# Controlling Gold Nanoclusters with Atomic Precision for Catalytic Applications

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### Abstract

The major goal of this thesis is synthesis and structure determination of stable, ligand-protected, gold nanoclusters in the ~ 1 nm size regime. These structurally well-characterized clusters are then tested as catalysts in probe chemical reactions to gain an atomic-level understanding of size- and/or structure-dependent catalytic pathways.

Chapter 2 describes the synthesis and structure determination of a new mixed phosphine/thiolate-protected  $[Au_{24}(PPh_3)_{10}(SC_2H_4Ph)_5X_2]^+$  (where, X= Cl/Br) nanocluster. This cluster, which differs by a single Au atom, shows drastic differences in properties from the previously reported biicosahedral  $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5X_2]^{2+}$  nanocluster protected by the same type and number of phosphine and thiolate ligands.

Chapter 3 describes the synthesis and atomic structures of some of the smallest members of the crystallographically characterized thiolate-protected Au<sub>n</sub>(SR)<sub>m</sub> clusters, where *n* and *m* represent the number of metal atoms and thiolate ligands respectively. These ultra-small nanoclusters lie at the interface between organo-gold complexes and plasmonic gold nanoparticles, i.e. the origin of the first metallic bonds and the nucleation of clusters from organometallic precursors occur in this domain. Total structure determination of thiolate-protected small Au<sub>24</sub>, Au<sub>23</sub> and Au<sub>18</sub> clusters has revealed new types of Au core packing structures and surface ligand binding motifs, which offer mechanistic insights into nucleation and size evolution of gold clusters.

Chapter 4 discusses the role of protecting ligands in dictating the size and structure of gold clusters. Here, the electronic and steric effects of ligands on the structure and properties of a nanocluster are illustrated, through the case study of a Au<sub>36</sub>(SR)<sub>24</sub> nanocluster. These insights are expected to offer some new standpoints in terms of structural and size control in nanoclusters, as well as the factors dictating the stability of nanoclusters.

In chapter 5, the newly synthesized Au nanoclusters mentioned above have been tested as catalysts in the model catalytic reaction involving reduction of 4-nitrophenol by NaBH<sub>4</sub>. Preliminary results suggest that the detailed atomic structures, rather than the nominal size (n) in  $Au_nL_m$  clusters, dictate their catalytic properties.

Finally, chapter 6 summarizes the major achievements of this thesis and some future directions in this field.

This thesis is dedicated to my parents: Santa & Debasish Das

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## **List of Abbreviations**

fcc	face-centered cubic
PPh <sub>3</sub>	triphenylphosphine
SR	thiolate
DFT	density functional theory
TGA	thermogravimetric analysis
DPV	differential pulse voltammogram
CV	cyclic voltammogram
SAM	self-assembled monolayer
PAGE	polyacrylamide gel electrophoresis
MALDI	matrix-assisted laser desorption ionization
ESI	electrospray ionization
MS	mass spectrometry
TOF	time-of-flight
DAD	diode array detector
$HSC_2H_4Ph$	2-phenylethanethiol
HSPh- <i>t</i> -Bu	4-tertbutylbenzenethiol
HSCH₂Ph- <i>t</i> -Bu	4-tert-butylbenzylmercaptan
p-MBA	p-mercaptobenzoic acid
TOA⁺	tetraoctylammonium ion

$CH_2CI_2$	dichloromethane
THF	tetrahydrofuran
CsOAc	cesium acetate
DCTB	trans-2-[3-(4-tert-butylphenyl)-2-methyl-2
	propenyldidene]malononitrile
SG	glutathione
TOAB	n-tetraoctylammonium bromide
HAuCl <sub>4</sub>	tetrachloroauric(III) acid
NaBH <sub>4</sub>	sodium borohydride
TBAPF <sub>6</sub>	tetrabutylammonium hexaflurophosphate
Х	halide, either CI or Br
HS-c-C <sub>6</sub> H <sub>11</sub>	cyclohexanethiol
$HS-c-C_5H_9$	cyclopentanethiol
4-NP	4-nitrophenol
4-AP	4-aminophenol
TOF	turnover frequency
SPR	surface plasmon resonance

### Chapter One

Literature Survey: Atomically Precise Ligand-Protected Gold Nanoclusters

#### 1.1 Motivation and Introduction

Catalysis, a term coined by Jöns Jakob Berzelius back in 1836, is now responsible for approximately 90% of all chemical processes and production of more than 60% of chemical products worldwide. These numbers are further expected to show a steep rise in future years to meet the current necessity to resort to environment-friendly production processes and improve their commercial viability.<sup>1</sup> While new catalysts are in great demand in modern industry, their search is largely based on trial-and-error experiments due to the non-uniform nature of conventional catalysts that preclude systematic studies on their catalytic mechanisms.

Heterogeneous catalysts employing metal particles have significantly contributed to the development of chemical technology since the early 19<sup>th</sup> century.<sup>2</sup> The particle sizes of majority of these catalytically active metal particle catalysts are found to lie in the nanometer range (i.e. ~1-100 nm in size). However, due to the lack of proper nanometer-range imaging tools in the past, information about the true nature and form of the active catalysts remained a mystery.

With the advent of nanotechnology in the mid-1980s, there have been significant advances in synthesizing uniform metal nanoparticles with fine control over their morphologies, size and chemical compositions.<sup>3-9</sup> Parallel developments in electron microscopy techniques have made it possible to map out the metal core structures of sufficiently large nanoparticles (typically  $\geq$  2 nm). However, the surface structure, which is of tremendous importance in catalysis,

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cannot be studied by electron microscopy. As a result, a precise atomic-level correlation between catalytic activity and the catalyst's surface structure is largely missing in previous research. In order to address this major limitation, it is crucial to synthesize atomically precise metal nanoparticles followed by their total structure determination (i.e., the metallic core + surface ligand binding modes). This is ultimately expected to afford atomic-level structure-activity and structure-selectivity correlations in catalytic studies.

#### 1.2 The Gold Standard: Ligand-Protected Gold Nanoclusters

The metal gold is chosen as a paradigm system for this thesis research due to its inherent chemical stability and elegant photo-physical properties. Although bulk gold metal is considered to be chemically inert, research has shown that the same is not true for the nanometer sized form of gold. In fact, the most active nano-gold catalysts have been shown to be  $\leq \sim 1-3$  nm in size and are henceforth, referred to as "nanoclusters" or simply "clusters" to distinguish them from their larger metallic nanoparticle counterparts.<sup>10,11</sup> The high catalytic activity of these smaller nanoclusters is attributed to generally two effects:<sup>12</sup>

(1) Scalable effects: A decrease in particle size results in increased surface-tovolume ratios which translate into a higher ratio of low-coordinated surface atoms and unique surface geometries. These surface atom arrangements in turn bestow upon these nanoclusters special "bonding powers" which allow for efficient breaking and making of bonds in catalytic cycles. (2) Quantum confinement effects: The ultra-small size of nanoclusters stimulates distinctive quantum confinement effects which result in discrete energy levels and single electron transitions of HOMO-LUMO type as opposed to the collective mode of electron excitation in the form of surface plasmon resonance seen in larger nanoparticles. The discrete energy level structure of these nanoclusters dictates the availability of electrons for redox processes and the interactions with the adsorbate reactant molecules in catalytic processes.

To estimate the threshold nanocluster size for exhibition of quantum effects, one might use the free-electron model which has previously been shown to effectively describe the 6s electron in bulk gold to a first order approximation. However, it is worthy to note that this model does not take into consideration the predominant surface effects (prevailing in small clusters) and contribution of ligands to the electronic structure. Hence, the obtained results would be a rough estimate as we will see later that all stable gold nanoclusters are protected by organic ligands.

According to the free electron model, if  $E_f$  is the Fermi energy and *N* is the number of gold atoms in the nanocluster, the average spacing ( $\delta$ ) of the electronic energy levels can be described as,<sup>13</sup>

$$\delta = \frac{E_f}{N}$$

Hence, we observe that the  $\delta$  increases as the number of gold atoms (or the nanocluster size) decreases. Further, for electronic energy quantization to become apparent,  $\delta$  should be comparable or larger than the thermal energy ( $k_B$ T) at room temperature (298 K), i.e. when,

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After substituting the Fermi energy of gold,  $E_f = 5.5 \text{ eV}$  (=  $8.8 \times 10^{-19} \text{ J}$ ),  $k_B = 1.3806488 \times 10^{-23} \text{ J/K}$  and T = 298 K, into the equations, the threshold number of gold atoms (*N*) comes out to be ~220. In order to relate *N* to the particle size, we first find that the net number of gold atoms in the fcc unit cell is,

$$\frac{1}{8}(8 \text{ vertices}) + \frac{1}{2}(6 \text{ face centers}) = 4$$

Since the edge length of a fcc unit cell is 0.408 nm, the number density of gold atoms is can be calculated as,

$$\frac{4}{(0.408\,nm)^3} = \sim 59\,nm^{-3}$$

Hence, the volume of a nanocluster comprising of ~220 gold atoms is found to be ~4 nm<sup>3</sup> corresponding to a particle diameter of 1.6 nm or roughly 2 nm since the free electron model provides only a rough estimation.

Thus, ~2 nm is the critical particle size at and below which quantum confinement effects will dominate and collective modes of electron excitation like surface plasmon resonance (SPR) would disappear. Also, in the  $\leq$  2 nm size regime, the nanoclusters are composed of countable number of atoms and their properties are extremely sensitive to their exact atomic composition. Hence, these ultra-small entities are best denoted as Au<sub>n</sub>L<sub>m</sub>, where *n* and *m* are the number of gold atoms and protecting ligands, respectively. In light of this fact, Chapter 1 of this thesis will primarily address only those gold nanoclusters the sizes and chemical compositions of which have been precisely determined by mass spectrometry and/or single crystal X-ray crystallography.

#### 1.2.1 Synthesis of atomically precise gold nanoclusters

The synthetic route to metal nanoclusters typically relies on reduction of a metal salt in presence of suitable protecting ligands. In order to ensure precise size control, a key task involves terminating the growth of nanoclusters through ligand passivation at an early stage before Ostwald ripening begins to yield metallic nanoparticles.

Further, an atomic level precision in the nanocluster synthesis usually occurs via a universal "size-focusing" phenomenon, which is based on the inherent stability properties of different-sized nanoclusters.<sup>14</sup> Herein, the less stable nanoclusters in the initially polydisperse ligand-passivated nanocluster sample either decompose or convert to the most stable nanocluster under the reaction conditions over a period of time. The underlying principle of this process is hence *Survival of the robustest*, similar to Darwin's law for nature- "*Survival of the fittest*". Some critical factors which help bring about size-focusing to yield atomically precise gold nanoclusters are highlighted below:

(1) Nature and concentration of protecting ligand: Stronger passivating ligands like thiols and phosphines are chosen to achieve ultra-small gold nanoclusters. In addition, a higher ratio of ligand to gold concentration is found to be essential for early termination of the growth of nanoclusters into larger nanoparticles.

(2) Reaction temperature: The temperature at which reduction of Au(III) to Au(I) occurs dictates the structure of Au(I)-ligand complexes and hence, the structure and composition of the final nanocluster product. In addition, higher

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reaction temperatures ( $\geq$  80°C) can expedite "size-focusing" of nanoclusters, whereby, monodisperse clusters are obtained with very high purity.<sup>14</sup>

(3) **Reaction solvent:** The polarity of the reaction solvent plays a major role in dictating the size and structure of nanoclusters. For example, polar solvents like methanol are found to precipitate out nanoclusters protected by organic-soluble ligands, thereby limiting their growth.<sup>15</sup>

(4) **Reducing agent:** The nature and concentration of the reducing agent used affects the kinetics of the Au(I) to Au(0) reaction, thereby influencing the formation of final nanocluster products.<sup>16</sup>

#### 1.2.2 Origin of stability in gold nanoclusters

In previous gas phase cluster research, discrete sizes of clusters were observed to exhibit particular stability, which are sometimes called *magic sizes*.<sup>17-</sup><sup>19</sup> The same was observed in solution phase gold nanoclusters protected by ligands. Regarding this, two views are prevalent in literature;

(a) Geometric shell closing: Special geometric metallic core arrangements (e.g, icosahedron and cuboctahedron-based) and associated surface structures are believed to confer special stability to the whole nanocluster structure.

(b) Electronic shell closing: Those gold nanoclusters with the number of Au 6s free electrons satisfying electron-shell closing (i.e.,  $1S^21P^61D^{10}2S^2...$ ) exhibit peculiarly high stability just like the atoms of noble gas elements (i.e.,  $1s^22s^2p^6...$ ) in the Periodic Table. Hence, such gold nanoclusters are often referred to as 'superatoms'.

# 1.2.3 Early work on gold nanoclusters: phosphine-protected gold nanoclusters

In early work on gold nanoclusters, researchers advocated the use of phosphines as protecting ligands. Stronger Au-P interactions compared to previously used ligands like citrates for larger gold nanoparticles allowed the isolation of the phosphine-protected gold nanoclusters in the solid form which could then be redispersed in appropriate solvents.

The first examples of such Au:PPh<sub>3</sub> nanoclusters can be traced back to the mid-1960s through reports published by Malatesta and coworkers.<sup>20</sup> For example, McPartlin et al. reported an 11-gold atom containing Au<sub>11</sub>(PPh<sub>3</sub>)<sub>7</sub>(SCN)<sub>3</sub> cluster in 1969.<sup>21</sup> Following this report, Mingos et al. predicted the centered icosahedral Au<sub>13</sub> clusters<sup>22</sup> and later successfully synthesized and experimentally determined this structure in 1981.<sup>23</sup> Later. Teo et al. synthesized comparatively larger bimetallic Au-Ag  $[Au_{13}Ag_{12}(PR_3)_{10}Br_8]^+$ , clusters including [Au<sub>18</sub>Ag<sub>19</sub>(PR<sub>3</sub>)<sub>12</sub>Br<sub>11</sub>]<sup>2+</sup>, [Au<sub>18</sub>Ag<sub>20</sub>(PR<sub>3</sub>)<sub>14</sub>Cl<sub>12</sub>]<sup>2+</sup> and eventually an even larger allgold containing [Au<sub>39</sub>(PPh<sub>3</sub>)<sub>14</sub>Cl<sub>6</sub>]Cl<sub>2</sub> cluster.<sup>24-26</sup> Meanwhile, the hitherto largest Au-phosphine cluster, formulated as Au<sub>55</sub>(PPh<sub>3</sub>)<sub>12</sub>Cl<sub>6</sub> was reported by Schmid et al. which has since garnered much interest but its crystal structure has not been solved till date.27

#### 1.2.3.1 Crystal structures of phosphine-protected gold nanoclusters

The atomic structures of most gold:phosphine nanoclusters are commonly based on a centered icosahedral Au<sub>13</sub> metal core (Figure 1.1.a), which is capped



**Figure 1.1.** (a) Icosahedral  $Au_{13}$  and (b) Incomplete icosahedral  $Au_{11}$  cores of  $Au:PPh_3$  nanoclusters

by a sheath of phosphines and a smaller number of ligands like halides, cyanides, thioisocyanides. Of note, the smaller  $Au_{11}(PPh_3)_7(SCN)_3$  cluster is based on an incomplete centered  $Au_{11}$  icosahedron, which is obtained by replacing a three-Au atom facet of a centered  $Au_{13}$  icosahedron with a single Au atom (Figure 1.1.b).<sup>21</sup> These packing structures are in stark contrast to gold nanoparticles  $\geq ~2$  nm which like bulk gold, adopt a face-centered cubic (*fcc*) structure. This is because with decreasing nanoparticle size, the *fcc* structure often collapses and the ultra-small nanoparticle adopts its lowest energy structure by transforming into a centered icosahedron. It is worthy to note that by doing so, the coordination number of the central Au atom becomes 12 just like

the Au atoms in *fcc* structures.<sup>12</sup> With regard to the pattern of growth of the nanoclusters containing >13 Au atoms, there are two possible routes:

(1) The Au<sub>13</sub> icosahedron serves as a basic building block, which undergoes further growth by sharing a common Au vertex with other Au<sub>13</sub> units to form polyicosahedral supraclusters. The latter are hence often referred to as "clusters of clusters". Examples of such entities include the biicosahedral and triicosahedral structures found in phosphine-protected Au-Ag bimetallic nanoclusters reported by Teo et al.<sup>25</sup>

(2) As opposed to fusion growth, a layer-by-layer cluster growth is possible where a second atomic layer of 42 gold atoms is added to the  $Au_{13}$  icosahedral core, yielding a  $Au_{55}$  cluster. The  $Au_{55}(PPh_3)_{12}Cl_6$  cluster is believed to adopt this structure, but it is yet to be confirmed experimentally.<sup>28</sup>

#### 1.2.3.2 Limitations of phosphine-protected gold nanoclusters

Phosphine-protected gold nanoclusters suffer from stability issues. For example, their solutions have a tendency to undergo photo-degradation under ambient conditions and thus, are of limited value in practical applications like industrial catalysis. In addition, it is difficult to analyze their chemical compositions by common characterization techniques like mass spectrometry. For example, the exact composition of phosphine-protected Au<sub>55</sub> cluster is still under debate even after three decades of discovery.

To combat these issues, researchers decided to use thiols as alternate protecting ligands, inspired by the discovery of strong gold-thiol interactions in

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self-assembled monolayers (SAM) of thiols on bulk gold surfaces during late 1980s. Hence in order to increase the stability of gold nanoclusters, two viable strategies are: (1) incorporation of thiols along with phosphines in the gold nanocluster structure and, (2) replacing phosphine ligands completely with thiols.

#### 1.2.4 Mixed phosphine/thiolate-protected gold nanoclusters

The primary difference between phosphines and thiolates as ligands is that while phosphines prefer to bind to the top sites of gold atoms, thiolates typically tend to bridge two gold atoms. This fact is reflected explicitly in a mixed phosphine/thiolate-protected  $[Au_{25}(PPh_3)_{10}(SC_2H_5)_5Cl_2]^{2+}$  nanocluster reported by Shichibu et al. in 2007, which was synthesized by reacting phosphine-protected  $Au_{11}$  clusters with excess ethanethiol.<sup>29</sup> The gold core of this cluster can be viewed as being composed of two centered icosahedral  $Au_{13}$  units joined by



**Figure 1.2.** Total structure of  $[Au_{25}(PPh_3)_{10}(SR)_5Cl_2]^{2+}$  nanocluster; -R groups of ligands are not shown for clarity. Color codes: Au, magenta; S, yellow; P, orange; Cl, green. (Adapted with permission from ref. 31. Copyright 2011 American Chemical Society.)

sharing a common vertex gold atom. With regard to the protecting ligands, 10 PPh<sub>3</sub> ligands bind to the peripheral gold atoms of the two Au<sub>13</sub> units; 5 ethanethiolate ligands bridge the gold atoms of the two middle Au<sub>5</sub> pentagons while two halides coordinate to the two apical gold atoms. The structure of this vertex-sharing gold nanocluster is related to the previously reported all-phosphine protected bimetallic  $[Au_{13}Ag_{12}(PR_3)_{10}Br_7]^{2+}$  cluster and can be said to belong to the category of "clusters of clusters".<sup>25</sup>

Subsequently, Jin and co-workers used a different thiol (HSC<sub>2</sub>H<sub>4</sub>Ph) to convert polydisperse 1-3.5 nm Au:phosphine nanoparticles (as opposed to Au<sub>11</sub>:phosphine clusters) into monodisperse  $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]^{2+}$  clusters and solved the crystal structure.<sup>30,31</sup> The Au core framework of the cluster turned out to be identical to the  $-SCH_2CH_3$  counterpart reported by Shichibu et al. earlier. Interestingly, the authors found some orange colored crystals in addition to those of the darker  $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]^{2+}$  cluster in their crystallization trials. These were then determined to be that of a small  $[Au_2(PPh_3)_2(SC_2H_4Ph)]^+$  complex.

#### 1.2.4.1 Mechanism of formation of [Au<sub>25</sub>(PPh<sub>3</sub>)<sub>10</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>5</sub>Cl<sub>2</sub>]<sup>2+</sup>

The finding of a  $[Au_2(PPh_3)_2(SC_2H_4Ph)]^+$  by-product in the  $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]^{2+}$  nanocluster sample offered important mechanistic insights into the conversion of polydisperse Au:PPh<sub>3</sub> nanoparticles into monodisperse Au<sub>25</sub> clusters. The proposed mechanism involves etching of the initial polydisperse nanoparticles capped by phosphines and/or chlorides by

thiols due to strong Au-thiol interactions. This thiol etching of surface Au atoms releasing  $[Au_2(PPh_3)_2(SC_2H_4Ph)]^+$ . The nanoparticle surface, hence left partially bare would further undergo thiol etching until its size becomes smaller and smaller, and finally the structure would size-focus to the thermodynamically stable  $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]^{2+}$  nanocluster.<sup>31</sup>



**Figure 1.3.** Proposed mechanism for the formation of  $[Au_2(PPh_3)_2(SC_2H_4Ph)]^+$  complex and  $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]^{2+}$  from size-mixed Au:PPh<sub>3</sub> nanoparticles. (Reproduced with permission from ref. 31. Copyright 2011 American Chemical Society.)

#### 1.2.5 Thiolate-protected gold nanoclusters

An early solution-phase synthetic route for thiolate-protected gold nanoparticles was reported by Brust et al in 1994.<sup>32</sup> Here, the major reaction steps involved, (a) phase transfer of a Au(III) salt to organic phase followed by (b) its reduction to Au(I) polymers by reacting with thiolate ligands and finally, (c)

reducing Au(I)-polymers further to Au(0) nanoparticles by using a strong reducing agent like NaBH<sub>4</sub>. By modifying these basic steps, Whetten and coworkers successfully isolated a series of stable Au-thiolate nanoclusters through solubility-based size fractionations. The core masses of these clusters were determined to be ~ 8, ~14, ~22 and ~29 kDa by laser desorption ionization (LDI) mass spectrometry.<sup>33</sup> However, monodispersity at an atomic level was not achieved.

In an effort to prepare a series of monodisperse nanoclusters, in 2005 Negishi et al. used a high-resolution PAGE separation to successfully achieve the isolation of well-defined clusters from size-mixed  $Au_n(SG)_m$  (where, SG= glutathionate) clusters.<sup>34</sup> Using electrospray ionization (ESI) mass spectrometric analysis, they assigned the obtained clusters to well-defined chemical formulae



**Figure 1.4.** Isolation and identification of atom-precise Au:SG clusters through PAGE separation of  $Au_n(SG)_m$  cluster mixture followed by ESI-MS analyses (Reprinted with permission from ref. 34. Copyright 2005 American Chemical Society.)

of Au<sub>15</sub>(SG)<sub>13</sub>, Au<sub>18</sub>(SG)<sub>14</sub>, Au<sub>22</sub>(SG)<sub>16</sub>, Au<sub>22</sub>(SG)<sub>17</sub>, Au<sub>25</sub>(SG)<sub>18</sub>, Au<sub>29</sub>(SG)<sub>20</sub>, Au<sub>33</sub>(SG)<sub>22</sub>, and Au<sub>39</sub>(SG)<sub>24</sub>. Jin and coworkers later developed a kinetically controlled one-step method for synthesizing Au<sub>25</sub>(SR)<sub>18</sub> clusters with high purity, eliminating the need for nontrivial separation techniques.<sup>16</sup> Subsequently, the "size-focusing" technique was discovered which in conjunction with ESI mass spectrometry, led to the discovery of a host of Au-thiolate clusters including Au<sub>19</sub>(SR)<sub>13</sub>,<sup>35</sup> Au<sub>20</sub>(SR)<sub>16</sub>,<sup>36</sup> Au<sub>24</sub>(SR)<sub>20</sub>,<sup>37</sup> Au<sub>36</sub>(SR)<sub>24</sub>,<sup>38</sup> Au<sub>38</sub>(SR)<sub>24</sub>,<sup>39</sup> Au<sub>40</sub>(SR)<sub>24</sub>,<sup>40</sup> Au<sub>55</sub>(SR)<sub>31</sub>,<sup>41</sup> Au<sub>102</sub>(SR)<sub>44</sub><sup>42</sup> and Au<sub>144</sub>(SR)<sub>60</sub>.<sup>43</sup> In addition, single crystal X-ray crystallography has unraveled the atom packing structures of some of these nanoclusters. In the following section, we highlight the structures and properties of some of the Au clusters which have been characterized fully by ESI-MS and Single crystal X-ray diffraction.

#### 1.2.5.1 The case of Au<sub>102</sub>(SR)<sub>44</sub> nanoclusters

The first X-ray crystal structure of a Au-thiolate nanocluster was that of a  $Au_{102}(p-MBA)_{44}$  (where, *p*-MBA represents *p*-mercaptobenzoic acid) cluster which was reported by Kornberg and coworkers in 2007.<sup>44</sup> The structure was found to be a core-shell structure containing a  $Au_{79}$  core (highlighted in magenta in Figure 1.5) and a shell of  $Au_{23}(p-MBA)_{44}$ . Of note, the Au atoms in the latter shell carrying partial positive charges  $\delta^+$  have been colored light blue in order to distinguish them from the e<sup>-</sup> rich Au core atoms. The  $Au_{79}$  core can be viewed as being composed of a  $Au_{49}$  Marks decahedral kernel face-capped by a pair of  $Au_{15}$  rhombicosidodecahedral fragments. The  $Au_{23}(p-MBA)_{44}$  shell, on the other

hand, is arranged in the form of 19 RS-Au-SR monomeric and 2 RS-Au-SR-Au-SR dimeric ligand bonding modes commonly referred to as 'staple motifs'. The latter finding shattered the prevalent point of view based on early research on SAMs that the –SR group was directly attached to a close-packed gold core in nanoparticles. In addition,  $Au_{102}(p-MBA)_{44}$  cluster was found to be chiral, due to the arrangement of equatorial gold atoms and the associated surface thiolates.



**Figure 1.5.** Total structure of  $Au_{102}(p-MBA)_4$ ; color codes: Au, magenta or light blue; S, yellow; -R groups of ligands are omitted for clarity. (Adapted with permission from ref. 44. Copyright 2007 AAAS.)

#### 1.2.5.2 The case of Au<sub>25</sub>(SR)<sub>18</sub> nanoclusters

The second successful example of a X-ray crystal structure in the field was that of a  $[Au_{25}(SC_2H_4Ph)_{18}]^-$  cluster reported by Jin and Murray groups independently.<sup>45,46</sup> The structure of this cluster can be viewed as being

composed of a  $Au_{13}$  centered-icosahedron core which is covered by a  $Au_{12}$  shell arranged in the form of six dimeric staple motifs. Subsequently, Zhu et al.



**Figure 1.6.** Total structure of  $[Au_{25}(SC_2H_4Ph)_{18}]^{-}$  cluster; color codes: Au, magenta or light blue; S, yellow; -R groups of ligands are omitted for clarity. (Adapted with permission from ref. 45. Copyright 2008 American Chemical Society.)

determined the structure of the charge neutral  $[Au_{25}(SC_2H_4Ph)_{18}]^0$  cluster which was revealed to have the same structural arrangement of gold and thiolate ligands as the anionic form.<sup>47</sup> Here, it is interesting to note that the 12 surface atoms in the staple motifs of both anionic and neutral  $Au_{25}(SC_2H_4Ph)_{18}$  clusters cap only 12  $Au_3$  faces of the icosahedral  $Au_{13}$  core, leaving 8  $Au_3$  faces uncapped, which are free to serve as binding sites in applications like catalysis.

#### (a) Electronic structure and optical properties

With respect to the electronic structure of  $Au_{25}(SC_2H_4Ph)_{18}$  cluster, DFT calculations on a model  $Au_{25}(SH)_{18}$  cluster show that the HOMO and the lowest three LUMOs are mainly composed of *6sp* orbitals of gold, which comprise the

quantized *sp* band consisting of discrete energy levels.<sup>45</sup> The HOMO-1 to HOMO-5 orbitals are mainly contributed by the  $5d^{10}$  atomic orbitals of gold and hence form the *d* band (Figure 1.7.a). The HOMO is found to be triply degenerate, corresponding to a set of superatomic *P* orbitals delocalized over the Au<sub>13</sub> core



**Figure 1.7.** (a) Kohn-Sham orbital level diagram; (b) Peak assignment for the UV-visible spectrum of  $[Au_{25}(SC_2H_4Ph)_{18}]^-$  cluster. (Adapted with permission from ref. 45. Copyright 2008 American Chemical Society.)

while the LUMO (doubly degenerate) and LUMO+1 (triply degenerate) correspond to the split superatomic *D* orbital.

Further, the simulated optical spectrum of the model Au<sub>25</sub> cluster was found to be in good agreement with the experimentally determined one. As shown in Figure 1.7.b, the absorption spectrum of  $[Au_{25}(SC_2H_4Ph)_{18}]^-$  cluster shows prominent bands at 670 nm, 450 nm and 400 nm. All of these bands are found to arise from single-electron transitions. For example, the band at 670 nm
arises from a HOMO-LUMO transition, which is essentially an intraband (*sp-sp*) transition. The band at 450 nm, on the other hand, comes from mixed intraband (*sp-sp*) and interband (*d-sp*) transitions while the band at 400 nm corresponds to an interband (*d-sp*) transition.

## (b) Photoluminescence properties

Ramakrishna and coworkers have reported the ultrafast relaxation dynamics of the  $Au_{25}(SR)_{18}$  cluster, where two emission bands at ~500 and 700 nm were observed.<sup>48</sup> The 500 nm emission band was attributed to electron hole



**Figure 1.8.** Cartoon depicting relaxation pathways in  $Au_{25}(SR)_{18}$  cluster involving the Au core states as well as surface staple motif states (Adapted with permission from ref. 48. Copyright 2010 American Chemical Society.)

recombination within the icosahedral  $Au_{13}$  core, while the 700 nm band was assigned to recombination of holes in the ground core state and electron decay from the core excited state to the surface dimeric staple motifs. In other words, while the shorter wavelength emission at 500 nm has almost no influence from protecting ligands on the surface, the 700 nm emission band could be governed by the chemical nature of the protecting thiolates. Wu et al demonstrated the latter assumption by demonstrating photoluminescence enhancement at 700 nm in  $Au_{25}(SR)_{18}$  clusters through the use of a series of electron-rich thiolates (i.e. containing O, N atoms).<sup>49</sup>

## 1.2.5.3 The case of Au<sub>38</sub>(SR)<sub>24</sub> nanoclusters

After the initial identification of the  $Au_{38}(SR)_{24}$  nanoclusters through ESI-MS by Tsukuda et al. in 2008,<sup>50</sup> Qian et al. reported a large-scale synthetic



**Figure 1.9.** Total structure of  $Au_{38}(SC_2H_4Ph)_{24}$  cluster; color codes: Au, magenta or light blue; S, yellow; -R groups of ligands are omitted for clarity. (Adapted with permission from ref. 39. Copyright 2010 American Chemical Society.)

route<sup>51</sup> and subsequently solved the crystal structure of the Au<sub>38</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>24</sub> cluster.<sup>39</sup> The total structure of this cluster can be viewed as being composed of a bi-icosahedral Au<sub>23</sub> core formed by sharing a common Au<sub>3</sub> face of two icosahedra Au<sub>13</sub> units (Figure 1.9). The remaining Au<sub>15</sub>(SR)<sub>24</sub> part makes up the shell in the form of three Au(SR)<sub>2</sub> monomeric staples (RS-Au-SR) and six Au<sub>2</sub>(SR)<sub>3</sub> dimeric staples (i.e., RS-Au-S(R)-Au-SR). The structure is reminiscent of previous vertex-sharing "clusters of clusters" supraclusters seen in phosphine-and mixed phosphine/thiol protected clusters (described earlier in Sections 1.2.3. and 1.2.4).<sup>25</sup> However, face-sharing structure based on bi-icosahedral structure was observed for the first time in the Au<sub>38</sub>(SR)<sub>24</sub> structure. In addition, the cluster was shown to be chiral, stemming from the dual-propeller-like rotating arrangement of its six dimeric staples.

#### 1.2.5.4 The case of Au<sub>36</sub>(SR)<sub>24</sub> nanoclusters

Using molecularly pure Au<sub>38</sub>(SR)<sub>24</sub> nanoclusters as precursors, Zeng et al. reported the synthesis of a new Au<sub>36</sub>(SR)<sub>24</sub> cluster through complete thiol-to-thiol ligand exchange with a bulky aromatic thiol ligand of 4-tertbutylbenzenethiol (henceforth, abbreviated as TBBT).<sup>38</sup> The crystal structure of Au<sub>36</sub>(SR)<sub>24</sub> cluster was found to be drastically different from the parent Au<sub>38</sub>(SR)<sub>24</sub> cluster. While the Au<sub>38</sub> structure was based on a face-sharing bi-icosahedral Au<sub>23</sub> core, the new Au<sub>36</sub> cluster was found to exhibit a truncated tetrahedral face-centered-cubic (*fcc*) Au<sub>28</sub> kernel. The latter is protected by two pairs of Au<sub>2</sub>(SR)<sub>3</sub> dimeric staple motifs

and 12 simple bridging thiolate ligands. In addition, the  $Au_{36}$  structure is found to be achiral unlike the  $Au_{38}$  precursor structure.



**Figure 1.10.** Total structure of Au<sub>36</sub>(TBBT)<sub>24</sub> cluster; color codes: Au, magenta or light blue; S, yellow; -R groups of ligands are omitted for clarity. (Adapted with permission from ref. 38. Copyright 2012 John Wiley and Sons.)

The finding of a *fcc* Au core in the Au<sub>36</sub>(SR)<sub>24</sub> cluster shattered the previously accepted general trend in atom packing structures, starting from icosahedral (e.g., Au<sub>25</sub>(SR)<sub>18</sub> and Au<sub>38</sub>(SR)<sub>24</sub>) to decahedral (e.g., Au<sub>102</sub>(SR)<sub>44</sub>) to *fcc* structure in plasmonic nanoparticles and bulk gold. Further in order to understand the ligand-induced size and structure transformation of Au<sub>38</sub> to Au<sub>36</sub>, Zeng et al. carried out time-dependent mass spectrometry and optical spectroscopy analyses.<sup>52</sup> Based on these results, the TBBT ligand-induced reaction pathway was found to consist primarily of four stages: (1) ligand exchange, (2) structure distortion, (3) disproportionation, and (4) size-focusing (Figure 1.11). Although a detailed map of Au<sub>36</sub> structure formation was revealed,

a major question remained as to whether it was the conjugation effect of the aromatic TBBT ligand or its bulkiness which initiated the structure and size change from Au<sub>38</sub> to Au<sub>36</sub>.



**Figure 1.11.** Reaction pathway for ligand-induced size and structure transformation of  $Au_{38}$  to  $Au_{36.}$  (Reproduced with permission from ref. 52 Copyright 2013 American Chemical Society.)

# 1.3 Thesis Overview

This thesis focuses on the synthesis and structure determination of a family of stable ligand-protected gold nanoclusters containing  $\leq$  25 Au atoms. These clusters are then tested as catalysts in probe reactions to attain an atomic-level understanding of catalytic mechanisms.

Chapter 2 describes the synthesis and structure determination of a new mixed phosphine/thiolate-protected  $[Au_{24}(PPh_3)_{10}(SC_2H_4Ph)_5X_2]^+$  (where, X=

Cl/Br) nanocluster. Single crystal X-ray crystallography revealed its structure to be composed of two incomplete (i.e., one vertex missing) icosahedral  $Au_{12}$  units joined by five thiolate linkages. This cluster shows interesting differences from the previously reported biicosahedral  $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5X_2]^{2+}$  nanocluster protected by the same type and number of phosphine and thiolate ligands.

Chapter 3 describes the synthesis and atomic structures of a series of thiolate-protected gold nanoclusters, all of which are smaller than the previously reported  $Au_{25}(SR)_{18}$  nanocluster. The discovery of new types of Au cores and surface ligand binding motifs in the new thiolate-protected  $Au_{24}$ ,  $Au_{23}$  and  $Au_{18}$  clusters offer clues regarding stability of Au clusters at the smaller end.

Chapter 4 discusses the role of protecting ligands in dictating the size and structure of gold clusters. Here, the electronic and steric effects of ligands on the structure and properties of a nanocluster are illustrated, through the case study of a  $Au_{36}(SR)_{24}$  nanocluster.

In Chapter 5, the newly synthesized Au nanoclusters are tested as catalysts in probe reactions. Preliminary results suggest that the detailed atomic structures, rather than the nominal size (n) in Au<sub>n</sub>L<sub>m</sub> clusters, dictate its catalytic properties.

Finally, Chapter 6 summarizes the major achievements of this thesis and some future directions in this field.

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# **Chapter Two**

Single Au Atom Manipulation in Mixed Phosphine/Thiolate-Protected Gold Nanoclusters: The Case of  $[Au_{24}(PPh_3)_{10}(SR)_5X_2]^+$ 

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DFT calculations were carried out by Prof. Nobusada.

# 2.1 Introduction

To achieve a fundamental understanding of quantum size effects in nanoclusters and their size evolution, unraveling the atom packing structures of metal nanoclusters is of critical importance. Over the past few years, the total structures of a number of thiolate-protected gold nanoclusters with sizes larger than 15 gold atoms have been reported.<sup>1-5</sup>

However with respect to mixed phosphine/thiolate gold nanoclusters, reports have been scarce. Apart from a small  $Au_{11}(PPh_3)_7(SR)_3$  cluster,<sup>6</sup> the only other example has been a  $[Au_{25}(PPh_3)_{10}(SR)_5Cl_2]^{2+}$  cluster discovered by Schichibu et al. in 2007.<sup>7</sup> This biicosahedral cluster was synthesized from phosphine-protected  $Au_{11}$  cluster precursors through thiol etching. Subsequently, Jin and coworkers demonstrated the conversion of polydisperse 1-3.5 nm Au:phosphine nanoparticles into the same  $[Au_{25}(PPh_3)_{10}(SR)_5Cl_2]^{2+}$  cluster, indicating its enhanced stability under the 'size-focusing' thiol-etching conditions.<sup>8,9</sup> The  $[Au_{25}(PPh_3)_{10}(SR)_5Cl_2]^{2+}$  cluster has a total of 16 formal valence electrons, i.e.,

$$25(Au 6s) - 5(thiolates) - 2(chloride) - 2(charge) = 16e \quad (eq. 2.1)$$

This *16e* count can be considered as a dimer of two *8e* units. Hence, the  $[Au_{25}(PPh_3)_{10}(SR)_5Cl_2]^{2+}$  cluster exhibits electron shell closing. Of note, PPh<sub>3</sub> does not localize Au (*6s*) electrons and is therefore not counted. More recently, Lee and coworkers have studied the electrochemical properties of the  $[Au_{25}(PPh_3)_{10}(SR)_5Cl_2]^{2+}$  clusters capped with various thiolate ligands and found

them to be quite different from the electrochemical behavior of the all-thiolate protected  $Au_{25}(SR)_{18}$  clusters.<sup>10</sup>

In this chapter, we report a new  $[Au_{24}(PPh_3)_{10}(SR)_5X_2]^+$  cluster (where X = Cl/Br) which is just one atom smaller than the previous  $[Au_{25}(PPh_3)_{10}(SR)_5Cl_2]^{2+}$  cluster. Although, this new cluster is capped by the same number and type of protecting ligands, its structural features and properties are distinctly different from those of the Au<sub>25</sub>. In other words, a single Au atom dislodgement from the  $[Au_{25}(PPh_3)_{10}(SR)_5Cl_2]^{2+}$  cluster induces significant differences in the optical, electronic and electrochemical properties.

# 2.2 Experimental

#### 2.2.1 Chemicals

Tetrachloroauric(III) acid (HAuCl<sub>4</sub>·3H<sub>2</sub>O, 99.99%, Sigma Aldrich), 2-Phenylethanethiol (PhC<sub>2</sub>H<sub>4</sub>SH, 99%, Sigma Aldrich), Triphenylphosphine (PPh<sub>3</sub>, 98%, Acros Organics), Tetraoctylammonium Bromide (TOAB, 99%, Fluka), Sodium borohydride (NaBH<sub>4</sub>, 99.99%, Sigma Aldrich), Tetrabutylammonium hexaflurophosphate (TBAPF6, 98%, Fluka), Toluene (HPLC grade, 99.9%, Sigma Aldrich), Ethanol (HPLC grade, Sigma Aldrich), Methanol (HPLC grade, 99%, Aldrich), Dichloromethane (HPLC grade, 99.9%, Aldrich) and Hexane (HPLC grade, 99%, Sigma Aldrich) were used as received.

# 2.2.2 Synthesis of the [Au<sub>24</sub>(PPh<sub>3</sub>)<sub>10</sub>(SR)<sub>5</sub>X<sub>2</sub>]<sup>+</sup> cluster

HAuCl<sub>4</sub>·3H<sub>2</sub>O (0.090 g, 0.228 mmol) was first dissolved in 5 mL water, then added to 10 mL toluene solution of tetraoctylammonium bromide (TOAB, a phase transfer agent, 0.145 g, 0.265 mmol). The two-phase solution was vigorously stirred for 15 min to effect phase transfer of gold salt from aqueous to toluene phase. The aqueous layer was then removed, and PPh<sub>3</sub> (0.180 g, 0.686 mmol) was added under vigorous stirring. The solution turned cloudy white immediately. A freshly prepared ethanolic solution of NaBH<sub>4</sub> (0.026 g, 0.684 mmol, 5 mL) was rapidly added to the whitish suspension to reduce Au<sup>I</sup>(PPh<sub>3</sub>)X (X=CI or Br) to clusters. After 2-16 h (this reaction time is not critical), toluene was rotavaporated and the reddish brown product was extracted with dichloromethane. Excess Phenylethylthiol (200 µL) was added to this solution and then heated to 313 K The reaction was allowed to proceed at 313 K for ~ 4-6 h, during which the optical spectrum of the crude product exhibited features of  $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5X_2]^{2+}$  (Figure 2.5.b). Then, to the crude product solution (without any processing), excess  $PPh_3$  (~1.20 g, powders) was added. The reaction was continued for extra 24 h at 313K. Finally, the obtained product was washed with hexane: dichloromethane (15:1) and extracted with toluene. The as- $[Au_{24}(PPh_3)_{10}(SC_2H_4Ph)_5X_2]^+$ obtained clusters were determined to be (counterion = X, where X is CI and/or Br).

Alternatively, the Au<sub>24</sub> clusters can be obtained by reacting pure  $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5X_2]^{2+}$  clusters (~5 mg) with excess PPh<sub>3</sub> (200 mg) dissolved in dichloromethane (500 µL) at 313 K. Single crystal growth of the Au<sub>24</sub>

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clusters was achieved by vapor diffusion of hexane into a concentrated solution of the cluster in toluene (5-10 mg in 1 mL toluene).

#### 2.2.3 Characterization

Electrospray ionization mass spectrograms (ESI-MS) were collected on a Waters Q-TOF mass spectrometer equipped with a Z-spray source. UV-vis spectra of clusters in  $CH_2Cl_2$  were recorded on Hewlett- Packard (HP) 8453 diode array spectrophotometer. Fluorescence spectra were recorded on a Fluorolog-3 spectrofluorometer (HORIBA Jobin Yvon); excitation: 500 nm/slit width 5 nm (from a Xe arc source). Cyclic voltammograms (CV) of  $Au_{24}$  nanoclusters were collected on a CHI 620C electrochemical station at room temperature under N<sub>2</sub> atmosphere. A platinum wire (the counter electrode), platinum working electrode, and Ag/Ag<sup>+</sup> quasi-reference electrode were used in the analysis.  $Au_{24}$  cluster solution (~15 mg) was prepared in ~6 mL electrolyte solution (0.1 mol/L TBAPF<sub>6</sub> in anhydrous  $CH_2Cl_2$ ). The solution was bubbled with dry N<sub>2</sub> and blanketed under N<sub>2</sub> throughout the electrochemical measurements to minimize O<sub>2</sub> and moisture interference.

## 2.3 Results and Discussion

## 2.3.1 Synthesis of [Au<sub>24</sub>(PPh<sub>3</sub>)<sub>10</sub>(SR)<sub>5</sub>X<sub>2</sub>]<sup>+</sup> cluster

The synthesis of  $[Au_{24}(PPh_3)_{10}(SR)_5X_2]^+$  cluster started with a Au(III) salt HAuCl<sub>4</sub>·3H<sub>2</sub>O which was first dissolved in water followed by phase transfer to toluene with the aid of tetraoctylammonium bromide (TOAB). Then, PPh<sub>3</sub> was

added to convert Au(III) to Au(I), followed by further reduction by NaBH<sub>4</sub>. After 16 h, toluene was rotavaporated and the reddish brown product was extracted with



**Scheme 2.1.** Synthetic scheme for the  $[Au_{24}(PPh_3)_{10}(SR)_5X_2]^+$  cluster

dichloromethane. Phenylethylthiol was then added to this solution and then reacted at 313 K for ~4 h, after which excess PPh<sub>3</sub> was added and the reaction continued for ~24 h, after which monodisperse  $[Au_{24}(PPh_3)_{10}(SR)_5X_2]^+$  cluster (counterion (X) = halide ions) was obtained. The first stage of the  $Au_{24}$  synthesis is similar to that of Au<sub>25</sub> which prompted us to test if pure Au<sub>25</sub> could be used as a synthesizing precursor for Au<sub>24</sub>. When we reacted pure  $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5X_2]^{2+}$  clusters with excess PPh<sub>3</sub> dissolved in dichloromethane at 313 K, we obtained the same  $[Au_{24}(PPh_3)_{10}(SR)_5X_2]^+$  cluster. Hence, the addition of excess excess PPh<sub>3</sub> in the final step is critical for obtaining Au<sub>24</sub> nanoclusters.

### 2.3.2 Total structure of [Au<sub>24</sub>(PPh<sub>3</sub>)<sub>10</sub>(SR)<sub>5</sub>X<sub>2</sub>]<sup>+</sup> (counterion: X=halide) cluster

Single crystals of the  $[Au_{24}(PPh_3)_{10}(SC_2H_4Ph)_5X_2]^+$  cluster were grown by vapor diffusion of hexane into a toluene solution of the nanocluster. As shown in Figure 2.1, the rod-like core framework of  $[Au_{24}(PPh_3)_{10}(SC_2H_4Ph)_5X_2]^+$ comprises a  $Au_{24}$  metal core which may be viewed as two incomplete (i.e. onevertex missing) icosahedral  $Au_{12}$  units joined together in an eclipsed fashion through five thiolate linkages. The diameter of the rod is 0.5 nm (Au atomic



**Figure 2.1.** The  $Au_{24}P_{10}S_5X_2$  core framework (left) and the two incomplete icosahedrons bridged by five thiolates (right). (Color labels: Au, magenta; S, yellow; P, orange; Cl, green; Br, brown)

center-to-center distance) or 0.8 nm (edge-to-edge distance), and the length of the rod is 1.1 nm (Au center-to-center) or 1.4 nm (edge-to-edge), where the diameter of Au atom is taken to be ~0.3 nm. The Au-S bond length is 2.375 $\pm$ 0.004 Å. The top and bottom Au<sub>5</sub> pentagons (Figure 2.1, atomic planes *a* and *d*) are coordinated to ten PPh<sub>3</sub> ligands (Au-P bond length: 2.293 $\pm$ 0.007Å).

The two apex gold atoms (Figure 2.1, labeled 1 and 4) are coordinated by halides (X = Br or Cl); both halide sites show partial occupancy of Cl and Br, resulting in three combinations, Br<sub>2</sub>, Br/Cl and Cl<sub>2</sub> (confirmed by mass spectrometry, *vide infra*), and the average Au-X bond length is 2.454 Å. The remaining two uncoordinated gold atoms are located in the centers of the two incomplete icosahedrons (Figure 2.1, labeled 2 and 3). Overall, the Au<sub>24</sub> core adopts a quasi- $D_{5h}$  symmetry. The total structure of [Au<sub>24</sub>(PPh<sub>3</sub>)<sub>10</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>5</sub>X<sub>2</sub>]<sup>+</sup> is shown in Figure 2.2.



**Figure 2.2.** Total structure of  $[Au_{24}(PPh_3)_{10}(SC_2H_4Ph)_5X_2]^+$  (Color labels: Au, magenta; S, yellow; P, orange; Cl, green; Br, brown, C, grey; H are omitted for clarity).

Compared to the previously reported  $[Au_{25}(PPh_3)_{10}(SR)_5Cl_2]^{2+}$  (R=C<sub>2</sub>H<sub>5</sub> or C<sub>2</sub>H<sub>4</sub>Ph) cluster—which exhibits a *vertex-sharing* biicosahedral structure,<sup>7-9</sup> the intriguing feature of  $[Au_{24}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]^+$  lies in that the central Au atom (i.e. the shared vertex atom in biicosahedral Au<sub>25</sub>) is missing. The dislodgement

of this central Au atom results in much stronger interactions between the two Au<sub>12</sub> incomplete icosahedrons in Au<sub>24</sub>, manifested in the significantly shorter Au<sub>5</sub>-Au<sub>5</sub> interplane distance (Figure 2.1, planes *b* and *c*): 2.925±0.011 Å in Au<sub>24</sub> versus  $3.053\pm0.035$ Å in Au<sub>25</sub>. The 0.13 Å difference (-4.2% relative to Au<sub>25</sub>) is

Table 2.1. Comparison of Au-Au distances in  $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5X_2]^+$  and  $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]^{2+}$ 

Au-Au distances	Au <sub>24</sub> , Å	Au <sub>25</sub> , Å	Difference
Au <sub>(1)</sub> to pentagon a	2.990±0.013	2.920±0.030	+2.4%
within plane a	2.925±0.010	2.929±0.030	-0.1%
$Au_{(2)}$ to pentagon <i>a</i>	2.728±0.011	2.755±0.034	-1%
Au <sub>(2)</sub> to pentagon b	2.761±0.008	2.801±0.024	-1.4%
between a and b	2.923±0.072	2.931±0.021	-0.3%
within plane b	2.802±0.007	2.903±0.022	<b>-3.5%</b>
between <i>b</i> and <i>c</i>	2.925±0.011	3.053±0.035	<b>-4.2%</b>
within plane <i>c</i>	2.802±0.013	2.886±0.012	<b>-3%</b>
between <i>c</i> and <i>d</i>	2.922±0.056	2.894±0.030	+0.9%
Au <sub>(3)</sub> to pentagon c	2.756±0.004	2.801±0.026	-1.6%
$Au_{(3)}$ to pentagon d	2.721±0.008	2.744±0.022	-0.8%
within plane d	2.915±0.011	2.953±0.027	-1.3%
$Au_{(4)}$ to pentagon d	2.976±0.026	2.983±0.040	-0.2%

quite significant. Moreover, the Au-Au distances within planes *b* and *c* are also shorter (–3.5% and –3%, respectively) than the corresponding values in  $Au_{25}$  (Table 2.1). The other Au-Au distances in  $Au_{24}$  are less affected when compared with  $Au_{25}$ . Overall, the observed shrinking at the "waist" of the cluster due to one-

atom loss is quite distinct and may induce significant perturbation to the electronic structure and optical properties.

The  $Au_{24}$  nanocluster structure is interesting in that it exhibits two  $Au_{12}$ incomplete icosahedrons with two pentagonal planes joined together by five thiolate linkages. This configuration does not involve the commonly observed structural modes<sup>11</sup> such as vertex-sharing via one gold atom in the  $[Au_{25}(PPh_3)_{10}(SR)_5X_2]^{2+}$  rod<sup>7,8</sup> or edge-sharing via two atoms in the  $[Au_{20}(PPhpy_2)_{10}Cl_4]^{2+}$  rod,<sup>12</sup> or face-sharing via three atoms in the Au<sub>38</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>24</sub> rod.<sup>5</sup> The Au<sub>24</sub> core structure observed in this work is different from the "cluster of clusters" model discussed earlier by Teo et al,<sup>11</sup> according to which, sequential accretion of 13-atom icosahedral clusters (as basic building blocks) leads to larger supraclusters via vertex sharing. One may argue that the clusters reported by Teo et al involved phosphine and halide ligands without thiolate and that halide (X=CI, Br) would be different from thiolate in terms of ligation. But recent theoretical studies by Jiang et al. implies that halides as ligands behave in much the same way as thiolate.<sup>13</sup> Therefore, introducing thiolate ligands should not be the cause of the new structure of Au<sub>24</sub> and its production as opposed to Au<sub>25</sub>.



**Figure 2.3.** A different anatomy of the  $Au_{24}$  structure. Left: a non-centered  $Au_{12}$  pentagonal prism, right: capping by two roof-like  $Au_6$  units.

An alternative view of the  $Au_{24}$  structure is a *non*-centered  $Au_{12}$  bicapped pentagonal prismatic core (Figure 2.3, left) capped by two pentagonal units (Figure 2.3, right). To the best of our knowledge, this *non*-centered pentagonal prismatic structural motif is unprecedented in gold cluster structures.

# 2.3.3 Confirmation of formula and charge state of the Au<sub>24</sub> cluster

To confirm the formula and probe the charge state of the cluster, we further performed electrospray ionization (ESI) mass spectrometric analysis. Positive ion mode ESI-MS (Figure 2.4) revealed a set of prominent peaks of intact cluster ions **1**–**3** at m/z = 8196.63 (peak **1**,  $[Au_{24}(PPh_3)_{10}(SC_2H_4Ph)_5Br_2]^+$ ), 8151.76 (peak **2**,  $[Au_{24}(PPh_3)_{10}(SC_2H_4Ph)_5BrCI]^+$ ) and 8107.42 (peak **3**,

 $[Au_{24}(PPh_3)_{10}(SC_2H_4Ph)_5CI_2]^+)$ . Of note, fragmentation (i.e. loss of *one phosphine*) occurred quite severely in ESI process, with fragment peaks **1**'-**3**'



**Figure 2.4.** ESI-MS spectrum of  $[Au_{24}(PPh_3)_{10}(SC_2H_4Ph)_5X_2]^+$  (positive mode). 1-3 corresponding to intact cluster ions (z = +1) with X=Br, Br/Cl (0.5/0.5), and Cl, respectively; 1'-3' corresponding to one-PPh<sub>3</sub> lost cluster ions (z = +1) with X=Br, Br/Cl (0.5/0.5), and Cl, respectively.

observed at m/z = 7934.57 (peak 1',  $[Au_{24}(PPh_3)_9(SC_2H_4Ph)_5Br_2]^+$ ), 7889.41 (peak 2',  $[Au_{24}(PPh_3)_9(SC_2H_4Ph)_5BrCl]^+$ ) and 7844.71 (peak 3',  $[Au_{24}(PPh_3)_9(SC_2H_4Ph)_5Cl_2]^+$ ), respectively. The loss of phosphine in ESI-MS was also observed in  $[Au_{20}(PPhpy_2)_{10}Cl_4]^{2+}$  as reported recently.<sup>12</sup>

#### 2.3.4 Electronic structure and optical properties of the Au<sub>24</sub> cluster

Besides the X-ray crystal structural features, the difference between Au<sub>24</sub> and Au<sub>25</sub> nanoclusters (both capped by the same type and number of ligands) also lies optical properties. The UV-Vis in the spectrum of  $[Au_{24}(PPh_3)_{10}(SC_2H_4Ph)_5X_2]^+$  in dichloromethane (Figure 2.5a) shows prominent bands ~383 ~560 at nm and nm (broad). In contrast. [Au<sub>25</sub>(PPh<sub>3</sub>)<sub>10</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>5</sub>Cl<sub>2</sub>]<sup>2+</sup> nanoclusters<sup>8,9</sup> show absorption bands at ~415 and 670 nm (Figure 2.5b, similar to the  $SC_2H_5$  counterpart<sup>7</sup>). Density functional theory (DFT) calculations on the Au<sub>25</sub> nanocluster by Nobusada et al.<sup>14</sup> revealed that the 670 nm band was the HOMO-LUMO transition in the Au<sub>25</sub> cluster and is caused by the interactions between the two complete icosahedral Au<sub>13</sub> units. The observed differences in optical spectra between Au<sub>24</sub> and Au<sub>25</sub> nanoclusters indicate the distinct effects of a single gold atom on the cluster's electronic structure and optical properties.

To gain insight into the geometric and electronic structure of  $[Au_{24}(PPh_3)_{10}(SC_2H_4Ph)_5X_2]^+$ , we performed density functional theory (DFT) calculations. In the calculations, the cluster was mimicked by a model system of  $[Au_{24}(PH_3)_{10}(SCH_3)_5Cl_2]^+$ . Such a simplification of the ligands has frequently been used in previous calculations to reduce the computational demand and appears to be reasonable. The DFT results are in good agreement with the experimental observations of the geometric structure and optical absorption spectrum. The optimized geometric structure of the Au<sub>24</sub> core cluster slightly expands (< ~ 2.5)

%) in comparison with the determined crystal structure, while the  $Au_{12} - Au_{12}$  distance is more prolonged (~ 5.5 %) than the experimental structure.



**Figure 2.5.** (a) Experimental optical spectrum of  $[Au_{24}(PPh_3)_{10}(SC_2H_4Ph)_5X_2]^+$  (in dichloromethane), (b) Experimental optical spectrum of  $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5X_2]^{2+}$  (in dichloromethane), (c) DFT simulated optical spectrum of  $[Au_{24}(P(CH_3)_3)_{10}(SCH_3)_5X_2]^+$  model cluster, and (d) The LUMO+2 molecular orbital of  $[Au_{24}(P(CH_3)_3)_{10}(SCH_3)_5X_2]^+$ .

The computed absorption spectrum, which is convoluted by the Lorentz function with appropriate width, is shown in Fig. 2.5c. The peak positions and spectral pattern are reasonably reproduced by DFT calculations. The simulated, lowest-energy peak is at 510 nm, which corresponds to the experimentally observed broad band at ~560 nm; the ~0.2 eV discrepancy is in large part due to

the limitation of accuracy of DFT calculations.<sup>15</sup> This absorption peak arises from the HOMO-1 to LUMO+2 electronic transition. The LUMO+2 is a localized molecular orbital and mainly distributes around the  $Au_{12}$ – $Au_{12}$  junction (Fig 2.5d). Thus, this electronic transition of  $Au_{24}$  has a character similar to the  $Au_{25}$  cluster's HOMO to LUMO transition<sup>14</sup> (i.e. the lowest-energy peak at ~670 nm, see Fig 2.5b) in the sense that both are caused by interactions between the two units:  $Au_{12}$ – $Au_{12}$  in the  $Au_{24}$  cluster and  $Au_{13}$ – $Au_{13}$  in the  $Au_{25}$  cluster.

For other optical features of  $Au_{24}$ , the calculated peak at ~440 nm (Fig 2.5c) is well assigned to the experimental 415 nm shoulder (Fig 2.5a), and the simulated ~380 nm peak to the experimental 383 nm band; both spectral features are primarily due to the electronic transitions related to the localized electronic structures of the individual  $Au_{12}$  unit.

## 2.3.5 Photoluminescence properties of the Au<sub>24</sub> cluster

With respect to the photoluminescence (PL) properties of the phosphine/thiolate-capped  $Au_{24}$  cluster, it exhibits a weak PL band centered at ~818 nm and the excitation spectrum for this PL band resembles the absorption spectrum. The 818 nm emission of  $Au_{24}$  is comparable to that of  $Au_{25}$  clusters<sup>10</sup> and may involve surface states.



**Figure 2.6.** (a) Photoluminescence spectrum of  $[Au_{24}(PPh_3)_{10}(SC_2H_4Ph)_5X_2]^+$  in  $CH_2CI_2$  (excit.=500 nm, slit width: 5 nm, concentration: 0.1 OD absorbance at 560 nm measured by UV-vis); (b) excitation spectrum corresponding to the 818 nm PL band.

# 2.3.6 Electrochemical properties of the Au<sub>24</sub> cluster

Since HOMO-LUMO transition was found to be forbidden in optical absorption spectrum of the Au<sub>24</sub> cluster, we performed cyclic voltammetry (CV) measurements to probe the HOMO-LUMO gap. The gap between oxidation onset (+0.3 V vs. Ag/Ag<sup>+</sup>) and reduction onset (-1.05 V vs. Ag/Ag<sup>+</sup>) is ~1.35 eV (Figure 2.7), slightly smaller than that of Au<sub>25</sub> (~1.54 eV).<sup>10</sup>



**Figure 2.7.** Cyclic voltammogram (CV) of Au<sub>24</sub> nanoclusters (scan rate: 100 mV/s, room temperature).

# 2.3.7 Proposed mechanism for formation of [Au<sub>24</sub>(PPh<sub>3</sub>)<sub>10</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>5</sub>Cl<sub>2</sub>]<sup>+</sup>

As described before in section 2.1, the robust  $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5X_2]^{2+}$  was shown to exhibit enhanced stability under excess thiol etching conditions.<sup>8,9</sup> Hence, its size-transformation to  $Au_{24}$  in presence of excess of another reactant, i.e., PPh<sub>3</sub> was a big surprise. Of note, the  $Au_{24}$  clusters have a total of 16 valence electrons and hence exhibit electron shell closing just like the  $Au_{25}$  cluster (see eq. 2.1 in section 2.1).

$$24(Au\ 6s) - 5(thiolates) - 2(halide) - 1(charge) = 16e \qquad (eq.\ 2.2)$$

However, unlike the ubiquitous biicosahedral structure of Au which has been observed previously in many phosphine-protected bimetallic clusters (e.g., Au<sub>13</sub>Ag<sub>12</sub>) and trimetallic clusters (e.g., Au<sub>12</sub>Ag<sub>12</sub>Pt, Au<sub>12</sub>Ag<sub>12</sub>Ni), the one-vertex missing biicosahedral structure has not been observed before.

With regard to this intriguing Au<sub>25</sub> to Au<sub>24</sub> transformation, we obtained the first clue in the form of colorless needle shaped crystals which appeared along with those of brown colored  $[Au_{24}(PPh_3)_{10}(SC_2H_4Ph)_5X_2]^+$  clusters during our crystallization trials for the latter (These are highlighted with red arrows in Figure 2.8).



**Figure 2.8.** Optical microscope image of single crystals of  $[Au_{24}(PPh_3)_{10}(SC_2H_4Ph)_5X_2]^+$  clusters and  $Au(PPh_3)_2Br$  complex (the latter are highlighted with red arrows).

These colorless crystals were analyzed with single crystal X-ray crystallography (Figure 2.9) and ESI mass spectrometry (Figure 2.10), both of which confirmed its identity to be a  $Au(PPh_3)_2Br$  complex.



Figure 2.9. Crystal structure of the Au(PPh<sub>3</sub>)<sub>2</sub>Br complex (color labels are same

as in Figure 2.2, H atoms are omiited for clarity)



Figure 2.10. ESI spectrum of the Au(PPh<sub>3</sub>)<sub>2</sub>Br crystals

The identification of the intermediate Au(PPh<sub>3</sub>)<sub>2</sub>Br complex in the Au<sub>24</sub> cluster product gives us important insights into the size-transformation of Au<sub>25</sub> to Au<sub>24</sub>. Excess PPh<sub>3</sub> reacts with  $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5X_2]^{2+}$  clusters, dislodging the central Au atom leading to the simultaneous formation of  $[Au_{24}(PPh_3)_{10}(SC_2H_4Ph)_5X_2]^+$  clusters and Au(PPh<sub>3</sub>)<sub>2</sub>Br complex (Scheme 2.2).

Additionally we have discovered that when polar solvents like methanol and ethanol are added to  $[Au_{24}(PPh_3)_{10}(SC_2H_4Ph)_5X_2]^+$  clusters, they convert to the Au<sub>25</sub> counterpart. This single-atom shuttling can easily be observed by monitoring their optical absorption spectra since both clusters have different UVvisible spectroscopic fingerprints. Work is currently underway to understand this phenomenon and provide additional support for the proposed mechanism of the formation of  $[Au_{24}(PPh_3)_{10}(SC_2H_4Ph)_5X_2]^+$  clusters.

**Scheme 2.2.** Proposed mechanism for formation of  $[Au_{24}(PPh_3)_{10}(SC_2H_4Ph)_5X_2]^+$  clusters and  $Au(PPh_3)_2Br$  complex



## 2.4 Conclusion

A single Au-atom dislodgement in [Au<sub>24</sub>(PPh<sub>3</sub>)<sub>10</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>5</sub>X<sub>2</sub>]<sup>+</sup> results in major differences in structural, optical, electronic and electrochemical properties when compared to the parent Au<sub>25</sub> counterpart. Hence, by synthesizing Au<sub>24</sub> and Au<sub>25</sub> clusters protected by the same types and numbers of ligands, we have provided a "proof-of-concept" that every metal atom counts in determining the properties of a nanocluster. Identification of the Au(I) complex (i.e., Au(PPh<sub>3</sub>)<sub>2</sub>Br) by-product provides mechanistic insights into the Au<sub>25</sub> to Au<sub>24</sub> size transformation.

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# **Chapter Three**

Single Au Atom Manipulation in Thiolate-Protected Gold Nanoclusters: Towards

Smaller Clusters

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# 3.1 Introduction

Atomically precise metal nanoclusters have recently emerged as an exciting class of materials in nanoscience research.<sup>1</sup> Significant progress has been made in identifying discrete sized nanoclusters protected by thiolate<sup>2-13</sup> and/or phosphine<sup>14-19</sup> and determining the unique properties.<sup>1,20-25</sup> Gold nanoclusters protected by thiolate ligands (denoted as  $Au_nL_m$ , where *n* and *m* represent the number of metal atoms and ligands, respectively) are of particular interest due to their extraordinary stability and a wide range of potential applications.<sup>26-28</sup> In fundamental research, a major question is what determines the stability of the size-discrete  $Au_nL_m$  nanoclusters. In order to elucidate this issue, it is of critical importance to solve the total structures (i.e., both the metallic core arrangement as well as the surface ligand binding modes) of nanoclusters and carry out electronic structure analysis.

Thus far, four total structures of different-sized gold nanoclusters protected by thiolates have been successfully determined, including  $[Au_{36}(SPh-t-Bu)_{24}]^{0,32}$ 0),<sup>29-31</sup>  $[Au_{25}(SCH_2CH_2Ph)_{18}]^q$ (q=-1, $[Au_{38}(SCH_2CH_2Ph)_{24}]^{0,33}$  and  $Au_{102}(SPh-p-COOH)_{44}$ .<sup>34,35</sup> Among them, some characteristic structural features have been identified. First of all, all the gold cores exhibit high symmetry, such as icosahedral Au<sub>13</sub> in Au<sub>25</sub>(SCH<sub>2</sub>CH<sub>2</sub>Ph)<sub>18</sub>,<sup>29-</sup> <sup>31</sup> face-sharing biicosahedral Au<sub>23</sub> in Au<sub>38</sub>(SCH<sub>2</sub>CH<sub>2</sub>Ph)<sub>24</sub>,<sup>33</sup> truncated tetrahedral two-shelled Au<sub>28</sub> in Au<sub>36</sub>(SPh-t-Bu)<sub>24</sub>,<sup>32</sup> and decahedral Au<sub>79</sub> in Au<sub>102</sub>(SPh-p-COOH)<sub>44</sub>.<sup>34,35</sup> On the other hand, the protecting motifs of these four nanoclusters can be categorized into three types, the dimeric staple-like motif (i.e. -SR-AuSR-Au-SR-)<sup>29-35</sup> with the *-mer* referring to the number of incorporated gold atoms, the monomeric staple motif (i.e. -SR-Au-SR-),<sup>33-35</sup> and simple bridging -SR- thiolate ligand without incorporating any gold atom.<sup>32</sup> These surface motifs can be collectively represented by Au<sub>x</sub>(SR)<sub>x+1</sub> (x=0, 1, 2). Some questions arise naturally, such as whether these staple motifs form the complete set and what other highly symmetric kernel structures would exist in nanoclusters. In order to answer some of these questions, we chose sterically hindered thiolate ligands containing rigid rings (e.g. cyclohexanethiol) or bulky tert-butyl groups (e.g., 4-*tert*-butylbenzylmercaptan, abbreviated as TBBM henceforth) as protecting ligands for making gold clusters. Our choice of these ligands stemmed from our hypothesis that bulky ligands may (i) alter the regular structures of clusters due to their rigid structures.

Herein, we have discovered new types of gold kernels in three different bulky thiolate-protected Au<sub>24</sub>, Au<sub>23</sub>, and Au<sub>18</sub> nanoclusters, all of which are smaller than the magic-sized  $[Au_{25}(SR)_{18}]^{0,-1}$  cluster. Moreover, we have experimentally identified the trimeric staple motif in cyclohexanethiolate-protected  $[Au_{23}(S-c-C_6H_{11})_{16}]^-$  (counterion: tetraoctylammonium ion, TOA<sup>+</sup>) nanocluster and the tetrameric staple motif in TBBM-capped  $[Au_{24}(SCH_2Ph-t-Bu)_{20}]^0$  and cyclohexanethiol-capped  $[Au_{18}(S-c-C_6H_{11})_{14}]^0$  nanoclusters . Detailed analyses on the geometric and electronic structures offer insight into their interesting features and stability of these nanoclusters. The knowledge of the total structures of these nanoclusters further opens possibilities for exploration in applications such as catalysis, optoelectronics, and sensor design.<sup>36</sup>

#### 3.2 Experimental

### 3.2.1 Chemicals

Tetrachloroauric(III) acid (HAuCl<sub>4</sub>·3H<sub>2</sub>O, 99.99%, Sigma Aldrich), 2-Phenylethanethiol (PhC<sub>2</sub>H<sub>4</sub>SH, 99%, Sigma Aldrich), Triphenylphosphine (PPh<sub>3</sub>, 98%, Acros Organics), Tetraoctylammonium Bromide (TOAB, 99%, Fluka), Sodium borohydride (NaBH<sub>4</sub>, 99.99%, Sigma Aldrich), Tetrabutylammonium hexaflurophosphate (TBAPF6, 98%, Fluka), Toluene (HPLC grade, 99.9%, Sigma Aldrich), Ethanol (HPLC grade, Sigma Aldrich), Methanol (HPLC grade, 99%, Aldrich), Dichloromethane (HPLC grade, 99.9%, Aldrich) and Hexane (HPLC grade, 99%, Sigma Aldrich) were used as received.

## 3.2.2 Synthesis and crystallization of [Au<sub>23</sub>(S-c-C<sub>6</sub>H<sub>11</sub>)<sub>16</sub>]

HAuCl<sub>4</sub>·3H<sub>2</sub>O (0.3 mmol, 118 mg) and tetraoctylammonium bromide (TOAB, 0.348 mmol, 190 mg) were dissolved in methanol (15 mL) in a 50 mL trineck round-bottom flask. After vigorously stirring for 15 min, the solution color changed from yellow to dark reddish orange. Then, excess 1-cyclohexanethiol (1.6 mmol, 196 µL) was added to the mixture at room temperature. The reddish orange solution turned yellowish almost immediately indicating the conversion of Au(III) to Au(I) complexes. After ~15 min, NaBH<sub>4</sub> (3 mmol, 114 mg dissolved freshly in 6 mL of cold Nanopure water) was rapidly added to the solution under vigorous stirring. The solution turned black immediately indicating formation of Au

clusters, which then precipitated out of the methanol solution. The reaction mixture was further allowed to stir overnight to yield pure  $[Au_{23}(S-c-C_6H_{11})_{16}]^{-1}$  nanoclusters (yield ~20%, Au atom basis). Single crystal growth of the nanoclusters was performed by first dissolving ~4 mg  $[Au_{23}(S-c-C_6H_{11})_{16}]^{-1}$  clusters in 1 mL dichloromethane. This was followed by vapor diffusion of pentane into the cluster solution for 1-2 days.

# 3.2.3 Synthesis and crystallization of [Au<sub>24</sub>(SCH<sub>2</sub>Ph-t-Bu)<sub>20</sub>]<sup>0</sup>

The  $[Au_{23}(S-c-C_6H_{11})_{16}]^{-}$  nanocluster was used as the starting material for obtaining the  $[Au_{24}(SCH_2Ph-t-Bu)_{20}]^{0}$  nanocluster via a ligand exchange reaction with TBBM. Typically, ~5 mg pure  $[Au_{23}(S-c-C_6H_{11})_{16}]^{-}$  clusters were dissolved in ~0.5 mL dichloromethane containing 0.5 mL TBBM ligand. The mixture was then stirred for 24 h at 40 °C under reflux conditions. After 24 h, pure  $[Au_{24}(SCH_2Ph-t-Bu)_{20}]^{0}$  clusters were obtained (yield ~50%, Au atom basis). Crystallization of the clusters was performed in the same manner as  $[Au_{23}(S-c-C_6H_{11})_{16}]^{-}$ .

# 3.2.4 Synthesis and crystallization of [Au<sub>18</sub>(S-c-C<sub>6</sub>H<sub>11</sub>)<sub>14</sub>]<sup>0</sup>

In a typical reaction, HAuCl<sub>4</sub>·3H<sub>2</sub>O (0.2 mmol, 78.8 mg, dissolved in 0.5 mL ethanol) was added to 10 mL dichloromethane solution of tetraoctylammonium bromide (TOAB, 0.232 mmol, 127 mg). After vigorously stirring for 15 min, the solution colour changed from yellow to dark reddish orange. Then, excess 1-cyclohexanethiol (125  $\mu$ L, neat) was added to the mixture at room temperature. The reddish orange solution turned colourless in 15-20 minutes indicating the conversion of Au(III) to Au(I) complexes. Then,
NaBH<sub>4</sub> (0.5 mmol, 19 mg dissolved freshly in 1.5 mL of ethanol) was added dropwise to the solution under vigorous stirring. The solution turned green slowly, indicating the formation of clusters (identified to be Au<sub>18</sub>(S-c-C<sub>6</sub>H<sub>11</sub>)<sub>14</sub>). The mixture was further allowed to react for 4-5 h under stirring, after which it was centrifuged to remove insoluble Au(I)-polymers. The supernatant was then dried under rotary evaporation and the product was washed several times with methanol to remove excess reactants. The purified nanocluster product was then extracted with dichloromethane and recrystallized by vapor diffusion of pentane into the dichloromethane solution of the cluster for 1-2 days. The latter step was repeated 2-3 times to obtain high quality single crystals of the nanocluster for Xray crystallography.

#### 3.2.5 Characterization

X-ray diffraction data of Au clusters were collected on a Bruker X8 Prospector Ultra equipped with an Apex II CCD detector and an I $\mu$ S micro-focus Cu K<sub>a</sub> X-ray source ( $\lambda$  = 1.54178 Å). Data collection was performed under cold N<sub>2</sub> flow at 230 K. The structure was solved by direct methods using Bruker program SHELXTL which located all the Au and S atoms. ESI mass spectrograms of the clusters were recorded using a Waters Q-TOF mass spectrometer equipped with Z-spray source with source temperature kept at 70 °C. To prepare the ESI sample, the clusters were dissolved in dichloromethane (~1 mg/mL) and diluted (2:1 v) by dry ethanol containing 50 mM CsOAc in order to forming Cs<sup>+</sup>-cluster adducts. The cluster sample was directly infused into the chamber at 5 µL/min. The spray voltage was kept at 2.20 kV and the cone voltage at 60 V. The quantum yield (QY) was measured with dilute solutions of clusters (~0.02 - 0.1 OD absorption at 514 nm) at 514 nm excitation (slit width: 5 nm) using Au<sub>25</sub>(SG)<sub>18</sub><sup>-</sup> as the reference (QY: 0.2%).

### 3.3 Results & Discussion

### 3.3.1 Single Au-atom level manipulation: The case of $[Au_{23}(S-c-C6H_{11})_{16}]^{\circ}$ and $[Au_{24}(SCH_2Ph-t-Bu)_{20}]^{\circ}$

We first discuss the  $[Au_{23}(S-c-C6H_{11})_{16}]^{-}$  nanocluster. The synthesis involved a one-phase method using methanol as the solvent. Briefly, HAuCl<sub>4</sub>·3H<sub>2</sub>O and tetraoctylammonium bromide (TOAB) were first dissolved in methanol, followed by the addition of excess 1-cyclohexanethiol. The reddish orange solution turned yellowish, indicating the conversion of Au(III) to Au(I) complexes. The Au(I) species was further reduced by NaBH<sub>4</sub>, and the reaction was continued overnight, which finally yielded pure  $[Au_{23}(S-c-C_6H_{11})_{16}]^{-}$ nanoclusters via spontaneous size-focusing. Methanol was intentionally chosen as a solvent for this reaction due to its polar nature, which would bring about precipitation of organic-soluble cyclohexanethiolate-protected nanoclusters, thereby leading to size-control of clusters. Single crystal growth of the nanoclusters was performed via vapor diffusion of pentane into a concentrated solution of the nanoclusters in dichloromethane for 1-2 days.



**Figure 3.1.** Total structure of  $[Au_{23}(S-c-C_6H_{11})_{16}]^{-1}$  nanocluster (Color labels: Au, magenta; S, yellow; C, grey; H are omitted due to clarity)

The total structure (Figure 3.1) of the cluster was solved by single crystal X-ray crystallography. The counterion (TOA<sup>+</sup>) for the anionic cluster was also found, albeit the carbon chains of TOA<sup>+</sup> were heavily disordered. To reveal the details of the structure, we start with the Au<sub>23</sub>S<sub>16</sub> framework (Figure 3.2). The kernel of [Au<sub>23</sub>(S-c-C<sub>6</sub>H<sub>11</sub>)<sub>16</sub>]<sup>-</sup> is composed of a Au<sub>13</sub> cuboctahedron (Figure 3.2 A, highlighted in magenta), in contrast with the Au<sub>13</sub> icosahedron in [Au<sub>25</sub>(SCH<sub>2</sub>CH<sub>2</sub>Ph)<sub>18</sub>]<sup>*q*</sup> (*q*=-1, 0).<sup>29-31</sup> Starting from the center of the cuboctahedron, the radial Au-Au bond lengths give rise to an average of 2.96±0.28 Å, in comparison to the 2.79±0.01 Å in the icosahedral Au<sub>13</sub> for [Au<sub>25</sub>(SCH<sub>2</sub>CH<sub>2</sub>Ph)<sub>18</sub>]<sup>*q*</sup>.<sup>29-31</sup> The periphery Au-Au contacts give an average of 3.00±0.27 Å.



**Figure 3.2.** (A) the Au<sub>23</sub>S<sub>16</sub> framework with the cuboctahedron core highlighted in magenta and the two 'extra' surface atoms in dark blue, (B) thiolate-binding motifs in  $[Au_{23}(S-c-C_6H_{11}))_{16}]^-$ : (I)  $Au_3(SR)_4$  trimeric staple, (II)  $Au(SR)_2$  monomeric staple, and (III) simple thiolate bridging mode. (color labels: magenta/dark blue/light blue=Au, yellow=S, C and H atoms are omitted for clarity).

The cuboctahedral kernel is protected by two trimeric  $Au_3(SR)_4$  staples (Figure 3.2 B, labeled *I*), two monomeric  $Au(SR)_2$  staples (Figure 3.2 B, labeled *II*), and 4 simple bridging SR ligands (Figure 3.2 B, labeled *III*). Among these surface-protecting motifs, the trimeric  $Au_3(SR)_4$  staple is for the first time observed experimentally, and its configuration is comparable with the theoretically constructed trimeric staple in structural prediction of the  $Au_{20}(SR)_{16}$  nanocluster.<sup>37,38</sup> The theoretical structure of  $Au_{20}(SR)_{16}$  was predicted to possess a prolate  $Au_8$  kernel with four trimeric staple motifs.<sup>37-39</sup> Recently,  $Au_{18}(SR)_{14}$  was also predicted to possess the prolate  $Au_8$  kernel protected by two trimeric staples

and two dimeric staples.<sup>40</sup> In the theoretical trimeric staple, the Au-Au distance  $(3.6-3.7 \text{ Å})^{38}$  is larger than the Au-Au distance (3.4 Å) in the experimental trimeric staple.

Interestingly, we also found two extra surface Au atoms in  $[Au_{23}(S-c-C_6H_{11})_{16}]^-$  (Figure 3.2 B, marked in dark blue), each serving as a "hub" for linking to the trimeric and monomeric staples (Au<sub>hub</sub>-Au<sub>staple</sub> distance ~2.93 Å). By measuring the Au<sub>hub</sub>-Au<sub>kernel</sub> distances, these two extra surface Au atoms appear to be more strongly associated with the kernel (~2.7 Å to the underlying kernel's gold atoms, even shorter than the average radial Au-Au distance (2.96 Å) within the cuboctahedron). In this sense, the kernel is better described to be the Au<sub>15</sub> bipyramid, rather than the Au<sub>13</sub> cuboctahedron. The Au<sub>15</sub> bi-pyramidal structure can be roughly viewed as a bi-capped cuboctahedron along its 4-fold axis.

The cluster formula and charge state were confirmed by electrospray ionization mass spectrometry (ESI-MS) analysis. ESI-MS (negative ion mode) revealed a prominent peak at m/z = 6373.13 (Figure 3.3.A), corresponding to the formula of the intact cluster ion  $[Au_{23}(S-c-C_6H_{11})_{16}]^-$  (calculated formula weight: 6373.16). The TOA<sup>+</sup> counterion was also found in the positive mode mass spectrum (Figure 3.3.B, expected mass: 466.53, observed: 466.52 Da), confirming the -1 charge of the cluster. The purity of the product was further confirmed by thermogravimetric analysis, and a 33.8 wt % loss was observed (Figure 3.4), consistent with the formula (calculated loss: 33.8%).

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**Figure 3.3.** ESI-MS analysis of  $[Au_{23}(S-c-C_6H_{11})_{16}]^{-}[TOA]^{+}$ . (A) ESI-MS (negative ion mode) spectrum of  $[Au_{23}(S-c-C_6H_{11})_{16}]^{-}$ ; (B) positive mode spectrum for the counterion  $[TOA]^{+}$ , where TOA= N(C<sub>8</sub>H<sub>17</sub>)<sub>4</sub><sup>+</sup>.



**Figure 3.4.** Thermogravimetric analysis of the  $[Au_{23}(S-c-C_6H_{11})_{16}]^{-}[TOA]^{+}$ . clusters. The weight loss of 33.8% agrees well with the formula (cal. 33.8%).

To achieve insight into the newly observed trimeric staple motif and address to what extent the two extra surface Au atoms contribute to the electronic structure of the whole cluster, we carried out DFT calculations. In the calculations we adopted a  $[Au_{23}(SCH_3)_{16}]^-$  model cluster mimicking the experimental one by simplifying its ligands with -SCH<sub>3</sub>.<sup>41,42</sup> Figure 3.5 A-B shows the experimental and theoretical optical absorption spectra. The theoretical spectrum is convoluted by the Lorentz function with appropriate width.



**Figure 3.5.** (A) Experimental  $[Au_{23}(S-c-C_6H_{11})_{16}]^{-}$  and (B) theoretical  $[Au_{23}(SCH_3)_{16}]^{-}$  optical absorption spectra. (C) Schematic diagrams of HOMO (top) and (D) LUMO (bottom) of  $[Au_{23}(SCH_3)_{16}]^{-}$ 

The DFT result reasonably reproduces the spectral profile and peak positions of the experimental observation. The distinct peak at ~570 nm in the experimental spectrum corresponds to the simulated peak at ~530 nm; the ~0.16 eV discrepancy is primarily due to the limitation of accuracy of DFT calculations.<sup>43,44</sup> This peak involves both the HOMO to LUMO (529 nm, intense) and HOMO to LUMO+1 (507 nm, less intense) electronic transitions (Figure 3.5 B). Figure 3.5 C-D illustrates schematic diagrams of HOMO and LUMO of the nanocluster. In the HOMO diagram, we see two large blue lobes of MO clouds. The extra surface Au atoms that serve as the hubs indeed contribute to these lobes of MO. The third lump (red) of the HOMO is located within the cuboctahedron (Figure 3.5 C). On the other hand, in the LUMO diagram (Figure 3.5 D), two blue and two red lobes are exhibited; the surface "hub" Au atoms are also relevant to constructing the electronic state of LUMO. Therefore, the lowest-lying peak (experiment: 570 nm, theory: 530 nm) in the optical spectrum uniquely arises from the transition within the Au<sub>15</sub> kernel.

While we were further exploring the ligand exchange reactions of clusters with *4-tert-butylbenzylmercaptan* (abbreviated as TBBM), we surprisingly found that the  $[Au_{23}(S-c-C_6H_{11}))_{16}]^-$  cluster can be used as the starting material to obtain a new cluster,  $[Au_{24}(SCH_2Ph-t-Bu)_{20}]^0$ . Briefly, pure  $[Au_{23}(S-c-C_6H_{11}))_{16}]^-$  clusters were dissolved in dichloromethane and then reacted with excess TBBM at 40 °C. After 36 h, pure  $[Au_{24}(SCH_2Ph-t-Bu)_{20}]^0$  clusters were obtained. Crystallization was performed in the same manner as  $[Au_{23}(S-c-C_6H_{11}))_{16}]^-$ .

**Scheme 3.1.** TBBM ligand-induced formation of Au<sub>24</sub>(SCH<sub>2</sub>Ph-*t*-Bu)<sub>20</sub> nanocluster.



The total structure of  $[Au_{24}(SCH_2Ph-t-Bu)_{20}]^0$  is shown in Figure 3.6. The  $Au_{24}(SCH_2Ph-t-Bu)_{20}$  structure comprises a bi-tetrahedral  $Au_8$  kernel, which is



**Figure 3.6.** Total structure of  $[Au_{24}(SCH_2Ph-t-Bu)_{20}]^0$  nanocluster (Color labels: Au, magenta; S, yellow; C, grey; H are omitted due to clarity)



**Figure 3.7.** Anatomy of  $[Au_{24}(SCH_2Ph-t-Bu)_{20}]^0$  nanocluster comprising of a bitetrahedral Au<sub>8</sub> kernel which is protected by two pairs of tetrameric Au<sub>4</sub>(SCH<sub>2</sub>Ph*t*-Bu)<sub>5</sub> staple motifs

quite small and came as a surprise, for that we initially expected that, compared to Au<sub>23</sub>(S-c-C<sub>6</sub>H<sub>11</sub>))<sub>16</sub> that contains a 15-atom bi-capped cuboctahedral kernel, the larger Au<sub>24</sub>(SCH<sub>2</sub>Ph-*t*-Bu)<sub>20</sub> nanocluster would consist of a larger kernel. The two tetrahedrons in the Au<sub>24</sub>(SCH<sub>2</sub>Ph-*t*-Bu)<sub>20</sub> kernel structure are antiprismatically joined together through two triangular faces of the two tetrahedrons, forming an elongated structure. The average Au-Au distance in the Au<sub>8</sub> kernel of Au<sub>24</sub>(SCH<sub>2</sub>Ph-*t*-Bu)<sub>20</sub> is  $2.87\pm0.22$  Å. The Au-Au distances in individual Au<sub>4</sub> tetrahedrons range from 2.70 to 2.75 Å, while the Au-Au distances at the interface of the two tetrahedrons are larger (3.13±0.14 Å).

Interestingly, four tetrameric staples (i.e.  $Au_4(SR)_5$ ) were found to protect the  $Au_8$  kernel (one pair is shown in Figure 3.7). The  $Au_4(SR)_5$  tetramers resemble a 'chair' and are assembled onto the  $Au_8$  kernel via bi-dentate bonding. It is worth noting that one of the theoretical structures of  $Au_{24}(SR)_{20}$  modeled by Pei *et al*<sup>45</sup> is close to the X-ray crystal structure of  $Au_{24}(SCH_2Ph-t-Bu)_{20}$ , but surprisingly the theoretical structure (Iso3, specified in ref 45), which contains an Au<sub>8</sub> kernel protected by four tetrameric staples, was not the lowest-energy structure. The theoretical tetrameric staple is comparable to the experimental one observed in our present work, but the theoretical bi-tetrahedral Au<sub>8</sub> kernel configuration in Au<sub>24</sub>(SCH<sub>3</sub>)<sub>20</sub> is different from the experimental *face-joining* bi-tetrahedral Au<sub>8</sub> kernel in Au<sub>24</sub>(SCH<sub>2</sub>Ph-*t*-Bu)<sub>20</sub>. It is also worth noting that another theoretical structure of Au<sub>20</sub>(SCH<sub>3</sub>)<sub>20</sub> contains a bi-tetrahedral Au<sub>8</sub> kernel,<sup>38,39</sup> but it was predicted to be protected by four trimeric Au<sub>3</sub>(SR)<sub>4</sub> staples, rather than four tetrameric Au<sub>4</sub>(SR)<sub>5</sub> staples as observed in the Au<sub>24</sub>(SCH<sub>2</sub>Ph-*t*-Bu)<sub>20</sub> nanocluster.



**Figure 3.8.** ESI-MS (positive ion mode) spectrum of  $[Au_{24}(SCH_2Ph-t-Bu)_{20}]^0$ . For mass spectrometry analysis, the charge-neutral clusters were first adducted with Cs<sup>+</sup> by mixing with cerium acetate (CsOAc) in solution.

No counterions was found in the unit cell of Au<sub>24</sub>(SCH<sub>2</sub>Ph-*t*-Bu)<sub>20</sub>, indicating that the cluster should be charge neutral. To further confirm the formula and the charge state of the cluster, we performed ESI-MS analysis. Either positive or negative mode gave no signals due to the charge neutral cluster; thus, the cluster was mixed with Cs(OAc) to form positively charged MCs<sup>+</sup> adducts (where M represents the cluster) in subsequent ESI-MS analysis (Figure 3.8). Two peaks were observed at *m/z* 8445.84, and 4289.08. The *m/z* 8445.84 peak is the mono-cation adduct peak, thus the cluster mass is determined to be 8312.94 after subtracting one Cs<sup>+</sup>. The more prominent *m/z* 4289.08 peak is 2+ charged, as revealed by the isotope peak spacing ( $\delta$ =0.5, hence 2+ charged); thus the cluster mass is determined to be 8312.36 after subtracting two Cs<sup>+</sup> ions. Therefore, both peaks gave rise to the identical cluster mass (8312.65), and the experimental mass matches perfectly with the calculated value of Au<sub>24</sub>(SCH<sub>2</sub>Ph-*t*-Bu)<sub>20</sub> (cal: 8313.26 Da, deviation: 0.6 Da).

To elucidate the electronic properties of the newly observed  $Au_{24}(SCH_2Ph-t-Bu)_{20}$  structure with tetrameric staple motifs, we further carried out DFT calculations for a model cluster,  $Au_{24}(SCH_3)_{20}$ . The procedures of the calculation are similar to those of  $Au_{23}(SCH_3)_{16}$ . Figure 3.9 A-B shows the experimental and theoretical optical absorption spectra. The DFT result reasonably reproduces the spectral pattern and peak positions of the experimental observation. The spectrum of  $Au_{24}(SCH_2Ph-t-Bu)_{20}$  is less prominent than that of  $Au_{23}(S-c-C_6H_{11})_{16}$ ; only a broad peak appears at ~ 500 nm (Figure 3.9A), which corresponds to the simulated peak at ~460 nm (Figure 3.9

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B). The ~0.22 eV discrepancy is again primarily due to the limitation of accuracy of DFT calculations.<sup>43,44</sup>



*Figure 3.9.* (A) Experimental UV-vis absorption spectrum of  $Au_{24}(SR)_{20}$ , (B) theoretical  $Au_{24}(SCH_3)_{20}$  optical absorption spectrum, (C) Schematic diagrams of the HOMO of  $Au_{24}(SCH_3)_{20}$ , and (D) the LUMO of the cluster.

The peak is mainly contributed by the HOMO-LUMO transition and also in less part by the HOMO-2 to LUMO transition. Figure 3.9C-D illustrates schematic diagrams of HOMO and LUMO orbitals. Both are distributed around the bitetrahedral  $Au_8$  kernel, thus the HOMO-LUMO transition occurs within the  $Au_8$  kernel.

It is worth comparing the optical absorption spectrum of  $Au_{24}(SCH_2Ph-t-Bu)_{20}$  with that of the previously reported  $Au_{24}(SCH_2CH_2Ph)_{20}$ .<sup>46</sup> We found that these two  $Au_{24}$  nanoclusters show striking differences in optical spectra, implying that they might adopt different structures. Future work on different ligand-capped  $Au_{24}(SR)_{20}$  may reveal more details on the potential ligand-caused structural isomerization in  $Au_{24}(SR)_{20}$ .



**Figure 3.10.** UV-Vis spectrum of  $[Au_{24}(SCH_2CH_2Ph)_{20}]^0$  (ref 5).

# 3.3.2 Comparison of properties of "a trio of nanoclusters"- $Au_{23}$ , $Au_{24}$ and $Au_{25}$ protected by thiolates

(a) Structural framework including the gold kernel and protecting staple motifs

Although the sizes of the three thiolate-protected  $Au_{23}$ ,  $Au_{24}$  and  $Au_{25}$  clusters are almost the same (~1 nm), they exhibit very different atomic

structures. In terms of the Au cores, while the Au<sub>25</sub> cluster features a ubiquitous icosahedral Au<sub>13</sub> core, the Au<sub>23</sub> and Au<sub>24</sub> clusters feature bipyramidal Au<sub>15</sub> and bi-tetrahedral Au<sub>8</sub> cores, respectively. With respect to surface staple motifs, highly elongated tetramers and trimers are found in Au<sub>24</sub> and Au<sub>23</sub>, respectively, while the Au<sub>25</sub> cluster exhibits only dimers in its structure. The observation of these new staple motifs in turn demonstrates that the ligand determines the size and geometry of the Au kernel to a large extent.



**Figure 3.11.** Total atomic structures of (a)  $Au_{25}(SCH_2CH_2Ph)_{18}$ , (b)  $Au_{24}(SCH_2Ph-t-Bu)_{20}$  and (c)  $Au_{23}(S-c-C_6H_{11})_{16}$ 

### (b) Optical properties

The lowest-lying electronic transition at ~500 nm in Au<sub>24</sub>(SCH<sub>2</sub>Ph-*t*-Bu)<sub>20</sub> blue-shifts blue-shifted compared to the gap of one-gold-less  $[Au_{23}(S-c-C_6H_{11})_{16}]^-$  nanoclusters (570 nm) as well as gap of one-gold-more  $[Au_{25}(SCH_2CH_2Ph)_{18}]^q$  nanoclusters (680 nm). Therefore, the HOMO-LUMO gap energies in  $[Au_{23}(S-c-C_6H_{11})_{16}]^-$ ,  $Au_{24}(SCH_2Ph-t-Bu)_{20}$  and  $[Au_{25}(SCH_2CH_2Ph)_{18}]^{-1/0}$  do not scale with size in a monotonic trend, instead, exhibiting zig-zag behaviour in this "trio" of

nanoclusters. This behaviour indicates the importance of the detailed structures of nanoclusters.

### (c) Photoluminescence properties

The Au<sub>24</sub>(SCH<sub>2</sub>Ph-*t*-Bu)<sub>20</sub> nanocluster exhibits red photoluminescence at ~620 nm (see Figure 3.12A) and the emission is indeed stronger than that of both Au<sub>23</sub>(S-*c*-C<sub>6</sub>H<sub>11</sub>)<sub>16</sub> and Au<sub>25</sub>(SCH<sub>2</sub>CH<sub>2</sub>Ph)<sub>18</sub>. Using the more luminescent Au<sub>25</sub>(SG)<sub>18</sub> (where SG represents glutathione) as a reference (QY~0.2%), we



**Figure 3.12.** (A) Photoluminescence of Au<sub>24</sub>(SCH<sub>2</sub>Ph-*t*-Bu)<sub>20</sub> nanoclusters: (a) Solid Au<sub>24</sub> crystals under UV light ( $\lambda$  = 365 nm) with red emission, (b) Photograph of a ~0.1 OD (at 500 nm) solution of Au<sub>24</sub> in toluene under visible light, (c) The same solution under under UV ( $\lambda$  = 365 nm). (B) Photoluminescence spectrum (blue curve) of Au<sub>24</sub> in toluene (blue curve, excit.=514 nm, slit width: 5 nm, concentration: 0.08 OD absorbance at 514 nm measured by UV-vis) and the excitation spectrum (black curve) corresponding to the 618 nm emission band.

found that the quantum yield of  $Au_{24}(SCH_2Ph-t-Bu)_{20}$  is ~25 times higher than that of  $Au_{25}(SG)_{18}$ . The enhancement fluorescence in  $Au_{24}(SCH_2Ph-t-Bu)_{20}$  might be due to the high fraction of Au atoms in the staple motifs and the electronic interaction between the staple Au atoms and the kernel Au atoms. The  $Au_{24}(SCH_2Ph-t-Bu)_{20}$  structure provides some structural hint for a recent study by Luo *et al.*,<sup>47</sup> which demonstrates that Au nanoclusters with oligomeric staple motifs on the surface are highly luminescent.

Table 3.1. Summary of differences between thiolate-protected Au\_{23}, Au\_{24} and Au\_{25}

Au Clusters Properties	Au <sub>25</sub>	Au <sub>24</sub>	Au <sub>23</sub>
Au core	Icosahedral Au <sub>13</sub>	Bitetrahedral Au <sub>8</sub>	Bipyramidal Au <sub>15</sub>
Surface motifs	Au <sub>2</sub> (SR) <sub>3</sub> (6)	Au <sub>4</sub> (SR) <sub>5</sub> (4)	$\begin{cases} Au_3(SR)_4 (2) \\ Au(SR)_2 (2) \\ Bridging thiolate (4) \end{cases}$
HOMO-LUMO gap	1.3 eV	2.2 eV	1.9 eV
Fluorescence quantum yield	0.2 %	5 %	0.1 %

## 3.3.3 Toward smaller Au nanoclusters: The total structure determination of the hitherto smallest cyclohexanethiolate-protected Au<sub>18</sub> cluster

Ligand-protected gold nanoclusters lie at the interface between organogold complexes (e.g. Au<sup>1</sup>SR) and plasmonic gold nanoparticles.<sup>1</sup> Understanding the nucleation of Au<sup>1</sup>SR complexes into clusters (i.e. Au<sub>n</sub>L<sub>m</sub>, where *n*>*m*) is of critical importance for understanding the origin of metallic bonds in clusters and the nucleation of clusters from organometallic precursors. To accomplish this, discrete-sized clusters should be made and their structures solved by X-ray crystallography. In the case of thiolate-protected Au<sub>n</sub>L<sub>m</sub> nanoclusters, following the initial efforts of structural elucidation of Au<sub>25</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>18</sub>, Au<sub>38</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>24</sub> and Au<sub>102</sub>(SPh-*p*-COOH)<sub>44</sub>, several new crystal structures toward the smaller end (*x*<25) have been attained recently, including Au<sub>24</sub>(SCH<sub>2</sub>Ph-*t*-Bu)<sub>20</sub> featuring a Au<sub>8</sub> kernel protected by four tetrameric Au<sub>4</sub>(SR)<sub>5</sub> staples (see section 3.3.2), Au<sub>23</sub>(S-c-C<sub>6</sub>H<sub>11</sub>)<sub>16</sub> with a Au<sub>15</sub> kernel protected by various surface motifs, and Au<sub>20</sub>(SPh-*t*-Bu)<sub>16</sub> exhibiting a Au<sub>7</sub> kernel and unprecedented Au<sub>8</sub>(SR)<sub>8</sub>

Crystallization of even smaller Au<sub>n</sub>L<sub>m</sub> clusters (e.g. n<20), however, has not been successful, although small sizes of Au<sub>n</sub>(SR)<sub>m</sub> clusters were reported a decade ago.<sup>49,50</sup> Negishi *et al.* first isolated Au<sub>10-12</sub>(SG)<sub>10-12</sub> complexes and clusters of Au<sub>15</sub>(SG)<sub>13</sub>, Au<sub>18</sub>(SG)<sub>14</sub>, etc, where –SG refers to glutathione.<sup>50</sup> In recent work, Hamouda *et al.* also observed similar sizes together with chargeneutral Au<sub>16</sub>(SG)<sub>14</sub> and Au<sub>20</sub>(SG)<sub>16</sub> clusters.<sup>51</sup> Ghosh *et al.* reported a one-step, slow reduction route for the synthesis of pure Au<sub>18</sub>(SG)<sub>14</sub> and further studied the photoluminescence.<sup>52</sup> Yao *et al.* recently devised a pH-controlled method for onepot synthesis of Au<sub>15</sub>(SG)<sub>13</sub> and Au<sub>18</sub>(SG)<sub>14</sub> without the need of isolation.<sup>53</sup> In theoretical work, Tlahuice *et al.* predicted the Au<sub>18</sub>(SR)<sub>14</sub> structure to be a prolate bitetrahedral Au<sub>8</sub> core capped by two dimers (-SR-Au-SR-Au-SR-) and two trimers (-SR-Au-SR-Au-SR-Au-SR-).<sup>40</sup> Despite the identification of Au<sub>18</sub>(SG)<sub>14</sub> has not been successful thus far; the barrier could be the –SG ligand. We rationalize that, if one can devise a synthetic strategy to obtain organic-soluble thiolate-protected Au<sub>18</sub> clusters, crystallization may be realized, since the majority of the reported crystal structures were obtained with organic soluble thiolates. Based on our experience in achieving single crystal growth of  $[Au_{23}(S-c-C_6H_{11})_{16}]^-$  clusters, we chose cyclohexanethiol to attempt (and eventually achieved) the synthesis of Au<sub>18</sub>(SR)<sub>14</sub> clusters.

The Au<sub>18</sub>(S-c-C<sub>6</sub>H<sub>11</sub>)<sub>14</sub> nanoclusters were synthesized in a one-pot reaction at room temperature via a kinetically controlled approach.<sup>54</sup> Briefly, HAuCl<sub>4</sub>·3H<sub>2</sub>O and tetraoctylammonium bromide (TOAB) were first dissolved in an ethanol-dichlomethane mixture, followed by the addition of excess 1-cyclohexanethiol. The reddish orange solution turned colorless, indicating the conversion of Au(III) to Au(I) complexes. The Au(I) species was further reduced by drop-wise addition of an ethanolic solution of NaBH<sub>4</sub> and the reaction was continued for 4-5 h, which finally yielded pure Au<sub>18</sub>(S-c-C<sub>6</sub>H<sub>11</sub>)<sub>14</sub> nanoclusters evidenced by the optical spectrum closely resembling that of Au<sub>18</sub>(SG)<sub>14</sub>.<sup>[13,14]</sup> Recrystallization and single crystal growth of the nanoclusters were performed

via vapor diffusion of pentane into a concentrated solution of the nanoclusters in dichloromethane for 1-2 days.

The total structure (Figure 3.13) of the cluster was solved by single crystal X-ray crystallography. The structure of  $[Au_{18}(S-c-C_6H_{11})_{14}]^0$  nanocluster comprises a face-fused bi-octahedral Au<sub>9</sub> kernel (Figure 3.14 a), where two Au<sub>6</sub> octahedra are fused together by sharing a common Au<sub>3</sub> face. The Au-Au bond distances in the Au<sub>9</sub> kernel range from 2.67 to 3.00 Å (average: 2.82 Å), which is comparable to the Au-Au distance (2.88 Å) in bulk gold. Alternatively, the face-fused bi-octahedral Au<sub>9</sub> kernel of the cluster may be viewed as three layers of Au<sub>3</sub> planes arranged in hexagonal close-packing (hcp) (with ABA layers, Figure 3.14-c).



**Figure 3.13.** Total structure of  $[Au_{18}(S-c-C_6H_{11})_{14}]^0$  nanocluster (Color labels: Au, magenta; S, yellow; C, grey; H are omitted for clarity)



**Figure 3.14.** (a) The Au<sub>9</sub> bi-octahedral kernel of  $[Au_{18}(S-c-C_6H_{11})_{14}]^0$  nanocluster. The common Au<sub>3</sub> face is highlighted in purple. (b) Another view of Au<sub>9</sub> showing 3 layers of three Au atoms arranged in *hcp* fashion. (c) The Au<sub>9</sub> kernel in spacefill model.

Of note, the Au-Au bonds within each of the three  $Au_3$  planes range from 2.67 to 2.81 Å and are considerably shorter than the Au-Au bonds connecting the three planes which range from 2.78 to 3.00 Å.

This hcp-layered Au<sub>9</sub> kernel is encapsulated by one Au<sub>4</sub>(SR)<sub>5</sub> tetramer, one Au<sub>2</sub>(SR)<sub>3</sub> dimer and three Au(SR)<sub>2</sub> monomers. Specifically, the two sulfur ends of the Au<sub>4</sub>(SR)<sub>5</sub> tetrameric staple are bonded with two Au atoms of the middle Au<sub>3</sub> plane of the Au<sub>9</sub> kernel and the tetramer spans across the front Au<sub>3</sub> face (Figure 3.15 B). The three Au(SR)<sub>2</sub> monomers, on the other hand, connect Au atoms of the front and back Au<sub>3</sub> faces (Figure 3.15 C) and are symmetrically distributed. Finally, a dimeric staple spans from the middle Au<sub>3</sub> plane to the back Au<sub>3</sub> face (rotated 180° to the front, Figure 3.15 D).



**Figure 3.15.** Anatomy of the  $[Au_{18}(S-c-C_6H_{11})_{14}]^0$  nanocluster, starting with the bioctahedral Au<sub>9</sub> kernel (A), to which one tetrameric staple motif is added giving rise to (B), followed by addition of three monomeric staples to give (C), and finally addition of a dimeric staple motif yields the total structure of  $Au_{18}(S-c-C_6H_{11})_{14}$  (D). (Color labels: magenta/purple = Au in the kernel; light blue = Au in the staples; yellow = S; carbon tails of thiolates are omitted for clarity).

In addition, the Au atoms in all three types of staple motifs residing on the Au<sub>9</sub> kernel share strong contacts with the Au atoms of the kernel (Au-Au distances ranging from 2.88-3.58 Å, average 3.23 Å), giving rise to a compact cluster structure. Of note, the cluster is non-chiral, as a symmetry plane is existent. It is worth noting that Tlahuice *et al.* performed theoretical calculations and predicted the structure of Au<sub>18</sub>(SR)<sub>14</sub> to be composed of a bitetrahedral Au<sub>8</sub>

kernel protected by two dimers and two trimers.<sup>40</sup> The predicted structure does not match with our experimental structure.



**Figure 3.16.** ESI-MS (positive ion mode) spectrum of  $[Au_{18}(S-c-C_6H_{11})_{14}]^0$ . For mass spectrometry analysis, the charge-neutral clusters were first adducted with Cs<sup>+</sup> by mixing with cerium acetate (CsOAc) in solution.

No counterions was found in the unit cell of Au<sub>18</sub>(S-c-C<sub>6</sub>H<sub>11</sub>)<sub>14</sub>, and the charge neutrality of the cluster was further confirmed by electrospray ionization mass spectrometric (ESI-MS) analysis; no signals was observed in both positive and negative mode analyses prior to the addition of cesium acetate (CsOAc). With CsOAc, the clusters form a positively charged mono-Cs<sup>+</sup> adduct which was detected in positive mode ESI-MS (Figure 3.16). A strong peak was observed at

m/z 5291.12, which corresponds to Au<sub>18</sub>(S-c-C<sub>6</sub>H<sub>11</sub>)<sub>14</sub> -Cs<sup>+</sup>. The isotope pattern further revealed the isotope peak spacing to be unity, thus, confirming the ionized cluster to be +1 charged. The cluster mass is determined to be 5158.22 after subtracting one Cs<sup>+</sup>, which is in excellent agreement with the theoretical mass (5158.42, deviation 0.2 Da).



**Figure 3.17.** UV-vis absorption spectrum of  $[Au_{18}(S-c-C_6H_{11})_{14}]^0$  nanocluster (green curve). Inset: Excitation (blue) and emission (black) and UV-vis absorption (green) profiles.

With regard to the optical properties of  $Au_{18}(S-c-C_6H_{11})_{14}$ , the UV-vis spectrum exhibits prominent bands at 450, 570 and 630 nm (Figure 3.17), and the optical energy gap ( $E_g$ ) is 1.70 eV by extrapolating the absorbance to zero. Electrochemical measurements give the first reduction peak at -0.95V (vs. Ag/AgCl) and the first oxidation at +0.87V (Figure 3.18). By extrapolating the

peaks to the baseline we obtain the electrochemical gap energy of ~1.66 eV, in good agreement with the optically measured gap of 1.7 eV. The absorption spectrum



**Figure 3.18.** Cyclic voltametry (CV, left panel) and differential pulse voltametry (DPV, right panel) analyses of the  $Au_{18}(S-c-C_6H_{11})_{14}$  nanocluster.

closely match with that of water-soluble  $Au_{18}(SG)_{14}$  reported previously by Negishi *et al.*,<sup>50</sup> indicating that both  $Au_{18}(S-c-C_6H_{11})_{14}$  and  $Au_{18}(SG)_{14}$  clusters share the same structure. Photoluminescence measurements revealed that the  $Au_{18}(SC_6H_{11})_{14}$  cluster gives rise to red emission centered at ~735 nm (excitation: 450 nm). The corresponding excitation spectrum exhibits multibands resembling the absorption spectrum (Figure 3.17, inset). The quantum yield of  $Au_{18}(S-c-C_6H_{11})_{14}$  was measured to be is ~0.05% using the well-studied  $Au_{25}(SG)_{18}^-$  as the reference (QY: 0.2%). Of note, the quantum yield of the -SG protected counterpart is typically 10-100 times higher due to the surface ligand effect.<sup>55</sup> The origin of the luminescence is largely ascribed to the surface effect, while the inner metal core plays a less important role.

To gain insight into the electronic and optical absorption properties of the cluster, we carried out density functional theory (DFT) calculations. The simulated optical absorption spectrum is shown in Figure 3.19A, in which the lowest-energy peak arises from the HOMO to LUMO electronic transition. Unlike other nanoclusters previously reported, an interesting feature of  $Au_{18}(S-c-C_6H_{11})_{14}$  is that the HOMO extends to the  $Au_4(SR)_5$  staple (Figure 3.19B), and indeed all the four gold atoms and five sulfur atoms of this extended staple are involved in the HOMO. The LUMO, on the other hand, distributes over the 3 layers of the  $Au_9$  kernel. Thus, the HOMO-LUMO transition exhibits charge transfer from the  $Au_4(SR)_5$  staple to the  $Au_9$  kernel, a feature not found in other nanoclusters. The simulated optical absorption spectrum reproduces well the experimental observation, except for a small redshift (0.22 eV) of the computed result. The DFT results also verify the tetrameric gold-thiolate motif assigned in the above structural anatomy.



**Figure 3.19.** (A) Simulated absorption spectrum of  $[Au_{18}(S-c-C_6H_{11})_{14}]^0$  nanocluster; (B) HOMO distribution; (C) LUMO distribution.

It is worth commenting on the crystal structures of the close sizes.<sup>37-40,</sup> <sup>45,46,56,57</sup> Previous studies (both experiment and theory) have predicted reduction in gold kernel size with decreasing size of the cluster (Table 3.2), and a small kernel encapsulated by extended staple motifs is believed to stabilize the cluster structure.<sup>38-40,56,57</sup> However, on careful analysis of the gold cores in experimentally determined crystal structures of small Au<sub>n</sub>L<sub>m</sub> clusters (where, n <25), we find that the predicted trend does not hold (Table 3.2 and Figure 3.20). This indicates the structures of clusters at the smaller end are much more diverse than previously predicted.

Au <sub>n</sub> (SR) <sub>m</sub>	Au kernel (experiment)	Au kernel (theory)		
Au <sub>15</sub> (SR) <sub>13</sub>	_	Au <sub>4</sub>		
Au <sub>18</sub> (SR) <sub>14</sub>	Au9	Au <sub>8</sub>		
Au <sub>20</sub> (SR) <sub>16</sub>	Au <sub>7</sub>	Au <sub>8</sub>		
Au <sub>22</sub> (SR) <sub>18</sub>	-	Au <sub>8</sub>		
Au <sub>23</sub> (SR) <sub>16</sub>	Au <sub>15</sub>	_		
Au <sub>24</sub> (SR) <sub>20</sub>	Au <sub>8</sub> (different configuration from theory)	Au <sub>8</sub>		

Table 3.2. Au	n(SG)m	clusters	and	their	Au	kernels
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The successful determination of the  $Au_{18}(SR)_{14}$  structure leaves the smallest  $Au_{15}(SR)_{13}$  to be solved in future efforts. No cluster sizes was found

between  $[Au^{I}SR]_{10-12}$  complexes and  $Au_{15}(SR)_{13}$ . In contrast, phosphineprotected gold clusters ranging continuously from Au<sub>2</sub> to Au<sub>14</sub> have identified.<sup>58-61</sup> The four-electron (4e) family of Au<sub>n</sub>(SR)<sub>m</sub> nanoclusters include Au<sub>18</sub>(SR)<sub>14</sub>,<sup>40</sup> Au<sub>20</sub>(SR)<sub>16</sub>,<sup>37-39</sup> and Au<sub>24</sub>(SR)<sub>20</sub>,<sup>45,46</sup> as well as Au<sub>24</sub>(SePh)<sub>20</sub>.<sup>62</sup> From Au<sub>24</sub> to Au<sub>20</sub>, one sees a reduction in Au kernel size from the face-joined bitetrahedral Au<sub>8</sub><sup>4+</sup> in Au<sub>24</sub>(SR)<sub>20</sub> to vertex-shared bitetrahedral Au<sub>7</sub><sup>3+</sup> in Au<sub>20</sub>(SR)<sub>16</sub>. However, the present Au<sub>18</sub>(SR)<sub>14</sub> does not follow the shrinking trend and instead a larger Au<sub>9</sub><sup>5+</sup> kernel is observed in Au<sub>18</sub>(SR)<sub>14</sub>. This Au<sub>9</sub><sup>5+</sup> kernel comprises three layers of gold atoms and may be viewed as two Au<sub>6</sub> octahedral units sharing a common face, in contrast with the linking of Au<sub>4</sub> tetrahedra in the larger members of the thiolateprotected 4e gold clusters.



**Figure 3.20.** Experimentally determined gold kernels of (A)  $Au_{18}(S-c-C_6H_{11})_{14}$ , (B)  $Au_{20}(SPh-t-Bu)_{16}$ , (C)  $Au_{23}(S-c-C_6H_{11})_{16}$ , and (D)  $Au_{24}(SCH_2Ph-t-Bu)_{16}$ .

In summary, we have devised a facile one-pot synthesis for obtaining molecularly pure  $Au_{18}(S-c-C_6H_{11})_{14}$  cluster and successfully solved its total structure. This cluster constitutes the smallest member in the crystallographically characterized thiolate-protected  $Au_n(SR)_m$  clusters. The observation of a face-fused  $Au_9$  bi-octahedral (or hexagonal close-packing) kernel in a small  $Au_{18}(S-c-C_6H_{11})_{14}$  cluster is remarkable and it offers insights into nucleation and size evolution of gold clusters.

### 3.4 Conclusion

We have experimentally identified new staple motifs, including trimeric Au<sub>3</sub>(SR)<sub>4</sub> motifs in Au<sub>23</sub>(SR)<sub>16</sub> and tetrameric Au<sub>4</sub>(SR)<sub>5</sub> motifs in Au<sub>24</sub>(SR)<sub>20</sub> and Au<sub>18</sub>(SR)<sub>14</sub> clusters together with the cuboctahedron-based Au<sub>15</sub>, bi-tetrahedral Au<sub>8</sub> and bi-octahedral Au<sub>9</sub> kernel structures. An implication from the present work is that the ligand plays a critical role in dictating the size of Au<sub>n</sub>(SR)<sub>m</sub> and the structure, especially the TBBM-induced up-conversion from [Au<sub>23</sub>(S-c-C<sub>6</sub>H<sub>11</sub>)<sub>16</sub>]<sup>-</sup> to Au<sub>24</sub>(SCH<sub>2</sub>Ph-*t*-Bu)<sub>20</sub>. The emergence of new trimeric or tetrameric staples is expected to be closely related to the curvatures of the kernel structures. Of note, the kernel curvature increases with decreasing particle size and hence, cannot be sufficiently protected by conventional ligand binding modes found in larger clusters. The observations of new staple motifs indicate that the ligand determines the size and geometry of the Au kernel to a large extent; therefore, one can potentially control the electronic structures of gold-thiolate nanoclusters by the ligand or the staple motif.

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### Chapter Four

Insight into the steric & electronic effects of ligand for nanoclusters

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### 4.1 Introduction

As highlighted in previous chapters, metal clusters have enjoyed considerable research interest in chemical and physical sciences.<sup>1</sup> Recent efforts focus on ligand-protected nanoscale clusters (typically >13 metal atoms). Among the metals, gold nanoclusters have garnered significant interest owing to their elegant optical properties and a wide range of applications.<sup>2</sup> Thiolate-protected gold nanoclusters<sup>3-12</sup> (typically denoted as  $Au_n(SR)_m$ ) in particular, exhibit high stability, both in solid and solution forms, which makes them highly suitable for real-world applications.<sup>13-16</sup> for example, the availability of robust  $Au_n(SR)_m$  clusters and their crystal structures have allowed precise correlation of catalytic activity with atomic structure, offering a much deeper understanding of the catalytic mechanism<sup>17</sup> and new knowledge basis for future design of highly efficient gold nanocluster catalysts.<sup>15-17</sup>

As mentioned in chapter 1, there are two point of views in literature regarding the stability of certain magic-sized clusters (including those in the  $Au_n(SR)_m$  cluster family)<sup>18-32</sup>. These are (i) electronic shell closing, and (ii) geometric shell closing. The argument of electronic shell closing roots in the atomic electron-shell closing (such as  $1s^2$  for chemically inert He atoms,  $1s^22s^22p^6$  for Ne atoms), but the multiple nuclearity in metal clusters (as opposed to single nuclearity in atoms) gives rise to a different sequence of electron shells, i.e.  $1S^21P^61D^{10}2S^21F^{14}2P^6...$ ), and those nanoclusters having closed electron (sub)shells are often termed superatoms, such as the gas phase 40-valence-electron icosahedral  $Al_{13}^-$  superatom<sup>33</sup> and the 8-electron  $Au_{25}(SCH_2CH_2Ph)_{18}^-$ 

superatom (counterion: tetraoctylammonium ion) by assuming that each thiolate ligand localizes one Au 6s electron.<sup>23</sup> However, controversies exist and nonsuperatomic nanoclusters such as  $[Au_{25}(SCH_2CH_2Ph)_{18}]^0$  and  $[Au_{23}(S-c-C_6H_{11})_{16}]^-$  are also robust.<sup>8,34</sup>

Next, we look at the geometry or structural features of  $Au_n(SR)_m$  clusters. The X-ray crystal structure of  $[Au_{25}(SCH_2CH_2Ph)_{18}]^{0/-1}$  consists of an icosahedral Au<sub>13</sub> inner core (i.e. kernel) protected by six staple-like dimeric -SR-Au-SR-Au-SR- motifs.<sup>34-36</sup> A larger 38-atom Au<sub>38</sub>(SCH<sub>2</sub>CH<sub>2</sub>Ph)<sub>24</sub> nanocluster was found to adopt a biicosahedral Au<sub>23</sub> kernel protected by three -SR-Au-SR- monomers and six -SR-Au-SR-Au-SR- dimers.<sup>37</sup> Zeng et al. recently reported the first face-centered cubic (fcc) structure in a Au<sub>36</sub>(SPh-*t*-Bu)<sub>24</sub> nanocluster protected by 4-tert-butylbenzenethiolate ligand.<sup>38</sup> The observation of fcc structure in such a small 36-gold-atom cluster<sup>38,39</sup> was indeed a surprise, especially given the prevalent view and observation of icosahedral structures to be the most stable structural motif at small sizes of metal clusters protected by thiolate and/or phosphine ligands,<sup>34-37,40-51</sup> while fcc is expected to appear only in sufficiently large nanoclusters (e.g. at least a few hundred atoms).<sup>24</sup> More interestingly, a disproportionation mechanism was mapped out in the thermal transformation from Au<sub>38</sub>(SCH<sub>2</sub>CH<sub>2</sub>Ph)<sub>24</sub> to Au<sub>36</sub>(SPh-*t*-Bu)<sub>24</sub> via thiol ligand exchange.<sup>52</sup> Clearly, the type of thiol ligand plays a critical role in determining the structure and size, which is fundamentally different than gas phase clusters.

Since the transformation involves a substitution reaction of the aromatic HSPh-*t*-Bu (i.e., the functional sulfur atom is directly linked to the aromatic phenyl

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ring) for the non-aromatic  $-SCH_2CH_2Ph$  ligands on the starting Au<sub>38</sub> cluster, it was previously believed that the size and structure alteration from Au<sub>38</sub> to Au<sub>36</sub> could be induced by the electronic conjugation effect of the -SPh-*t*-Bu ligand.<sup>38</sup> On the other hand, -SPh-*t*-Bu is noticeably bulkier than  $-SCH_2CH_2Ph$ . Thus, the ligand bulkiness might also play some role in the ligand-induced thermal transformation of Au<sub>38</sub> to Au<sub>36</sub>. In order to gain further insight into the explicit roles of bulkiness and electronic effects of ligand, it is necessary to pursue non-aromatic ligand-capped Au<sub>36</sub> nanoclusters for comparative studies. Such a pursuit will address how the properties (e.g. optical absorption) of nanoclusters are affected by the chemical nature of the ligand (e.g., aromatic vs. non-aromatic).

In this chapter, we report our success in the synthesis and crystallization of Au<sub>36</sub> nanocluster protected by non-aromatic cyclopentanethiolate ligand (S-c- $C_5H_9$ ). We follow the same route of ligand-induced conversion from Au<sub>38</sub>(SCH<sub>2</sub>CH<sub>2</sub>Ph)<sub>24</sub> to Au<sub>36</sub>(SPh-*t*-Bu)<sub>24</sub> except using HSC<sub>5</sub>H<sub>9</sub> to replace the aromatic HSPh-<sup>t</sup>Bu thiol. The two systems, Au<sub>36</sub>(S-*c*-C<sub>5</sub>H<sub>9</sub>)<sub>24</sub> and Au<sub>36</sub>(SPh-*t*-Bu)<sub>24</sub>, permits a close comparison of their structure, optical absorption and other properties, which offers deep insight into the electronic and bulkiness effects of the ligands in dictating the Au<sub>36</sub> FCC structure. We found that the geometric structure of the ligand plays a more important role in controlling the structure of nanoclusters. This outlook is expected to guide future rational synthesis of nanoclusters with controlled size and structure.

#### 4.2 Experimental

#### 4.2.1 Synthesis and crystallization of Au<sub>36</sub>(S-c-C<sub>5</sub>H<sub>9</sub>)<sub>24</sub> nanoclusters

The Au<sub>38</sub>(SCH<sub>2</sub>CH<sub>2</sub>Ph)<sub>24</sub> nanoclusters were used as the starting material for obtaining the Au<sub>36</sub>(S-c-C<sub>5</sub>H<sub>9</sub>)<sub>24</sub> nanoclusters via a ligand exchange reaction with cyclopentanethiol (HSC<sub>5</sub>H<sub>9</sub>). Typically, ~5 mg pure Au<sub>38</sub>(SCH<sub>2</sub>CH<sub>2</sub>Ph)<sub>24</sub> nanoclusters were dissolved in ~0.5 mL toluene containing 0.5 mL cyclopentanethiol. The mixture was stirred for 24 h at 80 °C. The resulting crude product was washed with methanol several times and then extracted with dichloromethane. The as-obtained nanoclusters were identified to be Au<sub>36</sub>(S-c-C<sub>5</sub>H<sub>9</sub>)<sub>24</sub>. UV-vis spectra of the nanoclusters were acquired on an HP Agilent 8453 diode array spectrophotometer at room temperature. Single crystal growth of the nanoclusters was performed by first dissolving ~3-4 mg nanoclusters in 1 mL dichloromethane, followed by vapor diffusion of pentane into the cluster solution for 1-2 days. Single crystal X-ray diffraction data of Au<sub>36</sub>(S-c-C<sub>5</sub>H<sub>9</sub>)<sub>24</sub> was collected on a Bruker X8 Prospector Ultra system equipped with an Apex II CCD detector and an IµS micro-focus Cu K<sub>α</sub> X-ray source ( $\lambda = 1.54178$  Å).

#### 4.3 Results and Discussion

#### 4.3.1 Atomic structure

The Au<sub>36</sub>(S-c-C<sub>5</sub>H<sub>9</sub>)<sub>24</sub> nanoclusters were synthesized by ligand exchange of Au<sub>38</sub>(SCH<sub>2</sub>CH<sub>2</sub>Ph)<sub>24</sub> with cyclopentanethiol following the method reported by Zeng *et al.*<sup>38</sup> Single crystal X-ray crystallographic analysis reveals that the total structure of the Au<sub>36</sub>(S-c-C<sub>5</sub>H<sub>9</sub>)<sub>24</sub> nanocluster (Figure 4.1) is composed of a 28gold atom core of *fcc*-based truncated tetrahedron, which is protected by two pairs of  $Au_2(SR)_3$  dimeric staple motifs and 12 simple bridging thiolate ligands (Figure 4.2).



Figure 4.1. (A) Total structure of  $Au_{36}(S-c-C_5H_9)_{24}$  nanocluster (color labels: Au,

magenta; S, yellow; C, grey; H are omitted due to clarity)



**Figure 4.2.** The 28-Au-atom truncated tetrahedral kernel (highlighted in magenta) surrounded by 4 dimeric  $Au_2(SR)_3$  staple motifs and 12 simple bridging thiolate ligands. (Color codes: Au, magenta or light blue; S, yellow; C, grey)

Indeed, the basic framework of this non-aromatic thiolate-protected  $Au_{36}(S-c-C_5H_9)_{24}$  nanocluster is essentially the same as that of the previously reported aromatic thiolate-protected  $Au_{36}(SPh-t-Bu)_{24}$ .<sup>38</sup> Of note, one pair of dimeric staples (Figure 4.2, indicated by arrows) exhibit a zigzag fashion, in contrast with the other pair of nearly planar dimeric staples (on the left and right sides of the structure, Figure 4.2). The attainment of the same size and structure reveals that the electronic conjugation effect in the aromatic -SPh-*t*-Bu ligand is not necessary for the formation of the size and FCC structure of  $Au_{36}(SR)_{24}$ .

A detailed comparison of the bond lengths of Au-Au and Au-S between the two Au<sub>36</sub> structures is listed in Table 4.1. While the Au-Au bond length within the Au<sub>28</sub> kernel is almost the same between the two clusters (2.908±0.149 vs. 2.910±0.148 Å), the average Au<sub>(staple)</sub>-Au<sub>(kernel)</sub> bond length is found to undergo a considerable shrinkage (-3.1%) in the  $Au_{36}(S-c-C_5H_9)_{24}$  cluster as compared to the Au<sub>36</sub>(SPh-*t*-Bu)<sub>24</sub>, that is, 3.559±0.302 versus 3.669±0.314 Å. In addition, the average Au-S bond length is also found to be slightly shorter (-0.6%) in the  $Au_{36}(S-c-C_5H_9)_{24}$  cluster compared to  $Au_{36}(SPh-t-Bu)_{24}$ . The distinct difference (3.1%) in the Au<sub>(staple)</sub>-Au<sub>(kernel)</sub> bond length between the two clusters should be attributed to the electronic effect of the ligands (i.e., non-aromatic vs aromatic). The average S-C bond lengths are 1.90 Å and 1.81 Å for  $Au_{36}(S-c-C_5H_9)_{24}$  and Au<sub>36</sub>(SPh-*t*-Bu)<sub>24</sub>, respectively, indicating that the electronic conjugation effect in aromatic thiol ligands makes the S-C bond shorter and stronger; such a conjugation effect apparently further extends over to the S-Au bonds, resulting in larger separation between the staple motifs and the Au<sub>28</sub> kernel (hence, longer

Au<sub>(staple)</sub>-Au<sub>(kernel)</sub> bonds for aromatic ligands). The stronger influence of ligands on the S-Au bond but less on the Au-Au bond in the kernel is reasonable.

**Table 4.1.** Comparison of the  $Au_{36}(S-c-C_5H_9)_{24}$  and  $Au_{36}(SPh-t-Bu)_{24}$  crystal structures. The bond length difference (%) was calculated using  $Au_{36}(SPh-t-Bu)_{24}$  as the reference.

Bond lengths	Au <sub>36</sub> (S- <i>c</i> -C <sub>5</sub> H <sub>9</sub> ) <sub>24</sub>	Au <sub>36</sub> (SPh- <i>t</i> -Bu) <sub>24</sub>	Difference	
$Au_{(staple)}$ - $Au_{(kernel)}$	3.559±0.302 Å	3.669±0.314 Å	-3.1%	
Au-Au (within the Au <sub>28</sub> kernel)	2.908±0.149 Å	2.910±0.148 Å	-0.07%	
Au-S bond	2.310±0.047 Å	2.324±0.035 Å	-0.6%	
S-C bond	1.896±0.172 Å	1.813±0.119 Å	+4.5%	

#### 4.3.2 Mass spectrometric analyses

For obtaining further evidence of formation of the Au<sub>36</sub>(S-c-C<sub>5</sub>H<sub>9</sub>)<sub>24</sub> cluster, we performed electrospray ionization mass spectrometric analysis. No signals were observed either in positive or negative mode indicating the cluster to be charge neutral. Hence, the cluster was mixed with CsOAc to form positively charged Cs<sup>+</sup>- cluster adducts in subsequent ESI-MS analysis (Figure 4.3). A prominent peak was observed at *m*/*z* 9651.62, corresponding to the mono-cation  $[Au_{36}(S-c-C_5H_9)_{24}Cs]^+$  adduct peak. Thus, the cluster mass is determined to be 9518.71 after subtracting one Cs<sup>+</sup>, which matches perfectly with the calculated

value of Au<sub>36</sub>(S-c-C<sub>5</sub>H<sub>9</sub>)<sub>24</sub> (cal: 9519.35 Da, deviation: 0.64 Da). Also, peaks corresponding to small quantities of Au<sub>32</sub>(S-c-C<sub>5</sub>H<sub>9</sub>)<sub>20</sub> (m/z = 8458.60) and Au<sub>28</sub>(S-c-C<sub>5</sub>H<sub>9</sub>)<sub>20</sub> (m/z = 7671.77) were observed, indicating they are less stable as compared to the Au<sub>36</sub>(S-c-C<sub>5</sub>H<sub>9</sub>)<sub>24</sub> cluster under the synthetic size-focusing conditions. Here it is worth noting that during the matrix-assisted laser ionization mass spectrometric (MALDI-MS) analysis of the Au<sub>36</sub>(S-c-C<sub>5</sub>H<sub>9</sub>)<sub>24</sub> cluster, we did not observe the one-ligand lost Au<sub>36</sub>(SR)<sub>23</sub> product peak typically seen in the



**Figure 4.3**. (A) Electrospray ionization mass spectrum (ESI-MS) of the Au<sub>36</sub>(S-c- $C_5H_9$ )<sub>24</sub> cluster. CsOAc was added to form Cs<sup>+</sup> adducts with the charge-neutral nanoclusters. The asterisks indicate peaks corresponding to small amounts of  $[Au_{32}(S-c-C_5H_9)_{20}Cs]^+$  and  $[Au_{28}(S-c-C_5H_9)_{20}Cs]^+$  cluster ions. (B) Matrix-assisted laser desorption ionization mass spectrum (MALDI-MS) of the Au<sub>36</sub>(S-c-C<sub>5</sub>H<sub>9</sub>)<sub>24</sub> cluster (using DCTB matrix). The asterisks denote the fragments generated due to MALDI.

MALDI-MS spectrum of aromatic thiol-protected Au<sub>36</sub>(SR)<sub>24</sub> clusters (where, SR = 4-*tert*-butylbenzenethiolate or thiophenol).<sup>52,60</sup> Instead, the highest observed cluster peak was that of Au<sub>32</sub>(S-c-C<sub>5</sub>H<sub>9</sub>)<sub>19</sub> (even at very low laser intensities), which denotes a further  $-Au_4(SR)_4$  fragment loss from the one-ligand lost Au<sub>36</sub>(SR)<sub>23</sub> product. Here, it is worthy to note that such a tetrameric Au<sub>4</sub>(SR)<sub>4</sub> fragment loss has been reported previously in the MALDI-MS spectrum of clusters like Au<sub>25</sub>(SR)<sub>18</sub>.<sup>56</sup> Hence, the MALDI-MS analysis of the Au<sub>36</sub>(S-c-C<sub>5</sub>H<sub>9</sub>)<sub>24</sub> cluster indicates that the chemical nature of the ligand plays a role in gas-phase production of specific cluster ions.

#### 4.3.3 Optical properties

We next compare the optical spectra of the two nanoclusters. While their spectral profiles are quite similar (Figure 4.4), the peak wavelengths of the Au<sub>36</sub>(S-c-C<sub>5</sub>H<sub>9</sub>)<sub>24</sub> nanocluster indeed shows large blue shifts compared to those of Au<sub>36</sub>(SPh-*t*-Bu)<sub>24</sub>; specifically, the peaks of Au<sub>36</sub>(S-c-C<sub>5</sub>H<sub>9</sub>)<sub>24</sub> are at ~345 nm and ~555 nm (Figure 4.4.a) *versus* 375 nm and 570 nm for the aromatic thiolate-capped Au<sub>36</sub>(SPh-*t*-Bu)<sub>24</sub> analogue (Figure 4.4.b), respectively. These changes are also reflected in the somewhat different colors of dichloromethane solutions of the two clusters, with the Au<sub>36</sub>(S-c-C<sub>5</sub>H<sub>9</sub>)<sub>24</sub> solution being coral pink (Figure



**Figure 4.4.** UV-vis spectra of (A)  $Au_{36}(S-c-C_5H_9)_{24}$  and (B)  $Au_{36}(SPh^{-t}Bu)_{24}$  cluster solutions in dichloromethane. Inset: photographs of the nanocluster solutions.

4.4A, inset) while the Au<sub>36</sub>(SPh-*t*-Bu)<sub>24</sub> solution being a greenish color (Figure 4.4.b, inset). The ~30 nm blueshift (~0.29 eV) for the short-wavelength peak is much larger than the blueshift of the long-wavelength peak (~15 nm, ~0.06 eV). These differences reflect the above structural differences: the long-wavelength peak is primarily due to electronic transitions within the Au<sub>28</sub> kernel<sup>52</sup> and is less affected by the ligands, while the short-wavelength peak involves more contribution from the surface (including the staple Au atoms and ligands as well)

and is expected to be more affected. Further insight into the subtle differences in the electronic structure calls for density functional theory (DFT) calculations on the genuine structures of  $Au_{36}(S-c-C_5H_9)_{24}$  and  $Au_{36}(SPh-t-Bu)_{24}$  without simplifying the ligands to  $-SCH_3$ .<sup>53,54</sup>

#### 4.3.4 Conversion of $Au_{38}(SCH_2CH_2Ph)_{24}$ to $Au_{36}(S-c-C_5H_9)_{24}$

With regard the  $Au_{36}(SPh-t-Bu)_{24}$ formation to from the Au<sub>38</sub>(SCH<sub>2</sub>CH<sub>2</sub>Ph)<sub>24</sub> nanoclusters, Jin and coworkers recently elucidated the structure and size transformation mechanism.<sup>52</sup> The reaction pathway is found to primarily consist of four stages: (1) ligand exchange, (2) structure distortion, (3) disproportionation, and (4) size-focusing.<sup>52</sup> All of these steps could be conveniently monitored by UV-visible spectroscopy. Herein we monitored the conversion process for the case of non-aromatic cyclopentanethiol and observed similar UV-visible spectral features of the intermediate products. As shown in Figure 4.5, the starting  $Au_{38}(SCH_2CH_2Ph)_{24}$  cluster shows prominent peaks at 490, 620, 750 and 1050 nm. With time, a new peak at ~540 nm starts to appear in addition to the Au<sub>38</sub> features (Figure 4.5), indicating structural distortion to the Au<sub>38</sub>(S-c-C<sub>5</sub>H<sub>9</sub>)<sub>x</sub>(SCH<sub>2</sub>CH<sub>2</sub>Ph)<sub>24-x</sub> cluster when more and more cyclopentanethiol ligands are exchanged onto the Au<sub>38</sub> surface. This peak eventually disappeared and a peak at ~560 nm emerged and persisted; the latter peak is indicative of the formation of the  $Au_{36}(SC_5H_9)_{24}$  nanoclusters. These observations show that the transformations of Au<sub>38</sub> to Au<sub>36</sub> in non-aromatic HSC<sub>5</sub>H<sub>9</sub> vs. aromatic HSPh-*t*-Bu share some common features. However, the reaction in the case of

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cyclopentanethiol took a longer time to complete (~6 h versus 2 h in the HSPh-*t*-Bu case), indicating that the size-focusing step takes a longer time to occur in the cyclopentanethiol case.



**Figure 4.5.** Time-dependent UV-vis spectra of the transformation of  $Au_{38}(SCH_2CH_2Ph)_{24}$  to  $Au_{36}(S-c-C_5H_9)_{24}$  clusters. Grey arrows show the signature peaks during the course of the reaction.

### 4.3.5 Effect of ligands

We further comment on the bulkiness and electronic effects of  $SC_5H_9$  and SPh-*t*-Bu ligands. When we first observed the transformation of Au<sub>38</sub> to Au<sub>36</sub>,<sup>38</sup> we suspected that the electronic conjugation effect of the HSPh-*t*-Bu ligand, instead of the steric or geometric hindrance, triggered such a conversion. This

view was based on the fact that, in previous syntheses of Au<sub>25</sub>(SR)<sub>18</sub> and  $Au_{38}(SR)_{24}$  (where, SR represents multiple types of thiolate ligands),<sup>53-59</sup> even very bulky thiolate ligands (such as glutathione (HS-G), a tripeptide) readily yielded  $Au_{25}(SG)_{18}$  and  $Au_{38}(SG)_{24}$  nanoclusters, rather than the  $Au_{36}(SR)_{24}$ nanocluster. After we performed a detailed mechanistic study of this transformation process,<sup>52</sup> we further found that it is indeed the bulkiness of the HSPh-*t*-Bu ligand that induces the structural distortion and further transformation of the starting Au<sub>38</sub>(SR)<sub>24</sub>. Of note, Nimmala et al<sup>60</sup> previously observed the transformation of larger clusters protected by nonaromatic ligand to Au<sub>36</sub>(SPh)<sub>23</sub> via ligand exchange with HSPh,<sup>60</sup> in which the one-ligand difference (Au<sub>36</sub>(SPh)<sub>23</sub> vs. Au<sub>36</sub>(SR)<sub>24</sub> in our work) was caused by destructive matrix-assisted laser desorption ionization mass spectrometric analysis.<sup>52</sup> Herein, with the successful crystallization of a non-conjugated  $Au_{36}(S-c-C_5H_9)_{24}$ , it can now be concluded that the hindrance of the thiolate ligand plays a key role here in determining the structure and size of ligand-protected gold nanoclusters. By comparing the various ligands (Scheme 4.1) and their resultant cluster sizes, we further point out that the steric effect of the thiolate ligand at the  $\alpha$  position is more important than the generally discussed steric effect-i.e. the steric cone angle in previous literature works.<sup>61</sup> The  $\alpha$ -position directly connects to the sulfur atom, hence the steric effect of this position can affect more the bonding between the sulfur atom and gold atom.

**Scheme 4.1.** Molecular structures of (A) HSPh-*t*-Bu, (B) HSCH<sub>2</sub>CH<sub>2</sub>Ph, (C) HSC<sub>5</sub>H<sub>9</sub> and (D) glutathione.



While the ligand *bulkiness* triggers the initial transformation process due to bulkiness-caused distortion to the original Au<sub>38</sub> structure, the effect of electronic conjugation of aromatic ligand is also in operation in the conversion process; With the aromatic HSPh-*t*-Bu thiol, Au<sub>36</sub> nanoclusters were exclusively formed (yield ~90%, Au atom basis),<sup>52</sup> while using non-aromatic HSC<sub>5</sub>H<sub>11</sub> in the present work the yield is much lower (~50%), indicating some difference in the latter steps of the four-stage transformation pathway, albeit the first two steps (i.e. ligand exchange and structural distortion) are essentially the same (see discussions above and Figure 4.5). In the case of cyclohexanethiol exchange process, previous results yielded more polydispersed products.<sup>52</sup> All these results imply that the electronic conjugation effect of the aromatic ligand is also important for exclusive formation and stabilization of Au<sub>36</sub>. Taken together, both the steric bulkiness and electronic factors of the ligand are important for the

transformation from  $Au_{38}$  to  $Au_{36}$  and their respective effects are manifested in the different stages of the transformation process.

#### 4.4 Conclusion

In this chapter, we have achieved the synthesis and crystallization of a non-aromatic cyclopentanethiolate–protected  $Au_{36}(S-c-C_5H_9)_{24}$  nanocluster. This attainment rules out that the fcc structures of aromatic-thiolate-protected Au<sub>36</sub>(SPh-*t*-Bu)<sub>24</sub> and Au<sub>28</sub>(SPh-*t*-Bu)<sub>20</sub> nanoclusters is dictated by the aromatic ligand. Close comparison of the two structures offers insight into the electronic conjugation and steric effects of HSC<sub>5</sub>H<sub>9</sub> and HSPh-t-Bu in governing the structure and properties of the Au<sub>36</sub>(SR)<sub>24</sub> nanocluster. Our results show that the steric structure of the ligand plays a more important role in the formation of the Au<sub>36</sub> cluster structure, while the electronic structure of the ligand is more important for exclusive formation of Au<sub>36</sub>(SR)<sub>24</sub> nanoclusters. Unlike the view of the cone angle of the whole ligand previously discussed in the literature, we specifically point out that the steric hindrance at the  $\alpha$  position in HSC<sub>5</sub>H<sub>9</sub> and HSPh-t-Bu is critically important in triggering the initial transformation of Au<sub>38</sub> due to bulkiness-caused distortion to the Au<sub>38</sub> structure, with the electronic conjugation effect exerted in the later stages of the four-stage transformation process. In addition, the electronic effect of aromatic vs. nonaromatic ligands is also manifested in the optical absorption properties, i.e. the distinct shift in optical absorption peaks of the nanoclusters. These insights are expected to offer some

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new perspectives in terms of structural and size control in nanoclusters, as well as what factors dictate the stability of nanoclusters.

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# Chapter Five

Catalytic Applications of Atomically Precise Gold Nanoclusters

#### 5.1 Introduction

Catalysis by nanomaterials has garnered immense research interest in the last few decades due to their attractive catalytic properties, which stem from their unique geometric and electronic structures. Specifically, the area of gold nanocatalysis began in the mid-1980s when Haruta et al. demonstrated the high catalytic power of gold nanoparticles (<10 nm) loaded on inorganic supports for low temperature oxidation of carbon monoxide.<sup>1,2</sup> Since this seminal discovery, gold nanoparticles (especially those which fall under the nanocluster regime, i.e., < 3 nm) have been shown to efficiently catalyze a wide range of organic reactions.<sup>3-5</sup>

However, a precise structure-activity correlation was not achieved in early work on gold nanocatalysis due to the polydisperse nature of the synthesized gold nanoparticles. In other words, it was difficult to correlate the observed catalytic activity and selectivity (which averaged out due to contributions from non-uniform nanoparticles) to the structure of an individual nanoparticle catalyst. The discovery of truly monodisperse ligand-protected gold nanoclusters in the last decade has allowed researchers to overcome this obstacle and gain an atomic level understanding of catalytic mechanisms.<sup>6</sup> Among these atomically precise gold clusters, the Au<sub>25</sub>(SR)<sub>18</sub> cluster, owing to its ease of synthesis, high stability and ability to exist in (-1,0) charge states, has been extensively investigated as catalysts for wide-ranging organic transformations.<sup>4,5</sup>

For some of these reactions, size-dependent catalytic activities of ligandprotected gold nanoclusters have been reported. For example, Yan et al.

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investigated the cluster size effect in partial oxidation of styrene. The general order of observed activity was found to be  $Au_{25}(SR)_{18} > Au_{38}(SR)_{24} > Au_{144}(SR)_{60}$ . In other words, the smaller nanoclusters were found to be more efficient than larger ones, especially when  $O_2$  was used as the oxidant.<sup>7</sup> This result is in good agreement with a previous report which showed that larger nanoclusters have lower  $O_2$ -activating capability.<sup>8</sup>

However, exact identification of the catalytically active sites in the gold clusters has remained a challenge in the field of nanocatalysis. In this regard, since the properties of gold clusters are extremely sensitive to the number of Au atoms, addition or removal of a single Au atom is expected to induce significant changes in its structure and properties. Investigating such similar-sized clusters in probe catalytic reactions is expected to reveal the true nature of active sites and pave the way for atomic level tuning of catalytic properties in clusters.

The previous chapters of this thesis describe the synthesis and structure determination of a series of gold nanoclusters, all of which are composed of  $\leq 25$  Au atoms and hence, lie in the catalytically active size regime (Figure 5.1). Interestingly, all of these clusters were found to exhibit very different Au kernels and surface ligand binding modes, which encouraged us to test these as catalysts to gain atomic-level structure-activity and structure-selectivity correlations in catalytic studies.



**Figure 5.1.** Total structures of newly synthesized  $Au_nL_m$  clusters where  $x \le 25$ ;

Specifically, we chose to investigate catalytic properties of Au<sub>n</sub>L<sub>m</sub> clusters where n = 23, 24 or 25, since these clusters are most closely-related size-wise.<sup>9-</sup> <sup>16</sup> Coming to our choice of a probe reaction, we decided to test the Au catalysts in the reduction of 4-nitrophenol (4-NP) at room temperature under homogeneous conditions.<sup>17</sup> This reaction features all the characteristics of a "model catalytic reaction"; (a) Reduction of 4-NP does not proceed without a catalyst, (b) Highest level of selectivity is achieved, since only a single product is formed, and (c) The reaction occurs under ambient conditions (e.g., room temperature), which ensures stability of the catalyst during and after the reaction.<sup>18,19</sup>

#### 5.2 Catalytic reduction of 4-nitrophenol (4-NP) by NaBH<sub>4</sub>

#### 5.2.1 Motivation and significance

Nitroaromatic compunds including 4-NP are human health hazards and feature in the EPA's list of priority pollutants for environmental remediation. The nitro group's electron-withdrawing nature in conjunction with the stability of the aromatic ring makes them resistant to oxidative biodegradation. The reduction product of 4-NP, i.e., 4-aminophenol (4-AP), has diverse applications ranging from medicinal chemistry and natural product synthesis to photographic film development.<sup>17,20</sup>

#### 5.2.2 Mechanism of catalytic 4-NP reduction by NaBH<sub>4</sub>

The 4-NP reduction by NaBH<sub>4</sub> catalyzed by Au nano-catalysts in aqueous medium can easily be monitored by UV–vis spectroscopy. The 4-nitrophenolate ion shows an absorption maximum at 400 nm while the product 4-AP peak appears at 295 nm. During the reaction, the decrease of the 4-NP peak at 400 nm is treated as a pseudo first-order decay reaction due to the presence of excess NaBH<sub>4</sub>. The rate of this decay is then measured to compare catalytic activity of various catalysts.<sup>17</sup>

#### 5.2.3 Experimental

The catalytic reduction of 4-NP was carried out in 3 mL Quartz cuvette using a using a Hewlett-Packard (HP) Agilent 8453 diode array spectrophotometer. Stock solutions of Au clusters were made in THF (~1 mg/

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mL). 150  $\mu$ L of aqueous 4-NP solution (0.1 mM) was added to 1.5 mL THF in the cuvette. Then 5  $\mu$ L of stock catalyst solution was added to the above mixture followed by 1 ml of freshly prepared NaBH<sub>4</sub> solution (0.2 M). The cuvette was then placed in the sample holder without stirring and the UV-vis absorption spectra recorded with time.

#### 5.2.4 Results and discussion

To study the reduction rate of 4-NP, the change of absorbance at 400 nm with time was used for kinetic analysis.<sup>17-19</sup> The typical UV-visible absorption spectral changes that occur after a certain period of induction time ( $\leq$  10 minutes) during this catalytic reaction are shown in Figure 5.2. For the thiolate-protected Au<sub>23</sub>, Au<sub>24</sub> and Au<sub>25</sub> clusters, the complete reduction time of 4-NP ranged between 2-6 minutes. Figure 5.3 shows the ln (A<sub>t</sub>/A<sub>0</sub>) versus reaction time data for the reduction of 4-NP over the thiolate-protected Au clusters. Using these plots, the corresponding rate constants, *k*, were determined and are shown in Table 5.1. Here, A<sub>0</sub> and A<sub>t</sub> are the absorption peaks at 400 nm initially and at time t, respectively.



Figure 5.2. UV/Vis absorption spectra during the catalytic reduction of 4-NP over

Au<sub>23</sub>(S-c-C<sub>6</sub>H<sub>11</sub>)<sub>16</sub> (representative example)



**Figure 5.3.** Plots of  $ln(A_t/A_0)$  and the reaction time for 4-NP reduction by thiolateprotected Au<sub>23</sub>, Au<sub>24</sub> and Au<sub>25</sub> clusters, where A<sub>0</sub> and A<sub>t</sub> are the absorption peaks at 400 nm initially and at time *t*, respectively.

Table	5.1.	Pseudo-first	order	rate	constants	for	thiolate-protected	Au	cluster
catalyz	zed 4	-NP reductior	).						

Au <sub>n</sub> (SR) <sub>m</sub>	Rate constant (s <sup>-1</sup> )
[Au <sub>23</sub> (S-c-C <sub>6</sub> H <sub>11</sub> ) <sub>16</sub> ] <sup>-</sup>	$0.0370 \pm 0.0045$
[Au <sub>24</sub> (SCH <sub>2</sub> Ph- <i>t</i> -Bu) <sub>20</sub> ] <sup>0</sup>	$0.0090 \pm 0.0004$
[Au <sub>25</sub> (SCH <sub>2</sub> CH <sub>2</sub> Ph) <sub>18</sub> ] <sup>-</sup>	$0.0242 \pm 0.0027$

From kinetic analysis of the 4-NP reduction reaction, the order of catalytic activity is found to be,  $[Au_{23}(S-c-C_6H_{11})_{16}]^- > [Au_{25}(SCH_2CH_2Ph)_{18}]^- >$ [Au<sub>24</sub>(SCH<sub>2</sub>Ph-*t*-Bu)<sub>20</sub>]<sup>0</sup>. Since the metal nanocatalyst initiates this catalytic reduction by relaying electrons from the donor BH4<sup>-</sup> to the acceptor 4-NP on adsorption of both reactants on their surfaces, this trend appears to be related to the electron transfer capabilities of our Au clusters (i.e., their electronic structures). Of note, the  $Au_{25}(SCH_2CH_2Ph)_{18}$  cluster has been shown to be able to shuttle between -1 and 0 charge states and is found to be quite stable in both its anionic and charge-neutral forms.<sup>21</sup> Such differently charged forms have not yet been discovered in the thiolate-protected Au<sub>23</sub> and Au<sub>24</sub> clusters and future work in this area is expected to shed more light on the observed trend of catalytic activity. In addition, all three Au clusters exhibit different core and surface structures. Hence, DFT calculations on preferred 4-NP adsorption geometry in future studies is expected to offer greater insight into the catalytic activity of these clusters.

With respect to mixed phosphine/thiolate-protected clusters, we discovered that the  $[Au_{24}(PPh_3)_{10}(SC_2H_4Ph)_5X_2]^+$  cluster immediately converted to the  $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5X_2]^{2+}$  cluster in mixed solvent of THF-water which is the solvent used for the present 4-NP reduction reaction. Hence, this cluster was not evaluated as a catalyst for this reaction.

The mixed phosphine/thiolate-protected Au<sub>25</sub> cluster, on the other hand, was found to catalyze the 4-NP reduction reaction. However, unlike the reactions catalyzed by thiolate-protected Au clusters, which were complete in 2-6 minutes,



**Figure 5.4.** (a) UV-vis absorption spectra and, (b) Plot of  $ln(A_t/A_0)$  and the reaction time for the catalytic reduction of 4-NP over the  $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5X_2]^{2+}$  cluster.

the reaction catalyzed by the  $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5X_2]^{2+}$  cluster took > 1 h for completeion (Figure 5.5.a). The rate constant for this reaction was determined to be 0.000488 ± 0.000022 s<sup>-1</sup>, which is ~20 times lower than the worst  $Au_n(SR)_m$ cluster (i.e., the  $Au_{24}(SCH_2Ph-t-Bu)_{20}$  cluster). Here it is worthy to note that the non-core-shell  $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5X_2]^{2+}$  cluster has previously been found to be less catalytically active as compared to its only-thiolate protected  $Au_{25}$ counterpart.<sup>22</sup> In these studies, differences in their electronic structures were shown to be the primary reason for their differing catalytic properties.

#### 5.2.5 Summary

Although all of the tested Au clusters are roughly 1 nm in size, they exhibit different catalytic properties in the 4-NP reduction reaction. This in turn proves that rather than their nominal size, it is the detailed atomic and electronic structure that dictate the catalytic properties of nanoclusters.

# 5.3 Application of atomically precise nanoclusters in multi-component A<sup>3</sup>coupling reaction

#### 5.3.1 Motivation and significance

Propargylamines are important intermediates in therapeutic drug molecules and natural products synthesis. The traditional method for synthesis of propargylamines involves addition of a metal acetylide to an imine through the use of strong bases such as butyllithium to form metal acetylides. However, such a reaction path requires stoichiometric amounts of reactants and is highly moisture-sensitive, which makes the process highly cumbersome.<sup>23</sup> An attractive atom-economical alternative approach to the synthesis of propargylamines was introduced by C.J Li's group in 2003 which involves a catalytic coupling of alkyne, aldehyde, and amine, where, water is the only by-product.<sup>24</sup> This reaction is commonly referred to as *A*<sup>3</sup>-*coupling reaction*. Following the initial report, Kidwai et al. demonstrated the ability of gold nanoparticles (10-70 nm) to catalyze this reaction.<sup>25</sup> However, this reaction was found to require a very high catalyst loading (10 mol%). In order to combine the advantages of homogeneous and heterogeneous catalysis, Corma et al. used supported-gold nanoparticle catalysts having both Au(III) and Au(I) sites for this multi-component reaction.<sup>26</sup> It was proposed that Au(III) sites on the inorganic supports (e.g., CeO<sub>2</sub>, ZrO<sub>2</sub>) were the active catalytic sites. However, it was determined that Au(I) sites could also contribute to the catalytic reaction.

## 5.3.2 Mechanism of A<sup>3</sup>-coupling reaction

The mechanism of the A<sup>3</sup>-coupling reaction is not well-understood. However, a tentative reaction pathway involves C-H activation of the alkyne forming an intermediate  $\pi$ -metal-alkyne complex, which then reacts with the iminium ion, resulting in the formation of propargylamine with simultaneous regeneration of the metal catalyst (scheme 5.2).<sup>23</sup> **Scheme 5.1.** Tentative mechanism for the A<sup>3</sup>-coupling reaction. (Reproduced with permission from ref. 23. Copyright 2012 Royal Society of Chemistry.)



# 5.3.3 Ligand-protected Au nanoclusters as catalysts for the A<sup>3</sup>-coupling reaction

Based on the tentative mechanism and Corma et al.'s previous claim that Au(I) sites could contribute to the A<sup>3</sup>-coupling reaction,<sup>23,26</sup> we hypothesized that thiolate-protected atomically precise Au nanoclusters may act as efficient catalysts for this reaction. Here, our hypothesis is based on the fact that thiolate-protected Au nanoclusters exhibit a core shell structure,<sup>4-6</sup> comprising of-(i) An electron rich Au(0) core (highlighted in magenta in Figure 5.5) and (ii) a shell comprising of Au atoms carrying partial positive charges ( $\delta^+$ ) (highlighted in light blue in Figure 5.5) on account of bonding to thiolates in the staple motifs.<sup>27</sup> We

envision that use of atomically precise Au nanoclusters will help us attain fundamental understanding of this reactions' mechanism.

Since this reaction occurs at moderately high temperatures (80-100  $^{\circ}$ C), we chose the Au<sub>38</sub>(SR)<sub>24</sub> cluster as our model catalyst, owing to its high solution phase stability.<sup>27</sup>



**Figure 5.5.** Total structure of Au<sub>38</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>24</sub> cluster; color codes: Au, magenta or light blue; S, yellow; -R groups of ligands are omitted for clarity. (Adapted with permission from ref. 27. Copyright 2010 American Chemical Society.)

#### 5.3.4 Experimental

#### 5.3.4.1 Synthesis of Au<sub>38</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>24</sub> clusters

The  $Au_{38}(SC_2H_4Ph)_{24}$  cluster was synthesized according to a previously reported method.<sup>27</sup> Briefly, HAuCl<sub>4</sub>·3H<sub>2</sub>O (0.5 mmol) and GSH powder (2.5 mmol) were mixed in 20 mL acetone at room temperature under vigorous stirring for  $\sim 20$  min, after which a solution of NaBH<sub>4</sub> (5 mmol, dissolved in 6 mL cold Nanopure water) was rapidly added to the suspension under vigorous stirring. The color of the solution immediately turned black indicating the formation of Au nanoclusters. After ~15 minutes, the black  $Au_n(SR)_m$  nanoclusters were found to precipitate out and stick to the inner wall of the flask. The clear acetone solution was decanted and 6 mL water was added to dissolve the  $Au_n(SR)_m$  clusters. Monodisperse  $Au_{38}(SC_2H_4Ph)_{24}$  nanoclusters were obtained by reacting  $Au_n(SR)_m$  nanoclusters in water with excess  $PhC_2H_4SH$  in toluene-ethanol mixture at 80 °C for ~36-40 h. The organic phase was then thoroughly washed with ethanol (or methanol) to remove excess thiol, following which the Au<sub>38</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>24</sub> nanoclusters were simply separated from Au(I)-SG (poorly soluble in almost all solvents) by extraction with dichloromethane or toluene.

#### 5.3.4.2 Catalytic experiment

Typically, 1 equiv of benzaldehyde (1mmol), 1.2 equiv of piperidine, and 1.3 equiv of phenylacetylene were added to a 10 mL round-bottom flask containing ~1 mg of the Au<sub>38</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>24</sub> cluster (0.1  $\mu$ mol). This reaction mixture

was then stirred at 80 °C for 6 h. The products of this catalytic reaction were analyzed by NMR spectroscopy.

## 5.3.5 Results and discussion

Preliminary catalytic runs suggest the  $Au_{38}(SC_2H_4Ph)_{24}$  cluster is a highly efficient catalyst for the A<sup>3</sup>-coupling reaction involving benzaldehyde, piperidine and phenylacetylene. An excellent conversion of 93% to the propargylamine product in 5 h was determined using NMR spectroscopy. Figure 5.6 depicts time-



**Figure 5.6.** NMR spectra of (A) Benzaldehyde, (B) Phenylacetylene, (C) Piperidine, (D) Reaction mixture after 1 h and, (E) Reaction mixture after 6 h.



**Figure 5.7.** Conversion of benzaldehyde, phenylacetylene and piperidine as a function of reaction time over  $Au_{38}(SC_2H_4Ph)_{24}$  catalyst.

dependent NMR spectra of the reaction products. We see continuous increase of peaks corresponding to the propargylamine product while the reactant peaks decrease with time.

The reaction kinetics was studied by monitoring the conversion of reactants at different time intervals (Figure 5.7). We found that the conversion to propargylamine increased rapidly during the first few hours, reached a maximum (> 90%) within 4 h time and was maintained thereabouts for prolonged period of time. The TOF calculated at 50 % conversion turns out to be 3333  $h^{-1}$ .

We further characterized our  $Au_{38}(SC_2H_4Ph)_{24}$  catalyst after the A<sup>3</sup>coupling reaction by UV-visible spectroscopy (Figure 5.8) and ESI-mass spectrometry (Figure 5.9).



**Figure 5.8.** UV-vis spectra of  $Au_{38}(SC_2H_4Ph)_{24}$  catalyst before (black curve) and after the A<sup>3</sup>-coupling reaction (red curve).

Figure 5.8 shows that the signature peaks of Au<sub>38</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>24</sub> cluster at 450 nm, 630 nm and 750 nm are maintained after the A<sup>3</sup>-coupling reaction, indicating the stability of the Au<sub>38</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>24</sub> cluster under the reaction conditions. This was further confirmed by the ESI-mass spectrum of the Au<sub>38</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>24</sub> catalyst taken after the reaction, which shows peaks corresponding to only the Au<sub>38</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>24</sub> cluster (Figure 5.9).



**Figure 5.9.** ESI-mass spectrum of  $Au_{38}(SC_2H_4Ph)_{24}$  cluster after the A<sup>3</sup>-coupling reaction

On the basis of the observed catalytic activity, we propose a mechanism where Au(I) sites in the staple motifs of the Au<sub>38</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>24</sub> cluster activate phenylacetylene in the first step forming a  $\pi$ -Au<sub>38</sub>-phenylacetylene complex, which then reacts with the spontaneously formed iminium ion. We believe the electron rich core could further help in facilitating positively charged iminium ions to react with the activated  $\pi$ -Au<sub>38</sub>-phenylacetylene complex. Theoretical input in the form of DFT calculations are needed in future to confirm our proposed mechanism.

#### 5.4 Conclusions

We have demonstrated interesting comparative catalytic activities of similar sized  $Au_nL_m$  clusters (where n = 23-25) in the model catalytic reaction involving reduction of 4-nitrophenol by NaBH<sub>4</sub>. The observed catalytic activities of these clusters suggest that, rather than their nominal size, it is their detailed structure and electronic properties which dictate their catalytic properties.

We further investigated a thermally stable  $Au_{38}(SC_2H_4Ph)_{24}$  cluster as a catalyst for multi-component A<sup>3</sup>-coupling reaction. This cluster was found to catalyze this reaction very efficiently (>94% conversion). We believe the coreshell structure of this cluster is responsible for the observed high catalytic activity. DFT calculations in future are expected to reveal the exact catalytically active sites in the  $Au_{38}(SC_2H_4Ph)_{24}$  cluster.

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# Chapter Six

**Conclusions and Future Directions** 

## 6.1. Conclusions

In this thesis, we have succeeded in synthesizing and determining the crystal structures of a family of stable ligand-protected gold nanoclusters containing  $\leq 25$  Au atoms. These clusters, which include  $[Au_{18}(S-c-C_6H_{11})_{14}]^0$ ,  $[Au_{23}(S-c-C_6H_{11})_{16}]^{-}$ ,  $[Au_{24}(SCH_2Ph-t-Bu)_{20}]^0$  and  $[Au_{24}(PPh_3)_{10}(SC_2H_4Ph)_5X_2]^+$  (where, X= Cl/Br) nanoclusters, are all protected by either all-thiolate or mixed ligands of phosphine and thiolate. Interestingly, these clusters, all of which are ~ 1 nm in size, are found to exhibit great variety in their total structures (i.e., the metallic cores as well as the surface structures). The discovery of these new Au kernels offer new insights into the structure evolution of gold nanoparticles and refute the classical point of view that that icosahedral structures should be the most stable structure for small clusters.

Through the case study of a  $Au_{36}(SR)_{24}$  nanocluster, we have demonstrated the role of the protecting ligands' steric structure in dictating the precise structure of the resulting nanocluster. The observations of new ligandbinding modes or the staple motifs in thiolate-protected  $Au_{18}$ ,  $Au_{23}$  and  $Au_{24}$ clusters confirm the latter assumption and are expected to offer some new perspectives in structural and size control of nanoclusters.

We further chose to investigate catalytic properties of  $Au_n(SR)_m$  clusters where n = 23, 24 or 25 (since size-wise, these clusters are most closely-related) in the reduction of 4-nitrophenol at room temperature under homogeneous conditions. The observed catalytic activities of these clusters suggest that the detailed atomic structures, rather than the nominal size (*n*) in  $Au_n(SR)_m$  clusters, dictate their catalytic properties.

# **6.2. Future Directions**

Single crystal growth of precious metal nanoclusters has long been a huge challenge in the field. Indeed, coaxing these large "molecules" containing dozens of metal atoms and ligands to form single crystals has always seemed like a herculean task. Hence, the experience gained from growing single crystals of gold nanoclusters (≤ 40 Au atoms) using rigid ligands could be guiding principles in attempt to crystallize much larger ligand-protected gold nanoclusters (> 100 gold atoms) and even possibly plasmonic ones (> 250 gold atoms). Apart from catalysis, such efforts will have important implications for other surface-dependent research areas like self-assembled monolayers (SAMs) on gold surfaces.

Similarly, the knowledge gained through synthesis and structural characterization of gold nanoclusters is expected to drive the generation of stable atomically precise nanoclusters of non-noble metals (e.g. copper, nickel, etc). Synthesizing and solving the crystal structures of such nanoclusters will help us gain a clear insight into their quantum confinement effects, structure evolution with increasing size, as well as their surface structures. These fundamental studies will in turn lead to the development of their practical applications.

Finally, investigating the exciting catalytic properties of the closely-sized new library of Au clusters (containing  $\leq 25$  Au atoms) in probe reactions is expected to lead to identification of the catalytically active sites– which continues to be a huge challenge in the field of nanocatalysis. Further, such endeavors

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could pave the way for the ultimate control in catalyst synthesis, i.e., atom-byatom level of tuning catalytic properties in clusters. Department of Chemistry Carnegie Mellon University 4400 Fifth Ave Pittsburgh, PA, 15213, USA

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Department of Chemistry, Carnegie Mellon University Advisor: Prof. Rongchao Jin	Aug 2010 – Aug 2015
Thesis: "Controlling gold nanoparticles with atomic precision for catalytic ap	plications"
National Chemical Laboratory (NCL), Pune, India Advisor: Dr. Sayam Sen Gupta	Dec 2008 – May 2010
Project: "Synthesis of mesoporous silica-polypeptide hybrid materials using and click chemistry"	NCA polymerization
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Internship: Training in organic synthesis	
Awards & Recognition	
<ul> <li>McWilliams Fellowship, Carnegie Mellon University (CMU)</li> </ul>	June 2014 – May 2015

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- A. Das, T. Li, K. Nobusada, C. Zeng, N. L. Rosi, & R. Jin, "Non-superatomic [Au<sub>23</sub>(SR)<sub>16</sub>] Nanocluster Featuring Bipyramidal Au<sub>15</sub> Kernel and Trimeric Au<sub>3</sub>(SR)<sub>4</sub> Motif" J. Am. Chem. Soc. 2013, 135, 18264.
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#### **Conference Presentations**

- 1. A. Das & R. Jin, "Extended Surface Staple Motifs in Thiolate-Protected Au<sub>23</sub> and Au<sub>24</sub> Nanoclusters: Implications for Nano-Gold Catalysis" **249th ACS National Meeting**, Denver, Colorado, 2015. (Oral)
- 2. A. Das & R. Jin, "A Trio of Nanoclusters: Au<sub>23</sub>, Au<sub>24</sub> and Au<sub>25</sub> Protected by Thiolates" *45th ACS Central Regional Meeting*, Pittsburgh, Pennsylvania, 2014. (Oral)
- 3. A. Das & R. Jin, "Controlling Gold Nanoparticles with Atomic Precision for Catalytic Applications" *IPMI 38th Annual Conference*, Orlando, Florida, 2014. (Invited talk)
- 4. **A. Das** & R. Jin, "One Gold Atom Makes a Difference:  $[Au_{24}(PPh_3)_{10}(SR)_5X_2]^+$  vs.  $[Au_{25}(PPh_3)_{10}(SR)_5X_2]^{2+}$ " **246th ACS National Meeting**, Indianapolis, Indiana, 2013. (Oral)
- 5. A. Das & R. Jin, "Towards Stabilization of Quantum-Sized Gold Nanoparticles: A Sol-Gel Approach" 244th ACS National Meeting, Philadelphia, Pennsylvania, 2012. (Poster)

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<ul> <li>Graduate Teaching Assistant, CMU</li> </ul>	Aug 2010 – May 2014
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#### **Technical Skills**

#### Synthesis

- Noble metal nanoparticles / Bimetallic nanoparticles
- Small organic molecules and organometallic complexes
- Mesoporous silica-polypeptide hybrid materials

# Characterization techniques

- Spectroscopy UV-Vis, NMR, FTIR, Raman, fluorescence
- Electrochemical cyclic voltammetry, differential pulse voltammetry
- Chromatography HPLC, size exclusion chromatography, GC-MS
- Analytical XRD, SEM & TEM, TGA, MALDI & ESI-MS, catalytic activity evaluation
- Biological protein labeling, dialysis