	$-20 \leq h \leq 20$, $-26 \leq k \leq 26$, $-32 \leq l \leq 32$
Collected reflections	123374
Independent reflections	33785 (R_{int} = 0.0669)
Data/restrains/parameters	33785/1516/914
Goodness-of-fit on F^2	1.087
Final $R^{a,b}$ indices [$I > 2\sigma(I)$]	R_1 = 0.0584, wR_2 = 0.1430
Final $R^{a,b}$ indices [all data]	R_1 = 0.0687, wR_2 = 0.1514
$(\Delta\rho)_{max,min}$ (e Å^{-3})	4.831, -3.226

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$, where $p = [\max(F_o^2, 0) + 2F_c^2]/3$.

two-dimensional ordered structure. $Au_{13}(dppe)_4(SPy)_4$ can be viewed as a counter part of the known cluster, $[Au_{13}(diphosphine)_4Cl_4]^+$ whose geometric structure was not determined.[19, 20] At this moment, the net charge of **2** cannot be determined unambiguously because of some residual electron density in XRD data.

Figure 12. X-ray structure of **2**. Yellow, blue, green gray, and light green balls represent the gold, phosphorus, sulfur, carbon, and nitrogen atoms, respectively. Hydrogen atoms and disordered parts are omitted for clarity. Organic parts of dppe are depicted by gray sticks.

Figure 13. Positive-ion mode MALDI-MS spectrum of **2**. Asterisk indicates the fragment species by laser irradiation (loss of one pyridyl group).

However, it is highly likely that **2** is a neutral species because the synthetic system did not contain any free cations and anions.

3.4. Summary

In this chapter, I reported the result of the attempts to construct an ordered assembly of protected Au superatoms. First, I synthesized $[Au_{25}(4\text{-PyET})_{18}]^{-}$ bearing pyridyl groups on the outer most shell for the first time. I tried to synthesize an assembly by the coordination with metal ions such as Ni^{2+} and Zn^{2+}. Although the assembly was obtained, the Au_{25} clusters were assembled into amorphous structure. Based on these experiences, I designed an Au cluster suitable for controlled assembly and synthesized $Au_{13}(dppe)_4(SPy)_4$ by the synthesis method developed in Chapter 2. The cluster has highly ordered linking unit on their monolayer and the charge state is tentatively assigned to be neutral. The construction of highly ordered assembly of **2** is a future subject.

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Chapter 4.

Synthesis of one-dimensional pentamer of Au_{13} superatomic molecule

4.1. Introduction

Since Au superatoms can be viewed as a nanoscale atom equivalent, we can synthesize quasi molecule composed of the superatoms ("superatomic molecules"). The key structural parameters of those superatomic molecules are the number and the bonding scheme of the constituents. Figure 1 summarizes the selected superatomic molecules reported so far as functions of those structural parameters.[1-7] Di-superatomic molecules with various bonding schemes have been reported. Those di-superatomic molecules show different optical absorption spectra suggesting that the bonding schemes strongly affect their fundamental properties as in the case of conventional molecules. However, there are a few examples of superatomic molecules having higher nuclearity than two because the synthesis is based on try and error approach. This situation hinders understanding of evolutional behavior of superatomic molecules and a bonding theory of superatoms. Theoretical works have predicted the Au cluster having one-dimensional anisotropy exhibits photoabsorption bands at IR region and that the

Figure 1. Examples of reported superatomic molecules.[1-7]

absorption energy is dependent on their length.[1] This prediction indicates that the synthesis of one-dimensional superatomic molecule is important not only for the study of their fundamental properties, but also for the biological usage such as photo-thermal application. In order to circumvent this situation, a method to synthesize a superatomic molecule with an aimed structure is strongly required. The aim of this chapter is to develop an aimed synthesis of superatomic molecules.

In order to develop the aimed synthesis of superatomic molecules, I adopted a template-mediated method frequently used in the nanoparticle synthesis. An example can be found in the synthesis of ultra-thin Au nanowire whose diameter is ~1.7 nm.[8-10] Figure 2a shows the proposed mechanism of the synthesis of the Au nanowires. The first step is the formation of one-dimensional template in the solution. Au(I) ions self assemble into one-dimensional structure because of the aurophillic interaction between

Figure 2. (a) The reported mechanism of a synthesis of ultra-thin Au nanowires.[9] (b) A schematic of synthetic strategy and hypothesis in this work.

them. The Au ions in the template are reduced by a weak reducing reagent such as alkylsilane to achieve the template-mediated growth of Au ultrathin nanowires. Similar template-mediated method is applicable for a synthesis of thiolate protected Au clusters (Au:SR) since Au(I)–thiolate complex has a one-dimensional oligomer or polymer structure (Figure 2b). In this chapter, I report a slow reduction synthesis of one-dimensional Au superatomic molecule showing an intense NIR absorption band.

4.2. Experiment

4.2.1. Chemicals

Tetrachloroauric acid tetrahydrate ($HAuCl_4 \cdot 4H_2O$), Sodium borohydride ($NaBH_4$), acetone-d_6, ethanol (EtOH), thiourea, methanol (MeOH), acetonitrile, and 2-methyltetrahydrofuran (MeTHF), triethylamine (Et_3N), chloroform, and sodium hydroxide (NaOH) were purchased from Wako Pure Chemical Industries. 4-(2-Bromoethyl)benzoic acid, 2-(phenylethyl)amine, and 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMT-MM) were purchased from Tokyo Chemical Industry. Bulk Au powder was purchased from The Nilaco cooperation. Water of Milli-Q grade (ρ > 18 M$\Omega \cdot$cm) was used. All commercially available reagents were used as received.

4.2.2. General

Ultraviolet-visible-Near-infrared (UV-vis-NIR) spectra were measured by V-670 spectrophotometer (JASCO, Japan). Thin films for optical absorption measurements were prepared by a drop-casting method on a calcium fluoride (CaF_2) substrate (OHYO KOKEN, japan). ^{1}H (400 MHz) and ^{13}C{^{1}H} (100 MHz) NMR spectra were recorded

by ECX-400 spectrometer (JEOL, Japan) using acetone-d_6 as a solvent at 292 K. Chemical shifts of the NMR spectra were referenced to the residual peaks of the solvent (^{1}H: δ = 2.05 ppm; ^{13}C: δ = 29.84 ppm). Positive-ion mode high-resolution mass spectrum was measured by JMS-T100LP AccuTOF (JEOL, Japan) with direct analysis in real time (DART) apparatus. Negative-ion mode electrospray ionization mass spectra (ESI-MS) were measured by homemade apparatus.[11] At first, the cluster sample was dissolved in 50 % aqueous MeOH with the concentration of 2 mg/mL. To enhance the ionization efficiency, small amount of Et_3N (0.1 vol%) was added to the sample solution. The solution was directly electrosprayed at a bias voltage of -3 kV. The mass spectra were calibrated by reference to $(CsI)_nI^-$ cluster ions generated from a 50 % aqueous methanol solution of CsI. Thermogravimetric (TG) measurement was conducted by TG-DTA 7200 instrument (SII, Japan) under N_2 gas flow (50 mL/min). The sample (~2 mg) was placed in Al_2O_3 crucible. Powder X-ray diffraction (PXRD) experiments were measured by using SmartLab-3 (Rigaku, Japan) in the Bragg-Brentano configuration with CuKα radiation. The powder samples were finely ground and placed in Si low background sample holder (Rigaku, Japan). The PXRD patterns were corrected by subtracting the patterns of sample holder. The temperature dependence of UV-vis-NIR absorption spectra were measured by using HR-4000-CG-NIR or NIRQuest 256 (Ocean Optics, USA). The incident light was generated by DH-2000-BAL (Ocean Optics, USA) deuterium-halogen lump and irradiated through optical fibers. The filmed sample was placed on a copper holder, which is placed on a S030 ^{4}He cryostat (Iwatani Industrial Gases, Japan) evacuated by a Hi Cube 80 Eco turbo-molecular pump (Pfeiffer Vacuum, Germany). The temperature of the sample was controlled by a resistive heater. Fourier transformed infrared (FT-IR)

spectra was measured by FT/IR-4200 spectrophotometer (JASCO, Japan). The sample was prepared as KBr pellets for the organic molecule and as thin film on CaF_2 substrate for the cluster compounds.

4.2.3. Synthesis

4.2.3.1. 4-(2-Mercaptoethyl)benzoic acid (4-MEBA)

Scheme 1.

4.12 g of 4-(2-bromoethyl)benzoic acid (18 mmol) was added to a 30 mL aqueous solution of thiourea (1.6 g, 21 mmol). The white dispersion was refluxed for 4 h and then the clear solution was cooled to room temperature. Next, to the solution, 8 mL of 10 % (w/v) aqueous NaOH solution was added and the white dispersion was refluxed again for 1h. After the clear solution was cooled in an ice bath, 6M aqueous HCl was added dropwise to the solution with stirring until the pH value became around 2. The precipitate formed was filtered and thoroughly washed with water and dried *in vacuo*. Crystallization in EtOH gave title compound as white needles; yield 3.00 g (16.5 mmol, 91.7 %); mp 156-158 ºC; ^{1}H NMR (400 MHz, acetone-d_6): δ 11.06 (br, 1H), δ 7.98 (d, J = 8.2 Hz, 2H), δ 7.39 (d, 8.2 Hz, 2H), δ 2.99 (t, J = 7.6 Hz, 2H), δ 2.82 (q, J = 7.8 Hz, 2H), δ 1.75 (t, J = 7.8 Hz, 1H) (Figure 3a); ^{13}C{^{1}H} NMR (100 MHz, acetone-d_6): δ 167.6, δ 146.6, δ 130.6, δ 129.7, δ 129.5, δ 40.8, δ 25.9 (Figure 3b); Found (%): C

59.27; H 5.48; S 17.14. Calc. for $C_9H_{10}O_2S_1$ (%): C 59.32; H 5.53; S 17.59. No nitrogen was found; HRMS (DART, positive, *m/z*): 183.04873 ($[M+H]^+$, +4.11 ppm).

Figure 3. (a) ^{1}H and (b) ^{13}C NMR spectra of 4-MEBA. Asterisks indicate the residual solvent signals.

4.2.3.2. Cluster 1

Scheme 2.

To an aqueous solution of $HAuCl_4 \cdot 4H_2O$ (30.5 mL; 0.125 mmol Au), an ethanolic solution of 4-MEBA (7.13 mL; 0.5 mmol) was added at once with vigorous stirring at 293 K. The solution immediately became clear yellow to cloudy white. Soon after the addition of thiol, the pH value of the solution was adjusted to above 12 by the addition of 25 % (w/v) aqueous NaOH solution (500 μL). The solution gradually became transparent. After 1 h stirring, aqueous $NaBH_4$ solution (10 mL; 0.375 mmol), which was prepared by dissolving $NaBH_4$ powder in cold water just before the addition, was added to the solution in one portion. The color of the solution stared to change to yellowish brown gradually. After keeping the stirring and the temperature for 96 h, the solution was divided into two 50 mL centrifuge tubes and 25 mL of EtOH was added to each tubes. Then, the tubes were centrifuged at 3500 rpm for 30 minutes and the supernatants were decanted. The pellets were suspended in 25 mL EtOH and centrifuged at 3500 rpm for 30 minutes and the supernatants were discarded. This washing process was repeated at least two times. Finally, the pellets were dried *in vacuo*. The obtained crude product was around 25 mg for one batch. The products from eight individual synthetic batches were combined and the mixture was purified by gel filtration on a Superdex 200pg column (16 mm i.d. × 600 mm) equilibrated by 20 %

aqueous EtOH containing 30 mM Tris·HCl (pH 8.8). The sample was dissolved in water (20 mg/mL) and the solution was filtered by membrane filter with 0.2 μm pore diameter. 1.8 mL of filtrate (~1.5 % CV) was injected to the column with elution speed of 0.5 mL/min. The first greenish band (K_{av} ~ 0.32) was collected and dried by evaporating the solvent *in vacuo*. The dried sample was washed with MeOH to remove organic salts and the residue was dried again *in vacuo*. Finally, cluster **1** was obtained as a black powder. The typical yield was 4~5 mg (1~2 % based on Au).

4.2.3.3. Cluster 2

Scheme 3.

A crude product of Au:4-MEBA cluster (200~220 mg) prepared by the same procedure as mentioned above was dissolve in water (50 mL) and filtered. To the black filtrate, 40 mL of MeTHF was added under vigorous stirring and then 2-(phenylethyl)amine (300 μL) and DMT-MM (900 mg) were successively added at room temperature. On addition of the DMT-MM, the color of the MeTHF layer started to change to black. After about 12 h, 100 mL of $CHCl_3$ was added to the reaction mixture and the mixture was quietly stirred for additional 1 h. The mixture was transferred to a separatory funnel and the organic layer was separated. The organic layer was washed successively with 1 M aqueous HCl (3 × 25 mL) and water (3 × 25 mL).

After removing the organic solvent by rotary evaporator, the black residue was washed three times with MeOH by centrifugation and the crude product was dried *in vacuo*. The crude product was purified by fractional precipitation. Firstly, the crude product was dissolved in $CHCl_3$ (~50 mg/mL) and the solution was centrifuged at 2300 rpm for 30 min. Secondly, the precipitate was removed and then CH_3CN was added to the supernatant with the final solvent ratio to 1:1 ($CHCl_3$:CH_3CN; v/v). The mixture was centrifuged again and the supernatant was discarded. Thirdly, the pellet was dissolved again in 2 mL of $CHCl_3$ and the solution was centrifuged. 1 mL of CH_3CN was added to the supernatant and the mixture was centrifuged. Finally, the black pellet was dried *in vacuo*. The typical yield was ~5 mg (~2 % based on Au).

4.2.4. High-Energy XRD (HEXRD) experiment

HEXRD experiment was conducted at beamline BL04B2 of the SPring-8 facility with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (proposal no. 2015A1258 and 2015B1478). The incident monochromatic X-ray was obtained by a Bragg reflection of Si(200) bending mirror with the energy of 61.7 keV (λ = 0.2009 Å). The cluster **2** was dissolved in minimum amount of THF and the solution was placed in a quartz glass capillary (2 mm i.d., 0.01 mm wall thickness). The solvent was carefully evaporated to dryness and the black precipitate was used as a sample. The measurement configuration was Guinier transmission geometry and the measurement 2θ range was 1.0 ~ 49.5º using three CdTe solid state detectors. The obtained raw data was corrected for absorption, polarization, and background from capillary, and then the scattering signal of the three detectors were combined using standard analysis procedures.[12] The corrected and combined data was normalized to give the Faber-Ziman

total structure factor $S(Q = 4\pi\sin\theta/\lambda)$ before subtracting the contribution of Compton scattering.[13] The total function $T(r)$ was obtained by a Fourier transformation of $S(Q)$ in the Q range of 0.5~26.015 Å^{-1} with the below formula.

$$T(r) = 4\pi\rho r + \frac{2}{\pi}\int_{Q_{min}}^{Q_{max}} Q[S(Q) - 1]sin(Qr)dQ \qquad (1)$$

4.2.5. Simulation of the PXRD patterns

The powder XRD pattern was simulated by using the Debye formula as shown below,[14-17]

$$I(s) = \sum_{i}\sum_{j\neq i}\frac{(1+\alpha cos^2 2\theta)}{(4sin^2\theta cos\theta)}exp(-\frac{Bs^2}{2})f_i f_j\frac{sin(2\pi s d_{ij})}{2\pi s d_{ij}} + atomic\ scattering \quad (2)$$

where $s = 2\sin\theta/\lambda$ is the diffraction vector length. λ and α correspond to the wavelength of incident X-ray (0.15418 nm) and polarization factor of incident X-ray (α = 1 for the experimental setup in this work). B is a factor of thermal or static displacement damping and was set to be 0.01 nm^2. f is an atomic scattering factor of gold atoms and the value was calculated by the analytical approximation with given coefficients.[18] d_{ij} is the distance of two i-th and j-th atoms in the model structure.

The first term has three components: Lorentz polarization factor, t the displacement factor, and the two-body X-ray scattering interference pattern. In the simulation, the polarization factor was assumed to be unity because the total scattering patterns were not sensitive to this parameter. I also considered the effect of single atom atomic scattering for the simulation as the second term since the first term gives negative value at certain s value and the value is physically meaningless. The model structures shown later were constructed using the Au–Au bond distance of 2.88 Å for the ideal structures and given length for the reported structures.

4.3. Results and discussion

4.3.1. Synthesis

A slow reduction of Au ions is conventionally used for the synthesis of Au nanoparticles. In order to obtain a product having the cluster size regime using the slow reduction of Au-SR template, optimization of the synthetic condition is necessary. Therefore, I investigated the suitable thiol ligand at first. Since the formation of Au clusters strongly requires a fast nucleation step without subsequent growth step, the Au precursor complex is usually reduced with strong and large excess amount of reducing reagent such as $NaBH_4$. It has been reported that the reduction of Au-MBA (MBA = *p*-mercaptobenzoic acid) polymer in aqueous medium under high pH value (~13) gave 2~3 nm Au:SR particles.[19] In contrast, the same synthetic process at low pH value (~9) gave the $Au_{102}(MBA)_{44}$ cluster having 1.5 nm Au core.[20] This difference indicated that the cluster growth efficiently proceeds by the slow reduction process at the high pH value. Thus, I chose a thiol with hydrophilic carboxyl group for the synthesis. A variety of Au:SR clusters have been successfully synthesized using phenylethanethiol as protection ligands.[21] From these consideration, I have chosen 4-MEBA as a ligand for this study. 4-MEBA was synthesized for the first time according to the synthetic procedure of similar compound, 4-(mercaptomethyl)benzoic acid.[22] After the optimization of the synthesis and purification conditions, the target thiol was obtained with good yield (~90 %).

Next, I characterized the product obtained by the fast reduction of Au-4-MEBA polymer. Figure 4 shows UV-vis-NIR spectrum of a crude product obtained by the reduction of Au ions in the presence of 5 molar equivalents of 4-MEBA and 10 molar

Figure 4. UV-vis-NIR spectrum of the fast reduction product.

equivalents of $NaBH_4$ without adjusting pH value at room temperature. The color of the solution was changed immediately upon the addition of $NaBH_4$. The absorption spectrum of the product showed a featureless profile without surface plasmon band. This result suggested that the fast reduction product had a polydisperse nature and a small size less than 2 nm.

Then, I examined the slow reduction of Au-4-MEBA polymer. Firstly, I mixed the Au(III) ions and 4-MEBA in aqueous EtOH giving a white dispersion. This white dispersion indicated the reduction of Au(III) to Au(I) by 4-MEBA and the formation of Au(I)-4-MEBA polymer. Secondly, the addition of aqueous NaOH gave a clear solution indicating that the deprotonation of carboxylic group of 4-MEBA ligands occurred. Thirdly, aqueous $NaBH_4$ was added to the solution. On the contrary to the above case, the color of the solution did not change appreciably just after the addition of the solution and the color gradually changed. Figure 5 shows a time course of UV-vis-NIR absorption spectra under after the addition. Before the addition of $NaBH_4$ (t = 0 h), the spectrum showed no absorption in vis-NIR region, but a weak absorption at 350 nm.

Figure 5. A time course of UV-vis-NIR spectra under the reduction.

Two small peaks were appeared at around 700 and 800 nm after 1h. The peaks gradually disappeared and a peak at around 1000 nm appeared after 7h. The peak was prominent and kept the intensity in the period of 7 h to 12 h. After 12 h, the peak started to gradually decrease its intensity until 60 h and the absorption intensity at visible region and low energy region started to increase. The spectral profile ceased to change after 72 h and the reaction was kept for additional 24 h. The crude product after 96 h showed some humps in visible region and the absorption at NIR region showed an increasing feature towards long wavelength direction.

Figure 6. UV-vis-NIR absorption spectrum of the crude product obtained by slow reduction method as a film form.

Figure 6 shows a UV-vis-NIR absorption spectrum of the crude as a film form on CaF_2 substrate to minimize the interference of the solvent absorption. A distinct absorption peak was observed at 1350 nm. The peaked structure in NIR region was predicted for the one-dimensional superatomic polymer.[1] The discontinuous red shift of the peaks in NIR region during the reaction indicated that the stepwise cluster growth

Figure 7. Pictures of (a) SEC column and (b) collected band. (c) UV-vis-NIR absorption spectrum of the brown band.

occurred under the slow reduction condition.

I adopted size exclusion chromatography (gel filtration) for the purification of the crude product. A greenish band eluted as the first band in the chromatography and brownish band eluted after the green band (Figure 7a). In the gel filtration, the elution volume has an inverse logarithmic relationship between the hydrodynamic radius of the product. Therefore, I collected the first green band (Figure 7b) as **1** for the further analysis. The UV-vis-NIR absorption spectrum of the brown band showed featureless profile suggesting that that the product has a small size with a spherical structure (Figure 7c).

In order to examine the intrinsic optical property of the cluster, the absorption measurement in the solution phase is required without interference from the solvent. Because water has strong absorption in NIR region, the surface modification of the

Figure 8. IR spectra of 4-MEBA (top, green), Au:4-MEBA (middle, blue), and Au:4-MEBA after amidation (bottom, red).

cluster to dissolve the organic solvents such as chloroform is necessary. In addition, the ligand modification enables us to estimate the composition because the modification gives rise to mass difference from the pristine cluster. Carboxylic groups are located at the outer most shell of the cluster. After the reaction with DMT-MM, the cluster transferred to MeTHF layer indicating that the modification of the carboxylic groups was achieved. IR spectrum of the amidated crude showed almost one C=O stretching band at 1637 cm^{-1} (red curve in Figure 8). From the comparison with the C=O stretching bands of 4-MEBA and Au:4-MEBA (green and blue curves in Figure 8, respectively), I concluded that almost all the carboxylic groups of Au:4-MEBA formed amide bonds. The purification of the obtained crude was performed by fractional precipitation and cluster **2** was obtained. The identity of **1** and **2** was confirmed by PXRD and UV-vis-NIR absorption spectroscopy as shown later. Hereafter, the **1** and **2** are treated as the same cluster whose surfaces are passivated by different ligands.

4.3.2. Estimation of the composition

The composition of **1** was examined by mass spectroscopy. Figure 9 shows the negative-ion mode ESI-MS spectrum of **1**. In the spectrum, a strong set of peaks for multiply charged anions of $Au_n(4\text{-MEBA})_m$ cluster was observed in addition to weak unassigned peaks. When I consider that the peaks correspond to the deprotonation of 4-MEBA ligands, the molecular weight was calculated to be 22.9 kDa. Although the molecular weight was obtained, it is difficult to unambiguously determine the chemical composition of **1** due to the similar mass number of Au (= 197) and 4-MEBA (= 181) and the limited mass accuracy. In order to estimate the number of ligands, I conducted TG analysis of **1**. The observed weight loss of the ligands in **1** was 35.1 % (Figure 10),

thus I could reduce the number of the candidates of chemical formula of **1** (Table 1). In order to improve the estimation, I also conducted TG analysis of **2** (Figure 11). From these result, I tentatively assigned the chemical formula of **1** and **2** to be $Au_{76}(SR)_{44}$.

Figure 9. Negative-ion mode ESI-MS spectrum of **1**. The numbers shown in the spectrum correspond to a set of multiply charged anions of $[Au_n(4\text{-MEBA})_m\text{–}xH^+]^{x-}$.

Figure 10. TG chart of **1**. The first weight decrease was considered to be the evaporation of the crystalline water.

Figure 11. TG chart of **2**.

Table1. Estimation of the chemical compositions of **1** and **2**.

(n, m)[a]	Cluster **1**		Cluster **2**
	MW[b] (Da)	weight loss[c] (%)	weight loss[c] (%)
73, 47	22896	37.2	48.1
74, 46	22912	36.4	47.3
75, 45	22928	35.5	46.4
76, 44	22944	34.7	45.5
77, 43	22959	33.9	44.6
Experiment	22.9×10^3	35.1	45.3

[a] $Au_n(SR)_m$. [b] Molecular weight. [c] Calculated weight loss from the Au content.

4.3.3. Geometric structures of 1 and 2

Since the crystallization trial was not unsuccessful, I examined the geometric structures of **1** and **2** by PXRD technique. Figure 12 shows PXRD patterns of **1**, **2**, and bulk Au recorded at the same measurement configuration. **1** and **2** showed the similar patterns indicating that the geometric structures of these species are essentially same. In order to construct the structure model, I made the following assumption. Firstly, the

Figure 12. PXRD patterns of **1** (middle, red), **2** (top, green), and bulk Au (bottom, black).

Figure 13. Distributions of core Au atoms of the reported Au:SR clusters. For $Au_{25}(SR)_{18}$, $Au_{38}(SR)_{24}$, and $Au_{102}(SR)_{44}$ clusters, the values are evaluated from the SCXRD data[4, 20, 23, 24] and the value for $Au_{144}(SR)_{60}$ cluster is evaluated from the theoretical calculation.[17]

PXRD patters consist of the scattering X-ray by Au as the major contribution because Au is heavy element. Secondly, the structures of **1** and **2** are composed of the core Au cluster and surface protecting Au-SR oligomers as in the case of the conventional

Au:SR clusters.[21] The number of core Au atoms was estimated to be about 50 according to the reported Au:SR clusters (Figure 13) because the $Au_{76}(SR)_{44}$ locates between $Au_{38}(SR)_{24}$ and $Au_{102}(SR)_{44}$ clusters. Finally, the PXRD pattern of the clusters has a major contribution of the core since the number of core Au atoms is much larger than that of oligomers and the core has rigid structure. Based on these assumptions, I focused the geometric structure of the core of **1** and **2**.

In order to construct the core model, the symmetry of the atomic packing was examined in advance using icosahedral Au_{55}, decahedral Au_{49}, and cuboctahedral Au_{55} clusters as examples. Figure 14 shows the result of the simulation of PXRD patterns using Debye formula with those examples. All the simulated patterns show broad peak at s ~ 4 nm^{-1}. The most notable difference can be found in the region of s = 5~10 nm^{-1}. Cuboctahedral Au_{55} shows two humps at s ~ 7 and 8 nm^{-1}. These correspond to (220)

Figure 14. Simulate PXRD patterns of Au clusters with various symmetries. Cuboctahedral Au_{55} (top), decahedral Au_{49} (middle), and icosahedral Au_{55} (bottom). The inset figures correspond to those structures. For the Au_{49} cluster, atomic coordinates of $Au_{102}(SR)_{44}$ cluster was used for the simulation.[20]

and (311) plane reflections in bulk Au because the cuboctahedron has face-centered cubic (fcc) symmetry. In the case of decahedral Au_{49}, only one broad peak at around s = 8 nm^{-1} was observed. This clear difference enables us to distinguish the symmetry from fcc in this size region. Icosahedral Au_{55} shows a different profile from the cuboctahedron. The pattern shows a small peak at s ~ 5.5 nm^{-1} and a broad hump at s ~ 7.5 nm^{-1}. The former peak can be a hallmark of icosahedral symmetry. Icosahedral symmetry does not show two distinct humps observed in fcc symmetry. Based on these consideration, I assumed that **1** and **2** have fcc symmetry in the core because there were two distinct humps in the region of s = 6 to 8 nm^{-1}. (Figure 12)

Given that the core has fcc symmetry, the sharp peak at around s = 4.5 nm^{-1} observed in the experimental pattern was indexed to be a (200) plane reflection of fcc Au. The peak width was much narrower than the other peaks and humps indicating that the distribution of the corresponding interatomic distance is high. From these results, I concluded that the cores of **1** and **2** had an anisotropic structure towards [100] direction of fcc symmetry.

Figure 15. Structures of the building units. Cuboctahedral Au_{13} (left) and octahedral Au_{17} (right).

Figure 16. Structure models and PXRD patterns. Structure models of (a) Au_{49}, (b) Au_{52}, and (c) Au_{56} clusters. (d) Simulated PXRD patterns of Au_{49} cluster (red), Au_{52} cluster (blue), and Au_{56} cluster (orange) and experimental PXRD pattern of **1** (green).

Then, I construct the model structure of the core. I considered a cuboctahedral Au_{13} unit (Figure 15 left) and an octahedral Au_{17} unit (Figure 15 right), which has the cubooctahedral Au_{13} unit at the center, as a building unit for the comparison. Since cores of **1** and **2** have structural anisotropy towards [100] direction, the structure models can be constructed by sharing the (100) planes of the building units. Based on this

strategy, I constructed three models. The first one, Au_{49} cluster, is made from 5 cuboctahedral Au_{13} units sharing their (100) planes (Figure 16a). The second one, Au_{52} cluster, is made from 4 cuboctahedral Au_{13} units attaching on their (100) planes with 45° torsion angles (Figure 16b). The third one, Au_{56} cluster, is made from 4 octahedral Au_{17} units sharing their (100) planes (Figure 16c). Figure 16d shows the comparison of the simulated PXRD patterns for those models and experimental pattern of **1**. The simulation pattern for Au_{52} cluster differs significantly from the experimental one, whereas the patterns for Au_{49} and Au_{56} clusters show a similar profile to the

Figure 17. The expansion dependency of simulated PXRD patterns for Au_{49} cluster. The expansion direction is shown as the inset.

experimental one. This result suggests that the cores of **1** and **2** have bulk atom packing because the Au_{52} model is not the bulk fragment. When I compare the two simulation patterns of Au_{49} and Au_{56} clusters, I find that the peak at s ~ 5 nm^{-1} is prominent for Au_{49}. The two humps at s = 6~8 nm^{-1} are not so prominent for Au_{49} but is prominent for Au_{56}. These comparisons suggest that the model of Au_{49} is more plausible than Au_{56} model. The agreement of peak positions and total profile between simulation pattern of Au_{49} model and experimental pattern is improved after the expansion of the model structure by 5% along the [100] direction (Figure 17).

Although the linear pentamer of cuboctahedral Au_{13}, Au_{49} cluster, is the most considerable structure model, I also check the other structure models to avoid the accidental coincidence of the PXRD patterns. Firstly, I examined the anisotropic oligomer of icosahedral Au_{13}. Figure 18 shows the simulated patterns of a tetramer of

Figure 18. The comparison between simulated PXRD patterns for Au_{52} (top) and Au_{52} (middle) clusters and experimental pattern (bottom). Right figures show the model structures.

icosahedral Au_{13}, Au_{52} cluster, without sharing their atom and a pentamer of icosahedral Au_{13}, Au_{53} cluster, sharing their facets. In the case of icosahedral Au_{55}, a peak at s ~ 5 nm^{-1} is distinct, whereas the oligomers of icosahedral Au_{13} clusters do not show such peak. The total simulated patterns of the oligomers differ significantly from the experimental pattern.

Figure 19. The comparison between simulated PXRD patterns for Au_{43}, Au_{46}, and Au_{49} clusters (from top to bottom) and experimental pattern (bottom). Right figures show the model structures.

Secondary, I examine the oligomers of cuboctahedral Au_{13} clusters having the anisotropy towards different direction from [100]. Figure 19 shows the results of PXRD simulation for a tetramer of cuboctahedral Au_{13}, Au_{43} cluster, sharing their (111) facets, a tetramer of cuboctahedral Au_{13}, Au_{46} cluster, sharing their edges, and a tetramer of cuboctahedral Au_{13}, Au_{49} cluster, sharing their vertexes. All the simulated patterns do not show a peak at s ~ 4.5 nm^{-1}, but they show only one peak at s ~ 4 nm^{-1}.

Thirdly, I examine the other models having the anisotropy towards [100] direction.

A series of Au:SR clusters whose chemical compositions formulated by $Au_{(8n+20)}(SR)_{(4n+16)}$ (n = 1 ~ 4) have been already reported by Jin and coworkers, and $Au_{76}(SR)_{44}$ cluster suits the formulation.[25-27] Those reported clusters have fcc symmetry in the core and they have an anisotropic structure towards [100] direction except $Au_{44}(SR)_{28}$ cluster. From the construction rules of the Au_{28}, Au_{36}, and Au_{52} clusters, I can construct a tetragonal rod-shaped Au_{68} model. I also construct a fused dimer made from two tetramers of cuboctahedral Au_{13}, Au_{62} cluster, for comparison. Figure 20 shows the simulated patterns of those models. Since these are the fragments of bulk, they show similar profiles to the bulk pattern. They show similar patterns to the experimental one, however the peak at s ~ 4.5 nm^{-1} is not distinct. Based on these considerations, I concluded that the model of the Au_{49} cluster, a linear pentamer of cuboctahedral Au_{13}, is the most reliable one.

The Debye formula means that the obtained PXRD pattern is one of the Fourier

Figure 20. The comparison between simulated PXRD patterns for Au_{62} (top) and Au_{68} (middle) clusters and experimental pattern (bottom). Right figures show the model structures.

transformation of Au–Au distances locating inside the cluster. Thus, the Fourier transformation of a scattering pattern gives a distance distribution of the scatterers. In order to do this inverse process, the wide s range is required because the process of Fourier transformation is strongly affected by a length of transformation region. High energy X-ray (= short wavelength X-ray) enables us to measure the diffraction pattern for long s length because the length of a scattering vector is inversely proportional to the wavelength. To obtain the interatomic distance distribution of the $Au_{76}(SR)_{44}$ cluster, I conducted the HEXRD experiment at the SPring-8 facility. I measured a HEXRD pattern of **2** with the transmission configuration using 61.7 keV incident X-ray. The pattern obtained from HEXRD experiment was similar to that obtained from conventional PXRD measurement regardless of the measurement configuration (Figure 21). In the HEXRD pattern, humps were observed until high *Q* region in which the conventional Cu Kα experiment can not reach. The observed pattern contains the atomic scattering as a background, therefore normalizing of the observed pattern by the atomic

Figure 21. HEXRD pattern of **2** (top) and PXRD pattern of **1** (bottom).

Figure 22. The observed Faber-Ziman total structure factor $S(Q)$ of **2**.

scattering gives a structure factor originating from the atomic configuration. Figure 22 shows the experimental Faber-Ziman total structure factor $S(Q)$ of **2**. The $S(Q)$ showed a oscillation behavior centered at $S = 1$ indicating that the scattering from the atomic pairs approached to the atomic scattering factor. After a Fourier transformation of the $S(Q)$, I obtained the total correlation function $T(r)$ as a function of atomic distances. Although the $T(r)$ contains an overall bonding information including the every atom pair (Au–Au, Au–S, and S–S, etc.) inside the cluster, a distinct correlation between Au–Au pair should be prominent because Au is an electronically dense element. Figure 23 shows the experimental T(r) of **2** and Au–Au distances distribution of the elongated Au_{49} model. The sharp peaks and humps were observed in the $T(r)$ and the Au–Au distances distribution of the elongated Au_{49} model well reproduced the positions of those peaks and humps over the entire real space. In order to figure out the anisotropy of the $Au_{76}(SR)_{44}$ cluster, the precise evaluation of the structure of $T(r)$ in the long r region is necessary. In order to confirm that the humps observed in the $T(r)$ at long r are not an artifact in the Fourier transformation, I also analyzed an experimental $T(r)$ of

Figure 23. The experimental $T(r)$ of **2** (top, red) and a histogram of Au–Au distances in the expanded model of the Au_{49} (bottom, black). The right figure shows the size of the model.

$Au_{25}(SR)_{18}$ with the same analysis procedure because the structure of the cluster was already determined by SCXRD analysis.[23, 24] Figure 24 shows the $T(r)$ of $Au_{25}(SR)_{18}$ and the histogram of Au–Au distances of the cluster. The Au arrangement in $Au_{25}(SR)_{18}$ has two parts. The one is icosahedral Au_{13} core and the other is 12 Au atoms located at outer most shell, which are the part of surface protecting oligomers. In the experimental $T(r)$, there was no humps at long r region as shown in Figure 24 and the peaked structure in $T(r)$ was reproduced well by the distribution of Au–Au distances calculated from the SCXRD structure. This result clearly indicates that the humps of $T(r)$ observed at long r in **2** were not artifact. The tailed structure of $T(r)$ observed at the first intense peak in $Au_{25}(SR)_{18}$ corresponded to the correlation between Au atom at the oligomer site and Au atom at the core. The similar shoulder structure was observed in **2** also clearly indicated that the $Au_{76}(SR)_{44}$ might possess surface protecting Au–S oligomer supporting that the estimated core size was reasonable. Based on the above results and discussions for the geometric structure of **1** and **2**, I concluded that the $Au_{76}(SR)_{44}$

Figure 24. The experimental $T(r)$ of $Au_{25}(SR)_{18}$ (top, blue) and a histogram of Au–Au distances in the X-ray structure (bottom, black).[23] The right figure shows the X-ray structure and the size of the model. In the right figure, yellow and green balls represent Au and S atoms, respectively. The organic part is depicted as gray sticks.

cluster had a linear pentamer of cuboctahedral Au_{13} as its core and that the template method could work as an aimed synthetic method of Au superatomic oligomer and molecules passivated by thiolates.

4.3.4. Electronic structures of 1 and 2

The electronic structures of **1** and **2** were examined by optical absorption spectroscopy. Figure 25 shows UV-vis-NIR absorption spectra of **1** as a film form on CaF_2 substrate and a dispersion in water. Several humps were observed in the spectrum of a water dispersion indicating that the electronic structure of the cluster is quantized. An intense NIR absorption band was observed in the spectrum of a film form. The relative intensity between the NIR band and the hump at visible region was comparable. In the case of conventional Au:SR clusters having spherical structures, an absorption at

Figure 25. UV-vis-NIR absorption spectra of **1** measured at room temperature. The spectrum as a water dispersion (red) and as a film form (green).

NIR region is much weaker than that at visible region.[21, 28] This clear difference suggested that the structural anisotropy of the cluster generated the intense NIR absorption.

In the case of plasmonic nanoparticle, temperature dependence of LSPR is relatively small as pointed out by El-Sayed.[29] The small temperature dependence of the LSPR band was explained as follows. The LSPR intensity and bandwidth are related to the relaxation lifetime of the excited valence electrons. The dephasing time of the electrons is strongly affected by the electron-electron scattering rate in the case of Au nanoparticle. The scattering rate $1/\tau_{e\text{-}e}$ has a relationship between the excited energy E and Fermi energy E_F as follows.

$$\frac{1}{\tau_{e-e}} \propto (E - E_F)^2 \quad (3)$$

Because room temperature is too cold in the framework of the Fermi distribution, the dephasing rate has a small dependence when the sample is cooled to the lower

temperature. Kreibig has investigated the temperature dependence of the LSPR band of small Ag and Au nanoparticles in glass matrix at low temperature.[30-32] In that case, the resonance intensity and bandwidth became weaker and broader with increasing temperature from 1.5 K. The reason was explained by a contribution of electron–phonon scattering and thermal lattice expansion with increasing temperature. However, only small energy shift was observed. On the other hand, in the case of the quantized cluster such as $Au_{25}(SR)_{18}$ and $Au_{38}(SR)_{24}$, temperature dependences of absorption spectra are prominent.[33-34] By cooling the temperature, peaks became more clear and showed blueshift by 20~30 nm. Those responces indicate that the temperature dependence of optical absorption spectrum can be used as a tool to distinguish the nature of the transition. Figure 26 shows a temperature dependence of UV-vis-NIR spectrum of **1** as a film form. With decreasing the temperature, the absorption of humps at visible region became sharper and showed distinct blueshift. This result emphasized that the absorption of UV-vis region is due to the electronic transition between two

Figure 26. Temperature dependence of UV-vis-NIR absorption spectrum of **1** as a film form.

Figure 27. Temperature dependence of NIR absorption spectrum of **1** as a film form.

discrete states. Next, I investigated the temperature dependence of the NIR band. Figure 27 shows the temperature dependence of NIR absorption spectrum of **1** as a film form. The peak showed blueshift by 58 nm and narrowing of its full width half maximum by a factor of 86 %. This temperature dependence implied that the origin of the NIR peak is the electronic transition rather than LSPR.

In order to figure out the origin of the NIR absorption band, I examined the absolute value of the absorbance. Figure 28 shows UV-vis-NIR absorption spectrum of **2** dispersed in $CHCl_3$ to determine the molar absorption coefficient ε. The determined ε value at 1330 nm was ~2.5×10^5 M^{-1} cm^{-1}. There are two scenarios for the origin of the band. The one is simple one electron transition between two discrete states and the other is the longitudinal mode of localized surface plasmon resonance (LSPR).[10] In the latter case, the excitation is explained by the coherent oscillation of the free valence electrons by an oscillating electric field of the incident light. Therefore, I can estimate the contribution of one electron to the extinction from a LSPR active Au nanoparticle. Recently, Dass and coworkers have reported plasmonic $Au_{\sim500}(SR)_{\sim120}$ cluster and its

Figure 28. UV-vis-NIR absorption spectrum of **2** dispersed in $CHCl_3$ at room temperature. The asterisk indicates the absorption of the solvent.

extinction coefficient.[35] The number of valence electrons of the cluster is calculated to be ~380 and the extinction coefficient of 1.42×10^6 M^{-1} cm^{-1} at 498 nm. From those values, the contribution of one valence electron to the extinction coefficient is calculated to be 3.73×10^3 $atom^{-1}$. **2** has 32 valence electrons and the calculated contribution at 1330 nm is 7.8×10^3 $atom^{-1}$ and the value is the similar order to that of reported $Au_{\sim 500}(SR)_{\sim 120}$. From this analysis, I can not rule out the possibility of LSPR. The other measurements such as transient absorption spectroscopy are also required to unravel the nature of the absorption.

The quantized nature of the cluster is confirmed. Then the next consideration is the nature of the electronic transition of the NIR band. The quantized cluster often shows HOMO-LUMO band as the lowest optical excitation. So, is the NIR band HOMO-LUMO gap of the cluster? Theoretical work reported that the band gap of one-dimensional superatomic oligomer of Au:SR was low (<~ 0.1 eV) and the distinct peak in NIR region was not assigned as HOMO-LUMO gap of the cluster in the

calculation.[1] The authors pointed out the transition corresponded to "supercluster excitation". The supercluster excitation means that the number of nodes of delocalized orbital constructing from the localized superatomic orbitals on each superatomic components changes by 1. They also explained that the origin of the high intensity is due to the large induced dipole of the transition along the long axis.

In order to check the applicability of their explanation to the Au_{76} cluster, I measured a wide-range absorption spectrum of **1**. Figure 29 shows vis-NIR-IR spectrum of **1**. The peak at ~7500 cm^{-1} corresponds to the intense NIR peak 1330 nm. The spectrum shape suggested that the absorption in IR region had a contribution not only from the vibrational modes of the ligands, but also from the electronic transition of the cluster. The estimated band gap for the electronic contribution is ~950 cm^{-1} (~0.11 eV) suggesting that the band gap satisfying the theoretical prediction.

Figure 29. Vis-NIR-IR spectrum of **1** as a film form. The red line corresponds to the spectrum measured by UV-vis-NIR spectrophotometer and blue line corresponds to the spectrum measured by FT-IR spectrophotometer. The same sample was used both of the measurements.

Based on the above consideration, the NIR band does not correspond to the simple HOMO-LUMO transition of the entire molecule. The theoretical work also predicted that the intense NIR absorption corresponded to the transition of an electron confined in the core.[1] Since the *ab initio* calculation for the $Au_{76}(SR)_{44}$ cluster is not trivial, I investigated the electronic structure of the core using a primitive model, particles in a box.

In the framework of super valence bond model, the construction of superatomic oligomers Au_{49}^{17+}(32e) can be described as follows.

$$Au_{49}^{17+}(32e) = 5\times Au_{13}^{5+}(8e) - 4\times 4Au^{+} - 4\times 2e \quad (4)$$

In Au_{49}^{17+}(32e), five Au_{13}^{5+}(8e) superatoms are connected by sharing four Au atoms in (100) and two valence electrons. The HOMO of Au_{13}^{5+} is 1P superatomic orbital, therefore each two electrons shared by each superatoms can be viewed as π electrons of conventional conjugated molecules. Given that the Au_{49} is a linear pentamer of icosahedral Au_{13}, the most primitive model to explain the valence electronic state of the Au_{49} is the one-dimensional box. When I assume the infinite potential barrier at the outside of the core, the exact solution of eigenfunction (eq. 5) and eigenenergy (eq. 6) in the box are evaluated as follows,

$$\psi_n(x) = \sqrt{\frac{2}{L}} sink_n x \ (n = 1, 2, 3, \dots) \quad (5)$$

$$E = \frac{h^2}{8mL^2} n^2 \ (n = 1, 2, 3, \dots) \quad (6)$$

where *n*, *L*, *h*, and *m* correspond to quantum number, the length of the box, Planck constant, and electron mass, respectively. If I assumed that only the 8 π-like electrons take into account the electronic transition of the core, the transition energy corresponds to the difference of the eigenenergies of *n* = 4 and 5. The length of the pentamer is 2.44

nm, thus the calculated transition energy is 0.569 eV (= 2180 nm). Given that the experimental value of the NIR band is 0.932 eV, the matching between the experimental and the calculated value is not bad considering that the model used is primitive.

Figure 30. The dimension of the Au_{49} model.

Compared to the conventional atom, superatoms have large volumes. Thus, the shape of a potential well for the one-dimensional box must have a finite thickness. Then, I consider the three-dimensional box as a potential for the all valence electrons of the core. Figure 30 shows the size of the pentamer model. The aspect ratio is about 4 assuming the covalent bond radius. Schrödinger equation for the particle in three-dimensional box can be written as follows,

$$\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V_a(x)+V_b(y)+V_c(z)-E\right]\psi(x,y,z) = 0 \quad (7)$$

where $V_a(x)$, $V_b(y)$, and $V_c(z)$ correspond to the given potential along each directions. This equation can be solved by a variable separation and we can treat the equation as the problem in one-dimensional box. The resulting eigenfunctions and eigenenergies can be evaluated as follows,

$$\psi_{n_x n_y n_z}(x,y,z) = \sqrt{\frac{8}{abc}}\sin\frac{n_x\pi}{a}x\sin\frac{n_y\pi}{b}y\sin\frac{n_z\pi}{c}z \quad (8)$$

$$E = \frac{h}{8m}\left(\frac{n_x^2}{a^2}+\frac{n_y^2}{b^2}+\frac{n_z^2}{c^2}\right) \qquad (n_x, n_y, n_z = 1, 2, 3, \ldots) \quad (9)$$

where a, b, and c correspond to the length of the well in each directions. In order to

simplify the problem, I assume the lengths of the potential well as $1/4a = 1/4b = c$. Figure 32 shows the energy diagram using eq. (9). Since the z axis has a wide length, the deep energy levels are only occupied by its contributions. In the medium energy level, the contributions from the short axes appeared. Interestingly, there are three degeneracies at the HOMO level (= 32e). The one corresponds to the energy level of the high quantum number of z axis. And, the two correspond to the same quantum number with the one-dimensional box in the long axis having one node in orthogonal direction.

The LUMO have similar quantum numbers to the two states in the HOMO. This result indicates that the optical transition between HOMO and LUMO of the core shows the similar trend estimated in the one-dimensional box model since the dipole transition requires an odd parity between corresponding eigenfunctions. The corresponding energy gap is same to the one-dimensional box. Thus, the transition energy is same to the value described above.

Figure 31. Energy diagram obtained from the three-dimensional box. The indexes in the parentheses indicate the quantum numbers of the corresponding directions. The right numbers show the number of total electrons.

In order to improve the matching of energy difference, I consider a volume factor of the

actual potential. The estimated potential volume was 1.16 nm^3 for the rectangular box model whereas the Au_{49} model had ~0.83 nm^3. When I correct the overestimation, the calculated transition energy is improved to be 0.713 eV. Even though the primitive model cannot explain the experimental value quantitatively, I can say that the model succeeded in qualitatively explaining the electronic structure of the Au core. From those considerations, I concluded that the electronic state of the cluster can be elucidated by the particle in a box model and the electronic structure and the bonding nature of the superatomic molecule is similar to the conventional π bonding.

4.4. Summary

In this chapter, I investigated the aimed synthesis of superatomic molecule using template mediated method. The obtained cluster was assigned to $Au_{76}(SR)_{44}$ and the geometric structure of the cluster was examined by XRD. A linear pentamer of cubooctahedral Au_{13} superatoms, Au_{49} core model, was the most plausible model for the cluster and the one-dimensional anisotropy might be induced by the structural template. The cluster showed an intense NIR absorption band and the origin of the band was assumed to be a simple electronic transition between two discrete states.

A dimer of cubooctahedral Au_{13} superatoms sharing their (100) planes has been reported, very recently (Figure 32).[36] The Au superatom dimer, Au_{22}^{14+}, is the core of $[Au_{24}(C_2Ph)_{14}(TPP)_4]^{2+}$ (C_2Ph = phenylacetylene; TPP = triphenylphosphine) and the cluster shows an intense NIR emission.[36] The isolation and characterization of the intermediate species will reveal the evolution of the electronic structure of superatomic molecules (Figure 32). The synthesis of longer superatomic molecules such as hexamer, heptarmer, and octamer will also reveal the emergence of LSPR as already studied in

spherical clusters.[35]

Figure 32. A summary of cubooctahedral Au_{13} based Au clusters. The structure of Au_{22}^{14+} (left) has been determined.[36]

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Chapter 5.

Concluding remarks

In this thesis, I tackled three main themes to develop and deepen materials chemistry of protected Au superatoms.

In chapter 2, I developed a synthesis method to obtain protected Au superatom with open electronic structure. I successfully obtained $Au_{13}(TPP)_8(MBA)_3$ by reducing Au(I)–phosphine/thiolate complex in the absence of counter anions. SCXRD experiment revealed that the $Au_{13}(TPP)_8(MBA)_3$ cluster has an icosahedral-like Au_{11} core protected by $Au_2(MBA)_3$ motif. The formal number of valence electrons confined within the Au_{11} core was calculated to be 10 so that the electronic configuration of $Au_{13}(TPP)_8(MBA)_3$ can be described as $(1S)^2(1P)^6(1D)^2$. Theoretical calculation suggested that the $Au_{13}(TPP)_8(MBA)_3$ cluster is in the triplet spin state.

In chapter 3, I aimed to develop a method to assemble protected Au superatoms into an ordered structure. To this end, I synthesized pyridine modified $[Au_{25}(4\text{-PyET})_{18}]^-$ cluster as a building unit. The $[Au_{25}(4\text{-PyET})_{18}]^-$ cluster formed the precipitates by the coordination with certain metal ions such as Ni^{2+} and Zn^{2+}. However, the assembled structures are not crystalline-like, but amorphous-like probably because of too many binding sites on the surface of the clusters. To overcome this problem, I synthesized using the method in chapter 2 novel icosahedral Au_{13} cluster, $Au_{13}(dppe)_4(SPy)_4$, having only four binding sites symmetrically. I believe that these clusters will be assembled into a one-dimensional structure in the presence of coordinating ions.

In chapter 4, I developed an aimed synthesis method to obtain one-dimensional superaomic oligomers. I obtained a novel $Au_{76}(4\text{-MEBA})_{44}$ cluster by adopting a

template mediated and slow reduction method. I investigated the geometric structure of the cluster by various XRD techniques and elucidated that linear pentamer of cuboctahedral Au_{13} is the most plausible structural model. I examined the origin of an intense NIR absorption band of the cluster and found that the origin is the electronic transition between two discrete states localized on the anisotropic core like a conventional π-conjugated molecule.

In this thesis, I succeeded in synthesizing protected Au superatoms such as $Au_{13}(TPP)_8(MBA)_3$ and $Au_{13}(dppe)_4(SPy)_4$ with open electronic structures. However, further studies on the spin state are indispensable to establish correlations between electronic structures and magnetic properties. In addition, versatility of the method developed in chapter 2 must be tested for the synthesis of a symmetrical functionalized Au superatom with a variety of electronic structure. In this work, I used thiolate as a linker to assemble the clusters. This approach is promising because of high stability and well-developed synthesis of the thiolate protected Au superatoms. Once the assemble method of thiolate-protected metal clusters will be established, the next challenge is to use other ligands such as terminal alkyne and carbenes as linkers. These ligands will enhance the electronic interaction between superatoms and as a result new type of superatomic material will be obtained.

During the synthesis of $Au_{76}(SR)_{44}$ cluster, I optically observed the formation of transient species with life-time of > 24hs. I speculate from the peak position of their absorption spectra that these correspond to shorter intermediates of $Au_{76}(SR)_{44}$:

one-dimensional trimer or tetramer of cuboctahedral Au_{13} superatom. The isolation and characterization of these intermediates will unravel the evolutional behavior of optical properties of superatomic oligomers with the length. The identification of critical length at which one-electron transition is taken over by Localized Surface Plasmon Resonance in ultrathin Au wires is an interesting subject in the future. As described above, this work will open up new materials chemistry of protected metal superatom.

List of Publications

Publications related to the thesis

1. "Slow-reduction synthesis of a thiolate-protected one-dimensional gold cluster showing an intense near-infrared absorption", Shinjiro Takano, Seiji Yamazoe, Kiichirou Koyasu and Tatsuya Tsukuda, *J. Am. Chem. Soc.* **2015**, *137*, 7027.

Publications not related to the thesis

1. "Hierarchy of bond stiffnesses within icosahedral-based gold clusters protected by thiolates", Seiji Yamazoe, Shinjiro Takano, Wataru Kurashige, Toshihiko Yokoyama, Kiyofumi Nitta, Yuichi Negishi and Tatsuya Tsukuda, *Nat. Commun.* **2016**, *7*, 10414.
2. "Synthesis and catalytic application of Ag_{44} Clusters Supported on Mesoporous Carbon", Masaru Urushizaki, Hirokazu Kitazawa, Shinjiro Takano, Ryo Takahata, Seiji Yamazoe and Tatsuya Tsukuda, *J. Phys. Chem. C* **2015**, *119*, 27483.
3. "A critical size for Emergence of Nonbulk Electronic and Geometric Structures in Dodecanethiolate-Protected Au Clusters", Yuichi Negishi, Tafu Nakazaki, Sami Malola, Shinjiro Takano, Yoshiki Niihori, Wataru Kurashige, Seiji Yamazoe, Tatsuya Tsukuda and Hannu Häkkinen, *J. Am. Chem. Soc.* **2015**, *137*, 1206.
4. "Binding motif of terminal alkynes on gold clusters", Prasenjit Maity, Shinjiro Takano, Seiji Yamazoe, Tomonari Wakabayashi and Tatsuya Tsukuda, *J. Am. Chem. Soc.* **2013**, *135*, 9450.
5. "90-degree optical switching of output second harmonic light in chiral photomagnet", Shin-ichi Ohkoshi, Shinjiro Takano, Kenta Imoto, Marie Yoshikiyo, Asuka Namai and Hiroko Tokoro, *Nat. Photon.* **2014**, *8*, 65.
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Acknowledgements

First of all, I am deeply grateful to Prof. Dr. Tatsuya Tsukuda. He always gives me a rich research environment and many fruitful suggestions and discussions for all of this work. Without his mindful support, I could not accomplish this work at all. Also, he gives me much good influence on maturing my way of thinking, way of working, and way of life.

I would like to appreciate Prof. Dr. Hiroshi Nishihara and Prof. Dr. Shin-ichi Ohkoshi for providing me to access to their instruments.

I am thankful to Associate Prof. Dr. Kiichirou Koyasu for giving me much time to discuss about this work. He also gave me many important suggestions from the theoretical aspects and many excellent supports for vacuum experiments. I would like to greatly thank to Assistant Prof. Dr. Seiji Yamazoe for his daily support and fruitful discussions. His excellent experimental techniques provided me many important information of this work.

I wish to thank to Associate Prof. Dr. Yuichi Negishi, Dr. Yoshiki Niihori, and Assistant Prof. Dr. Wataru Kurashige (Tokyo Univ. of Science) for valuable discussions. I also wish to thank to Dr. Kiyofumi Nitta (JASRI) for his kind experimental support and advises. I am thankful to Assistant Prof. Dr. Jun-ichi Nishigaki (Tokyo Metropolitan Univ.) for giving me favorable experimental advises. I also thank to Lecturer Dr. Issey Osaka (JAIST) for his kind trial of mass spectrometric experiment.

I really thank to Ms. Yuka Sakurai for daily support. I am grateful to current group members, Dr. Hirokazu Kitazawa, Mr. Ryo Takahata, Mr. Satoru Muramatsu, Mr. Akimaro Yanagimachi, Mr. Shun Hayashi, Mr. Shota Matsuo Mr. Ryohei Tomihara, Mr. Keisuke Hirata, Mr. Ryo Ishida, Mr. Sojiro Emori, Mr. Kazuyuki Tsuruoka, Mr. Hiroki Yamada, Mr. Hiroki Yamamoto, and Mr. Toshiaki Yanase, for their kind attitudes. I am also grateful to the former members, Dr. Tomomi Watanabe, Dr. Md. Jafar Sharif, Mr. Masaru Urushizaki, Ms. Setsuka Arii, Ms. Tachamapan Yoskamtorn, Mr. Diego J. Guzman Mr., and Mr. Yuichiro Kawahara.

I wish to thank to a JSPS Research Fellowship for Young Scientists and a Spring-8 Budding Researchers Support (JASRI) for funding.

Finally, I deeply appreciate to my family for their ceaseless affection and support.

Shinjiro Takano