Synthesis and study of silver molecular nanoparticles

Sameera M. Wickramasinghe

University of Toledo

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A Thesis

entitled

Synthesis and Study of Silver Molecular Nanoparticles

by

Sameera M. Wickramasinghe

Submitted to the Graduate Faculty as partial fulfillment of the requirements for the

Master of Science Degree in Chemistry

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August 2015
Molecular nanoparticles have been intensely studied over the last two decades due to their unique physicochemical properties and potential applications in a wide range of fields, such as electronics, photovoltaics, catalysis, sensing, and medicine. As a result of intense research on nanoparticle synthesis over this time, synthetic conditions have been improved to provide conditions that favor a single-sized molecular product, often avoiding the polydisperse product formation observed in early nanoparticle syntheses. Despite being able to synthesize single-sized molecular nanoparticles, the knowledge of the formation mechanism for molecular nanoparticles is still limited. Herein, a study involving a particularly stable molecular nanoparticle, namely, $M_4Ag_{44}(SR)_{30}$, was used to explore the chemistry of yielding single-sized products, which will expand our knowledge on molecular nanoparticle stability and synthesis. During this study, a variety of protecting ligands with different functional groups and structures were used aiming to synthesize $M_4Ag_{44}(SR)_{30}$ nanoparticles. It was found that the formation of $M_4Ag_{44}(SR)_{30}$ nanoparticles is very sensitive to the structural features of the protecting ligands used in the synthesis.
To further understand molecular nanoparticle chemistry it is also important to understand the interactions of the metal with the protecting ligand, so that molecular nanoparticles may be tuned for future applications. The solved crystal structure of M₄Ag₄₄(SR)₃₀ revealed the structural motif of the silver-thiol interface, which was shown to differ from the gold-thiol interface for gold molecular nanoparticles. In order to understand and generalize the chemistry of silver molecular nanoparticles, there is a need to study more structures. In this study, a new silver molecular nanoparticle was successfully synthesized and characterized. This silver molecular nanoparticle was protected with aromatic thiols, and has the molecular formula, M₃Ag₁₇(TBBT)₁₂, (TBBT = 4-tert-Butylbenzenethiol). Furthermore, in combination with experimental data and computational calculations a possible crystal structure was predicted for M₃Ag₁₇(TBBT)₁₂. The predicted structure of M₃Ag₁₇(TBBT)₁₂ can be used to test the generalization of molecular nanoparticles structural motifs, which will lead to a deeper understanding of this class of materials.
Acknowledgements

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Table of Contents

Abstract........................................................................................................................................... iii

Acknowledgements ......................................................................................................................... v

Table of Contents ........................................................................................................................... vi

List of Tables ....................................................................................................................................... viii

List of Figures ..................................................................................................................................... ix

List of Abbreviations ....................................................................................................................... xi

1 Introduction ................................................................................................................................. 1

1.1 Nanoscale vs. bulk ................................................................................................................... 1

1.2 Molecular nanoparticles are different ..................................................................................... 2

1.3 Stability of molecular nanoparticles ....................................................................................... 6

1.4 Silver molecular nanoparticles ............................................................................................... 7

2 Ligands as structure directing synthons ..................................................................................... 11

2.1 Introduction ............................................................................................................................ 11

2.2 Experimental section .............................................................................................................. 13

   2.2.1 Chemicals ....................................................................................................................... 13

   2.2.2 Synthesis of silver nanoparticles with water soluble ligands......................... 14
2.2.3 Synthesis of silver nanoparticles with water insoluble ligands........15
2.2.4 Optical absorption spectroscopy.............................................16
2.2.5 Electrospray ionization mass spectrometry ................................16
2.3 Results and discussion..................................................................17

3 M$_3$Ag$_{17}$(TBBT)$_{12}$ molecular silver nanoparticles .......................24
3.1 Introduction...................................................................................24
3.2 Experimental section.................................................................25
  3.2.1 Chemicals................................................................................25
  3.2.2 Synthesis................................................................................25
  3.2.3 Optical absorption spectroscopy.............................................26
  3.2.4 Electrospray ionization mass spectrometry...............................26
  3.2.5 Computational calculations.....................................................27
3.3 Results and discussion..................................................................28

4 Conclusions ..................................................................................38

Appendix A

  Nuclear magnetic resonance spectroscopy.......................................40

Appendix B

  Structure of the irregular icosahedral-shell formed by the 12 sulfur atoms, Bader
  charge analysis of Na$_3$Ag$_{17}$(TBBT)$_{12}$....................................42

References.........................................................................................45
List of Tables

B.1 Bader charge analysis for the optimal structure of Na$_3$Ag$_{17}$ (TBBT)$_{12}$ ............... 44
B.2 Bader charge analysis for the optimal structure of Na$_4$Ag$_{44}$ (p-MBA)$_{30}$ ............... 44
List of Figures

1-1 Variation of size-dependent properties of clusters as a function of the number of cluster constituents, n ...............................................................3
1-2 A series of gold glutathione molecular nanoparticles separated by PAGE and their assigned molecular formulae by ESI-MS ..........................................................5
1-3 (a) The cluster abundance spectrum of gas phase sodium clusters. (b) The calculated effective potential for Na_{40} gas phase cluster with filled energy levels ..........................................................6
1-4 The optical absorption spectra of IBANs synthesized with different aryl thiol ligands .........................................................................................9
1-5 The crystal structure of Ag_{44}(p-MBA)_{30}^{4-} molecular nanoparticle ...............10
2-1 Structures of ligands used in this study ..........................................................14
2-2 Optical absorption spectra of M_{4}Ag_{44}(SR)_{30} nanoparticles in DMF. Inset: spectra of Ag-nanoparticles with other ligands .........................................................17
2-3 Electrospray ionization mass spectra of Ag-nanoparticles, showing Ag_{44}(L)_{30}^{4-} along with other species .................................................................19
2-4 Electrospray ionization mass spectra of Ag-nanoparticles synthesized with CHT (A), p-MMBA (B), TBBM (C), and PET (D) .........................................................20
3-1 Optical absorption spectrum of the reaction mixture before adding water. ..............29
3-2 Optical absorption spectrum of \( \text{M}_3\text{Ag}_{17}(\text{TBBT})_{12} \) nanoparticles in DMF. Inset: spectrum in energy. ................................................................. 30

3-3 Electrospray ionization mass spectrum of Ag:TBBT nanoparticles, showing \( \text{Ag}_{17}(\text{TBBT})_{12}^{3-} \) along with other species. ................................................................. 31

3-4 Spontaneous fragmentation (CE = 0.5eV) of isolated \( \text{Ag}_{17}L_{12}^{3-} \) ions. ................................................................. 31

3-5 Proposed structure for \( \text{M}_3\text{Ag}_{17}(\text{TBBT})_{12} \) nanoparticles, constructed and relaxed with DFT calculations. ......................................................................... 34

3-6 Electronic properties of \( \text{Na}_3\text{Ag}_{17}(\text{TBBT})_{12} \) structure. ................................................................. 36

3-7 Measured and TD-DFT calculated optical absorption spectra of \( \text{Na}_3\text{Ag}_{17}(\text{TBBT})_{12} \) nanoparticles. ......................................................................... 37

A-1 2D-NOESY spectrum of \( \text{M}_4\text{Ag}_{44}(\text{TBBT})_{30} \) nanoparticles in DMF-\( d_7 \). ............... 41

B-1 (a) Irregular icosahedral arrangement of 12 S atoms (b) The S-S distances correspond to edge lengths E1, E2, and E3. ................................................................. 43
**List of Abbreviations**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCA</td>
<td>Bader Charge Analysis</td>
</tr>
<tr>
<td>BM</td>
<td>Benzyl Mercaptan</td>
</tr>
<tr>
<td>BT</td>
<td>Benzenethiol</td>
</tr>
<tr>
<td>CHT</td>
<td>Cyclohexanethiol</td>
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<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl Sulfoxide</td>
</tr>
<tr>
<td>ESI-MS</td>
<td>Electrospray Ionization Mass Spectrometry</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum</td>
</tr>
<tr>
<td>GGA</td>
<td>Generalized Gradient Approximation</td>
</tr>
<tr>
<td>GSH</td>
<td>Glutathione</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>IBANs</td>
<td>Intensely and Broadly Absorbing Nanoparticles</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>MALDI</td>
<td>Matrix Assisted Laser Desorption/Ionization</td>
</tr>
<tr>
<td>MS</td>
<td>Mass Spectrometry</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>PAGE</td>
<td>Polyacrylamide Gel Electrophoresis</td>
</tr>
<tr>
<td>PAW</td>
<td>Projector Augmented Wave Method</td>
</tr>
<tr>
<td>PDOS</td>
<td>Projected Density of States</td>
</tr>
<tr>
<td>p-MBA</td>
<td><em>para</em>-Mercaptobenzoic Acid</td>
</tr>
<tr>
<td>p-MMBA</td>
<td><em>para</em>-Mercaptomethylbenzoic Acid</td>
</tr>
<tr>
<td>PET</td>
<td>2-Phenylethanol</td>
</tr>
</tbody>
</table>
SPR..................Surface Plasmon Resonance
TBBM..................4-tert-Butylbenzyl Mercaptan
TBBT...................4-tert-Butylbenzenethiol
TDDFT.................Time-Dependent Density Functional Theory

TOF..................Time of Flight

VASP-DFT..............Vienna Ab-initio Simulation Package-Density Functional Theory

XC....................Exchange-Correlation
Chapter 1

Introduction

1.1 Nanoscale vs. bulk

The universe we live in is made out of many different forms of matter. One type of matter can be easily differentiated from others based on its properties. This definition of matter seems universal as all the materials we come across in our day-to-day life have a very unique set of properties. In fact, our perception about materials had been unchallenged for millennia. This was until 1857, when an English scientist named Michael Faraday showed the world that gold does not have its golden color in all dimensions. Examined, his findings of matter might have inspired a new branch of science that emerged in the following century, known as nanoscience.

During the first half of the 20th century, the well-established theories of science were revolutionized by the new theories of quantum mechanics. Later, quantum mechanics and its consequences were used to explain the anomalous properties of matter at the nanoscale. Even though the theories were well developed, the impact of this new realm of science was not recognized until the well-known speech delivered by American
theoretical physicist Richard Feynman, entitled “There’s Plenty of Room at the Bottom”. It was his speech that inspired the scientific community to design new experiments, as well as new instruments, which are capable of probing objects at the nanoscale.

What truly fascinated scientists were the unprecedented and size-dependent properties of matter observed at the nanoscale. In fact, the history of this topic extends to ancient Rome where the Romans knew how to utilize the optical properties of colloidal metal particles in decoration, although they were completely unaware of the origins of the properties of these materials. After Richard Feynman’s speech, there were intense studies that discovered not only the optical properties of matter, but also structural, energetic, electronic, electromagnetic, thermodynamic, and chemical properties of matter are different at the nanoscale compared with its bulk counterpart. The size-dependent properties at the nanoscale were rationalized as collective effects of quantum confinement, the appearance of a band gap, and high surface-to-volume ratio of the nanoparticles. These size-dependent properties of nanoparticles have been used in many fields including electronics, photovoltaics, catalysis, sensing, and medicine indicating the broad applicability of matter in the nanoscale.

1.2 Molecular nanoparticles are different

Terminology in nanoscience continuously evolves as our knowledge of the subject expands. Generally, nanoparticles range in scale between 1 and 100 nm. In the early stages, nanoparticles were synthesized in the gas phase and called metal clusters.
These metal clusters are formed by aggregation of 2 to 10000 individual particles and show very unique physicochemical properties compared to its bulk.\textsuperscript{4} As a result, scientists invested time into analyzing the size-dependent properties of the clusters with the goal of identifying possible trends (Figure 1-1). Interestingly, two distinct trends were discovered based upon the variation of properties. The first trend observed was with large clusters, and how the properties smoothly changed with the number of cluster constituents. Therefore, those properties were predictable. Whereas, the other trend observed with small clusters is not linear, therefore those properties vary in an "unpredictable" manner.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{Variation of size-dependent properties of clusters as a function of the number of cluster constituents, \(n\).\textsuperscript{4} Reprinted with permission from reference 4. Copyright 1992 Springer-Verlag.}
\end{figure}

Furthermore, the nanoparticles from 5-100 nm, including the large clusters discussed above, can be classified as conventional nanoparticles. Nanoparticles with a
diameter less than 3 nm typically have a discrete molecular formula (and presumably a definite molecular structure) and therefore can be called molecular nanoparticles. Unlike conventional nanoparticles, where the constituents can be varied by hundreds to thousands of atoms without significantly changing their properties, the physicochemical properties of a molecular nanoparticle can be drastically different than its immediate neighbor with a one atom difference.

With advancements in both instrumentation and synthetic routes, the concept of molecular nanoparticles gradually started to establish itself among the scientific community in 1990s. Studies of nanoparticles were brought up to a whole new level with solution-phase synthesis; especially after development of the Brust-Schiffrin method. The solution-phase synthesis is generally considered more successful at producing nanoparticles than in the gas phase, and also solution-phase synthesis allows the nanoparticles to be characterized with multiple analytical techniques non-destructively. In 1996, Whetten et al. reported a series of gold nanoparticles prepared with alkyl thiols using the solution-phase route. In that study, they were able to separate and characterize highly abundant nanoparticles, which were termed “nanocrystal gold molecules”. Furthermore, Whetten et al. were able to assign approximate molecular formulae to the nanocrystals with mass spectrometry. In 1998, Schaaff et al. synthesized a series of gold nanoparticles protected with glutathione (GSH) and separated using polyacrylamide gel electrophoresis (PAGE). The separation of gold nanoparticles with PAGE enabled the researchers to analyze each band excised from the gel. In 2005, a Japanese research group used electrospray-ionization mass spectrometry (ESI-MS) coupled with soft instrumental conditions to assign accurate molecular formulae to this family of gold glutathione
nanoparticles, which included the well-known Au$_{25}$(SG)$_{18}$ molecular nanoparticle (Figure 1-2).$^{15}$

![Figure 1-2: A series of gold glutathione molecular nanoparticles separated by PAGE and their assigned molecular formulae with ESI-MS. Reprinted with permission from reference 15. Copyright 2005 American Chemical Society.](image)

Requirements for being classified as molecules were partly fulfilled by the assignment of unique molecular formulae for these nanoparticles, however they were missing the most important piece of evidence to firmly establish their identity as molecules: a definitive structure. It was in 2007 that the first ever crystal structure of a molecular gold nanoparticle was solved with Au$_{102}$(p-MBA)$_{44}$, which revealed important structural information about molecular nanoparticles.$^{16}$ Following the structure determination of Au$_{102}$(p-MBA)$_{44}$, many structures of molecular nanoparticles including MAu$_{25}$(SR)$_{18}$ and Au$_{38}$(SR)$_{18}$ have been solved, proving that these nanoparticles truly exist as molecules.$^{17,18}$
1.3 Stability of molecular nanoparticles

Generally, any element in the periodic table reacts with another element to form a molecule, achieving the electronic configuration of their nearest noble gas. As a consequence of that, both elements involved in the bond formation gain a greater stability than their ground states. Even though it seems very simple, this fundamental phenomenon is considered the driving force to make stable compounds, including gas phase clusters. In 1984, a study carried out with gas phase sodium clusters showed that some clusters appear in higher abundance than their neighbors in the cluster abundance spectrum (Figure 1-3a).27

![Figure 1-3: (a) The cluster abundance spectrum of gas phase sodium clusters. (b) The calculated effective potential for Na_{40} gas phase cluster with filled energy levels. Reprinted with permission from reference 5. Copyright 1993 American Physical Society.](image)

When they were analyzing the higher abundance of some sodium clusters with atoms of 8, 20, 40, and 58 in the cluster abundance spectrum, it was found that these
clusters achieved their greater stability due to complete electronic shells. These electronic shell structures have been calculated based on theoretical models to interpret the experimental data.\textsuperscript{5,27} The calculated electronic shell structure for Na\textsubscript{40} gas phase cluster is shown in Figure 1-3b. Once a stable cluster is formed with a complete electronic shell, it appears in the mass distribution with a higher intensity and vice versa.

Unlike the gas phase clusters, solution phase clusters require protecting ligands to avoid aggregation and a loss of their molecular nature. These protecting ligands can be either covalently or datively bonded to the metals in the cluster.\textsuperscript{19} Once the ligands bond to the metal cluster, it is considered a “superatom complex” and its great stability is attributed to its closed electronic shells, which is analogous to the stability of a noble gas electron configuration. These stable molecular clusters have filled their “superatomic orbitals”, 1S\textsuperscript{2} | 1P\textsuperscript{6} | 1D\textsuperscript{10} | 2S\textsuperscript{2} | 1F\textsuperscript{14} | ...., where S, P, D, F are angular momentum states.\textsuperscript{19} The electron counts corresponding to closed electronic shells of the molecular nanoclusters can be calculated using the following equation:

\[ n^* = N\upsilon - M - z \]

where \( n^* \) is the electron count for the superatom complex, \( N \) is the number of metal atoms, \( \upsilon \) is the valence of the metal atoms, \( M \) is the number of ligands, and \( z \) is the overall charge of the superatom cluster.

**1.4 Silver molecular nanoparticles**

Gold molecular nanoparticles have been intensively studied due to their great stability compared to other metals, well-established synthetic routes, and relative stability
and ease of analysis. Therefore, the field of molecular nanoparticles has been greatly
nourished by the knowledge obtained from gold molecular nanoparticles, especially after
the many crystal structures reported during the last decade. But it is fundamentally
required to have more models to generalize the theories of a field. Scientists in this field
have extended their work to other metals in the coinage group expecting to come up with
more models.

In 2010, Kumar et al. reported the first-ever synthesis and separation of a series of
molecular silver nanoparticles protected with glutathione (GSH). Further studies carried
out on these silver nanoparticles have shown that their mass distribution and optical
properties are different from previously reported gold-glutathione nanoparticles, implying
that there are different governing rules in gold and silver molecular nanoparticles.

One of the remarkable papers in the field of silver molecular nanoparticles was published
by Bakr et al. in which they reported the synthesis of a single-sized product with a very
unique optical absorption spectrum (Figure 1-4). They named those silver nanoparticles
intensely and broadly absorbing nanoparticles (IBANs) which were later identified as
Ag\(_{44}(SR)_{30}\)\(^{4-}\).\(^{23}\)
With the discovery of Ag$_{44}$(SR)$_{30}^{4+}$ molecular nanoparticles, the field of silver molecular nanoparticles was one step behind that of gold, a crystal structure. It was in 2013 that two research groups independently determined the first crystal structure of the silver molecular nanoparticle Ag$_{44}$(SR)$_{30}^{4+}$.$^{24,25}$ The crystal structure of Ag$_{44}$(p-MBA)$_{30}^{4+}$ revealed how the silver atoms interact with the protecting ligands to form different capping motifs than that of gold nanoparticles (Figure 1-5)$^{24}$. The Ag$_{44}$(SR)$_{30}^{4+}$ molecular nanoparticle, with a known structure and synthetic routes to produce a single-sized product, is an ideal candidate to deepen the understanding of the chemistry of molecular nanoparticles.
Figure 1-5: The crystal structure of Ag$_{44}$(p-MBA)$_{30}^{2+}$ molecular nanoparticle. Reprinted with permission from reference 24. Copyright 2013 Macmillan Publishers Limited.
Chapter 2

Ligands as structure-directing synthons

2.1 Introduction

The canonical thinking about the structure and stability of noble metal nanoparticles is that the core determines the overall structure and stability of the molecule, that is once the best core structure is formed the ligand shell simply passivates that core. This implies that the structure of the ligand shell is determined by the structure of the metal core and, consequently, the nature of the metal-thiolate interface.

Traditionally, different sizes and shapes of ligands have been used to modify the mass distribution. For example, using a bulky ligand can force a smaller radius of curvature in order to accommodate the bulky ligand. This strategy was first employed using glutathione to make molecular gold nanoparticles with a lower mass distribution than that of the Brust-Schiffrin method using n-alkanethiols. While ligands can be used to shift the overall mass distribution and the average mass, it is normally the case that it is possible to synthesize any particular size or species of gold nanoparticle with
little to no regard for the ligand properties. For example, MAu$_{25}$(SR)$_{18}$, where M is a counter cation and SR is a thiol containing ligand, can be made with a wide range of ligands, including aliphatic chains, aromatic thiols, and water soluble peptides and other small molecules, for example, captopril, glutathione, and PET.$^{15,17,35,38,39}$ While this relative insensitivity to the nature of the ligands is common for molecular gold nanoparticles, it remains to be seen whether silver will behave the same way. This is primarily due to the lack of reliable mass spectrometric data for molecular silver nanoparticles, which are needed for making formula assignments.

More recently, M$_4$Ag$_{44}$(SR)$_{30}$ has been synthesized with quite a few different ligands, however they share the same basic structure in that the ligands are all aromatic with a variety of substituents.$^{22-24}$ In contrast, syntheses with aliphatic ligands (for example, glutathione, cysteine, and captopril) and even PET have never yielded M$_4$Ag$_{44}$(SR)$_{30}$ among the products.$^{20,30-32}$ M$_4$Ag$_{44}$(SR)$_{30}$ is a notably stable nanoparticle, therefore the canonical notion that the core structure determines the stability of the nanoparticle would predict that it can be synthesized with any ligand, contrary to experimental observations.

The pi-pi interactions between the ligands on M$_4$Ag$_{44}$(p-MBA)$_{30}$ have been shown to be important.$^{24,33}$ In fact, inter-ligand interactions are so strong that bundling of ligands might persist in solution. The strong interactions between ligands in the case of aromatic ligands, through pi-pi interactions, are expected to be quite different than the interactions between aliphatic ligands, which begs the question: are aromatic ligands required for making M$_4$Ag$_{44}$(SR)$_{30}$? While the relatively large ~0.8 eV HOMO-LUMO gap and the compact 32-atom Ag core no doubt play an important role in the stability of
M₄Ag₄₄(SR)₃₀, it is an open question whether or not ligand-ligand interactions also play a key role in the remarkable stability of this unique nanoparticle. Here, we seek to evaluate the importance of ligand-ligand interactions in determining the stability of M₄Ag₄₄(SR)₃₀ nanoparticles and determine to what extent the outcome (products) of a reaction can be affected by the choice of ligands. A selection of derivatized phenyl ligands have been used to synthesize M₄Ag₄₄(SR)₃₀, wherein the polarity, bulkiness, flexibility and aromaticity of the ligands were varied (Figure 2-1). The products were evaluated primarily by optical spectroscopy and mass spectrometry in order to determine whether or not each ligand could successfully stabilize M₄Ag₄₄(SR)₃₀.

2.2 Experimental section

2.2.1 Chemicals

The following reagents were purchased from Fisher Chemical: sodium borohydride, cesium hydroxide, citric acid, N,N-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO). Silver nitrate, 4-mercaptobenzoic acid (p-MBA), benzenethiol (BT), 4-tert-butylbenzenethiol (TBBT), cyclohexanethiol (CHT), 4-(mercaptomethyl)benzoic acid (p-MMBA), benzyl mercaptan (BM), 4-tert-butylbenzyl mercaptan (TBBM), 2-phenylethanethiol (PET), and toluene were purchased from Sigma-Aldrich. p-MBA was further purified by extracting into methanol. All other reagents were used without further purification. Deionized water (18.2 MΩ cm) from a Millipore Synergy system was used.
Figure 2-1: Structures of ligands used in this study: p-mercaptobenzoic acid (p-MBA); 4-tert-butylbenzenethiol (TBBT); benzenethiol (BT); cyclohexanethiol (CHT); 4-(mercaptomethyl) benzoic acid (p-MMBA); 4-tert-butylbenzyl mercaptan (TBBM); benzyl mercaptan (BM); 2-phenylethanethiol (PET).

2.2.2 Synthesis of silver nanoparticles with water soluble ligands

The method used to synthesize silver nanoparticles with water soluble ligands such as p-MBA and p-MMBA was reported elsewhere (Figure 2-1). Silver nitrate (0.0121 g, 0.0714 mmol) and the ligand (0.1285 mmol) were dissolved in a solution of water (21 mL) and DMSO (12 mL). The mixture was stirred to produce the insoluble silver-thiolate precursor. Then, the pH of the reaction mixture was increased up to pH 12-13 (confirmed by pH papers) using a concentrated CsOH solution. At this point, the insoluble precursor was dissolved forming a clear, yellow solution. After that, the soluble precursor was reduced with a 9 mL aqueous solution of NaBH₄ (0.0162 g, 0.4284 mmol).
It is important to add the reducing reagent in three equal aliquots at 20 minute intervals. After completing the addition of NaBH₄ solution, the solution was stirred for another hour to complete the reaction. After one hour, the solution was centrifuged and the precipitate discarded. Finally, the product was precipitated with excess DMF and collected after centrifugation.

The product obtained at this point is required to protonate with citric acid as the carboxylic acid groups of the ligand were deprotonated during the pH adjustment. Therefore, the solid product was dispersed in 30 mL of DMF and approximately 1 g of citric acid was added. This solution was agitated until citric acid dissolves in the DMF solution. Then, the nanoparticles were precipitated with 30 mL of toluene. This protonation step was carried out three times to ensure complete protonation of the carboxylic acid groups.

2.2.3 Synthesis of silver nanoparticles with water insoluble ligands

Synthesis of silver nanoparticles with water insoluble ligands was reported previously²² and it was used to synthesize the nanoparticles with BT, TBBT, CHT, BM, TBBM, and PET (Figure 2-1). First, silver nitrate (0.0121 g, 0.0714 mmol) was dissolved in 7.20 mL DMF and stirred for 5 minutes. Then, the ligand (0.1428 mmol) was added to the solution and continued stirring for another 15 minutes. At this point, the silver-thiolate precursor has formed. A 28.60 mL DMF solution of NaBH₄ (0.0108 g, 0.2856 mmol) was added dropwise to reduce the precursor. The reaction was allowed to stir at
1100 rpm for 3 h. After 3 h, 4.20 mL of de-ionized water was added to the reaction and stirred for another 2 min. Finally, the solution was incubated in the freezer at -18 °C for 2 days to complete the reaction. The procedure was repeated for all ligands except for TBBM and BM, which were unstable under ambient conditions, therefore those two syntheses were carried out under an inert atmosphere (Ar gas was used).

2.2.4 Optical absorption spectroscopy

All optical absorption spectra were obtained using a PerkinElmer Lambda 950 spectrophotometer with a 5.00 mm path length quartz cuvette. A solution of DMF and a mixture of water and DMF were used as background solutions for the products obtained with the water-soluble ligands and water-insoluble ligands, respectively.

2.2.5 Electrospray ionization mass spectrometry

All mass spectra were collected on a Waters Synapt HDMS G1 quadrupole time-of-flight mass spectrometer in negative ion V-mode using a nanospray source with fused silica emitters made in house. Instrument parameters used for data collection were as follows: capillary voltage, 2.0-4.0 kV; sampling cone, 15 V; extraction cone, 4.0 V; nanoflow, 0.1 bar; cone gas, 0 L/h; trap collision energy, 0.5 V; transfer collision energy, 1.0 V; source temperature, 40 °C; desolvation temperature, 120 °C. Calibration was performed externally in the range of 100 ≤ m/z ≤ 4500 using cesium iodide. MassLynx 4.1 software (Waters Corp.) was used for processing spectra. Simulating isotopic patterns was performed using mMass freeware (copyright Martin Strohalm).\textsuperscript{34} Samples were taken directly from the reaction mixture and diluted using neat DMF.
2.3 Results and discussion

In this study, three main features of the protecting ligands were considered: functional groups on the ligand, aromaticity, and flexibility of the ligand. First, the protecting ligands with different substituents were used in silver nanoparticles synthesis. All shared a common structural feature, namely a thiol group directly bound to a phenyl ring. This included the well-known p-mercaptobenzoic acid (p-MBA) ligand, benzenethiol (BT), and 4-tert-butylbenzenethiol (TBBT). The products obtained from these syntheses were characterized by optical absorption spectroscopy (Figure 2-2).

![Optical absorption spectra](image)

**Figure 2-2:** Optical absorption spectra of $\text{M}_4\text{Ag}_{44}(\text{SR})_{30}$ nanoparticles in DMF (black-p-MBA, red-BT, and blue-TBBT). Inset: spectra of Ag-nanoparticles with other ligands (black-CHT, red-p-MMBA, blue-TBBM, and pink-PET).
Previously, it has been shown that p-MBA ligand could yield a single-sized product\(^{24}\) namely \(\text{M}_4\text{Ag}_{44}(\text{p-MBA})_{30}\), which has a characteristic optical spectrum with 8 distinguishable peaks broadly and intensely covering the entire range of the optical spectrum.\(^ {22,24}\) Therefore, it was used as the reference optical spectrum to identify formation of \(\text{M}_4\text{Ag}_{44}(\text{SR})_{30}\) in this study. The absorption spectra obtained for silver nanoparticles synthesized with p-MBA, BT, and TBBT all shared the same overall characteristics, indicating that the major (if not exclusive) product of each reaction was \(\text{M}_4\text{Ag}_{44}(\text{SR})_{30}\).

The final products of silver nanoparticles synthesized with p-MBA, BT, and TBBT were further analyzed by electrospray-ionization mass spectrometry (ESI-MS). The mass spectra are consistent with previous observations confirming the presence of \(\text{M}_4\text{Ag}_{44}(\text{SR})_{30}\) (see figure 2-3). Other peaks observed along with the peaks of \(\text{Ag}_{44}(\text{L})_{30}^{4-}\) were identified as silver thiolates, with the common formula \(\text{Ag}_n\text{L}_{n+1}^{-}\), in the lower \(m/z\) range along with species associated with \(\text{Ag}_{44}(\text{L})_{30}^{4-}\) which were previously reported.\(^ {24}\) The presence of silver thiolates may be due to the analysis of crude products. These findings indicate that \(\text{M}_4\text{Ag}_{44}(\text{SR})_{30}\) clusters can be formed using ligands with a thiol group directly bound to a phenyl ring regardless of other substituents on the phenyl ring. This is consistent with previous work done on \(\text{M}_4\text{Ag}_{44}(\text{SR})_{30}\) nanoparticles with a wide range of derivatized phenyl-ring-containing ligands.\(^ {22}\)
Figure 2-3: Electrospray ionization mass spectra of Ag-nanoparticles, showing Ag$_{44}$(L)$_{30}^{4+}$ along with other species. L is p-MBA (A), BT (B), and TBBT (C).

With that knowledge, our study was extended to test the requirement of having an aromatic ligand in order to form stable M$_{4}$Ag$_{44}$(SR)$_{30}$ nanoparticles. To test that requirement, silver nanoparticles were synthesized with cyclohexanethiol (CHT), which is saturated BT, that is the ligand contained a thiol group directly bound to a non-aromatic ring (Figure 2-1). The final product of this reaction did not show the characteristic features present in the optical spectrum of M$_{4}$Ag$_{44}$(SR)$_{30}$ (Figure 2-2 inset). This evidence suggests that M$_{4}$Ag$_{44}$(SR)$_{30}$ has not been formed with CHT. The absence of M$_{4}$Ag$_{44}$(SR)$_{30}$ clusters among the products yielded using CHT was confirmed by ESI-MS (Figure 2-4). These results strongly suggest that aromaticity of the protecting ligand is a key requirement to yield M$_{4}$Ag$_{44}$(SR)$_{30}$ clusters.
Finally, we carefully chose a set of ligands by preserving the aromaticity and derivatization to test the last structural requirement of flexibility of the protecting ligand. The set of ligands includes 4-(mercaptomethyl) benzoic acid (p-MMBA), 4-tert-butylbenzyl mercaptan (TBBM), benzyl mercaptan (BM), and 2-phenylethanethiol (PET) (Figure 2-1). In this way, the degrees of freedom of the protecting ligands was increased due to the methylene bridges (–CH₂) that were added between the phenyl ring and the thiol end group.

Interestingly, none of the products obtained with the flexible aromatic ligands showed the characteristic optical spectrum of \( \text{M}_4\text{Ag}_{44}(\text{SR})_{30} \) clusters (Figure 2-2 inset). This observation was further supported by ESI-MS of the products (Figure 2-4). Only the
peaks corresponding to silver thiolates were identified in the mass spectra confirming that M₄Ag₄₄(SR)₃₀ has not formed with any of the flexible aromatic ligands. It should be noted that products formed using benzyl mercaptan (BM) were not stable long enough to be characterized, however the product did not have the characteristic color of M₄Ag₄₄(SR)₃₀.

The sensitivity of the synthesis to the choice of ligands has generally not been observed in gold nanoparticles, with few exceptions.³⁶,³⁷ Gold is more tolerant to the choice of the ligand. Changing ligands, for example, bulky versus compact, can change the mass distribution, however the same set of species is still typically observed. For example, MAu₂₅(SR)₁₈ can be synthesized with a wide range of ligands, including aliphatic and aromatic, aqueous and non-aqueous, for example, captopril, glutathione, and PET.¹⁵,¹⁷,³⁵,³⁸,³⁹ This might be due to the difference in Au-Au and Au-S bond strengths compared to Ag-Ag and Ag-S bond strengths⁴⁰, that is the Au-Au and Au-S bonds dominate the cohesive energy and stability of the Au molecules and therefore the ligands play a lesser role in that case. In the case of Ag nanoparticles, the weaker Ag-Ag and Ag-S bonds would play less of a role in the cohesive energy and stability of the Ag molecules, therefore the relative importance of the interactions within the ligand shell would be greater in the case of silver. Based on the results in the present study, it could be argued that the ligands play a determinant role in the stability of M₄Ag₄₄(SR)₃₀ nanoparticles.

So far, M₄Ag₄₄(SR)₃₀ has not been observed in syntheses with aliphatic ligands implying that those aliphatic ligands could not provide the additional cohesivity needed for M₄Ag₄₄(SR)₃₀ stability. The significance of the pi-pi interactions was illustrated by the failure of cyclohexanethiol (CHT), the non-aromatic version of BT, to stabilize
M₄Ag₄₄(SR)₃₀. CHT ligands are unable to provide any stabilization through pi-pi interactions, which is likely a significant reason that M₄Ag₄₄(SR)₃₀ clusters were not formed during the synthesis and therefore were not observed by any characterization technique.

Likewise, aromatic rings with added methylene bridges between the benzene ring and the thiol end group apparently had too many degrees of freedom for pi-pi interactions to persist and stabilize M₄Ag₄₄(SR)₃₀ nanoparticles. Clearly it is not sufficient for the ligand to simply contain an aromatic ring; the connectivity and flexibility of the ligand (or lack thereof) is apparently of critical importance for being able to establish and maintain the pi-pi interactions that appear to be required for forming and stabilizing M₄Ag₄₄(SR)₃₀.

Contrastingly, the ligands with a thiol directly bound to an aromatic ring are capable of stabilizing M₄Ag₄₄(SR)₃₀ nanoparticles. This unique ability of the ligands can be attributed to experimentally observed pi-pi interactions between the ligands (Figure A-1), which contributes to the overall cohesive energy of the M₄Ag₄₄(SR)₃₀ nanoparticle.

The results obtained from Ag-nanoparticles synthesized with flexible ligands such as p-MMBA, TBBM, and PET clearly show that simply having an aromatic ring anywhere on the ligand is not sufficient to form M₄Ag₄₄(SR)₃₀ nanoparticles. It is important to have that thiol group directly bound to a phenyl ring, presumably to promote formation of favorable ligand-ligand interactions. This observation can be explained with two plausible reasons: (i) fewer degrees of freedom suppress motion of the ligands and (ii) the bond angles and relative positions of aromatic rings in the ligands with added
methylene bridges are not correct for strong pi-pi interactions. One could imagine that PET ligands with two methylene bridges in between the phenyl ring and the thiol end group would have the same relative bond angles as BT and therefore strong pi-pi interactions might be possible in this case. Experiments showed that PET ligands were still unable to provide the necessary stabilization for making $\text{M}_4\text{Ag}_{44}(\text{SR})_{30}$. This supports the notion that more degrees of freedom and disorder introduced by two methylene bridges interfere with the establishment of strong pi-pi interactions. Therefore, the rigidity of silver-thiolate framework of $\text{M}_4\text{Ag}_{44}(\text{SR})_{30}$ and the resulting ligand interaction make an important and in fact key contribution to its stability.
Chapter 3

$M_3Ag_{17}(TBBT)_{12}$ molecular silver nanoparticles

3.1 Introduction

Silver nanoparticles are of significant fundamental and practical interest due to their optical and biological properties, however very little is known about the principles that govern their structures. The precise atomic structures of molecular nanoparticles can be determined by single-crystal X-ray diffraction methods, however only one silver nanoparticle structure which is completely protected by thiols has been determined by single-crystal X-ray diffraction methods thus far: $M_4Ag_{44}(SPh)_{30}$, where $M$ is a single-charge cationic counterion and SPh is a thiolate ligand containing a phenyl ring. \cite{22,24,25,33} This provided the first picture of the silver-thiolate protective outer layer, which was shown to consist of three-dimensional $Ag_2(SPh)_5$ mounts. \cite{24} These mounts are very different from the one-dimensional staple motif in the case of thiolate-ligated gold nanoparticles. \cite{16-18,41} It remains to be seen, however, whether the $Ag_2(SPh)_5$ mounts are common to a variety of thiolated silver nanoparticles or whether they are unique for
protecting the 32 Ag-atom excavated decahedral core of M₄Ag₄₄(SPh)₃₀. Such information is critically important for understanding the principles behind silver nanoparticle structures and developing a general structural model for thiolated silver nanoparticles, as well as self-assembled monolayers on silver surfaces.

A large number of phenyl-ring containing ligands have been used to prepare M₄Ag₄₄(SPh)₃₀ nanoparticles.22 Interestingly, preparations of M₄Ag₄₄(SPh)₃₀ nanoparticles have yet to yield other species; all appear to be single-sized products. It is somewhat of a challenge, then, to produce other species that may be crystallized for comparison in structural studies since phenyl-ring containing ligands are important for crystallization. To this end, we have used a bulky phenyl-ring containing ligand, 4-tert-butylbenzenethiol (TBBT), to change the interligand interactions and thereby induce the formation of a new silver nanoparticle species. Herein we report the synthesis of M₃Ag₁₇(TBBT)₁₂ nanoparticles, their salient physical properties, and a compelling structural model that introduces a new silver-thiolate mount motif.

3.2 Experimental section

3.2.1 Chemicals

Sodium borohydride and N,N-dimethylformamide (DMF) were purchased from Fisher Chemical. Silver nitrate and 4-tert-butylbenzenethiol (TBBT) were purchased from Sigma-Aldrich. All the reagents were used without further purification. Deionized water (18.2 MΩ cm) from a Millipore Synergy system was used.

3.2.2 Synthesis
The synthesis of $\text{M}_3\text{Ag}_{17}(\text{SR})_{12}$ was based upon a synthesis that was reported elsewhere.\textsuperscript{22} Silver nitrate (0.1210 g, 0.714 mmol) was dissolved in 7.20 mL DMF and stirred for 5 minutes. Next, TBBT (0.086 mL, 0.500 mmol) was added to the solution, which was stirred for an additional 15 min. The silver-thiolate precursor formed during this time. A 28.60 mL DMF solution of NaBH$_4$ (0.1080 g, 2.85 mmol) was added dropwise to the reaction mixture in order to reduce the precursor. This reaction was allowed to stir at 1100 rpm for 3 h. After this time, 4.20 mL of deionized water was added to the reaction in order to increase the reduction potential of the NaBH$_4$ and consequently the kinetics. This mixture was stirred for another 2 min before storing in a freezer at -18 °C for 16 h. After 16 h in the freezer, the product was separated into a clear yellow supernatant and a dark precipitate. We attempted to purify $\text{M}_3\text{Ag}_{17}(\text{SR})_{12}$ nanoparticles found in the supernatant of the final product by chromatography and by precipitation with antisolvents. Unfortunately, the final product was unstable during the purification, therefore the supernatant obtained from the reaction was used to characterize $\text{M}_3\text{Ag}_{17}(\text{SR})_{12}$ nanoparticles.

### 3.2.3 Optical absorption spectroscopy

All optical absorption spectra were obtained using a PerkinElmer Lambda 950 spectrophotometer with a 1.00 mm path length quartz cuvette. An optical absorption spectrum was collected for the reaction mixture before water was added (Figure 3-1) and for the supernatant that was the final product (Figure 3-2).

### 3.2.4 Electrospray ionization mass spectrometry
All mass spectra were collected on a Waters Synapt HDMS G1 quadrupole time-of-flight mass spectrometer in negative ion V-mode using a nanospray source with fused silica emitters made in house. Instrument parameters used for data collection were as follows: capillary voltage, 2.0-4.0 kV; sampling cone, 15 V; extraction cone, 4.0 V; nanoflow, 0.1 bar; cone gas, 0 L/h; trap collision energy, 0.5 V; transfer collision energy, 1.0 V; source temperature, 40 °C; desolvation temperature, 120 °C. Calibration was performed externally in the range of 100 ≤ m/z ≤ 4000 using cesium iodide. MassLynx 4.1 software (Waters Corp.) was used for processing spectra. Simulating isotopic patterns was performed using mMass freeware (copyright Martin Strohalm). Samples were taken directly from the reaction mixture and diluted using neat DMF.

### 3.2.5 Computational calculations

The density functional theory (DFT) calculations for Bader charge analysis were performed using the VASP-DFT package with a plane-wave basis with a kinetic energy cutoff of 400 eV, PAW pseudopotentials, and the PW91 generalized gradient approximation (GGA) for the exchange-correlation potential. For structure optimization, convergence was achieved for forces smaller than 0.001 eV/Å. The rational design outlined in the text has been used as the starting point for the structural relaxation.

The calculations of the absorption spectra were carried out following the time-dependent density-functional theory (TDDFT) method with the formalism described in references 61 and 62, implemented in the real-space Octopus code. These calculations employed the norm-conserving non-local soft Troullier–Martins pseudopotentials (including the valence electrons for the elements in the molecule: Ag (4d^{10}5s^{1}), S (3s^{2}...
3p^4), C (2s^2 2p^2), H(1s^1), Na (3s^1)), using the generalized gradient-corrected PBE exchange–correlation (xc) potential.\textsuperscript{66}

The Na\textsubscript{3}Ag\textsubscript{17}(TBBT)\textsubscript{12} structure was relaxed with the use of the Born-Oppenheimer density functional theory (BODFT) code,\textsuperscript{67} employing the above soft pseudopotentials and PBE xc potential. In the subsequent absorption spectra calculations, the system was placed in a sphere of radius 21 Å such that the electron vanishes outside of that sphere. The grid spacing was taken as 0.2 Å, which corresponded to a 70 Ry plane-wave kinetic energy cutoff. The calculation involved 898 valence electrons. In the TDDFT calculations, we have used all states in the interval \( E_F = -3.476 \) eV to +3.106 eV, where the lower limit was chosen to coincide with a minimum in the density of states. This interval included 50 occupied states and 63 unoccupied states, and therefore 3,150 electron-hole (occupied-unoccupied) pairs. Convergence was tested by varying the number of states included in the spectral calculations.

Detailed interpretation of the optical absorption spectrum requires analysis of the states and matrix elements contributing to the optical transition probabilities; see for example a method developed on the basis of time-dependent density functional perturbation theory (TD-DFPT) that allows analysis of correlations between single-particle transitions within a given energy range\textsuperscript{25}, which we have adopted in our analysis of the TDDFT results.

3.3 Results and discussion

During the synthesis of M\textsubscript{3}Ag\textsubscript{17}(TBBT)\textsubscript{12} nanoparticles, silver nitrate and TBBT were mixed to form silver-thiolate precursor which was a yellow precipitate. This
precursor was reduced by a solution of NaBH₄ which turned the yellow precipitate into a clear orange solution that darkened over time as it was stirred for 3 h. The color at this stage was dominated by larger plasmonic species, as verified by absorption spectroscopy, however a new peak was also present near 433 nm (Figure 3-1).

**Figure 3-1**: Optical absorption spectrum of the reaction mixture before adding water.

After addition of water and incubation at the freezer for 16 h, a dark precipitate formed and the optical density of the solution decreased. Presumably the precipitate was formed from the larger silver nanoparticles that were observed before the addition of water. The final solution was clear and yellow in color.

The dark yellow supernatant had a single strong absorption peak located at 436 nm that dominated the optical absorption spectrum, unlike any previously observed, with two small features on either side and a slowly decaying low-energy tail (Figure 3-2). The prominent peak at 436 nm is much narrower (0.18 eV FWHM) and located to the red of a typical plasmon peak characteristic of a spherical silver nanoparticle. None of the
spectral features characteristic of Na₄Ag₄₄(TBBT)₃₀ were observed in the spectrum, which is consistent with the ESI-MS results.

Figure 3-2: Optical absorption spectrum of M₃Ag₁₇(TBBT)₁₂ nanoparticles in DMF. Inset: spectrum in energy.

The product of this reaction was analyzed by electrospray ionization mass spectrometry (ESI-MS), which revealed the presence of a new silver nanoparticle: Ag₁₇(TBBT)₁₂⁻ (Figure 3-3). Such an Ag₁₇(TBBT)₁₂⁻ species has not been observed in any other preparation of silver molecular nanoparticles with either aromatic²²,²₄,²₅,⁴₂ or aliphatic²⁰,³₂,⁴₃ thiolate ligands.
Figure 3-3: Electrospray ionization mass spectrum of Ag:TBBT nanoparticles, showing Ag$_{17}$L$_{12}$$_{3}^-$ along with other species. Inset: experimental (black) and simulated (red) isotopic patterns for Ag$_{17}$L$_{12}$$_{3}^-$, where L = TBBT, with a shift of 0.08 m/z to correct for a 63 ppm mass difference due to the external calibration.

Only a small amount of one fragment species was observed, namely Ag$_{17}$(TBBT)$_{11}$$_{2}^-$, indicating that Ag$_{17}$(TBBT)$_{12}^-$ was quite stable for the conditions of the measurement (Figure 3-4). No charge state distribution was observed since the TBBT ligand is aprotic. Other species observed included adducts of the parent compound along with Ag(TBBT)$_{2}^-$ and Ag$_{5}$(TBBT)$_{6}^-$, which may have been solution-phase decomposition products.$^{21}$ No Ag$_{44}$(TBBT)$_{30}^-$ was observed, consistent with optical measurements.

Figure 3-4: Spontaneous fragmentation (CE = 0.5eV) of isolated Ag$_{17}$L$_{12}^-$ ions.
The formula of $\text{M}_3\text{Ag}_{17}(\text{TBBT})_{12}$ is based upon the requirement that the molecule needs to be neutral in the solid state, wherein 3 monocationic counterions are needed to balance charge of the $\text{Ag}_{17}(\text{TBBT})_{12}^{3-}$ ion identified by ESI-MS. It is likely that the counterions are $\text{Na}^+$ given their abundance in the synthesis, therefore the formula is expected to be $\text{Na}_3\text{Ag}_{17}(\text{TBBT})_{12}$.

Fragmentation of isolated parent ions at low collision energy (Figure 3-4) showed that the $\text{Ag}_{17}\text{L}_{12}^{3-}$ ion is relatively stable in the gas phase. In order to reduce the charge on metallic core, however, it may undergo a Coulomb explosion. The two observed gas phase reactions can be summarized as:

\[
\text{Ag}_{17}\text{L}_{12}^{3-} \rightarrow \text{Ag}_{17}\text{L}_{11}^{2-} + \text{L}^-
\]

\[
\text{Ag}_{17}\text{L}_{12}^{3-} \rightarrow \text{Ag}_{16}\text{L}_{10}^{2-} + \text{AgL}^-
\]

The prediction of structures of gold and silver molecular nanoparticles has proven to be quite a challenging task due to a lack of guiding principles and therefore has yet to yield a definite successful example. The small size of $\text{M}_3\text{Ag}_{17}(\text{TBBT})_{12}$ as well as past lessons learned provide an opportunity to begin to formulate and formally define a set of guiding principles for structure prediction and attempt to successfully predict a verifiable structure of this molecular nanoparticle.

First, it is well known that very small metal particles tend to assume low energy icosahedral structures.\textsuperscript{46,47} Gold and silver molecular nanoparticles share this tendency as the cores of many known structures contain icosahedra, with few exceptions, therefore it is reasonable to begin a structural model with an icosahedral core. Second, it is also well known that the presence of a central atom in the icosahedral core affects primarily the $s$
orbitals, due to their nonzero amplitude at the origin, i.e. the center of the particle.\textsuperscript{48-50} For example, an 18-electron spherical core will have a $1S^2$, $1P^6$ and $1D^{10}$ occupied orbitals, and a $2S$ orbital as the lowest-unoccupied molecular orbital (LUMO),\textsuperscript{27} therefore an empty 12-atom icosahedron would be favored as it would raise the energy of the $2S$ LUMO and thereby increase the energy gap. This is the case for $M_{4}Ag_{44}(SPh)_{30}$,\textsuperscript{24,25}

Formal counting\textsuperscript{19} for $M_{3}Ag_{17}(TBBT)_{12}$ nanoparticles gives 8 delocalized electrons, which are expected to fill the $1S^2$ and $1P^6$ orbitals\textsuperscript{27} such that the highest-occupied molecular orbital (HOMO) is $1P$ and the LUMO is $1D$. This is indeed found from our density functional theory (DFT) electronic structure calculations (see below), therefore there is no electronic advantage to an empty 12-atom icosahedral core. This is generally the case for an 8-electron core, such as $MAu_{25}(SR)_{18}$,\textsuperscript{17,41} On the other hand, there is an energetic advantage to a 13-atom (atom-centered) icosahedral core due to the coordination of the central atom. We therefore predict $Na_{3}Ag_{17}(TBBT)_{12}$ to have a 13-atom icosahedral core, as shown in Figure 3-5.

Next we consider the ligand shell. In the case of gold molecular nanoparticles, the capping motif has consistently been shown to be monomer and dimer staples.\textsuperscript{16-18,41} These can be thought of as fragments of the linear gold-thiolate polymer, $p$-(AuSR)$_{n}$. For silver, the capping motif for $M_{4}Ag_{44}(SPh)_{30}$ nanoparticles was carefully analyzed and has been shown to be the aforementioned $Ag_{5}(SPh)_{5}$ mount.\textsuperscript{24} This is a three dimensional structure and therefore distinct from the linear gold-thiolate polymer. The fact that $Ag_{5}(SPh)_{5}$ mounts were observed instead of staples can be understood based on the topological difference between the bonding of gold and silver in metal thiolates, which are two-fold and three-fold coordinate, respectively.\textsuperscript{51}
Figure 3-5: Proposed structure for $M_3Ag_{17}(TBBT)_{12}$ nanoparticles, constructed and relaxed with DFT calculations. (a) The structure consists of an icosahedral $Ag_{13}$ core (red) capped with four tetrahedrally-located Ag atoms (green). (b) The 12 sulfur atoms (yellow) surround the silver core, with three S atoms forming an equilateral triangle around each tetrahedrally-located Ag atom, to form a distorted icosahedron (yellow lines); E1, E2, and E3 are different edge lengths. (c) Isolated view of a $Ag(TBBT)_3$ monomer mount structure; the S atoms form an equilateral triangle (yellow lines); carbon atoms are in grey and hydrogen atoms are in blue. (d) Isolated view of the $Ag_2(p$-MBA)$_5$ dimer mount structure found on the Na$_4Ag_{44}$(p-MBA)$_{30}$ molecule, for comparison (see reference 24); the S atoms form nearly equilateral triangles (yellow lines); oxygen atoms are in red. (e) View of the $M_3Ag_{17}(TBBT)_{12}$ structure down the three-fold axis, showing slight rotation between the mount and the underlying icosahedral core. (f) View showing face-to-face interactions of the phenyl rings of ligands on neighboring mounts, leading to an overall octahedral arrangement of the ligand bundles.
Using this example, the 4 Ag atoms and 12 ligands that remain after accounting for the Ag$_{13}$ core can be grouped into four trigonal planar Ag(SPh)$_3$ mounts, as shown in Figure 3-5c. These can be thought of as fragments of the two-dimensional silver-thiolate polymer.$^{52}$ In fact, the Ag(SPh)$_3$ mount could be considered to be the primitive capping unit for silver-thiolate ligands since Ag$_2$(SPh)$_5$ mounts can be constructed by fusing two Ag(SPh)$_3$ mounts (see Figure 3-5d), where two of the newly proposed Ag(SPh)$_3$ mounts are joined at the apex S atom with the elimination of a single thiolate). In analogy to monomer and dimer staples for gold-thiolate ligands,$^{16-18,41}$ the Ag(SPh)$_3$ and Ag$_2$(SPh)$_5$ capping units can be thought of as monomer and dimer mounts.

Since icosahedra contain the tetrahedral symmetry group it is possible to arrange the four trigonal planar Ag(SPh)$_3$ mounts symmetrically around the Ag$_{13}$ core, as shown in Figure 3-5e. Structural optimization of the molecule with the use of first-principles relaxation revealed that interactions between ligands on neighboring mounts lead to ligand-pair bundling,$^{53}$ resulting in a ligand shell structure with an overall octahedral arrangement (see Figure 3-5f). Here, the ligands tilt in order to maximize the interligand interaction, thereby facilitating face-to-face interactions between the rings with minimal interference from the tert-butyl groups. This ligand-pair bundling and the symmetry that it confers on the ligand shell are likely to assist in the crystallization of these molecular nanoparticles and influence the properties of the resulting superlattice.$^{54}$

The stability of the proposed structure is strongly supported by the results of our DFT calculations, which reveal a density of states (DOS) with a large HOMO-LUMO energy gap of 1.94 eV (see Figure 3-6a). Such a large predicted gap is consistent with
experimental ESI-MS measurements of marked gas phase stability. Furthermore, the projection of the wave functions onto their angular momenta components shows the expected superatom shell structure with occupied 1S² and a HOMO 1P⁶ delocalized orbitals, and a superatom LUMO 1D orbital (see wave function portraits in Figure 3-6b).

**Figure 3-6:** Electronic properties. (a) Projected DOS calculated for the relaxed Na$_3$Ag$_{17}$(TBBT)$_{12}$ structure. The color-coded angular momenta are given on the right. (b) Representative wavefunction portraits corresponding to the indicated energies are given at the bottom (blue and purple signify different signs). The nodal structures for the delocalized orbitals with eigenenergies -6.19, -1.00 and 0.89eV correspond to 1S, 1P (HOMO) and 1D (LUMO) superatom states. The Fermi energy, at $E_F = 0.0$ eV, is indicated by the dashed line.

The calculated time-dependent DFT (TD-DFT) optical absorption spectrum is in good correspondence with the measured one, lending further support to the proposed structural model (see Figure 3-7). The experimental spectrum was measured in DMF and
the theoretical spectrum was calculated in vacuum, therefore a rigid red-shift was applied to the calculated spectrum, in analogy to a solvatochromic effect, such that the main prominent absorption feature in each better matched. The main feature observed at 436 nm (2.84 eV) and calculated at 400nm (3.10 eV) originated from transitions between (i) states on the carbon atoms (around -2.32eV) and the 1D superatom LUMO state delocalized on the Ag core (0.87 eV), and (ii) the 1P superatom HOMO state delocalized on the silver core (-0.90 eV) and an unoccupied state located mostly on the carbon atoms (2.3 eV).

**Figure 3-7:** Measured (red line) and TD-DFT calculated (green and dotted black lines) optical absorption spectra of Na$_3$Ag$_{17}$(TBBT)$_{12}$ nanoparticles plotted vs. wavelength and vs. energy (inset). The dotted black line is the as-calculated spectrum, and the green line is obtained by red-shifting the as-calculated spectrum.
Chapter 4

Conclusions

In this study, we have presented experimental results showing how sensitive M₄Ag₄₄(SR)₃₀ nanoparticle formation is to the choice of protecting ligand. Experiments were carefully designed by varying three main structural features of the ligands, namely functional groups on the aromatic ring, aromaticity, and flexibility of the aromatic ligand. We found that functional groups on a ligand with a thiol group directly bound to an aromatic ring have no significant effect on formation of M₄Ag₄₄(SR)₃₀. In fact, the chemistry of the overall cluster can be tuned with different substituents.⁶⁸ It was determined that nonaromatic-ring containing ligands were unable to yield M₄Ag₄₄(SR)₃₀, indicating the importance of having pi-pi interactions between the ligands in these Ag-nanoparticles. Further, we could show that these interactions demand proper orientation of the ligands in the shell as more flexible ligands failed to yield M₄Ag₄₄(SR)₃₀. Therefore, it can be concluded that the structure of protecting ligand shell and the inter-
ligand interactions play a vital role in the formation and stabilization of \( \text{M}_4\text{Ag}_{44}(\text{SR})_{30} \) nanoparticles.

In chapter 3, experimental results were presented showing the existence of a new molecular silver nanoparticle, namely \( \text{Na}_3\text{Ag}_{17}(\text{TBBT})_{12} \), which is merely the second size of molecular silver nanoparticle with an aromatic thiolate ligand shell to be discovered and precisely identified. The structure of this new molecular silver nanoparticle is predicted to consist of a \( \text{Ag}_{13} \) icosahedral core that is surrounded by a tetrahedral arrangement of newly found \( \text{Ag(SPh)}_3 \) planar mounts. This compact structure and bundled aromatic ligand shell make it a promising candidate for crystallization.

We also presented a rational strategy for predicting the structure of this molecule and calculations that support the structural model. The predicted HOMO-LUMO energy gap of 1.94 eV and the calculated optical absorption spectrum are in good correspondence with the gas phase stability and the measured spectrum, respectively. This work presents an important step toward the goal of developing accurate predictive structural models in order to relieve the bottleneck of crystallization that currently limits the structural data available for silver and other metals.
Appendix A

Nuclear magnetic resonance spectroscopy

Completely protonated $\text{M}_4\text{Ag}_{44}(\text{p-MBA})_{30}$ nanoparticles were dried under flowing nitrogen for approximately six hours to remove the residual toluene, which was used to precipitate the final product of $\text{M}_4\text{Ag}_{44}(\text{p-MBA})_{30}$ nanoparticles synthesis. A DMF-$d_7$ solution was prepared from the dried nanoparticles with a concentration of 5 mg/mL. The 2D-NOESY spectrum was collected on a Bruker Avance III 600 MHz spectrometer.
Figure A-1: 2D-NOESY spectrum of $\text{M}_4\text{Ag}_{44}(\text{TBBT})_{30}$ nanoparticles in DMF-$d_7$. 
Appendix B

Structure of the irregular (distorted) icosahedral-shell (20 triangles) formed by the 12 sulfur atoms

The irregular icosahedral geometry of the 12 S atoms is shown in Figure B-1a. The 12 sulfur atoms (yellow) surround the silver core (13 Ag atoms, colored red), with three S atoms forming an equilateral triangle around each tetrahedrally-located Ag atom (4 Ag atoms colored green), to form a distorted icosahedron (yellow lines). There are 4 small equilateral triangles (12 E1 edges), 4 large equilateral triangles (12 E3 edges), and 6 pairs of large non-equilateral triangle having 6 common E2 edges. In the sulfur cage, each equilateral triangle made of the 3 sulfur atom that are bonded to an Ag atom shares its E1 edges with the non-equilateral triangles. The edge lengths of the 20 triangles that prescribe the distorted icosahedral cage made by the sulfur atoms are E1 = 4.39 Å ± 0.03 Å, E2 = 5.74 Å ±0.03 Å, and E3 = 6.54 Å±0.06 Å (see Figure B-1b).
Figure B-1: (a) Irregular icosahedral arrangement of 12 S atoms, composed of triangles with edge lengths E1, E2, and E3. Red spheres: 13 Ag atom icosahedral core; green spheres: tetrahedrally arranged 4 Ag atoms (part of the AgS$_3$ mounts); yellow spheres: 12 sulfur atoms. Connecting yellow sticks are drawn to visualize the irregular icosahedron formed by the 12 S atoms. (b) The S-S distances correspond to edge lengths E1, E2, and E3.

**Bader Charge Analysis Na$_3$Ag$_{17}$(TBBT)$_{12}$**

The Bader charge analysis (BCA)$^{24,55,56}$ provides an estimate of the local net charge in a prescribed region in the molecule by finding the difference between the number of electrons found in that region and the number of valence electrons associated with that region. Specifically, the BCA provides an estimate of the balance, $\Delta N(e^-)$, between the number of electrons, $N(e^-)$, found in a prescribed region about a selected atom or group of atoms and the number of valence electrons, $N_v(e^-)$, associated with that atom (or atoms) in that prescribed region when isolated from the molecule, such that $\Delta N(e^-) = N(e^-) - N_v(e^-)$ and the charge balance $\Delta Q(e^-) = -\Delta N(e^-)$.

The results of the BCA for Na$_3$Ag$_{17}$(TBBT)$_{12}$ (Table B.1) and Na$_4$Ag$_{44}$(p-MBA)$_{30}$...
(Table B.2), show the excess electronic charge ($\Delta Q < 0$), deficiency ($\Delta Q > 0$), or no change ($\Delta Q = 0$) in the various prescribed regions of the molecule. The number of valence electrons considered in the pseudopotential for each of the elements was 11 for Ag, 6 for S, 4 for C, and 1 for H.

**Table B.1:** Bader charge analysis for the optimal structure of $\text{Na}_3\text{Ag}_{17}(\text{TBBT})_{12}$

<table>
<thead>
<tr>
<th>Region</th>
<th>$\Delta Q(e^-)$</th>
<th>$\Delta Q(e^-)/\text{unit}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Ag (central)</td>
<td>-0.037</td>
<td>-0.037/atom</td>
</tr>
<tr>
<td>12 Ag (icosahedron)</td>
<td>1.606</td>
<td>0.134/atom</td>
</tr>
<tr>
<td>4 Ag (mounts)</td>
<td>1.240</td>
<td>0.310/atom</td>
</tr>
<tr>
<td>S</td>
<td>-4.326</td>
<td>-0.360/atom</td>
</tr>
<tr>
<td>$\text{C}_6\text{H}_4$</td>
<td>-2.172</td>
<td>-0.18/phenyl</td>
</tr>
<tr>
<td>$\text{C}_4\text{H}_9$</td>
<td>0.690</td>
<td>0.075/tert-butyl</td>
</tr>
<tr>
<td>3 Na</td>
<td>3</td>
<td>1/atom</td>
</tr>
</tbody>
</table>

The sum of all $\Delta Q = 0$, i.e. the 3 electrons on the $\text{Ag}_{17}(\text{TBBT})_{12}^{3+}$ ion came from the 3 Na atoms that became the Na$^+$ counterions. The total system (with the 3 Na$^+$) is

**Table B.2:** Bader charge analysis for the optimal structure of $\text{Na}_4\text{Ag}_{44}(\text{p-MBA})_{30}$ (see reference 24)

<table>
<thead>
<tr>
<th>Region</th>
<th>$N(e^-)$</th>
<th>$N_e(e^-)$</th>
<th>$\Delta Q(e^-)$</th>
<th>$\Delta Q(e^-)/\text{unit}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12 Ag in inner shell</td>
<td>132.01</td>
<td>132</td>
<td>-0.01</td>
<td>-0.001/atom</td>
</tr>
<tr>
<td>8 Ag in outer shell (cube)</td>
<td>85.73</td>
<td>88</td>
<td>2.266</td>
<td>0.283/atom</td>
</tr>
<tr>
<td>12 Ag in outer shell</td>
<td>129.34</td>
<td>132</td>
<td>2.658</td>
<td>0.222/atom</td>
</tr>
<tr>
<td>12 Ag in mounts</td>
<td>127.91</td>
<td>132</td>
<td>4.09</td>
<td>0.341/atom</td>
</tr>
<tr>
<td>inner 24 S</td>
<td>152.53</td>
<td>144</td>
<td>-8.53</td>
<td>-0.355/atom</td>
</tr>
<tr>
<td>bridging 6 S</td>
<td>37.71</td>
<td>36</td>
<td>-1.71</td>
<td>-0.285/atom</td>
</tr>
<tr>
<td>30 Ph rings</td>
<td>838.38</td>
<td>840</td>
<td>1.618</td>
<td>0.054/Ph ring</td>
</tr>
<tr>
<td>30 COOH</td>
<td>334.39</td>
<td>330</td>
<td>-4.388</td>
<td>-0.146/COOH</td>
</tr>
<tr>
<td>4 Na</td>
<td>0</td>
<td>4</td>
<td>4</td>
<td>1/atom</td>
</tr>
</tbody>
</table>
charge neutral. Likewise, the 4 electrons on the Ag_{44}(p-MBA)_{30}^{4+} ion came from the 4 Na atoms that became the Na\(^+\) counterions.

References


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