Bulky Thiolated Gold Nanomolecules: Synthesis, Characterization, Optical Properties, and Atomic Structure

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BULKY THIOLATED GOLD NANOMOLECULES: SYNTHESIS, CHARACTERIZATION,
OPTICAL PROPERTIES, AND ATOMIC STRUCTURE

A Dissertation
presented in the partial fulfillment of Doctor of Philosophy
in the Department of Chemistry & Biochemistry
The University of Mississippi

by

TANYA C. JONES

August 2018
ABSTRACT

Gold nanomolecules (NMs) have a distinct number of gold atoms and thiolate ligands, \( \text{Au}_x(\text{SR})_y \), with unique spectroscopic, electrochemical, and chiral properties which are dependent on “x” and “y”. The properties of NMs are dictated by the type of capping ligand. The overall structure, size, surface percentage of ligands, and structure of an entire gold NM is changed based on the type of ligand used to synthesize it. Ligand type, such as aliphatic, aromatic or bulky play a crucial role in determining the size and composition of such NMs. A NM’s composition and properties vary widely depending on the type of ligand employed, and bulky thiolated NMs need to be explored in-depth. Hence, there is a need to synthesize and characterize bulky thiolated NMs. The phenomenon of ligand dictation brings a lot of interest in the field, into the determination of the different sizes of NMs that can be made (within the 1-2nm range) and the specific mechanism that causes the dictation of the capping ligand. Literature to date, has shown that different thiolate ligands such as aliphatic, bulky and aromatic exhibit a unique series of NMs. While the bulky and aromatic thiolated nanomolecular series are less known. This dissertation addresses the need for synthetic protocols, characterization, and development of bulky thiolated NMs.

Chapter 2 of this dissertation details the discovery, synthetic protocol development, structural elucidation, characterization, optical properties, anisotropic properties, and atomic structure of bulky adamantane thiolated \( \text{Au}_{21}\text{S(Adm)}_{15} \).

Chapter 3 of this dissertation details the crystallographic structure of bulky \( t \)-butyl thiolated \( \text{Au}_{30}\text{S-(tBu)}_{18} \) nanomolecule, and investigation into it’s temperature dependent optical properties.
Chapter 4 of this dissertation details the discovery of the two largest \( t \)-butyl thiolated NMs \( \text{Au}_{46}(S-\text{tBu})_{24} \) and \( \text{Au}_{65}(S-\text{tBu})_{29} \) including their synthesis, structural elucidation, characterization, optical properties, and electrocatalytic properties. In this work the synthetic protocols were optimized, as well as investigation of the optical properties and electrocatalytic properties of \( \text{Au}_{23}(S-\text{tBu})_{16} \) and \( \text{Au}_{30}(S-\text{tBu})_{18} \).

Chapter 5 of this dissertation details the discovery of the first core size interconversion of bulky thiolated nanomolecule \( \text{Au}_{30}(S-\text{tBu})_{18} \) and aromatic thiolated nanomolecule \( \text{Au}_{36}(S\text{PhX})_{24} \), with complete MS, optical characterization, and theoretical energy calculations.

Chapter 6 of this dissertation details original research proposal and investigation into the ligand effect on bulky thiolated nanomolecule \( \text{Au}_{30}(S-\text{tBu})_{18} \) and aliphatic thiolated \( \text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18} \).
DEDICATION

This dissertation is dedicated to my daughter, Katelyn, who constantly inspires me in all that I do. Also, to my parents and Casey for their love, encouragement, and support.

To my doctoral advisor Dr. Amala Dass, who I have the greatest admiration for and who has taught me as much about life as chemistry.

To my undergraduate advisor Dr. Stephen Morgan, for openly welcoming me into his lab and his immense support.
### LIST OF ABBREVIATIONS AND SYMBOLS

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<tr>
<th>Abbreviation</th>
<th>Symbol</th>
<th>Description</th>
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<tr>
<td>Au</td>
<td>gold</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>silver</td>
<td></td>
</tr>
<tr>
<td>BHT</td>
<td>butylated hydroxytoluene</td>
<td></td>
</tr>
<tr>
<td>DCM</td>
<td>dichloromethane</td>
<td></td>
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<tr>
<td>DCTB</td>
<td>trans-2-[3[(4-tertbutyl-phenyl)-2-methyl-2-propenylidene] malononitrile</td>
<td></td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
<td></td>
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<tr>
<td>ESI-MS</td>
<td>electrospray ionization mass spectrometry</td>
<td></td>
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<tr>
<td>HAuCl$_4$•3H$_2$O</td>
<td>chlorauric acid</td>
<td></td>
</tr>
<tr>
<td>HER</td>
<td>hydrogen evolution reaction</td>
<td></td>
</tr>
<tr>
<td>HOMO</td>
<td>highest-occupied molecular orbital</td>
<td></td>
</tr>
<tr>
<td>KOH</td>
<td>potassium hydroxide</td>
<td></td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
<td></td>
</tr>
<tr>
<td>MALDI</td>
<td>matrix assisted laser desorption</td>
<td></td>
</tr>
<tr>
<td>MS</td>
<td>mass spectrometer</td>
<td></td>
</tr>
<tr>
<td>NaBH$_4$</td>
<td>sodium borohydride</td>
<td></td>
</tr>
<tr>
<td>nm</td>
<td>nanometer</td>
<td></td>
</tr>
<tr>
<td>NM</td>
<td>nanomolecule</td>
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<tr>
<td>ORR</td>
<td>oxygen reduction reaction</td>
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<tr>
<td>Pd</td>
<td>palladium</td>
<td></td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
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</tr>
<tr>
<td>Pt</td>
<td>platinum</td>
<td></td>
</tr>
<tr>
<td>RDE</td>
<td>rotating disk electrochemistry</td>
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<tr>
<td>SAdm</td>
<td>adamantane thiol</td>
<td></td>
</tr>
<tr>
<td>SAMs</td>
<td>self-assembled monolayers</td>
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<tr>
<td>SCH$_3$</td>
<td>methane thiol</td>
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<tr>
<td>SCH$_2$CH$_2$Ph</td>
<td>phenyl ethane thiol</td>
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<tr>
<td>SCy</td>
<td>cyclohexane thiol</td>
<td></td>
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<tr>
<td>SEC</td>
<td>size exclusion chromatography</td>
<td></td>
</tr>
<tr>
<td>SPh</td>
<td>thiophenol</td>
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</tr>
<tr>
<td>S-$p$-MBT</td>
<td>para-methyl butane thiol</td>
<td></td>
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<tr>
<td>SPh-$t$Bu</td>
<td>tert-butyl benzene thiol</td>
<td></td>
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<tr>
<td>S-$t$Bu</td>
<td>tert-butyl thiol</td>
<td></td>
</tr>
<tr>
<td>SWNTs</td>
<td>single walled carbon nanotubes</td>
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<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
<td></td>
</tr>
<tr>
<td>TOABr</td>
<td>tetraoctylammonium bromide</td>
<td></td>
</tr>
<tr>
<td>TOF</td>
<td>time of flight</td>
<td></td>
</tr>
<tr>
<td>UV-Vis</td>
<td>ultra violet-visible</td>
<td></td>
</tr>
<tr>
<td>XRD</td>
<td>x-ray diffraction</td>
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ACKNOWLEDGMENTS

I express my deepest appreciation to my advisor, Dr. Amala Dass and my committee members: Dr. Davita Watkins, Dr. James Cizdziel, Dr. Jared Delcamp, and Dr. Joel Mobley for their advice, support, and encouragement. I could not have financed my doctoral studies without the assistantship provided by the University of Mississippi, Department of Chemistry & Biochemistry, and the Graduate School and thank them for their financial support.

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My success did not happen upon me, it happened because of all of you.
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CHAPTER 1

INTRODUCTION TO GOLD NANOMOLECULES

1.1 Introduction to Gold Nanomolecules

Gold nanoparticles and gold colloids have been in use since the 4th century, in the Roman’s Lygrus cup.\textsuperscript{13-14} Prime examples of ancient colloids are further seen in the stained glass windows in the cathedral of Notre Dame and in the paint of ceramics from the Italian renaissance.\textsuperscript{14} In the 18th century, gold colloids were first recognized by Michael Faraday and Thomas Graham.\textsuperscript{14} Many colloid gold nanoparticles are not stable and usually decompose, therefore research since then and up to now has looked at focusing down the size of the colloids into nanoparticles and improving their stability; in order to harness and understand their unique properties. Research to date has been able to create gold nanoparticles which range from 1-100nm.\textsuperscript{15} Gold nanoparticles, which reside in the 1-2nm size range are termed as gold NMs because of their unique size dependent properties, atomic monodispersity, and increased surface ratio of ligands.\textsuperscript{16} One of gold NMs’ most notable features is their monodispersity, meaning that they have a precise number of a gold atoms and a precise number of ligands.\textsuperscript{15} The development of these smaller, more precise, thiolated gold NMs was brought about by the Brust-Schiffrin method.\textsuperscript{17} This method allows NMs to be made that are highly stable and monodisperse. This has enabled the field of ultra-small NMs to evolve allowing researchers to have a more precise manipulation of the material. Gold NMs have several interesting properties such as their stability, dispersion in solvents to form a solution unlike colloids, ability to remain stable in a dried powder state for years, and unique optical properties which are highly applicable in catalysis, medical technology, and medicine.\textsuperscript{18-21}
1.2 Experimental approach: General Synthesis, Isolation, and Structure

1.2.1 Synthesis. The two-phase Brust-Schiffrin method is the most commonly utilized method for the synthesis of gold thiolate NMs. In general, this method can be done by mixing gold salt (chloroauric acid, HAuCl₄•3H₂O) in distilled water and tetaoctylammonium bromide (TOABr) in toluene and stirring for approximately an hour to allow for the gold salt to transfer into the organic layer. Afterwards, the aqueous layer is removed leaving the gold salt, TOABr, and toluene mixture. A specified amount of thiol is then added to this mixture and reacted. This reaction is then reduced with sodium borohydride (NaBH₄) in ice-cold water, at a tuned gold to reducing agent ratio. The reaction is then carried out for several minutes, hours, or days depending on the specifics of the synthesis. This method has also been modified to exclude the phase transfer step by using tetrahydrofuran instead of toluene and water. This process is referred to as a one-phase method for the synthesis of NMs. In both methods, once a synthesis is complete the product is then dried and washed in methanol and water to remove any excess thiol and by-products. Once this is done the nanoclusters are generally soluble and re-dispersible in various organic solvents such as: THF, toluene, and dichloromethane (DCM).

1.2.2 Isolation and Purification: In general, the synthetic protocol described above makes a mixture of monodisperse NMs. Therefore, additional isolation and purification steps are used to obtain highly pure and stable NMs. These methods include: thermochemical etching, solvent fractionation and size exclusion chromatography (SEC) and are described below.

1.2.3 Thermochemical Etching. This process involves heating the obtained mixture of NMs in excess amounts of the same or different thiolate ligand in order to remove meta-stable clusters. This process can be used to facilitate core-sized conversion in order to synthesize a new nanocluster with a new thiolate ligand type.

1.2.4 Solvent Extraction/Fractionation. This process is generally done to isolate NMs that are specifically soluble in a certain solvent. For example, Au_{25}(S-tBu)_{16} and Au_{25}(SCH₂CH₂Ph)_{18} are soluble in acetonitrile while other NMs such as Au_{30}(S-tBu)_{18} and Au_{144}(SCH₂CH₂Ph)_{60}, which are generally synthesized in conjunction respectively, are not soluble in acetonitrile. Therefore, when Au_{25}(CH₂CH₂Ph)_{18}
is synthesized along with other monodisperse clusters it can be easily separated and extracted from the mixture with acetonitrile. Solvent fractionation involves addition of a non-solvent, such as methanol addition to toluene solution of NMs.

**1.2.5 Size Exclusion Chromatography (SEC).** This process is a separation technique based on the size (hydrodynamic) and molecular weight of the analyte. Specialized separation beads (Bio Rad SX1 support beads) are used as the stationary phase along with THF stabilized with BHT, which constitutes the mobile phase. These specialized beads have channels which force smaller sized (or molecular weight) NMs into them while larger molecules pass around the beads this allows for the separation of NMs with different molecular weights. This method commonly repeated in many cases, to accomplish the desired purity. Figure 1.1 shows a summary of the discussed synthesis and isolation techniques in Section 1.2.1, 1.2.3, 1.2.4, and 1.2.5. Figure 1.1 a, illustrates the one-phase and two-phase synthesis discussed in Section 1.2.1. Figure 1.1b illustrates using MALDI-MS spectra the thermochemical etching technique discussed

![Diagram](image-url)

**Figure 1.1.** Summary of the discussed (a) one and two-phase synthetic protocols and isolation methods including (b) MALDI-MS of thermochemical etching (top) and solvent fractionation (bottom). (c) Shows the SEC process of Au_{30}(S-tBu)_{18}
in Section 1.2.3 and the solvent fractionation discussed in Section 1.2.4. Figure 1.1 illustrates the SEC method discussed in Section 1.2.5.

1.2.6 Structure: The general structure of a gold thiolate NM consists of several layers: the innermost layer is an Au core, with surrounded Au shell(s) and an outer Au shell protected by the sulfur end of the ligand. The outer layer of the nanostructure is composed of staple motifs of \((\text{SR-Au-SR})_n\) which protect and cap the structure. There are a variety of staples motifs which can be arranged in several ways on the nanostructure. Common arrangements observed included: monomeric staple which is a motif consisting of \(\text{SR-Au-SR}\), a dimeric which is \(\text{SR-Au-SR-Au-SR}\), and trimeric \(\text{SR-Au-SR-Au-SR-Au-SR}\). Several structures also have bridging thiols where the ligand is directly attached to the core (or outermost shell).

Figure 1.2 shows the crystal structure model of \(\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}\) as an example, the core of this structure (red) consists of a \(\text{Au}_{13}\) icosahedral core, surrounded by 12 Au atoms in staple formation, making up a total of six dimeric staples surrounding the core.

1.3 Specialized Synthetic Techniques

1.3.1 Ligand Exchange and Transformations. Ligand exchange is commonly performed on gold NMs for two purposes. The first is to replace the existing ligands with a new incoming ligand while maintaining the original core size. The second purpose is to convert the number of gold atoms in the core.
to another sized core with a newly bound ligand. The second is known as core conversion or transformation. This is an essential technique to nanoparticle synthesis because NMs can generally be created in this method. Allowing us to make new NMs, in high yield quantities which is essential for application and manufacturing purposes. Ligand exchanges can be monitored using mass spectrometric techniques such as MALDI-MS and ESI-MS. Mass spectrometry can be used to monitor ligand exchanges and transformation reactions when there is a mass difference between the existing ligand and the incoming ligand. NMs’ unique optical properties also allow the ability to utilize UV-Vis spectroscopy to also be used to monitor these reactions.

**1.3.2 Metal Doping.** Metal doping is commonly done to incorporate other metal atoms while maintaining monodispersity into the nanostructure allowing its properties to be tuned. Various metals such as Ag, Pt, and Pd can be incorporated into these structures. Synthetic protocols are similar to gold NMs synthesis, with the incorporation of a second doping metal at a specified molar ratio between the two metals used. Characterization techniques are similar to those utilized in gold NM synthesis.

**1.4 Characterization Techniques**

**1.4.1 Mass Spectrometry:** Two mass spectrometry techniques are commonly utilized in the characterization of NMs. MALDI-TOF-MS (matrix assisted laser desorption ionization-time of flight mass spectrometer) is used in order to make compositional assignments, determine purity and monodispersity of NMs. ESI-MS is a softer ionization technique with little to no fragmentation and higher sensitivity which makes it a key component for compositional analysis based on the mass to charge ratio and isotopic distributions.

**1.4.2 UV-Vis Spectroscopy:** UV-Vis spectroscopy is commonly used to characterize gold NMs. This is because gold NMs which are < 2nm, exhibit molecular-like properties due to the HOMO-LUMO gap in molecular orbitals. Whereas larger nanoparticles exhibit surface plasmon resonance, which is the collective oscillation of the conduction band electrons in response to the incident radiation. Gold nanoparticles in this size range exhibit a surface plasmon resonance at 500-550nm. UV-Vis experiments
are generally carried out in toluene, THF, and dichloromethane. Generally, the 300-1100nm wavelength region is examined for electronic properties of the NMs.

1.4.3 Low Temperature UV-Vis spectroscopy. Low temperature UV-Vis spectroscopy is utilized to study the optical electronic properties of gold NMs. This is accomplished using a specialized cryostat which is used in place of a traditional UV stage. The cryostat is evacuated of air and filled with liquid nitrogen to cool the sample to 77K. At 77K the molecules within the samples have less rotational and vibrational energy. Therefore, absorbance peaks and valleys from electronic transitions, are amplified and more resolved.

1.4.4 Single Crystal X-ray Diffraction. X-ray diffraction is crucial in the determination of the atomic structures of gold NMs. Unlike mass spectrometric methods which only confirm the atomic composition and not the arrangement of atoms. Through X-ray diffraction we can determine the exact molecular structure of the NMs. Essential information such as physical and electronic properties can also be obtained from the models deduced by crystallography. The process of obtaining a single crystal includes: growing crystals generally through vapor diffusion set-ups, crystal screening, data collection, refinement, and structure fitting. Growing single crystals of gold NMs for X-ray methods is a defining step in this process, as growing crystals is a challenging task in the field. However, there have been several NMs crystallized including \( \text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18} \) to ones as large as \( \text{Au}_{246}(\text{S-p-MBT})_{60} \) and \( \text{Au}_{279}(\text{SPh-tBu})_{84} \).33-36

1.5 Bulky Thiolated Nanomolecules

A NM’s composition and properties vary widely depending on the type of ligand employed and bulky thiolated NM remains to explored in depth. Hence, there is a need to synthesize and characterize bulky thiolated NMs. This is because the properties of the NMs are dictated by the type of ligand that it is capped with. The overall structure, size, surface percentage of ligands, and structure of an entire gold NM is changed based on the type of ligand used to synthesize it.12 This phenomenon of ligand dictation brings a lot of interest in the field, into the determination of the different sizes of NMs that can be made (within the 1-2nm range) and the specific mechanism that causes the dictation of the capping ligand. Literature to date,
has shown that different thiolate ligands such as aliphatic, bulky and aromatic exhibit a unique series of NMs. For instance, the series of NMs capped with aliphatic-like thiolate ligands, such as phenylethane thiol, are well known throughout the field.\textsuperscript{15, 30, 34} The phenylethane thiol series includes: \(\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}\), \(\text{Au}_{38}(\text{SCH}_2\text{CH}_2\text{Ph})_{24}\), \(\text{Au}_{67}(\text{SCH}_2\text{CH}_2\text{Ph})_{35}\), \(\text{Au}_{144}(\text{SCH}_2\text{CH}_2\text{Ph})_{60}\), \(\text{Au}_{329}(\text{SCH}_2\text{CH}_2\text{Ph})_{84}\), and \(\text{Au}_{500}(\text{SCH}_2\text{CH}_2\text{Ph})_{120}\).\textsuperscript{15, 30, 34} While the bulky and aromatic thiolated nanomolecular series are less known. In the bulky thiolated series the largest known NMs are \(\text{Au}_{30}(\text{SR})_{18}\) (SR=HS-\(t\)-Bu or HSAdm) and \(\text{Au}_{38}\text{S}_2(\text{SAdm})_{20}\).\textsuperscript{37-43} Research has focused on expanding on the known series of bulky thiolated NMs and comparing this series with that of the aliphatic-like, and phenylethane series of NM to provide insight into the ligand effect on the core of the NM and their optoelectronic properties and applications.
CHAPTER 2

BULKY ADAMANTANE THIOLATED NANOMOLECULES: THE CASE OF

$\text{Au}_{21}\text{S(SAdm)}_{15}$

*Part of the text and figures in this chapter reprinted (adapted) with permission from: $\text{Au}_{21}\text{S(SAdm)}_{15}$: Crystal Structure, Mass Spectrometry, Optical Spectroscopy, and First-Principles Theoretical Analysis Tanya C. Jones, Luca Sementa, Mauro Stener, Kevin J. Gagnon, Viraj Dhanushka Thanthirige Guda Ramakrishna, Alessandro Fortunelli,* and Amala Dass* J. Phys. Chem. C, 2017, 121 (20), pp 10865–10869, Copyright 2017 American Chemical Society.

Author Contributions

Tanya Jones developed the synthetic protocol, isolation, structure elucidation, and characterization of $\text{Au}_{21}\text{S(SAdm)}_{15}$. Characterization techniques used were ESI-MS, MALDI-MS, and UV-Vis spectroscopy, resolution of the crystallographic structure, and temperature dependent optical studies. Kevin J. Gagnon conducted crystal diffraction and aided resolution of crystallographic structure. Viraj Dhanushka Thanthirige conducted transient absorption measurements and Luca Sementa, Mauro Stener conducted theoretical studies.

2.1 Summary

Here we report X-ray crystal structure, spectroscopic and theoretical characterization of $\text{Au}_{21}\text{S(SAdm)}_{15}$ (SAdm=adamantane thiol). Single crystal X-ray diffraction shows that the $\text{Au}_{21}\text{S(SAdm)}_{15}$ NM exhibits a $\text{Au}_{12}$ cuboctahedral core surrounded by a single $\mu_3$ sulfur atom (sulfide), 5 bridging thiols, 2 additional Au atoms, 1 monomeric Au(SR)$_2$ and 2 trimeric Au$_3$(SR)$_4$ staples, with the 2 trimeric staples being linked through a Au$_2$(SR) unit with a thiolate ligand in $\mu_4$ coordination. Compositional, electronic, optical and structural features of this compound are clarified via nESI-MS, MALDI-MS, low-temperature UV-Vis spectroscopy, and first-principles analysis.
2.2 Introduction

Gold NMs have a distinct number of gold atoms and thiolate ligands, Au$_x$(SR)$_y$, with unique spectroscopic, electrochemical, chiral properties.$^{1-10}$ The type of ligands such as aliphatic vs. aromatic or bulky vs. slim play a crucial role in determining the size and composition of such NMs. Aliphatic slim ligands, such as phenylethane thiol, HSCH$_2$CH$_2$Ph, have been shown to produce a series of NMs, such as: Au$_{25}$(SCH$_2$CH$_2$Ph)$_{18}$, Au$_{38}$(SCH$_2$CH$_2$Ph)$_{24}$ and Au$_{144}$(SCH$_2$CH$_2$Ph)$_{60}$,$^{44-48}$ whereas using bulky ligands, such as $t$-butyl thiol and adamantane thiol, species such as: Au$_{23}$(SC$_6$H$_{11}$)$_{16}$, Au$_{24}$(SAdm)$_{16}$, Au$_{30}$S(S-$t$Bu)$_{18}$ and Au$_{30}$S(S-$t$Bu)$_{18}$ can be produced.$^{49-53,15,19}$ Krommenhoek et al. synthesized somewhat larger Au$_{39}$(SAdm)$_{23}$, Au$_{65}$(SCy)$_{30}$ and Au$_{67}$(SCy)$_{30}$ NMs (with Cy cyclohexyl residues), and discussed how the bulkiness of the ligands affects the structure of these gold NMs and limits the size of the Au core.$^{54}$ In any case, the detailed knowledge of the atomistic structure enormously facilitates the application of computational methods in this field, allowing synergy between theoretical and experimental approaches and is the basis for establishing sound structure/property relationships.$^{7,4}$

Here we report a new species in the bulky thiolated ligand series, Au$_{21}$S(SAdm)$_{15}$, along with its characterization via single crystal X-ray diffraction analysis, mass spectrometry (nESI-MS and MALDI-TOF-MS), optical UV-Vis variable-temperature spectroscopy, and first-principles analysis of its energetics and electronic features. The X-ray resolved crystal structure of Au$_{21}$S(SAdm)$_{15}$ shows that this species features the simultaneous presence of Au$_x$(SR)$_{x+1}$ staple motifs of different size (monomeric and trimeric) in the protecting shell, together with an extra triply coordinated sulfur atom, $\mu_3$-S, and a tetra-coordinated sulfur atom, $\mu_4$-S. While the $\mu_3$-S atom has been previously observed in literature in the $t$-butyl thiolated Au$_{30}$S(SR)$_{18}$ NM$^{55}$, the $\mu_4$-S species is unusual. [After completion of this work, we came across a recent publication which
reported a different but related crystal structure of Au$_{21}$(SAdm)$_{15}$. A detailed comparison between the two structures is beyond the scope of this work. The structures reveal a similarity but the extra $\mu_3$-S sulfide in the present compound causes significant rearrangement in the outer layer of Au$_{21}$S(SAdm)$_{15}$. These features should confer Au$_{21}$S(SAdm)$_{15}$ promising properties in sensing, opto-electronic, and electrochemical applications.

2.3 Results and Discussion

2.3.1 X-ray Crystallography. Figures 2.1 a, b show the total structure of Au$_{21}$S(SAdm)$_{15}$, which crystallizes in the space group $C2/c$ with unit cell dimensions: $a=33.2480(14)$ Å, $b=30.4845(11)$ Å, and $c=35.8966(11)$Å, and $\beta=90.609(3)^\circ$. The structure was refined to a
resolution of ~1.1 Å with an R value of 6.65%. The 1.1 Å cutoff was chosen with an R_{merge} of ~0.38 and an I/σ(I) > 2, data beyond this limit were too weak to be considered significant. Figure 2.1d shows the Au_{12} cuboctahedra core, containing a central atom, and has a single missing vertex of a cuboctahedron. Figure 2.1c shows the Au_{12} core surrounded by its 6 bridging thiols. Two of the bridging thiols on the Au_{12} core are: (1) an extra triply coordinated sulfur atom, μ₃ S, and (2) a tetra-coordinated sulfur atom, μ₄ S denoted as cyan and lime green, respectively, in Figure 2.1. The Au_{12}S(SR)_4 structure is surrounded by two trimeric staples [SR-Au-SR-Au-SR-Au-SR] and one monomeric staple [SR-Au-SR] bound to two Au atoms surrounding the Au_{12} core. These staples are deconstructed in Figure 2.1c for clarity. Figures 2.1e and 2.1f depict the full Au_{21}S(S)_15 motif and its 90° rotated view respectively, displaying how the monomeric and trimeric staple motifs surround the Au_{12}S(SR)_4 structure.

2.3.2 Mass Spectrometry. ESI-MS was performed to provide complementary evidence to the composition derived from the XRD structure analysis. Assignment of Au_{21}(SAdm)_{15} was

![Figure 2.2. MALDI-MS and ESI-MS of Au_{21}(SAdm)_{15} nanomolecules. MALDI-MS spectra (blue) shows a major peak which denotes the +1 charge state of Au_{21}(SAdm)_{15} by fragmentation of Au(SR) and the peak denoted by asterisk is further fragmentation of the nanomolecule minus an Au₄(SR)_4. ESI-MS mass spectra (red inset) shows the neutral species can be seen by the addition of cesium acetate and gives a peak at 6778 m/z as a result of a Cs⁺ adduct. The inset displays the theoretical spectra compared to the experimental spectra obtained for Au_{21}(SAdm)_{15} • Cs⁺.

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obtained from addition of cesium acetate, which gives a predominating peak with a charge state of +1 at 6778 m/z. This peak represents the Au$_{21}$(SAdm)$_{15}$$\cdot$Cs$^+$ adduct. Experimental (red) ESI-MS spectra was then isotopically compared with theoretical (black) spectra, shown in Figure 2.2 along with the full spectra of Au$_{21}$(SAdm)$_{15}$. The MALDI-MS spectrum in blue shows the +1 charge state of Au$_{21}$(SAdm)$_{15}$, fragmented by one ligand. The asterisk denotes further fragmentation by Au$_4$(SR)$_4$. Note that observation of Au$_{21}$(SAdm)$_{15}$ in the mass spectra is expected rather than the total Au$_{21}$S(SAdm)$_{15}$ with the additional sulfur atom as previously in the case of Au$_{30}$S(S-tBu)$_{18}$, in which Au$_{30}$S(S-tBu)$_{18}$ was shown to be formed during the crystallization process, but only Au$_{30}$S(S-tBu)$_{18}$ was observed during mass spectrometry. Careful effort eventually led to crystallization of Au$_{30}$S(S-tBu)$_{18}$, but Au$_{30}$S(S-tBu)$_{18}$ crystals are much more common and more easily produced.

2.3.3 Experimental Optical Spectroscopy. UV-Vis spectroscopy measurements provide
the optical absorption spectrum of $\text{Au}_{21}\text{S(Adm)}_{15}$ as a function of temperature (Figure 2.3). At 78K, electronic transitions can be seen with a much higher resolution. Experimental low-temperature UV-Vis data (Figure 2.3a) shows absorbance peaks at 350, 390, 430, 465, 500, 580, and 695nm, whereas the peaks at 350 and 500nm are not appreciable at room temperature. Figure 2.3b also depicts the energy plot of photon energy of the $\text{Au}_{21}\text{S(Adm)}_{15}$ molecule obtained from the optical spectrum.

### 2.3.4 Structural and Energetic Analysis.

Starting from the experimentally determined structural model of $\text{Au}_{21}\text{S(Adm)}_{15}$ and assuming a zero total charge for the cluster, a local geometry relaxation was performed employing density-functional theory (DFT) and QuantumEspresso code\(^6\) and the Perdew–Burke–Ernzerhof (PBE) exchange-correlation (xc-) functional.\(^6\) Since the PBE xc-functional overestimates the length of Au-Au bonds whereas X-ray determination is especially accurate in determining the coordinates of this heavy element, the positions of Au atoms were frozen to those experimentally derived in the local relaxation while fully optimizing the coordinates of all other atoms. The $\text{Au}_{21}\text{S(Adm)}_{15}$ structure so obtained was then simplified by replacing the adamantyl with methyl residues, freezing the positions of Au, S, and C atoms, and relaxing the H atoms. The $\text{Au}_{21}\text{S(SCH}_3\text{)}_{15}$ model so obtained was used to speed up the simulation of the optical spectrum using higher-level DFT xc-functionals. The Cartesian coordinates of both the $\text{Au}_{21}\text{S(Adm)}_{15}$ and $\text{Au}_{21}\text{S(SCH}_3\text{)}_{15}$ relaxed geometries are reported in full in the Supporting Information.

To quantify the energetic stability of the ligand containing the unusual $\mu_4$-coordinated sulfur, we have calculated the energies of the following fragmentation reactions:\(^5\)

\[ \text{Au}_{21}\text{S(SCH}_3\text{)}_{15} \rightarrow \text{Au}_{21}\text{S(SCH}_3\text{)}_{14} + \text{SCH}_3 \quad S=\mu_4 \quad (1) \]

\[ \text{Au}_{21}\text{S(SCH}_3\text{)}_{15} \rightarrow \text{Au}_{21}\text{S(SCH}_3\text{)}_{14} + \text{SCH}_3 \quad S\neq\mu_4 \quad (2) \]
where the fragments on the right-hand-side are frozen in their interacting configurations, and the 
μ₄-coordinated sulfur is compared with a standard ligand with S ≠ μ₄ taken from a trimeric staple
(the one containing the green Au). The corresponding fragmentation energies are: ΔE(1) = 5.37
eV, and ΔE(2) = 4.47 eV, respectively, showing that the ligand containing the μ₄ S is significantly
more strongly bound than a ligand with a standard coordination. This increased stability is
associated with the increased (μ₄) coordination and the compensation of the dipole introduced by
the μ₃ sulfide.

2.3.5 Theoretical Optical Spectroscopy. The simulated optical spectrum (averaged over x,
y, z Cartesian components) of Au₂₁S(SCH₃)₁₅ is reported in Figures 2.3b, as obtained via time-
dependent DFT (TDDFT) calculations. We use three different exchange-correlation(xc-) functionals and two TDDFT codes and approaches: a time-evolution formalism to follow the
electron dynamics using the CP2K code⁶² and the B3LYP hybrid xc-functional,⁶³ or the Casida
approach⁶⁴ using the ADF code⁶⁵ and the SAOP and PBE xc-functionals⁶⁶,2¹ on the Au₂₁S(SCH₃)₁₅
species. The replacement of adamantyl with methyl residues does not alter the qualitative feature
of the spectrum, as shown by a comparison of the obtained using a computationally more
affordable LB94⁶⁷ xc-functional (see Figure S2.3 in Appendix 2). Moreover, for this cluster the
hybrid B3LYP xc-functional produces a similar spectrum as the SAOP xc-functional, as illustrated
in Figure S2.5 of Appendix 2, so that in Figure 2.3b we report the comparison between the
experimental spectrum and the TDDFT one simulated using the SAOP xc-functional on
Au₂₁S(SCH₃)₁₅. The overall agreement between the observed and simulated spectra in Figure3b is
fair, except for a shift of the experimental peak at 2.1 eV to higher energy, around 2.6 eV. This
shift is also probably connected with the strongly asymmetric features of this species, and
interestingly a PBE xc-functional in the present case is in slightly better agreement with
2.4 Experimental and Computational Analysis

2.4.1 Materials. Tetrachloroauric (III) acid (HAuCl₄·3H₂O, >99% metal basis, Aldrich), sodium borohydride (Acros, 99%), adamantane thiol (Acros, 95%), and trans-2-[3[(4-tertbutylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB matrix) (Fluka≥99%) were purchased and used as received. HPLC grade solvents such as acetone, tetrahydrofuran, toluene, methanol, butylated hydroxytoluene stabilized tetrahydrofuran, methyl cyclopentane, methyl cyclohexane, and acetonitrile were obtained from Fisher Scientific.

2.4.2 Synthesis. Au₂₁(SAdm)₁₅ NMs were synthesized by addition of HAuCl₄·H₂O and adamantane thiol at 1:3 mol ratio in toluene. The reaction was allowed to stir at 450rpm for 15 minutes. The reaction was then reduced with 110mg of NaBH₄ (1:10 molar ratio) in 10mL cold H₂O. The reaction was stopped after 20 minutes, dried via rotary evaporator then washed 3 times with methanol. Acetone was added to the crude product to extract nanoparticles the acetone fraction was then dried and separated using size exclusion chromatography (SEC). The SEC fraction containing Au₂₁(SAdm)₁₅ then underwent further solvent fractionation with acetone in order to obtain the pure material.

2.4.3 Instrumentation. Voyager DE PRO matrix assisted laser desorption time-of-flight (MALDI-TOF) mass spectrometer was used to acquire mass spectra using DCTB as the matrix. Compositional analysis was performed using a Waters Synapt HDMS nano-electrospray ionization mass spectrometer (nESI-MS), collected from using a THF / acetonitrile solvent mixture. 10μL of 10mM cesium acetate was added to sample. Temperature dependent UV-vis-NIR absorption measurements were collected with UV-vis-NIR Cary 5000 and JANIS VNF-100 low temperature cryostat using a 1:1 mixture of methyl cyclopentane and methyl cyclohexane as the solvent. A
Lakeshore Cyotronics temperature controller was used for temperature-dependent absorption measurements.

**2.4.4 Single-crystal X-ray diffraction.** Data for Au$_{21}$S(SAdm)$_{15}$ was collected on beamline 11.3.1 at the Advanced Light Source, Lawrence Berkeley National Laboratory. A 0.08 x 0.05 x 0.01 mm$^3$ red-brown plate was mounted on a MiTeGen kapton loop and placed in a 100(2) K nitrogen cold stream provided by an Oxford Cryostream 800 Plus low temperature apparatus on the goniometer head of a Bruker D8 diffractometer equipped with a PHOTON 100 CMOS detector operating in shutterless mode. Diffraction data were collected using synchrotron radiation monochromated using silicon (111) to a wavelength of 0.7749 Å. An approximate full sphere of data was collected using a combination of phi and omega scans with scan speeds of 1 second per 4 degrees for the phi scans, and 3 and 5 seconds per degree for the omega scans at 2theta = 0 and -45, respectively. Additional crystallographic information has been summarized in Table S1 and full details can be found in the crystallographic information file provided in the Supplementary Information. The quality of the anisotropic refinements is shown in Figure S2.1, as well as a photograph of the Au$_{21}$S(SAdm)$_{15}$ crystal in Figure S2.2.

**2.4.5 Theory: Computational Details.** QuantumEspresso geometry optimizations were performed using ultrasoft pseudopotentials and the PBE xc-functional. Values of 30 and 300 Ry were chosen as the cut-offs for the selection of the plane wave basis sets for describing the kinetic energy and the electronic density, respectively. One-electron levels were broadened using a Gaussian distribution with $\sigma = 0.002$ Ry. The TDDFT/B3LYP absorption spectra were obtained from real-time simulations using the CP2K package with DVZP primary basis set GTH pseudopotentials and an auxiliary cpFIT3 basis set. Starting from a ground-state calculation, optical response is obtained by subjecting the system to electrical pulses of 0.0005 au following
the electron dynamics for 15 fs using a time step of 0.012 fs and a time damping of 7.3 fs. The TDDFT/SAOP$^{66}$ and TDDDFT/PBE$^{69}$ spectra were calculated at the scalar relativistic ZORA$^{73}$ level, with the Amsterdam Density Functional (ADF) code$^{65}$ and a Triple Zeta plus Polarization (TZP) basis set, with discrete transition broadened with Lorenzian function with $\sigma = 0.3$ eV.

2.5 Conclusions

In this work, we synthesized and isolated of a new species in the bulky thiolated ligand series, $\text{Au}_{21}\text{S(SAdm)}_{15}$. We report the complete characterization of $\text{Au}_{21}\text{S(SAdm)}_{15}$, including: single crystal X-ray diffraction analysis, mass spectrometry (nESI-MS and MALDI-TOF-MS), the temperature dependent optical properties with UV-Vis spectroscopy, and a detailed first-principles analysis of its energetics and electronic features. The X-ray resolved crystal structure of $\text{Au}_{21}\text{S(SAdm)}_{15}$ reveals an unusual lack of symmetry. As well as, a unique structure with the both monomeric and trimeric staples protecting the shell, all-together with an extra triply coordinated sulfur atom, $\mu_3$ S, and a tetra-coordinated sulfur atom, $\mu_4$ S. The $\mu_3$ S atom has been previously observed in literature in the $\tau$-butyl thiolated $\text{Au}_{30}\text{S(SR)}_{18}$ NM.$^{41}$ However, to the best of our knowledge this is the first-time observation of a unique $\mu_4$ S species. Collaboration with theoretical researchers shows that the NM’s unusual lack of symmetry unique to this compound, and has a peculiar anisotropy of its chiro-optical absorption spectrum.$^{44}$ As well as, the appearance of asymmetric pockets of electrostatic potential next to the molecular frame. These properties make the NM very promising for sensing, opto-electronic, and electrochemical applications.$^{7, 57-58}$ The theoretical results published in *J. Phys. Chem. Lett.* 2017, 8, 457.
CHAPTER 3

BULKY TERTIARY BUTYL THIOLATED NANOMOLECULE: THE CASE OF

\( \text{Au}_{30}(S\text{-tBu})_{18} \)

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**Author Contributions**

Tanya Jones synthesized and characterized \( \text{Au}_{30}(S\text{-tBu})_{18} \) through MS, and UV-Vis spectroscopy, diffraction and resolving the crystallographic structure, and temperature dependent optical studies. Milan Rambukwella aided in temperature dependent optical studies and discussion. Kevin J. Gagnon aided in the resolution of the crystallographic structure. Luca Sementa, Martina De Vetta, Oscar Baseggio, Edoardo Aprà, and Mauro Stener contributed theoretical calculations and studies.

**3.1 Summary**

We report the complete X-ray crystallographic structure as determined through single crystal X-ray diffraction and a thorough theoretical analysis of the green gold \( \text{Au}_{30}(S\text{-tBu})_{18} \). While the structure of \( \text{Au}_{30}S(S\text{-tBu})_{18} \) with 19 sulfur atoms has been reported, the crystal structure of \( \text{Au}_{30}(S\text{-tBu})_{18} \) without the \( \mu_3 \)-sulfur has remained elusive until now, though MALDI-MS and ESI-MS data unequivocally shows its presence in abundance. The \( \text{Au}_{30}(S\text{-tBu})_{18} \) NM is not only distinct in its crystal structure but has unique temperature dependent optical properties. Structure determination allows a rigorous comparison and an excellent agreement with theoretical predictions of structure, stability, and optical response.
3.2 Introduction

Gold-thiolate NMs, $\text{Au}_n(SR)_m$, are compounds with a fixed number $n$ of gold atoms which are stabilized by passivating organic thiolate ligands $m$.\textsuperscript{74} For instance, $\text{Au}_{25}(SR)_{18}^{-1,0}$, $\text{Au}_{35}(SR)_{24}$, and $\text{Au}_{144}(SR)_{60}$, are some of the most commonly studied NMs, with size dependent and unique chemical and physical characteristics.\textsuperscript{46, 75-77} Griffin and coworkers and others showed that self-assembled monolayers (SAMs) on a Au (111) substrate with mixed tert-butane-thiol and n-octadecane thiol ligands were prepared, revealed less-densely packed monolayers with increasing amount of tert-butane-thiol, demonstrating that the bulkiness of the thiolate ligand modifies the packings of the SAMs.\textsuperscript{78} Less common NMs such as $\text{Au}_{30}$, $\text{Au}_{39}$, $\text{Au}_{41}$, $\text{Au}_{65}$ and other clusters, have in fact been reported,\textsuperscript{52-55, 59, 79} synthesized using sterically hindered bulky ligands. Aromatic thiolate ligands have also been shown to lead to uncommon altered cluster sizes.\textsuperscript{80-83} Aromatic thiols introduce an additional complication as aromaticity and bulkiness are coupled in an intricate way, so that it is not possible to attribute the changes in geometric and electronic structure to bulkiness only. Because of this complex panorama, structural and geometric studies are highly reliant on the identification of crystallographic structure of the NMs.

In this study we follow this line of research. We focus on a specific compound: $\text{Au}_{30}(S$-$t\text{Bu})_{18}$, which had been identified so far only through MALDI-MS and ESI-MS\textsuperscript{59} but whose crystallographic structure had remained elusive until now, and determine its crystallographic data. Its properties can so be thoroughly compared with that of a homologous $\text{Au}_{30}S(S$-$t\text{Bu})_{18}$ compound, whose structure had been previously reported,\textsuperscript{55} thus providing an in-depth analysis on the composition, electronic, optical, and chiroptical properties. In addition to reporting the first crystallographic structure of the $\text{Au}_{30}(S$-$t\text{Bu})_{18}$ NM in two distinct packing structures, (space groups P2$_1$/n and P-1), determined through the use of single crystal X-ray diffraction, we detail
the unique temperature-dependent optical properties of $Au_{30}(S-tBu)_{18}$ and compare these optical
properties with theoretical predictions obtained using time-dependent density-functional theory

3.3 Results and Discussion

$\text{Au}_{30}(\text{S-} \text{tBu})_{18}$ was synthesized in a one-pot THF method (see Experimental Section for details), and crystallization was performed via vapor / vapor diffusion of hexane into a toluene solution of $\text{Au}_{30}(\text{S-} \text{tBu})_{18}$. Small green needle-like crystals were obtained after 4-7 days. These needle-like crystals are different than the rhombic shaped plate-like crystals of $\text{Au}_{30}\text{S}(\text{S-} \text{tBu})_{18}$.

3.3.1 Structure Elucidation. Figure 3.1a presents the total structure of the bicuboctahedron $\text{Au}_{30}(\text{S-} \text{tBu})_{18}$ cluster, which crystallizes in the space group $P2_1/n$. The structure was refined to a resolution of 1.06 Å, and to value of $R_1 = 10.93\%$. Figure 3.1b shows the $\text{Au}_{30}$ skeleton with an interpenetrating bicuboctahedral core. The geometry, shown in Figure 3.1c represents the Au-SR staples and bond structures of $\text{Au}_5(\text{SR})_4$. Figure 3.1d represents the $\text{Au}_{30}\text{S}_{18}$ geometry highlighting the two monomeric [-SR-Au-SR-] units. The structure of $\text{Au}_{30}(\text{S-} \text{tBu})_{18}$ is an oblate configuration composed of a $\text{Au}_{20}$ polytetrahedral core with its tips symmetrically capped by two $\text{Au}_3(\text{S-} \text{tBu})_4$ units and its central body wrapped by four $\text{Au}(\text{S-} \text{tBu})_2$ units and two S-tBu groups in bridge sites between two Au atoms, see Figure 3.1. A second synthesis resulted in a different crystal structure

![Figure 3.2](image)

**Figure 3.2.** (a) Temperature-dependent UV-vis-NIR absorption spectra of $\text{Au}_{30}(\text{S-} \text{tBu})_{18}$ nanomolecules in 3-methyl-tetrahydrofuran solvent. (b) Temperature-dependent UV-vis-NIR $\text{Au}_{30}(\text{S-} \text{tBu})_{18}$ nanomolecules plotted as photon energy where peaks marked by asterisk shows an instrumental artifact.
containing the same bicuboctahedron Au$_{30}$(S-tBu)$_{18}$ cluster. It crystallizes in the space group P-1 and refined to a resolution of 0.81 Å, and to a value of R$_1$ = 5.26%. The local structure in the cluster is the same between the two structures; however, the P-1 structure contains more pronounced terminal S-Au-S disorder. The poor quality of the P2$_1$/n structure did not allow for anisotropic refinement of the carbon atoms in the t-butyl thiol groups. In both structures, the external solvent contents could not be identified and were removed utilizing the SQUEEZE$^{84}$ program as implemented in the program PLATON.$^{85}$

### 3.3.2 Optical Spectroscopy.
UV-vis-NIR absorption response of Au$_{30}$(S-tBu)$_{18}$ is measured in 2-methyltetrahydrofuran at predetermined temperatures upon equilibrating at each temperature for 3-5 minutes as shown in Figure 3.2a. Temperature dependent optical absorption spectra of the NMs showed increased absorption features, with no shift of absorption maxima, and well resolved new vibrionic peaks at lower wavelengths (~300 to ~550) nm. Figure 3.2b, Absorption intensity spectra plotted against photon energy, shows ~ five distinct peaks in between 2.25 eV and 3.75 eV range and two new peaks in low energy region.

### 3.3.3 Theory: Structural Analysis.
Local geometry relaxation employing density-functional theory (DFT) and the Perdew–Burke–Ernzerhof (PBE) exchange-correlation (xc-)
functional were performed on the crystallographic determined structural model of \( \text{Au}_{30}(S-t\text{Bu})_{18} \), reporting the full Cartesian coordinates in the Supplementary Information. It is interesting to compare the \( \text{Au}_{30}(S-t\text{Bu})_{18} \) atomistic arrangement here determined for the first time with that of the homologous \( \text{Au}_{30}S(S-t\text{Bu})_{18} \) compound whose stoichiometry differs only by addition of a S atom, determined in previous work.\(^{55}\) We recall that in the \( \text{Au}_{30}(S-t\text{Bu})_{18} \) structure a \( \text{Au}_{20} \) oblate core is protected by two \( \text{Au}_3(S-t\text{Bu})_4 \) and four \( \text{Au}(S-t\text{Bu})_2 \) units and two bridge \( S-t\text{Bu} \) groups, see Figure 3.1. The insertion of an S anion on a hollow site of a \( \text{Au}_3 \) facet provokes a local swelling of the coordination environment, with the added S anion-like species pushing away the S atoms of one \( \text{Au}_3(S-t\text{Bu})_4 \) unit, while the other atoms approximately preserve their configuration, as can be appreciated by comparing Figures 3.4a and 3.4c (see especially the top part of the cluster). A previously proposed structural model of \( \text{Au}_{30}(S-t\text{Bu})_{18} \) was obtained by erasing the added S atom in \( \text{Au}_{30}S(S-t\text{Bu})_{18} \) and performing a local geometry relaxation,\(^{55}\) a procedure which has been reproduced here and leads to the structure shown in Figure 3.4b. The local geometry relaxation maintains the swelling caused by the added S anion, so that in the structural model of Figure 3.4b, one of the \( \text{Au}_3(S-t\text{Bu})_4 \) units is somewhat detached from the rest of the cluster. A more compact and thus energetically more favorable coordination (lower in energy by 0.39 eV) is restored in the \( \text{Au}_{30}(S-t\text{Bu})_{18} \) crystal structure illustrated in Figure 3.4c, proving the structural fluxionality of these monolayer-protected systems. Knowledge of the correct structure improves the comparison of experimental and simulated optical absorption spectrum, vide infra.

3.3.4 Theory: Optical spectroscopy. The optical absorption spectrum of \( \text{Au}_{30}(S-t\text{Bu})_{18} \) was simulated via time-dependent DFT (TDDFT) using two different xc-functionals: B3LYP\(^{63,86}\) and SAOP\(^{66}\), see the Method section for more details. This allows us to compare the result of a hybrid (B3LYP) xc-functional and a semi-local Coulomb-corrected (SAOP) one, where a hybrid xc-
functional is here employed to the best of our knowledge for the first time to predict the optical response of monolayer-protected clusters. In Figure 3.2b the TDDFT/B3LYP spectrum is reported together with the experimental one. The agreement between experimental and simulated optical absorption spectra is excellent, and is here improved by the use of the correct structural model with respect to previous work, see Figure 3.4a of ref. 55. The intense peak at 2. eV in the experiment is predicted at 2.04 eV by theory, while minor features between 2.45 and 3 eV are also present which parallel the experimental ones in the same energy range. The TDDFT/SAOP spectrum is also reported in the Supplementary Information and compares well with both the TDDFT/B3LYP and experimental spectra. As the TDDFT/B3LYP simulation is obtained by a real time propagation of the electronic density, an analysis of the excitation components is not possible. This is instead readily available via the TDDFT/SAOP approach. Focusing on the band around 2 eV, which is the counterpart of the experimental peak at 620 nm in Figure 3.2a, we find that is contributed by many discrete transitions (see Figure S3.5 in Appendix B for Chapter 3 Supplementary Information), of which two are the most prominent:

- one at 1.92 eV with main single-particle components: 42% HOMO→LUMO+2; 18% HOMO-3→LUMO; 14% HOMO-4→LUMO
- one at 1.98 eV with main single-particle components: 43% HOMO→LUMO+4; 22% HOMO-5→LUMO; 12% HOMO→LUMO+2

![Figure 3.4](image-url)

**Figure 3.4.** Schematic depiction of the clusters investigated in the present work: (a) Au$_{30}$S(S-tBu)$_{18}$ with an arrow highlighting the additional S atom; (b) Au$_{30}$S(S-tBu)$_{18}$ as obtained by a local relaxation of Au$_{30}$S(S-tBu)$_{18}$ after erasing the additional S atom; (c) Au$_{30}$(S-tBu)$_{18}$. The methyl atoms are not shown for clarity of illustration.
where HOMO is the Highest-Occupied Molecular Orbital and LUMO is the Lowest-Unoccupied Molecular Orbital. The molecular orbitals involved in such transition are illustrated in Figure 3.5. It is interesting to note that: (i) the occupied orbitals display contribution from both gold and sulfur, while in the virtual orbitals the sulfur contribution is marginal (i.e., both excitations can be classified as transitions from the Au-S bonds to the Au 6s-6p conduction band), and (ii) the HOMO belongs essentially to the metal Au 6s band and therefore is very delocalized, whereas the other occupied orbitals are more located on the Au-S bonds, with the 5d contribution the largest one on the gold atom.

3.4 Experimental

3.4.1 Materials. Sodium borohydride (Acros, 99%), tertiary butyl thiol (Acros, 99%), and trans-2-[3][(4-tertbutyl-phenyl)-2-methyl-2-propenylidene] malononitrile (DCTB matrix) (Fluka≥99%) were purchased and used as received. HPLC grade solvents such as tetrahydrofuran, toluene, methanol, butylated hydroxytoluene stabilized tetrahydrofuran and acetonitrile were obtained from Fisher Scientific.

3.4.2 Synthesis. Au_{30}(S-tBu)_{18} NMs were synthesized by reacting 0.1 g HAuCl_{4}.3H_{2}O to 15 mL of HPLC grade THF. Followed by addition of 87 μL of HS-tBu (1:3 molar ratio) which was stirred at 450 rpm for 15 minutes. An excess of 12 mmols of NaBH_{4} 0.113 g in 10 mL cold H_{2}O was added. The reaction was stopped after 1 hour then washed with a combination of 5 mL water and 40 mL MeOH, ~3 times. The crude product 200 mg was combined with 1mL toluene and 1 mL HS-tBu. The mixture of excess thiol and crude nanomaterial were etched at 70 °C for 4 hrs. After etching the product, it was washed again with a combination of 5 mL water and 40 mL MeOH, 3 times. SEC (size exclusion chromatography) was performed in order to separate Au_{30}(S-tBu)_{18} from the etched mixture SEC was repeated 3-4 times to achieve ~20 mg of pure Au_{30}(S-
3.4.3 Instrumentation. Matrix assisted laser desorption time-of-flight (MALDI-TOF) mass spectrometer was used to acquire mass spectra with DCTB matrix on a Voyager DE PRO mass spectrometer. Compositional analysis was performed with electrospray ionization mass spectra (ESI-MS), collected from Waters Synapt HDMS using THF as the solvent. Temperature dependent UV-vis-NIR absorption measurements were collected with UV-vis-NIR Cary 5000 and JANIS VNF-100 low temperature cryostat using 1-methyltetrahydrofuran as the solvent and Lakeshore Cyotronics temperature controller was used for temperature-dependent absorption measurements.

3.4.4 Single Crystal X-ray Diffraction. Data for both Au$_{30}$(S-t-Bu)$_{18}$ structures ($P2_1/n$ and $P$-1) were collected on beamline 11.3.1 at the Advanced Light Source, Lawrence Berkeley National Laboratory. Samples were mounted on MiTeGen® kapton loops and placed in a 100(2) K nitrogen cold stream provided by an Oxford Cryostream 800 Plus low temperature apparatus on the goniometer head of a Bruker D8 diffractometer equipped with a PHOTON 100 CMOS detector operating in shutterless mode. Diffraction data were collected using synchrotron radiation monochromated using silicon (111) to wavelengths of 0.7293 and 0.7749 Å, respectively. An approximate full sphere of data was collected using a combination of phi and omega scans with scan speeds of 1 second per 4 degrees for the phi scans, and 3 and 5 second per degree for the omega scans at 2theta = 0 and -45, respectively. Additional crystallographic information has been summarized in the SI. Full details can be found in the crystallographic information files provided in the supplementary information in Appendix B for Chapter 3.

3.4.5 DFT Calculations. The optimized structure of the Au$_{30}$(S-tBu)$_{18}$ complex was obtained starting from the experimentally determined geometry and performing a local relaxation. The
Plane-Wave QuantumEspresso software\textsuperscript{60} was adopted in conjunction with ultra-soft pseudopotentials\textsuperscript{68} and the PBE xc-functional. Values of 30 and 300 Rydberg were used as the cut-offs for the selection of the plane wave basis sets for describing the kinetic energy and the electronic density, respectively. One-electron levels were broadened using a Gaussian distribution with $\sigma=0.002$ Rydberg.

3.4.6 \textit{TDDFT Simulations}. The TDDFT/B3LYP absorption spectra are the result of a real-time time dependent DFT (RT-TDDFT) simulation, carried out with the CP2K package\textsuperscript{62}. To reduce the computational effort, the CH\textsubscript{3} groups of the tert-butyl moieties were replaced with hydrogen atoms. DVZP primary basis set\textsuperscript{70}, GTH pseudopotentials\textsuperscript{71} and an auxiliary cpFIT3 basis set as described in Ref. \textsuperscript{72} were employed in the calculations. Starting from a ground-state calculation, optical response is obtained by subjecting the system to electrical pulses (with a strength of 0.0005 a.u) in each of the three Cartesian directions and using the time-evolution formalism to follow the electron dynamics. A total of 16.5 femtosec were sampled using a time step of 0.012 femtosec. A

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image}
\caption{Plot of the orbitals mainly involved in the peak around 2 eV: (a) HOMO-5; (b) HOMO-4; (c) HOMO-3; (d) HOMO; (e) LUMO; (f) LUMO+2; (g) LUMO+4. Red/orange and blue/light-blue, respectively, correspond to opposite signs of the wave function. Red/blue and orange/light-blue correspond to occupied and virtual orbitals.}
\end{figure}
time damping of 7.3 femtosec was chosen to broaden the predicted spectrum. The TDDFT/SAOP spectra were calculated at the scalar relativistic ZORA level, with the Amsterdam Density Functional (ADF) code\textsuperscript{87, 65} which solves the TDDFT equations with the Casida approach\textsuperscript{64}. The basis set consists of all-electron Slater Type Orbitals (STO) of Triple Zeta plus Polarization (TZP) size for all the atoms, taken from the ADF ZORA database. SAOP exchange-correlation potential\textsuperscript{66} was used, exhibiting a correct Coulombic asymptotic behavior. 200 lowest eigenvalues of the Casida matrix were extracted. The discrete transitions have been convoluted with Lorentzian functions of 0.15 eV of FWHM.

3.5 Conclusions

Determination of crystal structure of monolayer-protected gold clusters is a crucial step to achieve in-depth understanding and control of the properties and functionalities of this class of materials. In the present work we were able to determine the crystallographic structure of Au\textsubscript{30}(S-tBu)\textsubscript{18}, a compound exhibiting peculiar optical absorption in the visible region of the spectrum conferring it a characteristic color and making it a unique "green gold" species, whose structure had remained elusive until now despite its presence in massive form had been demonstrated via mass spectrometric techniques. Structure determination then allows us to pursue a stringent comparison between theory and experiment for this species, from which three major conclusions can be drawn: (i) a great structural fluxionality with the existence of low-energy, subtly different isomers, (ii) an extreme sensitivity of optical response to geometrical details, (iii) the possibility of achieving, through advanced computational tools, an excellent agreement between simulated and observed quantities. The present achievement opens the way to further investigations aimed at exploiting the unique optical features of this compound and tuning them to e.g. biochemical and opto-electronic applications.
CHAPTER 4

A SERIES OF BULKY TERTIARY BUTYL THIOLATED NANOMOLECULES


Author Contributions

Tanya Jones developed the synthetic protocol for $t$-butyl thiol series and nanomolecules $\text{Au}_{46}(\text{S-tBu})_{24}$ and $\text{Au}_{65}(\text{S-tBu})_{29}$. As well as, isolation, structure elucidation, characterization, and discovery of $\text{Au}_{46}(\text{S-tBu})_{24}$ and $\text{Au}_{65}(\text{S-tBu})_{29}$. Characterization techniques used were ESI-MS, MALDI-MS, and UV-Vis spectroscopy. Leigh Sumner contributed electrocatalysis studies. Mohammad bin Hatshan, Abubkr Abuhagr contributed transient absorption measurements.

4.1 Summary

Here we report the synthesis and size-dependent optical study of a series of bulky $t$-butyl thiolated monodisperse NMs (NMs): $\text{Au}_{23}(\text{S-tBu})_{16}$, $\text{Au}_{30}(\text{S-tBu})_{18}$, $\text{Au}_{46}(\text{S-tBu})_{24}$, and $\text{Au}_{65}(\text{S-tBu})_{29}$. We further employ this series of NMs to address, how the NM core size affects electrocatalytic oxygen reduction reactivity of these NMs in alkaline media. Though $\text{Au}_{23}(\text{S-tBu})_{16}$ and $\text{Au}_{30}(\text{S-tBu})_{18}$ have been reported before, the expansion of this series is brought about by the discovery, through the synthesis and characterization, of two new and larger species, in the bulky $t$-butyl thiolated NM series: namely $\text{Au}_{46}(\text{S-tBu})_{24}$ and $\text{Au}_{65}(\text{S-tBu})_{29}$. Furthermore, we take an in-depth look at the ligand effects in the bulky thiolated NM series and ligand dictation over the gold atoms to surface ligands. Assignments of molecular formulae are based on results obtained in high-resolution nESI-MS and purity was confirmed with MALDI-TOF-MS. Further analysis of the new bulky thiolated NMs, $\text{Au}_{46}(\text{S-tBu})_{24}$ and $\text{Au}_{65}(\text{S-tBu})_{29}$, was conducted using UV-vis-
NIR spectroscopy to observe their unique optical properties. With the expansion of this series, we conclude that the bulky \( t \)-butyl thiolated series is unique from those observed with aliphatic and aromatic ligands, i.e., how the bulky ligands dictate the size, composition and structure of the NM is distinct from those of aliphatic and aromatic ligands. This provides insight into the tunability and core size manipulation of gold thiolate NM, i.e., we can make different sizes of NMs using specific types of ligands by varying the gold to thiol ratio. The largest NM \( \text{Au}_{65}(S\text{-tBu})_{29} \) was found to facilitate 80% \( \text{OH}^- \) production while the smallest size NM \( \text{Au}_{23}(S\text{-tBu})_{16} \) produced 53% \( \text{OH}^- \). From the optical measurements we determined that the excited state lifetimes of this series of \( t \)-butyl thiolate protected gold NMs follow the energy gap law except for \( \text{Au}_{30}(S\text{-tBu})_{18} \) which can be ascribed to its symmetry.

### 4.2 Introduction

Nanomolecules (NMs) are atomically monodisperse gold nanoparticles with a specific number of gold atoms and protecting ligands, \( \text{Au}_m(\text{SR})_n \), with \( \pm 0 \) Au atoms and ligand variation. In larger nanoparticles (> 2 nm), polydispersity is generally observed and therefore variation in the number of gold atoms and ligands is observed. Polydispersity is observed in nanoparticles as small as \( \text{Au}_{-500}(\text{SR})_{-120} \) which is 2.4nm with a variation of \( \pm 10 \) Au atoms. This concept is summarized in Scheme 4.1(a) showing the range of nanoparticles (1-100nm) and NMs (1-2nm). Scheme 4.1(b) shows the range of the observed \( t \)-butyl thiolated series observed in this work. Not only are NMs highly unique due to their monodispersity, there is also a higher percentage of surface atoms, which in turn means more ligands can be capped onto its surface. Among the ligands that protect gold NMs, a unique phenomenon has been observed, in which the capping ligand dictates the number of Au atoms; including the overall size, structure, and geometry.
Due to the monodispersity of gold NMs and the ligand dictation over the size, there is tremendous interest in the discovery of different sizes of NMs that can be made within the 1-2nm range; as well as, the specific mechanism that causes the dictation of the capping ligand. Furthermore, literature has shown that different thiolate ligands such as aliphatic, bulky and aromatic thiolated NMs exhibit (1) a different number of Au atoms and ligands and (2) a different surface ratio of atoms.$^{11, 43}$ Due to the ligand dictation phenomenon of Au NMs discussed above, research to date has focused on studying the ligand effect through both direct synthesis, ligand exchange, and core conversion reactions of Au NMs and SAMs.$^{11, 54, 92-99}$ Weiss et al. first demonstrated this phenomenon on SAMs with 1-adamantane thiol.$^{13}$ It also has been shown through core size conversion that when gold NMs are capped with bulky thiolated ligands, their core size is altered due to steric and electronic effects of the ligands. Core size conversion occurs when gold NMs containing one ligand type are exposed to excess amounts of another. For instance, it was shown that $\text{Au}_{144}(\text{SCH}_2\text{CH}_2\text{Ph})_{60}$ (SCH$_2$CH$_2$Ph, phenylethane thiol, being an aliphatic-like ligand) converted to $\text{Au}_{99}(\text{SPh})_{42}$ through thermochemical etching with excess amounts of aromatic

![Scheme 4.1](image)

**Scheme 4.1.** Shows the scale of monodispersity of NMs (a) depicts the 1-100nm size regime showing that NMs range from 1-2nm in size while nanoparticles are larger and range from 2-100nm. Nanoparticles from 2-100nm are monodisperse however atomically polydisperse whereas NMs are monodisperse at the atomic level. (b) Shows where the t-butyl bulky nanomolecular series falls into this scheme for nanomolecular size distribution of gold thiolate nanomolecules which include: $\text{Au}_{23}(\text{S-tBu})_{16}$, $\text{Au}_{30}(\text{S-tBu})_{18}$, $\text{Au}_{46}(\text{S-tBu})_{24}$, and $\text{Au}_{65}(\text{S-tBu})_{29}$. 
It was also shown, that when $\text{Au}_{144}(\text{SCH}_2\text{CH}_2\text{Ph})_{60}$ is thermochemically etched with $t$-butylbenzene thiol, the NMs would transform to $\text{Au}_{133}(\text{SPh}-\text{tBu})_{52}$. \cite{100} Jin et al. have also shown that $\text{Au}_{38}(\text{SCH}_2\text{CH}_2\text{Ph})_{24}$ can convert to $\text{Au}_{36}(\text{SPh})_{24}$ through thermochemical etching with thiophenol.\cite{101} They also demonstrated that $\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}$ converts to $\text{Au}_{28}(\text{SPh}-\text{tBu})_{20}$ when subjected to thermochemical etching with $t$-butylbenzene thiol.\cite{102} Reversible interconversion was also shown for the first time between $\text{Au}_{30}(\text{S-tBu})_{18}$ and $\text{Au}_{36}(\text{SPhX})_{24}$.\cite{103-104} 

Crasto et al. showed that both bulky thiols such as, 1-adamantane thiol and $t$-butyl thiol, can be used to form $\text{Au}_{30}(\text{SR})_{18}$.\cite{43} Crasto et al. also synthesized the now well-known $\text{Au}_{30}(\text{S-tBu})_{18}$ NM, whose crystal structure and facile synthesis have been reported by two independent research groups.\cite{39,41-43} The crystal structure of both $\text{Au}_{30}\text{S}(\text{S-tBu})_{18}$ and $\text{Au}_{30}(\text{S-tBu})_{18}$ NM are reported.\cite{39,41} NMs $\text{Au}_{24}(\text{SAdm})_{16}$ and $\text{Au}_{23}(\text{S-tBu})_{16}$ have also been synthesized and reported.\cite{105-106} As well as the synthesis, characterization, and crystal structure of $\text{Au}_{21}(\text{SAdm})_{15}$ \cite{56,107-108} and $\text{Au}_{38}\text{S}_2(\text{SAdm})_{20}$ has also been reported.\cite{37} However, NMs in the larger size range of the bulky thiolated NMs series is lacking and to date no bulky $\text{S-tBu}$ thiolated NMs larger than $\text{Au}_{30}(\text{S-tBu})_{18}$ have been reported to date.

The core sizes observed with bulky ligands differs from the core sizes observed in NMs with aromatic and aliphatic thiolate ligands.\cite{33,90,100-101,105,109-112} This has been shown throughout the literature, however investigation into the underlying cause and inherent nature of gold NMs is still underway. An important step in understanding the ligand effects on the core of the nanomolecular structure is to characterize the NMs in these series of aromatic, aliphatic, and bulky thiolated NMs. The nanomolecular series capped with aliphatic-like thiolate ligand, phenylethane thiol is well, known throughout the field.\cite{15,30,34} and was summarized by Kumara et al.\cite{15} The phenylethane thiol series includes: $\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}, \text{Au}_{38}(\text{SCH}_2\text{CH}_2\text{Ph})_{24},$
Whereas the bulky and aromatic thiolated nanomolecular series are less known. \( \text{Au}_{30} \text{(S-} t\text{Bu})_{18} \) is the largest monodisperse NM in bulky \( t\)-butyl thiol series, known to date.

We also took this research a step further and investigated the electrocatalytic properties of the nanomaterials. The term “nanotechnology” has become the buzz word in the field of alternate energy research where significant effort is being expended on development of nanomaterial-based catalysts.\(^{113-115}\) Oxygen electrolysis is an important reaction in the industry since many energy producing technology including fuel cells,\(^ {116-118}\) metal ion batteries,\(^ {119}\) and electrocatalytic water splitting\(^ {120}\) depend on this chemistry. Oxygen reduction reaction (ORR) is a kinetically challenging yet an integral part of these devices. The irreversible and energy demanding nature of ORR (\( \text{O}_2+4\text{H}^++4e^- \rightarrow \text{H}_2\text{O} \) in acidic medium; \( \text{O}_2+2\text{H}_2\text{O}+4e^- \rightarrow 4\text{OH}^- \) in alkaline medium) continues to be a difficult reaction to achieve at close to zero overpotentials. Among others, Pt is widely employed as the fuel cell catalyst for ORR reactions.\(^ {121-122}\) However, due to limited supply of Pt, catalysts based on non-Pt group metals, as well as metal-free catalysts, for ORR are being developed.\(^ {123-130}\) One promising class of nanomaterials for alternate energy research is the gold NMs (AuNMs) that range from 1-2nm in size and exhibit molecular like properties.\(^ {1, 15-16, 88-90}\) These properties are interesting to researchers because gold NMs are promising tools in several applications such as cancer therapy, biomedical imaging,\(^ {18, 131-132}\) and catalysis including substrate oxidation,\(^ {133-135}\) hydrogenation,\(^ {136}\) \( \text{CO}_2 \) reduction,\(^ {137-138}\) ORR,\(^ {130, 139-140}\) oxygen evolution reaction (OER)\(^ {141}\) and hydrogen evolution reactions (HER).\(^ {142}\) An important feature that give gold NMs their distinctive nature is their monodispersity.

Here we expand on the known series of bulky thiolated NMs and compare this series with that of the aliphatic-like, phenylethane series of NM to provide insight into the ligand effect on the
core of the NM. This was accomplished by the synthesis, and characterization of two larger series in the bulky thiolated NMs: Au_{46}(S-tBu)_{24} and Au_{65}(S-tBu)_{29}. Furthermore, we demonstrate the synthesis of the series, and conditions which are favorable to each NM within the series through the variation of thiol and gold ratios.

In addition, we have investigated the electrocatalytic ORR activity of this series of NMs in alkaline media and demonstrate that the highest activity is observed for the largest size NM Au_{65}, while the smallest NM Au_{23} is the least active. The purity of these compounds were determined using MALDI-MS. These NMs where isotopically resolved in nESI-MS which was used to make the composition assignments. The optical properties of these NMs were studied using UV-Vis spectroscopy. We further aimed to examine the structures of these larger bulky thiolated NMs to understand their: optical properties, structure, effects of the ligand on the overall structure of the NMs, and we have investigated the electrocatalytic ORR activity of this series of NMs.

4.3 Experimental

4.3.1 Materials. Hydrogen tetrachloroaurate (III) (HAuCl₄·3H₂O), sodium borohydride (Acros, 99%), tertiary butylthiol (Acros, 99%), and trans-2-[3[(4-tertbutyl-phenyl)-2-methyl-2-propenylidene] malononitrile (DCTB matrix) (Fluka≥99%) were purchased and used as received. HPLC grade solvents such as tetrahydrofuran, toluene, methanol, butylated hydroxytoluene stabilized tetrahydrofuran and acetonitrile were obtained from Fisher Scientific.

4.3.2 Synthesis. Au_{46}(S-tBu)_{24} and Au_{65}(S-tBu)_{29} NMs were synthesized by reacting 0.1 g HAuCl₄.3H₂O to 15 mL of HPLC grade THF. Followed by addition of 33 μL of HS-tBu (1:1 molar ratio), this mixture was stirred at 450 rpm for 15 minutes. An excess of 12 mmols of NaBH₄ 0.113 g in 10 mL cold H₂O was added. The reaction was stopped after 1 hr, then washed, 3x, with a
A combination of 5 mL water and 40 mL MeOH. The crude product 200 mg was combined with 1mL toluene and 1 mL HS-tBu. The mixture of excess thiol and crude nanomaterial were etched at 70 °C for 4 h. After etching the product, it was washed again with a combination of 5 mL water and 40 mL methanol, 3 times. SEC (size exclusion chromatography) was performed in order to separate Au_{46}(S-tBu)_{24} and Au_{65}(S-tBu)_{29} from the etched mixture. SEC was repeated 3-4 times to achieve ~40 mg and ~10 mg of pure Au_{46}(S-tBu)_{24} and Au_{65}(S-tBu)_{29}, respectively.

### Synthesis via Variation of Conditions to Produce HS-tBu series

Synthesis of Au_{46}(S-tBu)_{24} and Au_{65}(S-tBu)_{29} are conducted under similar conditions to those published by Crasto et al. However the key difference between Crasto et al.’s method for Au_{30}(S-tBu)_{18} and the procedure detail in this manuscript to make Au_{46}(S-tBu)_{24} and Au_{65}(S-tBu)_{29} is the Au:thiol ratio. The ratio used in this synthesis as depicted in Scheme 4.2, shows a gold to thiol molar ratio of 1:1 while Crasto et al. uses a 1:3 molar ratio to synthesize Au_{30}(S-tBu)_{18}. Higaki et al. also

![Scheme 4.2](image-url)

**Scheme 4.2.** Method for the synthesis of the t-butyl thiol series: Au_{23}(S-tBu)_{16} (red), Au_{30}(S-tBu)_{18} (green), Au_{46}(S-tBu)_{24} (blue), and Au_{65}(S-tBu)_{29} (purple).

### Table 4.1

<table>
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<tr>
<th>Nanomolecule</th>
<th>Charge</th>
<th>Charge</th>
<th>ESI (m/z)</th>
<th>MALDI (m/z)</th>
<th>Ligand</th>
<th>UV (nm)</th>
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<td></td>
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<td>2</td>
<td>3</td>
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<td>1984</td>
<td>5867</td>
<td>4809</td>
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<td>90</td>
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<td>5601</td>
<td>3734</td>
<td>11111</td>
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<td>90</td>
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<td>14155</td>
<td>12303</td>
<td>90</td>
</tr>
</tbody>
</table>

1As observed in ESI-MS and MALDI-MS.
showed that under similar condition using a 1:6 gold to thiol molar ratio that \( \text{Au}_{23}(S-t\text{Bu})_{16} \) was produced.\(^{40}\) This trend is similar to the series phenylethane thiol NMs in which the larger the ratio of thiol to gold the smaller sized NMs are produced. Whereas, when a lower amount of thiol is used larger NMs are formed. The conditions listed in Scheme 4.2 demonstrate the tunability of the NM based on the gold to thiol ratio.

**4.3.4 Composite preparations for Electrocatalysis.** A 0.17% SWNT suspension was prepared in 23% ethanol, 77% water with 0.27% Nafion by sonicating for 30 min at RT. AuNMs were dissolved in toluene at 8 mg/mL and incubated for 30 min with an equal volume of SWNT suspension after a brief sonication, reaching a final AuNM concentration of 4mg/mL. 10\( \mu \)L of the AuNM/SWNT suspension was drop cast on the RDE (final AuNM loading 0.04 mg or 0.2 mg/cm\(^2\)), dried under N\(_2\) gas and dipped into O\(_2\) saturated 0.1 M KOH solution for data collected. Three different films were tested for each sample, and at least 3 repetitions of the same film were performed.

**4.3.5 Instrumentation.** Matrix assisted laser desorption time-of-flight (MALDI-TOF) mass spectra was acquired using DCTB matrix\(^30\) on a Voyager DE PRO mass spectrometer. Compositional analysis was performed with electrospray ionization mass spectra (ESI-MS) collected from Waters Synapt HDMS using THF:CH\(_3\)CN as the solvent.

**4.3.6 Optical Spectroscopy.** UV-vis-NIR absorption response of \( \text{Au}_{23}(S-t\text{Bu})_{16} \), \( \text{Au}_{30}(S-t\text{Bu})_{18} \), \( \text{Au}_{46}(S-t\text{Bu})_{24} \) and \( \text{Au}_{65}(S-t\text{Bu})_{29} \) were measured in carbon tetrachloride using a UV-vis-NIR Cary 5000.

**4.3.7 Electrochemistry.** All electrochemistry experiments were performed on a Wave Driver 20 bipotentiostat (PINE Instruments) using a standard three-electrode set up using 5 mm
OD glassy carbon RDE as the working electrode, Ag/AgCl reference electrode and Pt wire as counter electrode. Scan rates of 10 mV/s were used for all the experiments. NM samples were recovered from the electrode after electrocatalysis experiments by gentle washing of the electrode with toluene. Recovery of the samples were confirmed by observing the colors of the NMs in the toluene wash. Data was visualized using AfterMath software and exported to Excel then plotted in Origin. RDE measurements were performed at rotation rates of 676-2500 rpm using Levich increments as controlled by Wave Driver. Open circuit potential values of 0.86, 0.91, 0.89, and 0.91 V were used to obtain the overpotentials for Au$^{23}$, Au$^{30}$, Au$^{46}$, and Au$^{65}$, respectively.

4.3.8 Koutecký-Levich and Tafel analysis. K-L plots were obtained according to eq. i by plotting the inverse currents ($i/j$) vs inverse square root of rotation rate ($\omega^{1/2}$) at different potentials in the mixed kinetic-diffusion potential window. Calculation of the number of e$^-$ transferred was performed using equations ii) according to the slopes of the K-L plots in Figure 4.6. The intercepts of the plots correspond to inverse kinetic current ($1/j_k$), which was used to calculate the heterogenous rate constant of electron transfer ($k$). Plots of ln$k$ vs overpotential gave intercepts equal to ln$k^0$ and slope proportional to the transfer coefficient $\alpha$.

4.3.8 Time-resolved Optical Measurements. Femtosecond transient absorption measurements were carried out at the Center for Nanoscale Materials, Argonne National Laboratory. Briefly, a Spectra Physics Tsunami Ti:Sapphire, 75 MHz oscillator was used to seed a 5 KHz Spectra-physics Spit-Fire Pro regenerative amplifier. 95% of the output from the amplifier is used to pump a TOPAS optical parametric amplifier, which is used to provide the pump beam in a Helios transient absorption setup (Ultrafast Systems Inc.). A pump beam of 370 nm was used for the measurements. The remaining 5% of the amplified output is focused onto a sapphire crystal to create a white light continuum that serves as the probe beam in our
measurements (440 to 780 nm). The pump beam was depolarized and chopped at 2.5 kHz and both pump and probe beams were overlapped in the sample. Optical absorption spectra were taken before and after the measurements and the NMs have shown little degradation. Nanosecond transient absorption measurements were carried out in an EOS transient absorption spectrometer with 370 nm as the excitation and a picosecond fiber optic continuum laser as the probe. All the data analysis was carried out using Surface Xplorer Pro from Ultrafast Systems.

4.4 Results and Discussion

4.4.1 Mass Spectrometry. Figure 4.1. shows the ESI-MS of Au_{23}(S-tBu)_{16} (red), Au_{30}(S-tBu)_{18} (green), Au_{46}(S-tBu)_{24} (blue), and Au_{65}(S-tBu)_{29} (purple). Au_{23}(S-tBu)_{16} ionizes in the

![Figure 4.1](image-url)

Figure 4.1. (a) ESI-MS spectra of Au_{23}(S-tBu)_{16} (red), Au_{30}(S-tBu)_{18} (green), Au_{46}(S-tBu)_{24} (blue), and Au_{65}(S-tBu)_{29} (purple). Each inset corresponds by color, and within them, in black the theoretical isotopic patterns for each NM are shown. The Au_{23}(S-tBu)_{16} was collected in negative mode, while other spectra were collected in positive mode. (b) Photograph of the SEC column separation performed on final etch product to purify Au_{30}(S-tBu)_{18}, Au_{46}(S-tBu)_{24} and Au_{65}(S-tBu)_{29}. Au_{23}(S-tBu)_{16} was extracted prior to SEC with acetonitrile.
39

negative mode at -1 charge state at 5,957 Da. The isotopic pattern is compared with theoretical spectra and agrees with the published report. \(^\text{106}\) Au\(_{30}\)(S-tBu)\(_{18}\) ionizes in positive mode as +1 and +2 charge states with masses corresponding to 7,514 Da and 3,757 Da respectively. The theoretical isotopic pattern matches with both the +1 and +2 charge states, collected experimentally, and with the published reports. \(^\text{39, 41, 43}\) Au\(_{46}\)(S-tBu)\(_{24}\) ionizes in positive mode as +1 and +2 charge states. The calculated isotopic pattern (11,200.8 Da, calc. isotopic) corresponds with the experimental values of (11,201.2 Da) for Au\(_{46}\) (S-tBu)\(_{24}\)\(^+\). The isotopic pattern and mass to charge ratio correspond to the +2 charge state of Au\(_{46}\) (S-tBu)\(_{24}\) at 5,599.1 Da. The +2 and +3 charge states of Au\(_{65}\) (S-tBu)\(_{29}\) are also shown. The +2 charge state of Au\(_{65}\) (S-tBu)\(_{29}\) (7,693 Da), shown in blue in Figure 4.1. The +3 charge state is also indicated for Au\(_{65}\) (S-tBu)\(_{29}\) (5,128.7 Da). Negative mode for Au\(_{30}\)(S-tBu)\(_{18}\), Au\(_{46}\)(S-tBu)\(_{24}\), Au\(_{65}\)(S-tBu)\(_{29}\) are not shown because the NMs ionize in positive mode. The conformational assignment is confirmed by theoretical isotopic distribution spectra.
which is shown in black in Figure 4.1. The ESI spectra were obtained when the NMs were sprayed from a mixture of THF and acetonitrile (~100:5). The \( \text{Au}_{46}(S-tBu)_{24} \) and \( \text{Au}_{65}(S-tBu)_{29} \) were also analyzed using MALDI-MS as seen in Figure 4.2, to further confirm the assignment and purity of the NMs. The complete peak assignments for \( \text{Au}_{46}(S-tBu)_{24} \) and \( \text{Au}_{65}(S-tBu)_{29} \) are shown in Figure S4.3 of the Appendix for Chapter 4 supporting information. The \( \text{Au}_{23}(S-tBu)_{16} \) (red), \( \text{Au}_{30}(S-tBu)_{18} \) (green) MALDI spectra were in agreement with the composition.

**4.4.2 Optical Spectroscopy.** The optical properties were investigated using UV-Vis spectra as shown in Figure 4.3a. The NMs are displayed as follows in Figure 4.3a: \( \text{Au}_{23}(S-tBu)_{16} \) (red),
Au_{30}(S-tBu)_{18} (green), and Au_{65}(S-tBu)_{29} (purple). Au_{23}(S-tBu)_{16} is red in color and has a peak at 565 nm corresponding with the published report [ref.106]. Au_{30}(S-tBu)_{18} is green in color and has an absorbance peak at 620 nm. This also corresponds with published reports of the Au_{30}(S-tBu)_{18} NM [ref.39,41-43]. Au_{46}(S-tBu)_{24} is a dark brown in color and Au_{65}(S-tBu)_{29} is black in color. Both Au_{46}(S-tBu)_{24} and Au_{65}(S-tBu)_{29} have a monotonous curve with no discernable features in the UV-Vis region. Absorbance intensity was plotted as a function of photon energy from absorption spectra of each NM and is shown in Figure 4.3b. The ESI-MS, MALDI-MS, and UV features are summarized in Table 4.1. The spectra for Au_{23}(S-tBu)_{16} (red), Au_{30}(S-tBu)_{18} (green), Au_{46}(S-tBu)_{24} (blue), and Au_{65}(S-tBu)_{29} (purple) are shown in Figure 4.3a and the onset of absorption values were calculated to be ~1.6 ± 0.2 eV, 1.3 ± 0.2 eV, 1.1 ± 0.1 eV, and <0.5 ± 0.2 eV respectively. Figure S4.4 shows the optical spectra for all samples observed in carbon tetrachloride, including the onset of absorption that was determined by extrapolating the low energy absorption spectrum to zero. The onsets of absorption for all samples were used to determine the HOMO-LUMO gap and it has to be emphasized that the onset is only an estimate.
4.4.3 Time-resolved Absorption and Fluorescence Spectroscopy. Time-resolved absorption and fluorescence spectroscopic investigations are often carried out in recent years to probe the excited state relaxation dynamics of quantum-sized gold NMs, especially in molecule-like regime.\textsuperscript{143-149} To probe the excited state relaxation dynamics of the investigated S-tBu NMs, combined femtosecond to nanosecond transient absorption measurements were carried out after excitation at 370 nm. Several recent excited state measurements on quantum-sized Au NMs have revealed excited state lifetimes ranging from few picoseconds to 100s of nanoseconds and depend on the HOMO-LUMO energy gap and to some extent on the symmetry of the NM.\textsuperscript{149-150} To understand how the size of the NM influences the time-resolved optical properties of S-tBu protected Au NMs, ultrafast transient absorption measurements were carried out for Au\textsubscript{23}(S-tBu)\textsubscript{16}, Au\textsubscript{30}(S-tBu)\textsubscript{18}, Au\textsubscript{46}(S-tBu)\textsubscript{24}, and Au\textsubscript{65}(S-tBu)\textsubscript{29}. Figure 4.4 shows the excited state absorption (ESA) spectra at representative delays for all the investigated NMs. All NMs show short-lived and long-lived transients similar to what was observed for hexane-thiolate protected gold NMs.\textsuperscript{149-150} Complete excited state relaxation dynamics for Au\textsubscript{23}(S-tBu)\textsubscript{16} (Figure S4.5) shows 1.9 ps time

![Image](image_url)

**Figure 4.5.** (a) Comparison of normalized excited state decay traces for different S-tBu protected NMs. The solid lines represent best-fit lines. (b) Plot of ln(knr) vs HOMO-LUMO gap for Au NMs. The black solid line is the linear fit to energy gap law for hexane-thiolate protected Au NMs and the red solid line is the linear fit to energy gap law with the present data on S-tBu protected Au NMs (except the data point of Au\textsubscript{30}(S-tBu)\textsubscript{18}).
scale intra core-state relaxation followed by long-lived excited state decay, which was fit to a multi-exponential function with lifetimes of $0.75 \pm 0.05$ ns (40.9%), $43 \pm 2$ ns (16.5%), $1920 \pm 50$ ns (42.6%). Average lifetime was determined by: $\tau_{avg} = \sum_i a_i \tau_i / \sum_i a_i$ and corresponding data is presented in Table S4.9. As the excited state recombination did not follow single exponential decay, the average lifetime can be used as a measure of the excited state lifetime of the NM. Along similar lines, Au$_{30}$(S-tBu)$_{18}$ (Figure S4.6) and Au$_{46}$ (S-tBu)$_{24}$ (Figure S4.7) have shown ultrafast intra core-state relaxation followed by the lifetime in nanoseconds. In the case of Au$_{65}$ (S-tBu)$_{29}$,

![Figure 4.6](image)

**Figure 4.6.** RDE data (a-d) collected in O$_2$ saturated 0.1 M KOH, and the corresponding K-L plots (e-h) obtained from the RDE data in the mid overpotential range of mixed kinetic-diffusion currents obtained with rotation rates of 676-2500 rpm. The solid lines in e-h represent linear fits of the K-L plots. Au$_{23}$/SWNT (a,e), Au$_{30}$/SWNT (b,f), Au$_{46}$/SWNT (c,g), and Au$_{65}$/SWNT (d,h). Scan rate 10 mV/s.
(Figure S4.8) the excited state decayed fast and no transient signal was detected in nanosecond transient absorption measurements.

For comparing the excited state recombination dynamics of different sized S-tBu passivated NMs, transient decay traces obtained from combined femtosecond and nanosecond transient absorption measurements for all NMs are shown in Figure 4.5a. The changes in absorption signal at 500 ps time delay for both femtosecond and nanosecond transient absorption were matched to obtain the complete decay traces. The lifetimes were obtained by fitting the decay traces to a multi-exponential function and average lifetimes were obtained from the decay constants and corresponding data for all NMs is shown in Table S4.2. Note from the table that the decay of Au$_{23}$(S-tBu)$_{16}$ is slowest with an average lifetime of 830 ns while that of Au$_{65}$ is fastest with a lifetime of 630 ps. A general trend of decreasing lifetimes was observed with increase in the size of NM and is in line with the trend observed for hexane-thiolate protected gold NMs. One way to rationalize the excited state lifetimes as a function of NM size is to correlate them to HOMO-LUMO gap. It was shown in a recent study that the exciton recombination follows the energy gap law where the lifetimes decrease with a decrease in HOMO-LUMO energy gap.$^{149}$

To check if the energy gap law holds for the present NMs, the excited state lifetimes of S-tBu protected gold NMs is plotted as a function of HOMO-LUMO gap obtained from optical absorption onset. As the photoluminescence quantum yields are low for the investigated NMs, the average lifetime of the NM is mostly dominated by non-radiative recombination and the average lifetime ($\tau_{avg}$) was used to determine the $k_{nr}$ ($k_{nr} = 1/\tau_{avg}$) for each NM. The energy gap law$^{150-151}$ for weakly coupled electronic states can be presented as: $k_{nr} \propto e^{-\gamma\Delta E/\hbar\omega_M}$, where $\gamma$ is a term describing molecular parameters and $\omega_M$ is the highest energy vibrational mode involved in the nonradiative transition to ground state and $\Delta E$ is the energy gap. Figure 4.5B shows the plot of
\[
\ln(k_{nr}) \text{ vs HOMO-LUMO gap for S-tBu protected gold NMs. For comparison, the data of hexane-thiolate protected gold NMs}^{149} \text{ is also shown in Figure 4.5. The black solid line was the linear fit line with hexane thiolate protected gold NMs that yielded } \gamma \text{ value of } -8 \pm 2 \text{ eV}^{-1}. \text{ The red solid line is after including of the new data from S-tBu protected gold NMs (except that of } Au_{30}(S-tBu)_{18} \text{) which made the R2 better and yielded a } \gamma \text{ of } -8 \pm 2 \text{ eV}^{-1}. \text{ This result shows that the energy gap law is valid for quantum-sized gold NMs irrespective of the passivating ligand. However, note from Figure 4.5B that the data point for } Au_{30}(S-tBu)_{18} \text{ was significantly away from the trend line. The reason why } Au_{30}(S-tBu)_{18} \text{ NM has a unique behavior can be ascribed to its symmetry and intrinsic anisotropic nature, which is beyond the scope of this work.}
\]

4.4.4 Electro catalysis Studies. We investigated the dependence of NM size on ORR kinetics in O\textsubscript{2} saturated 0.1 M KOH (pH 13) at 25°C. Due to low solubility (1.26 \times 10^{-3} \text{ mol L}^{-1}) of O\textsubscript{2} under these conditions, the ORR experiments were performed employing rotating disk electrochemistry (RDE) to allow convective transport of O\textsubscript{2} to the electrode.\textsuperscript{152-156} Composites of the NMs at 4 mg/ml were prepared by mixing equal volume of 8 mg/ml of toluene stocks of the NMs with single walled carbon nanotubes (SWNTs)/nafion suspensions and incubated at room temperature for 30 min. 10 µl of the composites was drop cast on the RDE (final NM loading 0.04 mg or 0.2 mg/cm\textsuperscript{2}), dried under a gentle stream of N\textsubscript{2} and ORR measurements were performed at scan rate of 10 mV/s with rotation rates 676-2500 rpm. The resulting voltammograms of the NMs are shown in Figure 4.6 a-d. At all rotation rates, the overpotential to achieve a given current density was the highest for the smallest NM Au\textsubscript{23}/SWNT, and the lowest for the largest size NM Au\textsubscript{65}/SWNT, while the two intermediate size NMs Au\textsubscript{30}/SWNT and Au\textsubscript{46}/SWNT showed overpotentials in-between the smallest and the largest NMs. At 2500 rpm, the overpotentials to obtain a current density of −1 mA/cm\textsuperscript{2} were found to be 0.68, 0.25, 0.24, and 0.8 V for Au\textsubscript{23}, Au\textsubscript{30},
Au$_{46}$, and Au$_{65}$, respectively (Table 4.2). Figure 4.6a-d also shows a mixed kinetic-diffusion current in the intermediate potential range of 0.61-0.11 V vs RHE for Au$_{23}$/SWNT, 0.76-0.51 V for Au$_{30}$/SWNT, 0.76-0.53 V for Au$_{46}$/SWNT, and 0.76-0.61 V for Au$_{65}$/SWNT. At more negative potentials, mass transport limited currents are observed for Au$_{30}$/SWNT, Au$_{46}$/SWNT, and Au$_{65}$/SWNT, while no clear regime was observed for Au$_{23}$/SWNT (Figure 4.6a). In the mixed kinetic-diffusion regime the ORR kinetics is described by the Koutecký-Levich (K-L) analysis of the RDE data expressed as:\textsuperscript{157}

\[
\frac{1}{j} = \frac{1}{j_L} + \frac{1}{j_K} = \frac{1}{B_0^2} + \frac{1}{nFAkC_0} \tag{i}
\]

\[B = 0.62nFAC_0(D_0)^{2/3} \nu^{-1/6} \tag{ii}\]

\[j_K = nFAC_0 \tag{iii}\]

where $j$ is the measured current in Amperes; $j_L$ and $j_K$ are the diffusion-limited and kinetics currents, respectively; $n$ is the number of electrons transferred; $F$ is Faraday’s constant (96485 C mol$^{-1}$); $A$ is the electrode area (0.196 cm$^2$ for the electrode used here); $C_0$ is the O$_2$ concentration (1.2x10$^{-6}$ mol cm$^{-3}$) in 0.1 M KOH;\textsuperscript{158} $D_0$ is the diffusion coefficient of O$_2$ in solution (1.9x10$^{-5}$ cm$^2$s$^{-1}$);\textsuperscript{158} $\nu$ is the kinematic viscosity (0.01 cm$^2$s$^{-1}$);\textsuperscript{159} $k$ is the rate constant (cm s$^{-1}$) for electron transfer; and $\omega$ is the angular frequency of electrode rotation (s$^{-1}$). Plots of inverse current

<table>
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<th>Sample</th>
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<th>HO$_2^-$ (%)</th>
<th>$k_m$ cm$^{-2}$ s$^{-1}$</th>
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<tr>
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<td>4.7x10$^{-3}$</td>
<td>0.21</td>
</tr>
<tr>
<td>Au$_{65}$/SWNT</td>
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<td>3.2</td>
<td>80</td>
<td>4.6x10$^{-3}$</td>
<td>0.20</td>
</tr>
</tbody>
</table>

$a$ $\eta$ measured from $\eta = E - E_{eq}$. Open circuit potentials of 0.86, 0.91, 0.89, and 0.91 V were used to obtain the overpotentials for Au$_{23}$, Au$_{30}$, Au$_{46}$, and Au$_{65}$, respectively, calculated from the mixed kinetic-diffusion regimes. calculated from the intercepts, and slopes of the ln$k$ vs $\eta$ plots in Figure 4.7.
vs inverse square root of electrode rotation rate from the K-L equation yields linear plots (Figure 4.6 e-h) with the inverse of the slopes giving the values of B in eq. ii, from which the number of electrons transferred (n) were calculated. These plots were approximately parallel with respect to each other, suggesting first order dependence of ORR current with respect to O$_2$ concentration at the electrode.

The reduction of O$_2$ in alkaline media can occur via the 4e$^-$ (eq. iv-viii) reduction or 2e$^-$ (eq. ix-xiv) reduction pathway, both following multiple steps. The first electron transfer to the surface adsorbed O$_2$ (eq. v and x) is believed to be the rate limiting step for O$_2$ reduction in both the mechanisms.

\[ \text{O}_2,\text{b} \rightarrow \text{O}_2,\text{ads} \] \quad \text{(iv)}

\[ \text{O}_2,\text{ads} + e^- \rightarrow \text{O}^-_2,\text{ads} \] \quad \text{(v)}

\[ \text{O}^-_2,\text{ads} + \text{H}_2\text{O} + e^- \rightarrow \text{HO}_2^-_\text{ads} + \text{OH}^-_\text{ads} \] \quad \text{(vi)}

\[ \text{HO}_2^-_\text{ads} + \text{H}_2\text{O} + 2e^- \rightarrow 3\text{OH}^-_\text{ads} \] \quad \text{(vii)}

\[ \text{OH}^-_\text{ads} \rightarrow \text{OH}^-_\text{b} \] \quad \text{(viii)}

\[ \text{O}_2,\text{b} \rightarrow \text{O}_2,\text{ads} \] \quad \text{(ix)}

\[ \text{O}_2,\text{ads} + e^- \rightarrow \text{O}^-_2,\text{ads} \] \quad \text{(x)}

\[ \text{O}^-_2,\text{ads} + \text{H}_2\text{O} + e^- \rightarrow \text{HO}_2^-_\text{ads} + \text{OH}^-_\text{ads} \] \quad \text{(xi)}

\[ 2\text{HO}_2^-_\text{ads} \rightarrow \text{O}_2 + 2\text{OH}^- \] \quad \text{(xii)}

\[ \text{HO}_2^-_\text{ads} \rightarrow \text{HO}_2^-_\text{b} \] \quad \text{(xiii)}
\[ \text{HO}_{\text{ads}}^- \rightarrow \text{HO}_2^- \] (xiv)

From K-L analysis the number of electrons transferred for Au\textsubscript{23} was found to slightly increase from 1.8 at 0.61 V to 2.1 at 0.11 V (Table 4.2), indicating the partial 2e\textsuperscript{-} reduced HO\textsubscript{2}\textsuperscript{−} as the predominant species at these potentials and the final product of the reaction. In Au\textsubscript{30} 1.9-2.5 e\textsuperscript{-} were transferred in the potential window 0.76-0.51 V suggesting formation of HO\textsubscript{2}\textsuperscript{−} at this potential. Beyond 0.51 V the current slightly increased (Figure 4.6b) indicating formation of surface adsorbed HO\textsubscript{2}\textsuperscript{−}. A second reductive current was apparent at potentials more negative than 0.2 V, indicating further reduction of surface bound HO\textsubscript{2}\textsuperscript{−} to OH\textsuperscript{−}, consistent with the number of electrons transferred of 3.8 at potentials below 0.2 V. For Au\textsubscript{46}, n was 2 in the 0.76-0.53 V, beyond which n increased to 2.8 consistent with appearance of the second reductive current. Finally, in Au\textsubscript{65} the number of electrons found was almost a constant value of 3.2 in the entire potential range 0.76-0.61 V, increasing slightly to 3.5 at potentials more negative than 0.3V. These data suggest that in the mixed kinetic-diffusion regime, Au\textsubscript{65} is most selective for O\textsubscript{2} reduction to OH\textsuperscript{−} among the NMs studied here transferring 3.2 e\textsuperscript{-} amounting to 80% of OH\textsuperscript{−} (Table 4.2). To test the

![Figure 4.7](image_url)

**Figure 4.7.** Plots of lnk vs overpotential for the data obtained from the K-L plots in Figure 6e-h. The intercepts of the lines correspond to lnk\textsubscript{0} and the slopes are proportional to the transfer coefficient \( \alpha \). Open circuit potentials of 0.86, 0.91, 0.89, and 0.91 V were used to obtain the overpotentials for Au\textsubscript{23}(red), Au\textsubscript{30}(blue), Au\textsubscript{46}(orange), and Au\textsubscript{65} (green), respectively.
survivability of the NMs under electrocatalytic conditions, we have compared the solution colors and UV-vis spectra of the NMs before and after electrochemistry (Figure S4.9). The colors and spectra of all NM solutions recovered from the electrode are similar to those before electrochemistry.

The inverse of the intercept of the K-L plots correspond to the kinetic limited currents $j_K$, from which the rate constant of electron transfer ($k$ in cm s$^{-1}$) was calculated based on eq. iii. A plot of $\ln k$ vs overpotential ($\eta = E-E_{eq}$) which has an intercept of $\ln k^0$ and slope of $-\alpha F/RT$. The $\alpha$ values from the slopes were determined to be 0.16, 0.16, 0.21, and 0.20 for Au$_{23}$, Au$_{30}$, Au$_{46}$, and Au$_{65}$, respectively (Table 4.2). The $k^0$ values were obtained to be $2.0 \times 10^{-4}$, $1.9 \times 10^{-3}$, $4.7 \times 10^{-3}$ and $4.6 \times 10^{-3}$ cm s$^{-1}$ for Au$_{23}$, Au$_{30}$, Au$_{46}$, and Au$_{65}$, respectively (Table 4.2). These data indicate that the equilibrium rate constant of electron transfer for the largest NM Au$_{65}$ is approximately 23 times that of the smallest NM Au$_{23}$, ~2 times than Au$_{30}$, and very similar to that of Au$_{46}$.

Combined electrocatalysis and kinetic analysis data indicate that the largest NM Au$_{65}$ produces a significantly higher amount of OH$^-$, which shows the lowest overpotential to reach $-1$ mA/cm$^2$ and higher rate constant of electron transfer compared to the smallest NM Au$_{23}$. Recently, Jin and coworkers reported a similar trend for OER where the highest activity was observed for the largest NM following the trend (Au$_{333}$(SC$_2$H$_4$Ph)$_{79}$ > Au$_{144}$(SC$_2$H$_4$Ph)$_{60}$ > Au$_{25}$(SC$_2$H$_4$Ph)$_{18}$)$_{141}$. Similar trend in activity where the largest NM is the most catalytically active was observed for the hydrogenation of para nitrobenzaldehyde (Au$_{38}$(SG)$_{24}$ > Au$_{25}$(SG)$_{18}$ > Au$_{18}$(SG)$_{14}$ > Au$_{15}$(SG)$_{13}$)$_{160}$ and cyclohexane oxidation (Au$_{39}$(SG)$_{24}$ > Au$_{25}$(SG)$_{18}$ > Au$_{18}$(SG)$_{14}$ > Au$_{10}$(SG)$_{10}$)$_{133}$ using the glutathione ligand. These results are however, in contrast to other series of NMs showing both ORR, and styrene oxidation activity using the HSCH$_2$CH$_2$Ph ligand, where the highest activity was demonstrated by the smallest size NM following the trend Au$_{25}$(SCH$_2$CH$_2$Ph)$_{18}$ >
Au\textsubscript{38}(SCH\textsubscript{2}CH\textsubscript{2}Ph)\textsubscript{24} > Au\textsubscript{144}(SCH\textsubscript{2}CH\textsubscript{2}Ph)\textsubscript{60}. These data indicate that a prior prediction of catalytic trend of NMs is difficult since several factors in addition to the core size effect, influencing the core stability, electronic and ligand effects and overall NM structures can tune the surface properties including facile vs hindered adsorption/desorption of the substrate, electron transfer and subsequent reaction kinetics. All of these factors can contribute to the observed catalytic trends.

4.4.5 Nano-Scaling Law for HS-tBu Protected AuNMs. NMs like other molecules in nature form with a minimum surface area and compact organization.\textsuperscript{91} With AuNMs the surface coverage of thiolates on a AuNMs surface varies depending on the type of ligand employed. For instance, aliphatic ligands form Au\textsubscript{25} protected by 18 ligands, whereas bulky ligands form Au\textsubscript{23} protected by 16 ligands.\textsuperscript{34, 106} The role of geometry has been shown to play an important role in determining the surface coverage of AuNMs and their stability.\textsuperscript{91, 162} It has been observed that NMs follow a 2/3 scaling as observed in the Euclidean surfaces.\textsuperscript{91} We employed this methodology to compare the compactness, scaling, and surface coverage of the differing (in steric and reactivity) ligands, which cover the surface of these NMs, along with their unique sized Au core. In Table 4.3, we compare the ligand to Au atom ratio of both phenylethane thiolate NMs, which are aliphatic like ligands. As well as the ligand to Au atom surface ratios of the bulky t-butyl

<table>
<thead>
<tr>
<th>Aliphatic HSCH\textsubscript{2}CH\textsubscript{2}Ph NMs</th>
<th>Bulky HS-tBu NMs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free electrons</td>
<td>Au atoms</td>
</tr>
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<td>8</td>
<td>25</td>
</tr>
<tr>
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<td>58</td>
<td>102</td>
</tr>
<tr>
<td>84</td>
<td>144</td>
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thiolated NMs. In this comparison, we find that the bulkier thiolated ligand NMs in the $t$-butyl thiolated series have a lower ligand to Au atoms surface ratio and as size increases, ratio decreases more rapidly in bulky thiolated NMs. We find that the ligand to Au atom ratio is lower throughout the bulky thiolated series. Which correlates to reduced ligand coverage which is observed in the $t$-butyl thiolate NM series. Whereas, aliphatic like, phenyl ethane thiolated NMs show a much higher surface ratio to Au atoms in the core, which in turn means more ligands can cover the surface of the Au core. As NMs size increases the ligand to thiol ratio decreases. However, when using bulky ligands, we see this trend occurs at a faster rate, as the bulky capped NMs grow in size. For instance, $\text{Au}_{65}(S-t\text{Bu})_{29}$ and $\text{Au}_{67}(\text{SCH}_2\text{CH}_2\text{Ph})_{35}$, have a ligand to Au atom ratio of 0.52 and 0.45 respectively and a ratio difference of 0.07 in two similarly sized NMs, due to the effect of the capping ligand. This is most prominently observed in comparison of $\text{Au}_{65}(S-t\text{Bu})_{29}$ with $\text{Au}_{102}(\text{SCH}_2\text{CH}_2\text{Ph})_{44}$ and $\text{Au}_{144}(\text{SCH}_2\text{CH}_2\text{Ph})_{60}$. $\text{Au}_{102}$ and $\text{Au}_{144}$ which are approximately twice the size of $\text{Au}_{65}(S-t\text{Bu})_{29}$ but have similar ligand to thiol ratio. From this comparison, we observed

**Figure 4.8.** Nano-Scaling law for $\text{Au}_n(S-t\text{Bu})_m$ series in comparison with $\text{Au}_n(\text{SCH}_2\text{CH}_2\text{Ph})_m$ series. The allometric powerfit of Log-Log plot of number of Au atoms (N) vs thiolate groups (L). $\text{Au}_n(S-t\text{Bu})_m$ - Red – solid, squares; $\text{Au}_n(\text{SCH}_2\text{CH}_2\text{Ph})_m$ - olive – dash, spheres. The standard error for slope = $0.59\pm0.02$ and intercept = $2.48\pm0.23$. Reduced $\chi^2=0.17$; Adjusted $R^2=0.9952$. Refer Figure S10 for the plot with table of standard errors and associated values.
the bulkiness effect of the $t$-butyl thiolated NM series is more pronounced with increase in size of the NM.

To assess the scaling and compactness of these $t$-butyl bulky thiolated NMs series, as compared to the aliphatic like, phenyl ethane thiol series, the nano-scaling law for $\text{Au}_n(\text{S-}t\text{Bu})_m$ series was obtained through allometric fitting of the number of gold atoms and ligand groups in a log-log plot. The slope is a measure of scaling factor and $y$-intercept of the power fit is inversely related to the compactness. In addition, we have drawn a comparison with the nano-scaling law for phenylethane thiolate series AuNMs ($\text{Au}_{25}(\text{SR})_{18}$, $\text{Au}_{38}(\text{SR})_{24}$ and $\text{Au}_{67}(\text{SR})_{35}$) which are in the same range as $\text{Au}_n(\text{S-tBu})_m$ sizes reported in this work (Figure 4.8, S4.10). The $\text{Au}_n(\text{S-tBu})_m$ has a scaling factor of $\sim2/3$ (0.59) and compactness of 2.48, whereas $\text{Au}_n(\text{SCH}_2\text{CH}_2\text{Ph})_m$ follow $2/3$ (0.67) scaling factor and a compactness of 2.08 (Figure 8, S10). The difference in scaling factor and compactness can be attributed to the more cuboidal nature of kernels in bulky HS-$t$Bu series and spherical nature of icosahedral kernel supported by aliphatic ligands. The icosahedral cores have compact packing and high volumetric strain, whereas HS-$t$Bu series AuNMs might possess relaxed FCC kernels like $\text{Au}_{30}(\text{S-tBu})_{18}$, which is echoed in the compactness in comparison with the phenylethane thiolated NM series. The surface coverage is reduced due to the bulkiness of the ligand and high radius of curvature in these ultra-small AuNMs.

4.5 Conclusions

We have extended the S-$t$Bu Au NM series through the synthesis and characterization of the two largest NMs in the $t$-butyl thiol series of NMs: $\text{Au}_{46}(\text{S-tBu})_{24}$ and $\text{Au}_{65}(\text{S-tBu})_{29}$. We conclude that the bulky $t$-butyl thiolated series, $\text{Au}_{23}(\text{S-tBu})_{16}$, $\text{Au}_{30}(\text{S-tBu})_{18}$, $\text{Au}_{46}(\text{S-tBu})_{24}$, $\text{Au}_{65}(\text{S-tBu})_{29}$, is entirely unique from those observed with aliphatic and aromatic ligands. The $t$-
butyl series of NMs is can be synthesized in milligram quantities and are stable when dried and stored in ambient conditions. Furthermore, we note that the bulky thiolated series has a lower gold to ligand ratio than observed in both aliphatic and aromatic nanomolecular series. The $\text{Au}_n(\text{S-}t\text{Bu})_m$ series has a scaling factor of $\sim 2/3$ (0.59) and compactness of 2.48, whereas $\text{Au}_n(\text{SCH}_2\text{CH}_2\text{Ph})_m$ series follow $2/3$ (0.67) scaling factor and a compactness of 2.08. The dictation that bulky ligands, such as $t$-butyl thiol, have on the overall size and structure of the NMs is also observed within the NMs produced in this series. We have also shown that these sizes can be produced through the same synthetic method but that the gold to thiol ratio can be tuned to produce the desired sized NM. This provides insight in: the tuning of nanomolecular structures and core size manipulation of gold thiolate NMs. We further conclude from the optical measurements that the excited state lifetimes of $\text{S-}t\text{Bu}$ protected gold NMs follow the energy gap law except for $\text{Au}_{30}(\text{S-}t\text{Bu})_{18}$ which can be ascribed to the symmetry of NM. In conclusion we show, that we can make different sizes of NMs with precise ligand selection and have size selection by tuning the gold to thiolate NMs. The kinetics of ORR catalyzed by the NMs indicate that the largest NM $\text{Au}_{65}$ facilitated higher selectivity for $\text{O}_2$ reduction producing 80% $\text{OH}^-$ compared to 53% $\text{OH}^-$ produced by the smallest NM $\text{Au}_{23}$. While an overpotential of 80 mV is required to reach a current density of $-1 \text{ mA/cm}^2$ at an electrode rotation rate of 2500 rpm for $\text{Au}_{65}$, $\text{Au}_{23}$ on the contrary, requires a significantly higher overpotential of 680 mV to achieve similar current density. Electron transfer rate constant is also significantly higher (23 fold) for $\text{Au}_{65}$ compared to $\text{Au}_{23}$. 
CHAPTER 5

CORE SIZE INTERCONVERSIONS OF Au$_{30}$S-tBu$_{18}$ AND Au$_{36}$SPhX$_{24}$

*Part of the text and figures in this chapter are reprinted (adapted) with permission from: Core Size Interconversions of Au$_{30}$S-tBu$_{18}$ and Au$_{36}$SPhX$_{24}$ Amala Dass*, Tanya C. Jones, Shevanuja Theivendran, Luca Sementa, and Alessandro Fortunelli J. Phys. Chem. C, 2017, 121 (27), pp 14914–14919; Copyright 2017, American Chemical Society.

Author Contributions

Tanya Jones developed the synthetic protocol of the first core size interconversion isolation, structure elucidation, and characterization. Characterization techniques used were ESI-MS, MALDI-MS, and UV-Vis spectroscopy. Shevanuja Theivendran performed the Au$_{36}$(SPh-tBu)$_{24}$ conversion and characterization. Luca Sementa contributed theoretical calculations and studies.

5.1 Summary

We report for the first time the interconversion between two NMs: Au$_{36}$SPhX$_{24}$, (where X=H or -tBu) and Au$_{30}$(S-tBu)$_{18}$. This is accomplished through thermochemical etching, with HSPhX on Au$_{30}$(S-tBu)$_{18}$ which converts the NM to Au$_{36}$SPhX$_{24}$. We further show that the conversion is reversible from Au$_{36}$SPhX$_{24}$ to Au$_{30}$(S-tBu)$_{18}$ with tert-butyl thiol (HS-tBu) under the same thermochemical conditions. Not only is this the first reported interconversion between two NMs, but this report further demonstrates the conversion from a smaller to a larger sized NM, which is a rare occurrence. Experimental evidence for the reversible conversion is provided using MALDI-TOF-MS, nESI-MS, and UV-Vis-NIR spectroscopy. This discovery leads to valuable insight into the inherent nature of ligand dependency on the composition and atomic structure of gold-thiolate NMs. The NMs, Au$_{36}$SPhX$_{24}$ and Au$_{30}$(S-tBu)$_{18}$ have cuboctahedral atomic
structures with fcc arrangement, but have entirely different staple arrangements, with Au\textsubscript{28} and Au\textsubscript{20} cores, respectively. Theoretical studies show the difference between Au\textsubscript{30}(S-tBu)\textsubscript{18} and Au\textsubscript{36}(SPhH)\textsubscript{24} resides in the different fragmentation energy of the two species: conjugation in Au\textsubscript{36}(SPhH)\textsubscript{24} weakens the strength of ligand bonding to the Au cluster and thus makes it somewhat less stable than Au\textsubscript{30}(S-tBu)\textsubscript{18}. Furthermore, Au\textsubscript{30}(S-tBu)\textsubscript{18} appears to be slightly more stable than Au\textsubscript{36}(SPhH)\textsubscript{24} also in terms of atomization energy of the Au cluster and ligand/ligand interactions.

5.2 Introduction

Gold-thiolate NMs are a unique class of nanoparticles whose core metal diameter is in the size range of 2 nm.\textsuperscript{15-16, 88-90} NMs have a specific number of gold atoms and a specific number of thiolate ligands, and are highly studied for their unique properties.\textsuperscript{15} These features give researchers the potential to have manipulation over nanomaterials at the molecular and atomic level.\textsuperscript{16} Because gold NMs exhibit these unique properties, research is especially focused on their inherent nature, size, and what dictates the gold to thiol arrangement.\textsuperscript{21, 48, 77, 163-164}

NMs Au\textsubscript{30}(S-tBu)\textsubscript{18} [ref.\textsuperscript{39, 41, 43}] and Au\textsubscript{36}(SPhH)\textsubscript{24} [ref.\textsuperscript{11, 101, 109, 111}] have been directly synthesized, crystallized, and comprehensively studied.\textsuperscript{11, 39-43, 101, 109, 111, 165} However to date, there have been no reports showing that reversible interconversion between two NMs occurs, as demonstrated here between Au\textsubscript{30}(S-tBu)\textsubscript{18} and Au\textsubscript{36}(SPhX)\textsubscript{24}.

However, there have been reports of transformations in other nanomolecular structures in the literature. Au\textsubscript{144}(SCH\textsubscript{2}CH\textsubscript{2}Ph)\textsubscript{60} has been shown to be converted to Au\textsubscript{99}(SPhH)\textsubscript{42} through thermochemical etching with thiophenol.\textsuperscript{100} Au\textsubscript{144}(SCH\textsubscript{2}CH\textsubscript{2}Ph)\textsubscript{60} can also be transformed to Au\textsubscript{133}(SPh-tBu)\textsubscript{52}, through thermochemical treatment or core conversion with t-butylbenzene thiol (HSPh-tBu).\textsuperscript{33} It has also been shown that Au\textsubscript{38}(SCH\textsubscript{2}CH\textsubscript{2}Ph)\textsubscript{24} can convert to Au\textsubscript{36}(SPh-tBu)\textsubscript{24}.
through thermochemical etching with t-butylbenzene thiol. Other NMs, such as Au$_{104}$(SCH$_2$CH$_2$Ph)$_{45}$ and Au$_{67}$(SCH$_2$CH$_2$Ph)$_{35}$ are converted to Au$_{40}$(SCH$_2$CH$_2$Ph)$_{24}$, while NMs less than Au$_{67}$(SCH$_2$CH$_2$Ph)$_{35}$ have been shown to convert to Au$_{38}$(SCH$_2$CH$_2$Ph)$_{24}$ by core size conversion process. This demonstrates the importance of the size distribution of the starting material in core size conversion reactions.

The interconversion of Au$_{30}$(S-tBu)$_{18}$ and Au$_{36}$(SPhX)$_{24}$ is so far unknown and is especially interesting because conversion from Au$_{30}$(S-tBu)$_{18}$ and Au$_{36}$(SPhX)$_{24}$, (smaller to larger NM) is rarely seen in the literature. To date, the only larger NM known to convert from a smaller species, is Au$_{28}$(SPh-tBu)$_{20}$. In the case of Au$_{28}$(SPh-tBu)$_{20}$, the conversion results from thermochemical etching with HSPh-tBu on Au$_{25}$(SCH$_2$CH$_2$Ph)$_{18}$. However, the interconversion of two NMs has not been reported, until now. In this manuscript, we show not only that a smaller NM converts to a larger NM, but also the reversible interconversion between Au$_{30}$(S-tBu)$_{18}$ and Au$_{36}$(SPhX)$_{24}$.

This study also presents the opportunity to study Au$_{30}$(S-tBu)$_{18}$ and Au$_{36}$(SPhX)$_{24}$, as these NMs have published crystal structures which will allow us to extensively analyze the structural changes that are occurring upon conversion from one NM to another. [ref. 39, 109, 111] Direct
synthetic protocols, characterization, and optical studies have also been previously published for each, $\text{Au}_{30}(S-\text{tBu})_{18}$, $\text{Au}_{36}(S\text{-tBu})_{24}$ and $\text{Au}_{36}(S\text{PhH})_{24}$. [ref. 11, 39, 41, 43, 101, 109, 111] However, so far it has not been shown that interconversion between them is possible, until now.

**5.3 Experimental**

**5.3.1 Materials.** Hydrogen tetrachloroaurate (III) (HAuCl$_4$·3H$_2$O), sodium borohydride (Acros, 99%), thiophenol (Acros, 99%), $t$-butyl thiol (>99%, Sigma-Aldrich), $t$-butyl thiophenol (Acros, 99%), trans-2-[3[(4-tertbutyl-phenyl)-2-methyl-2-propenylidene] malononitrile (DCTB matrix) (Sigma Aldrich≥99%). Toluene, THF HPLC, methanol, and mineral oil were obtained from Fisher Scientific.

**5.3.2 Interconversion of $\text{Au}_{36}(S\text{PhX})_{24}$ to $\text{Au}_{30}(S-\text{tBu})_{18}$**

*Conversion of $\text{Au}_{30}(S-\text{tBu})_{18}$ to $\text{Au}_{36}(S\text{PhX})_{24}$. The starting material $\text{Au}_{30}(S-\text{tBu})_{18}$, was synthesized according to previously reported literature.$^{43}$ $\text{Au}_{30}(S-\text{tBu})_{18}$ and HSPh-X were reacted at a 1:4000 molar ratio of the initial ligand to the incoming ligand. 500µL of toluene was added to the mixture and the reaction was etched for 16 hours at 80°C stirring at 400rpm in an oil bath. The product was then washed in a mixture of water and methanol to produce the pure product, $\text{Au}_{36}(S\text{PhX})_{24}$. 

*Conversion of $\text{Au}_{36}(S\text{Ph-X})_{24}$ to $\text{Au}_{30}(S-\text{tBu})_{18}$. $\text{Au}_{36}(S\text{PhX})_{24}$ NMs are synthesized according to previously reported literature$^{11}$ and then purified using size-exclusion chromatography. 1mg of $\text{Au}_{36}(S\text{-tBu})_{24}$ is dissolved in 100µL toluene and 100 µL of $t$-butyl mercaptan. The mixture is stirred in an oil bath maintained at 75 °C for 30-40 mins. The resulting product is washed with excess methanol twice. The product from first etch is re-dissolved in 100µL of $t$-butyl mercaptan and etched again for another 40 minutes at 75 °C. Then, the final product is washed with methanol twice to obtain the pure final product, of $\text{Au}_{30}(S-\text{tBu})_{18}$. 

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5.3.3 Instrumentation. MALDI-TOF mass spectrometer was used to obtain mass spectra with 20mmol DCTB matrix in toluene on a Voyager DE PRO mass spectrometer. ESI-MS, collected from Waters Synapt HDMS with THF as the solvent, was used for compositional analysis. UV-visible-NIR absorption spectra were recorded in toluene from 300-1100 nm range using a Shimadzu UV-1601 spectrometer.
5.4 Results and Discussion

5.4.1 Monitoring the conversion of Au$_{30}$(S-tBu)$_{18}$ to Au$_{36}$(SPh-tBu)$_{24}$. The conversion of Au$_{30}$(S-tBu)$_{18}$ to Au$_{36}$(SPh-tBu)$_{24}$ was monitored using ESI-MS, MALDI-MS, and UV-vis-NIR spectroscopy. ESI-MS shown in figure 5.1 a, was used to monitor the reaction progress for the conversion of Au$_{30}$(S-tBu)$_{18}$ to Au$_{36}$(SPh-tBu)$_{24}$. The spectra in figure 5.1 a. (red) shows the +1 and +2 charge states of the starting material Au$_{30}$(S-tBu)$_{18}$ corresponds to 7514 m/z and 3757 m/z respectively. The blue spectra (Figure 5.1a.) indicates the intermediate material with partially exchanged ligands which are shown in the +2 charge state Au$_{36}$(SPh-tBu)$_{24}$ Cs$^+$ and Au$_{36}$(SPh-tBu)$_{23}$(S-tBu) Cs$^+$.$^2$. The +2 and +3 charge states of Au$_{30}$(S-tBu)$_{18}$ and Au$_{36}$(SPh-tBu)$_{24}$ respectively, are also observed and shown in the intermediate spectra (blue). The final product Au$_{36}$(SPh-tBu)$_{24}$ (green) shows the +2 charge state with two Cs$^+$ adducts at 5661 m/z. MALDI-MS was performed for each part of the reaction. Figure 5.1 b shows the starting material Au$_{30}$(S-tBu)$_{18}$ (red) with the molecular peak at Au$_{30}$(S-tBu)$_{17}$ and the fragment Au$_{26}$(S-tBu)$_{13}$. The blue spectra, in figure 5.1b, is the intermediate product (after 40 minutes of etching) showing the presence of both Au$_{30}$(S-tBu)$_{18}$ and Au$_{36}$(SPh-tBu)$_{24}$ (see Figure S5.1. for a list of assignments of the peaks in between). MALDI-MS was performed after 16 hours of etching, the final product, Au$_{36}$(SPh-tBu)$_{24}$, was determined, Figure 5.1 b (shown in green spectra) shows the +1 charge state at 10892 m/z of Au$_{36}$(SPh-tBu)$_{23}$. UV-vis-NIR was also used to monitor the conversion of Au$_{30}$(S-tBu)$_{18}$ to Au$_{36}$(SPh-tBu)$_{24}$. Figure 5.1c, shows the UV-vis-NIR of the starting product Au$_{30}$(S-tBu)$_{18}$ (top, green spectra) and the final product Au$_{36}$(SPh-tBu)$_{24}$, (bottom, red spectrum) in toluene. During the reaction, a color change was observed from the vivid green color of Au$_{30}$(S-tBu)$_{18}$ to the dark olive green color of Au$_{36}$(SPh-tBu)$_{24}$, further indicating the core conversion.
5.4.2 Monitoring the conversion of Au_{36}(SPh-tBu)_{24} to Au_{30}(S-tBu)_{18}. The conversion progress of Au_{36}(SPh-tBu)_{24} to Au_{30}(S-tBu)_{18} is monitored using ESI-MS and MALDI-MS (Figure 5.2a, b) in order to analyze the formation of Au_{30}(S-tBu)_{18} from Au_{36}(SPh-tBu)_{24}. ESI-MS was used to track the conversion of Au_{36}(SPh-tBu)_{24}, and Au_{30}(S-tBu)_{18}. The red spectra, shown in Figure 5.2a, shows a 5661 m/z peak which is the +2 charge state of Au_{36}(SPh-tBu)_{24} (the starting material) with two Cs adducts. After a first etching for 40 minutes, an envelope of peaks was observed corresponding to Au_{30}(S-tBu)_{18-x}(SPh-tBu)x with one Cs adduct. The core size conversion of Au_{36}(SPh-tBu)_{24} occurs within 5 minutes of the first etch (see Figure S5.2 for details), which could be observed by the color change of the reaction mixture. The color of the reaction mixture changes from dark olive green to a vivid green color. The peak to the far left of the blue spectra of figure 5.2a, corresponds to Au_{30}(S-tBu)_{18} with a Cs adduct and the remaining peaks correspond to Au_{30}(S-tBu)_{18-x} (SPh-tBu)x with one Cs adduct, (where x = 1, 2, and 3). Au_{30}(S-tBu)_{17}(SPh-tBu)_{1} is the most intense peak observed in the ESI mass spectra after the first etch. The bottom (green) spectra shows the second etching reaction used to complete the exchange of the un-exchanged ligands from first etch. In Figure 5.2b, the top red spectra shows the MALDI-MS of the starting material Au_{36}(SPh-tBu)_{23} (one ligand lost fragment peak observed in MALDI-MS) with molecular weight of 10892 m/z is shown. The blue spectra, shows the reaction progress after 40 minutes of thermochemical treatment and further exhibits the ligand exchange process after the core size conversion. The mass of t-butylbenzene thiol is 166 m/z and the mass of t-butyl thiol is 90 m/z, which gives a mass difference of 76 m/z. Therefore, the envelope of peaks shown in the blue spectra corresponds to the Au_{30}(S-tBu)_{18-x} (SPh-tBu)x, where x is the number of unexchanged ligands. The green spectrum shows that Au_{30}(S-tBu)_{18} is formed as the final product. The peak to the right corresponds to the species of one un-exchanged ligand, i.e. the Au_{30}(S-
The peak shown to the left of \( \text{Au}_{30}(S-t\text{Bu})_{18} \) is a fragment of the intact species in the MALDI-MS.

In Figure 5.2 a (green spectra), \( \alpha, \beta \) and \( \gamma \) peaks were investigated. \( \alpha \) corresponds to \( \text{Au}_{21}(S-t\text{Bu})_{15} \), \( \beta \) corresponds to \( \text{Au}_{30}(S-t\text{Bu})_{18} \), and \( \gamma \) corresponds to an 8800 m/z unidentified species. However, ESI-MS is a soft ionization technique in which the ionization efficiency of the analyte affects the intensity of the peaks within the spectra. Therefore, MALDI-MS – a hard ionization technique in which concentration of analyte is proportional to the intensity of the peak observed in the spectra – was used to determine the purity of the products and is shown in Figure 5.2 b. Since, MALDI-MS is a reliable tool for analyzing the purity of the sample, and the fraction of each species present in the mixture. At high laser MALDI mass spectrum the area under the peak corresponds to the relative amount of species present, however, in ESI the intensity of the peaks depends on the ionization efficiency. Even though ESI-MS shows the formation of \( \text{Au}_{21}(S-t\text{Bu})_{15} \) and 8800 m/z species as side products, both high laser and low laser MALDI-MS (see Figure S5.3 for details), and UV-vis spectra indicate that \( \text{Au}_{30}(S-t\text{Bu})_{18} \) is the major product.

UV-vis absorption spectra of the starting and final products were collected throughout the conversion and are shown in Figure 5.2 c, of \( \text{Au}_{30}(S-t\text{Bu})_{18} \) and \( \text{Au}_{36}(S\text{Ph}-t\text{Bu})_{24} \) in toluene. The optical spectra agrees with the assignments of \( \text{Au}_{36}(S\text{Ph}-t\text{Bu})_{24} \) and \( \text{Au}_{30}(S-t\text{Bu})_{18} \), as well as, published reports.\(^{11, 101, 111}\) \( \text{Au}_{36}(S\text{Ph}-t\text{Bu})_{24} \), shown in red, has major features at 360 and 570 nm as reported previously.\(^{111}\) \( \text{Au}_{30}(S-t\text{Bu})_{18} \), shown in green, has a major peak at 620 nm.\(^{43}\)

The interconversion was repeated for reproducibility and trials are compiled in Table S5.1 and Table S5.2. MALDI-MS and ESI-MS were repeated each time and the spectra from one of the reproducibility trials with HS\text{Ph}-tBu are shown again in Figure S5.4 and Figure S5.5. This interconversion of \( \text{Au}_{36}(S\text{PhX})_{24} \) and \( \text{Au}_{30}(S-t\text{Bu})_{18} \) was also repeated using thiophenol.
MS, ESI-MS, UV-vis, and pictures of the starting, intermediate, and final products are shown in Figure S5.6 and Figure S5.7.

5.4.3 Theory. Structural and energetic analysis. Local geometry relaxations were performed using the CP2K code\textsuperscript{167} whose DFT algorithms are based on a hybrid Gaussian/Plane-Wave scheme (GPW)\textsuperscript{168}. Pseudopotentials derived by Goedecker, Teter and Hutter\textsuperscript{169} were chosen to describe the core electrons of all atoms and DZVP basis sets\textsuperscript{170} to represent the DFT Kohn–Sham orbitals. Calculations were performed spin-restricted and at the Gamma point only. The semi-empirical Grimme-D3 correction\textsuperscript{171} was added to Perdew–Burke–Ernzerhof (PBE)\textsuperscript{61} exchange and correlation (xc-) functional to take into account dispersion interactions. The cut-off for the auxiliary plane wave representation of the density was 400 Ry. The equilibrium structure of $\text{Au}_{36}(\text{SPhH})_{24}$ and $\text{Au}_{30}(\text{S}-\text{tBu})_{18}$ NMs was obtained via fully relaxed local geometry optimizations starting from configurations derived from X-ray measurements in [refs. 111 and 39] respectively. Note that we simplify $\text{Au}_{36}(\text{SPh-tBu})_{24}$ to $\text{Au}_{36}(\text{SPhH})_{24}$ to reduce computational effort – this is legitimate because in the following we analyze only equilibrium energetics, thus kinetic effects\textsuperscript{33} due to the larger mass of the Ph-tBu residues with respect to Ph ones are not important. The cartesian coordinates of the $\text{Au}_{36}(\text{SPhH})_{24}$ and $\text{Au}_{30}(\text{S-tBu})_{18}$ species are also provided in the supplementary information (Table S5.4), as well as energy values used to calculate fragmentation and charging energies discussed in Table S5.3.

To provide theoretical information on the transformation processes investigated here, we focus on a comparison of the thermodynamic stability of $\text{Au}_{36}(\text{SPhH})_{24}$ and $\text{Au}_{30}(\text{S-tBu})_{18}$ NMs, using a previously proposed energy fragment decomposition analysis\textsuperscript{105,172-173} (note that we apply this analysis to electronic energies at equilibrium structures and zero temperature, neglecting vibrational and entropic contributions and kinetics effects).\textsuperscript{33}
We therefore decompose the formation energy of a Au$_N$(SR)$_M$ NM in three pieces: (1) cluster fragmentation, (2) metal atomization, (3) ligand separation. The first piece is the cluster fragmentation reaction into a metal cluster and a “crown” of ligands (normalized to the number of ligands, M):

\[
\text{Au}_{36}(\text{SPhH})_{24} \rightarrow \text{Au}_{36} + (\text{SPhH})_{24}^{\text{crown}} \quad \Delta E_{\text{fragm}}/M = 3.10 \text{ eV} \quad (1)
\]

\[
\text{Au}_{30}(\text{S-tBu})_{18} \rightarrow \text{Au}_{30} + (\text{S-tBu})_{18}^{\text{crown}} \quad \Delta E_{\text{fragm}}/M = 3.53 \text{ eV} \quad (2)
\]

where the coordinates of the Au$_{36}$, Au$_{30}$, (SPhH)$_{24}^{\text{crown}}$ and (S-tBu)$_{18}^{\text{crown}}$ fragments in the right-hand-side of the equations are frozen in their interacting configurations, \( \Delta E_{\text{fragm}} \) is the reaction (cluster fragmentation) energy and is reported per ligand (\( \Delta E_{\text{fragm}}/M \)).

From equations (1-2) it turns out that Au$_{36}$(SPhH)$_{24}$ has a fragmentation energy smaller by 0.43 eV with respect to Au$_{30}$(S-tBu)$_{18}$. This in keeping with the weakening of Au-S bond strength due to aromatic effects, i.e., in passing from an aliphatic to an aromatic thiol. For comparison, the strength of the S-H bond in H-S-tBu and H-SPhH, i.e., the reaction energy of the process: \( \text{HSR} \rightarrow \text{SR} + \text{H} \), differs by 0.36 eV in the two compounds, being 4.86 eV for HS-tBu and 4.50 eV for H-SPhH, respectively, and it is expected that this will similarly affect the strength of the Au-S covalent interactions. The second piece is the atomization energy of the resulting metal cluster:

\[
\text{Au}_{36} \text{[fromAu}_{36}(\text{SPhH})_{24}] \rightarrow 36 \text{ Au} \quad \Delta E_{\text{atmz}}/N = 2.058 \text{ eV} \quad (3)
\]

\[
\text{Au}_{30} \text{[fromAu}_{30}(\text{S-tBu})_{18}] \rightarrow 30 \text{ Au} \quad \Delta E_{\text{atmz}}/N = 2.064 \text{ eV} \quad (4)
\]

which is normalized by the number of Au atom. Despite a slight decrease from Au$_{30}$(S-tBu)$_{18}$ to Au$_{36}$(SPhH)$_{24}$, the atomization energy of the Au structure is therefore pretty similar, although a subtle destabilization of Au$_{36}$(SPhH)$_{24}$ can be noted since Au$_{36}$ – being larger than Au$_{30}$ – is expected to exhibit a monotonically increasing atomization energy. The third piece of formation
energy is the separation of the crown or shell of ligands into separated and relaxed thiol SR radicals:

\[(S\text{PhH})_{24}^{\text{crown}} \rightarrow 24 (S\text{PhH})_{\text{relax}} \quad \Delta E_{\text{ligsep}/M} = 0.159 \text{ eV} \quad (5)\]

\[(S-\text{tBu})_{18}^{\text{crown}} \rightarrow 18 (S-\text{tBu})_{\text{relax}} \quad \Delta E_{\text{ligsep}/M} = 0.179 \text{ eV} \quad (6)\]

and are pretty similar. This separation energy contains two terms: residual S-S binding (the sulfur atoms of the thiols in the interacting configuration are not too distant) and dispersion/repulsion interactions between the organic residues. Indeed, \(\Delta E_{\text{ligsep}/M}\) for \(\text{Au}_{36}(S\text{PhH})_{24}\) has some contributions from dispersion interactions between the organic residues, including \(\pi-\pi\) and T-stackings among phenyl rings.\(^{33}\) We can estimate this contribution by comparison with the separation energy of hydrogenated ligands, i.e., by hydrogenating the crown of thiol radical ligands by keeping their geometry frozen and evaluating the separation energy of the thus formed thiols.

We obtain a hydrogenated ligand separation energy for \(\text{Au}_{36}(S\text{PhH})_{24}\) of 0.253 eV (to be compared with 0.159 eV for thiol ligands), whereas for \(\text{Au}_{30}(S-\text{tBu})_{18}\) this quantity amounts to 0.178 eV, i.e., it is virtually identical to that of the thiol ligands. The smaller (by \(\approx 0.08-0.09\) eV per ligand) value of the separation energy for thiol with respect to thiols in the case of \(\text{Au}_{36}(S\text{PhH})_{24}\) is due to the weakening of residual S-S binding caused by conjugation as discussed above. To provide further insight into the thermodynamic comparison between the two MPC species, we can now consider the reaction:

\[\text{Au}_{30}(S-\text{tBu})_{18} + 6\text{Au} + 24(S\text{PhH}) \rightarrow \text{Au}_{36}(S\text{PhH})_{24} + 18(S-\text{tBu}) \quad (7)\]

which – in addition to total energies from QM simulations – require an estimate of the chemical potential of an Au atom, \(\mu (\text{Au})\), and the chemical potential of the ligand thiols, \(\mu (\text{HSPH})\) and \(\mu (\text{HS}\text{-tBu})\). This reaction can in fact be decomposed as follows:

Now the contribution within the first square bracket depends on the fragmentation (1,2) and separation (5,6) energies, and on the chemical potential of the ligand radical thiols, \( \mu(\text{SPhH}) \) and \( \mu(\text{S-}t\text{Bu}) \). Normalizing to the number of ligands, and assuming an equal concentration of HS-\( t \text{Bu} \) and HSPhH thiols, we see that this contribution equals 0.41 eV, which is basically similar to the difference in the strength of H-S-\( t \text{Bu} \) and H-SPhH bonds. Of course, working under experimental conditions in excess of one or the other ligand there will be a thermodynamic driving force to one or the other MPC species. The contribution within the second square bracket instead depends on the atomization energies and on the chemical potential of Au, \( \mu(\text{Au}) \). However, if the only source of Au is the MPC, \( \mu(\text{Au}) \) will equal the atomization energy per Au atom of the dominating cluster. As noted above, the atomization energies of the two clusters are pretty similar from equations (3,4), except that the value for Au\(_{30}(\text{S-}t\text{Bu})_{18} \) is slightly larger, thus providing a small thermodynamic driving force for the Au\(_{36}(\text{SPhH})_{24} \) into Au\(_{30}(\text{S-}t\text{Bu})_{18} \) conversion.

In summary, despite the fact that a thermodynamic difference between the two species exists, this difference amounts to \( \approx 0.4 \) eV, i.e., it nearly perfectly parallels the difference in the strength of RS-H bonds. The residual differential contribution will thus be not so large as to hinder the possibility that the two species can be inter-converted under appropriate conditions of temperature and reactant concentrations, as indeed experimentally observed in the present work.

Finally, it is interesting to compare the vertical electron affinity (i.e., minus the energy gained by adding an electron to the neutral species evaluated at the frozen geometry of the neutral species) and the vertical ionization potential (i.e., the energy needed to extract an electron from the neutral species again evaluated at the frozen geometry of the neutral species). From these quantities we evaluate Mulliken electronegativity\(^{174} \) and chemical hardness\(^{175} \) which provide a quantitative measure of chemical propensity. The vertical electron affinities and the vertical
ionization potentials are: 1.75 eV and 5.06 eV for Au$_{30}$($\text{S-tBu}$)$_{18}$, and 2.17 eV and 5.44 eV for Au$_{36}$($\text{SPhH}$)$_{24}$, respectively. Both quantities are larger by $\approx 0.4$ eV for Au$_{36}$($\text{SPhH}$)$_{24}$ with respect to Au$_{30}$($\text{S-tBu}$)$_{18}$, i.e., the energy levels of the former are rigidly shifted by $\approx 0.4$ eV with respect to those of the latter, implying that the Mulliken electronegativity of Au$_{36}$($\text{SPhH}$)$_{24}$ (3.80 eV) is 0.4 eV larger than that of Au$_{30}$($\text{S-tBu}$)$_{18}$ (3.40 eV) – both being much smaller than the work function of bulk Au = 5.1~5.4 eV, while the chemical hardness of the two species is basically the same (1.64 and 1.66 eV, respectively). The difference in Mulliken electronegativity should reveal in a different electrochemical behavior (redox potentials) of the two species.$^{176}$

5.5 Conclusions

The interconversion of Au$_{30}$($\text{S-tBu}$)$_{18}$ and Au$_{36}$($\text{SPhX}$)$_{24}$ provides new insight into (1) the inherent nature of gold-thiolate NMs and (2) ligand dictation of the core of the nanomolecular structure. When Au$_{30}$($\text{S-tBu}$)$_{18}$ is treated with aromatic thiophenol or tert-butyl thiophenol, the core converts to the preferred Au$_{36}$($\text{SPhX}$)$_{24}$ structure, as dictated by the ligand being used. This is further confirmed and observed in Au$_{36}$($\text{SPhX}$)$_{24}$, because when it is treated in excess amounts of the bulky $t$-butyl thiol, Au$_{36}$($\text{SPhX}$)$_{24}$ converts to the preferred and most stable structure Au$_{30}$($\text{S-tBu}$)$_{18}$.

Thermodynamic analysis further provides us with two main conclusions: (1) the difference between Au$_{30}$($\text{S-tBu}$)$_{18}$ and Au$_{36}$($\text{SPhH}$)$_{24}$ basically resides in the different fragmentation energy of the two species: conjugation in Au$_{36}$($\text{SPhH}$)$_{24}$ weakens the strength of ligand bonding to the Au cluster$^{105,173}$ and thus makes it somewhat less stable than Au$_{30}$($\text{S-tBu}$)$_{18}$ – otherwise the two species exhibit similar values of the other energy descriptors; (2) Au$_{30}$($\text{S-tBu}$)$_{18}$ appears to be slightly more stable than Au$_{36}$($\text{SPhH}$)$_{24}$ also in terms of atomization energy of the Au cluster and ligand/ligand interactions, although these contributions are quantitatively of lesser importance.
CHAPTER 6

LIGAND DICTATION EFFECTS ON \( \text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18} \) AND \( \text{Au}_{30}(\text{S}-t\text{Bu})_{18} \)

6.1 Summary

Since the discovery of the Brust-Schiffin synthesis, nanomaterials have been envisioned as the gateway to the manipulation of matter. However, we have found a more complex system at the molecular level than ever imagined from bulk metal. What is found, is a significant dependence in the self-assembly process of gold NMs, based on the capping ligand. To harness this power of manipulation over matter at the atomic level, we must first understand the ligand dependency phenomenon. This phenomenon must be understood, in order to start picking and placing atoms to make the molecules we want, to develop the materials we need. In this work the ligand dictation effect on two systems: \( \text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18} \) and \( \text{Au}_{30}(\text{S}-t\text{Bu})_{18} \) were investigated using different sterically hindered ligands: 2-propene-1-thiol, n-butane thiol, 2-methyl-1-propane thiol, 2-butane thiol, and 3-methyl-2-butane thiol.

6.2 Introduction

Ligand exchange is well known throughout the literature to induce core size conversion in gold thiolate NMs. However, there are limited studies which look at ligand exchange, and transformations with complete mass spectrometric and characterization data. Furthermore, literature tends to focus on the role of aliphatic, aromatic, and bulkiness of the ligand as the primary factor for dictation of the nanostructure. However, when looking at these systems from recently published literature, gold NMs deviate from this trend. Based on the compiled
literature in the field, and the crystallographic structures we take an in depth look at the steric
dictation of the ligand over the nanostructure.

This was accomplished through induction of ligand exchange/transformation on $\text{Au_{30}(S-tBu)}_{18}$ and $\text{Au_{25}(SCH_2CH_2Ph)}_{18}$. Using structurally differing ligands to elicit conversion of the $\text{Au_{30}(S-tBu)}_{18}$ and $\text{Au_{25}(SCH_2CH_2Ph)}_{18}$ and study the bulkiness effect of the ligand dictation over the NM. These observations, along with crystallographic data, show the need for systematic studies on well characterized NMs to observe the effects of changes at the primary, secondary, and tertiary structures of the thiol used in synthesis in order to understand the ligand dictation phenomenon.

6.2.1 Summary of Specific Objectives. In this work we aimed to determine the effect on the nanomolecular structure of $\text{Au_{25}(SCH_2CH_2Ph)}_{18}$ and $\text{Au_{30}(S-tBu)}_{8}$ through variation of the primary and secondary carbons of thiolated ligands to observe changes to nanomolecular structure. The NMs $\text{Au_{30}(S-tBu)}_{18}$ and $\text{Au_{25}(SCH_2CH_2Ph)}_{18}$ were chosen because they are highly studied, thoroughly characterized, can be produced in high yield, using facile synthetic protocols, and the nanostructures have contrasting primary carbon sterics. The incoming ligands for exchange/conversion also have varying sterics and include: 2-propene-1-thiol, n-butane thiol, 2-methyl-1-propane thiol, 2-butane thiol, and 3-methyl-2-butane thiol. The exchange with 1-butane thiol on $\text{Au_{25}(SCH_2CH_2Ph)}_{18}$ was used as the control, as $\text{Au_{25}(SCH_2CH_2Ph)}_{18}$ has been shown to be successfully exchanged with ethyl thiol and hexane thiol to produce the $\text{Au_{25}(SR)}_{18}$ NM.

6.2.2 Importance and Significance to the Field. When looking at the literature to date on gold thiolate NMs there is a lack of understating on the ligand dictation over the nanostructure at the atomic level. Not only is there overwhelming discussion in the literature regarding the ligand
dictation. This need has given nanomaterial scientists a major obstacle to overcome in order to understand this phenomenon and to harness the incredible self-assembly properties of gold thiolated NMs. Overcoming this road block would allow researchers to tune matter precisely at the atomic level. This idea has been envisioned since the birth of the Brust-Schiffin synthesis and nanomaterial research and can only be accomplished by harnessing the mechanism that causes ligand dictation on the structure. Not only do we need to build on our understanding of ligand dictation, we also need to be able to make monodisperse NMs through optimized, high yield, and simple methods. The discovery of new NMs and new crystallographic structures is a crucial part in understanding the mechanism of controlling ligand dictation.

In this study, the ligand dictation of gold NMs was determined. Specifically, to determine the effects on the overall structure of the NMs by alteration of the primary and secondary carbons of the thiolated ligands used in the exchange/ transformation. In order to study, the ligand dictation through the synthesis and characterization of new NMs through the ligand exchange/transformations on $\text{Au}_{30}(S\text{-}t\text{Bu})_{18}$ and $\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}$. This was accomplished using ligands with varied sterics at the primary and secondary carbons

**6.2.3 Literature Background.** There are an overwhelming number of reports in the nanomolecular field on the topic of ligand dictation over the nanostructure. Single-crystal XRD however is the gold-standard for structural determination of molecules and is crucial to the understanding of the complex atomic structures of NMs. This provides us with the most critical information needed to understand the ligand dictation. This is because scXRD provides us with atomic structure, and arrangement of atoms. Therefore, using the literature to date and a recent review in the field, Table 1 summarizes this wealth of information for all of the gold-thiolated NMs’ crystal structures published to date.
Table 6.1 summarizes several crucial things to examine the nanomolecular structure in terms of determining ligand dictation. These features include: core size, geometry, shell composition, the number of electrons in the closing shell (outer Au shell), and staple arrangement around the structure. Ligand dictation throughout the literature has looked at the dictation in terms of aliphatic, bulky, and aromatic. However, several resolved crystal structures contradict this generic means of categorizing ligands. The progression of the literature, has shown that there is in fact more specificity behind the ligand dictation of the nanostructure. Defining this dictation will allow nanomolecular chemists to gain a higher level of precision and control in developing and understanding new nanomaterials.

For instance, when looking at the crystal structures of Au$_{30}$(S-tBu)$_{18}$ and Au$_{30}$(SAdm)$_{18}$ both structures have the same number of gold atoms and ligands. However, when looking at their crystal structures have entirely different packing geometries resulting in different structural geometry, core size, and staple arrangement. These are two ligands that before this report were expected to produce the same sized and shaped NMs.\textsuperscript{39-41} This is because it was shown previously only through ligand exchange (and mass spectrometry data) on Au$_{30}$(S-tBu)$_{18}$.\textsuperscript{43} However, it wasn’t until identifying the crystal structures of both NMs that Au$_{30}$(S-tBu)$_{18}$ and Au$_{30}$(SAdm)$_{18}$ revealed entirely different cores, geometry, staples arrangement and packing.\textsuperscript{40-41} Not only is this a great example of why crystallographic data is essential to the field, but further demonstrates the need for crystallographic data to solve the mystery of ligand dictation over the NM. Furthermore, synthesis of the complete series of t-butyl thiolated NMs differs from that of adamantane’s series. The known series for t-butyl thiol include Au$_{23}$(SR)$_{16}$,\textsuperscript{106} Au$_{30}$(SR)$_{18}$,\textsuperscript{39} Au$_{46}$(SR)$_{24}$, and Au$_{65}$(SR)$_{29}$.\textsuperscript{183} While adamantane thiolated NMs have a series of Au$_{21}$(SR)$_{15}$, Au$_{24}$(SR)$_{16}$, Au$_{30}$(SR)$_{18}$, and Au$_{38}$S$_2$(SR)$_{20}$.\textsuperscript{37, 105, 107-108, 184}
Table 6.1. Summary of published crystallographic structures of gold-thiolated NMs. Including NM, capping ligand, electrons in closing shells, the number of Au atoms in core and shell of structures (* indicates specialized hep packing hexagonal closed packing and † indicates bcc- body centered cubic packing), shape, and staple arrangement (i.e. monomeric, dimeric, trimeric, specialized staples, bridging thiols) and corresponding literature reference.

<table>
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<th>Nanomolecule (Au SR)</th>
<th>Ligand (SR)</th>
<th>Shell e</th>
<th>Core (Shell)</th>
<th>Shape</th>
<th>Specialized Stampes</th>
<th>Bridging thiols (SR)</th>
<th>Ref</th>
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<td>20</td>
<td>cuboctahedron</td>
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<td>3 6</td>
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<td>34</td>
<td>cuboctahedron</td>
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<td>tetrahedral</td>
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<tr>
<td>Au24(SR)34</td>
<td>HSPh-tBu</td>
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<td>84°</td>
<td>tetragonal</td>
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<tr>
<td>Au102(SR)44</td>
<td>HSPh-pCOOH</td>
<td>58</td>
<td>79</td>
<td>dodecahedron</td>
<td>22 -</td>
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<td>199</td>
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<tr>
<td>Au102(SR)44</td>
<td>HSCH2-tBu</td>
<td>58</td>
<td>(32) (40)</td>
<td>Marks dodecahedron</td>
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<td>Au233(SR)30</td>
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<td>80</td>
<td>13 (42) (50)</td>
<td>(25°)</td>
<td>25 -</td>
<td>-</td>
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<td>HSPh-tBu</td>
<td>81</td>
<td>13 (42) (52)</td>
<td>(26)</td>
<td>26 -</td>
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<td>206</td>
<td>-</td>
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<td>Au249(SR)34</td>
<td>HSPh-tBu</td>
<td>195</td>
<td>13 (42) (92)</td>
<td>(102) (30)</td>
<td>18 6</td>
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Continuing to compare similar cores sizes, we see from examining, for instance Au24(SAdm)18 and Au24(SCH2Ph-tBu)20,105,187 these structures have the same number of gold atoms but different amounts of capping ligand on the surface. The adamantane thiol capped Au24 has a larger steric effect on the structure, which leads to the decreased number of ligands on the outer structure of
the nanostructure. While $\text{Au}_{24}(\text{SCH}_2\text{Ph}-t\text{Bu})_{20}$ has less steric hindrance, at the Au-S interface which leads to the increased number of capping ligands on the core of the structure, increasing the Au:SR surface ratio. Whereas in the $\text{Au}_{24}(\text{SAdm})_{16}$ structure, there is a decrease in the Au:SR surface ratio and a fewer number of ligands capping the structure. When looking at the crystal data comparison between $\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}$ and $\text{Au}_{25}(\text{SCH}_2\text{CH}_3)_{18}$ these structures agree with the hypothesis that major dictation of the ligand resides in the sterics around the primary and secondary carbon of the thiolate ligand. When looking at $\text{Au}_{25}(\text{SR})_{18}$ ($\text{SR}=\text{HSCH}_2\text{CH}_2\text{Ph}$ or $\text{HSCH}_2\text{CH}_2$) structures we see almost identical structures. This is because phenylethane thiol and ethane thiol contain similar carbon bulkiness at the primary site. $\text{Au}_{25}(\text{SR})_{18}$ structures exhibit identical structures with almost identical Au-Au and Au-S bonds with different lengths. While crystal structure $\text{Au}_{25}(\text{S-2-napthalene})_{18}$ aromatic has the same number of Au atoms in the core and staple arrangement however, the icosahedral core exhibits expansion with the addition of the bulkier thiol. The 1-napthalene thiolated $\text{Au}_{25}$ has a similar structure to other structures of $\text{Au}_{25}$ however this may be due to the tilt angle imposed on the structure from the 1 position of the sulfur atom on the naphthalene ring. Another comparison of the bulkiness effect is observed in the structures of $\text{Au}_{25}(\text{S-1-Nap})_{18}$ and the $\text{Au}_{102}\text{S}_2(\text{S-2-Nap})_{41}$. As 1-napthalene thiol acts as a traditional aliphatic-like ligand (i.e. HSEt and HSCH$_2$CH$_2$Ph) producing $\text{Au}_{25}(\text{S-1-Nap})_{18}$. While 2-napthalene thiol sterics are like a traditional aromatic producing a $\text{Au}_{102}\text{S}_2(\text{S-2-Nap})_{41}$ and contains structure very similar to the aromatic capped $\text{Au}_{102}(\text{S-Ph-pCOOH})_{44}$.

Looking at the structures of $\text{Au}_{28}(\text{SPh}-t\text{Bu})_{20}$ and $\text{Au}_{28}(\text{S-cC}_6\text{H}_{11})_{20}$ the cores again have the same number of gold atoms and bridging thiols however the Au:S interface is dramatically different. Where $\text{Au}_{28}(\text{SPh}-t\text{Bu})_{20}$ has 4 dimeric staples and $\text{Au}_{28}(\text{S-cC}_6\text{H}_{11})_{20}$ has 2 trimeric staples and 2 monomeric staples. Another example of how sterics of the ligand alter the structure
of the NM. The ligand dictation phenomenon is also observed in the crystal structures of \( \text{Au}_{36}(\text{SR})_{24} \) (where \( \text{SR}=\text{HSPh}, \text{HSPh}-t\text{Bu}, \text{or HS}-c\text{C}_5\text{H}_9 \)). Where cyclopentane thiol, \( t\)-butyl benzene thiol, and thiophenol ligands, all with similar primary carbon sterics, produce almost identical \( \text{Au}_{36}(\text{SR})_{24} \) crystal structures. With the cyclopentane thiolated \( \text{Au}_{36} \) structure having a minor difference in the twist angle of one of the dimeric ligands. When looking at structures \( \text{Au}_{38}(\text{SCH}_2\text{CH}_2\text{Ph})_{24} \) and \( \text{Au}_{38}\text{S}_2(\text{SAdm})_{20} \) we see a similar pattern when using contrasting ligands. Again, we see different packing, geometry, core size, core shape, and staple arrangement. Where the \( \text{Au}:\text{SR} \) ratio is higher with the less sterically hindering primary carbon. This same phenomenon is also observed when comparing the structures of \( \text{Au}_{44}(\text{SR})_{24-26} \) (where \( \text{SR}=2,4 \text{dimethylbenzene thiol or } t\)-butyl benzene thiol). The 2,4 dimethylbenzene thiolated ligand adds more bulkiness at the Au-S surface, leading to a change in the core geometry (bi-icosahedral versus tetrahedral), core size, shell size, and ligand arrangement.

The notion of primary carbon dictation was also discussed in a 2015 perspective article\(^{204}\) and mentioned again in an 2016 highlight article.\(^{205}\) These articles suggest there are simply 3 layers of dictation the ligand has over the nanostructure. These layers include (1) bulkiness in the \( \alpha \)-carbon, (2) bulkiness in the isomeric benzenethiol; (3) bulkiness in the para-position of benzenethiol. However, the crystal structures and new literature disagrees with this generalized trend. This is especially true in the case of the interconversion between \( \text{Au}_{30}(\text{S}-t\text{Bu})_{18} \) and \( \text{Au}_{36}(\text{SPhX})_{24} \) (where \( X=-\text{H or } t\text{Bu} \)). Furthermore, this observation and the subsequent hypothesis made, has never been tested. The authors do state however, in the highlight article “further analysis is required from the perspective of why particular ligands dictate nanoclusters”. Another, notable study done looking at the substituent effects of alternating the position of the methyl group of methylbenzene thiol from para, meta, and ortho was conducted in 2015\(^{206}\) and the reason why
aromatic ligands were not chosen for this proposal. This study involved a direct synthesis and thiol etching technique. The species that remained or “the survival of the robust” NM was concluded to be the most stable product. This study showed us that para-methylbenzene thiol produced \( \text{Au}_{130}(\text{SR})_{50} \), ortho-methylbenzene thiol produces \( \text{Au}_{40}(\text{SR})_{24} \), and that direct synthesis with meta-methylbenzene thiol produces \( \text{Au}_{104}(\text{SR})_{41} \). This robust method also agrees with the hypothesis and shows that the larger the steric hindrance, the greater the change and greater the decrease in the Au:SR ratio. However, these studies leave the reader and the field, with a lack of in-depth understanding of the ligand dictation phenomenon.

6.2.4 Hypothesis. In the field, it is well known that the ligand dictates the nanostructure of gold-thiolate NMs, however the underlying mechanism remains unknown. Furthermore, there is a correlation in the published crystallographic data and field literature, that the ligand dictation over the core structure of the NMs is directly affected by the steric of the surrounding the primary and secondary carbons. If there is causation for this phenomenon then, new nanoparticles can be
tuned and created through ligand exchange/transformation by varying steric bulkiness on the primary and secondary carbons to induce structural changes on the NM.

6.2.5 Objectives Study effects of changing the primary and secondary carbons through ligand exchanges/transformation on Au$_{25}$(SCH$_2$CH$_2$Ph)$_{18}$ and Au$_{30}$(S-\textit{t}Bu)$_{18}$. This will be accomplished by using ligands with alternating sterics on the primary and secondary carbons to induce specific changes in the NM. From characterization data, determine the effects of steric changes on the primary and secondary carbons to observe changes to nanomolecular structure. This will be synthetically accomplished through ligand exchange/core conversion on the starting materials: Au$_{30}$(S-\textit{t}Bu)$_{18}$ and Au$_{25}$(SCH$_2$CH$_2$Ph)$_{18}$. Structural analysis and assignments using UV-Vis spectroscopy, MALDI-MS, ESI-MS, and scXRD. The NMs Au$_{30}$(S-\textit{t}Bu)$_{18}$ and Au$_{25}$(SCH$_2$CH$_2$Ph)$_{18}$ were chosen because they are highly studied, thoroughly characterized, ease of synthesis, high yield, and contrasting primary carbon sterics. The incoming ligands for exchange/conversion include: 2-propene-1-thiol, n-butane thiol, 2-methyl-1-propane thiol, 2-butane thiol, and 3-methyl-2-butane thiol. The exchange with 1-butane on Au$_{25}$(SCH$_2$CH$_2$Ph)$_{18}$ was the control, as Au$_{25}$(SCH$_2$CH$_2$Ph)$_{18}$ has been shown to be successfully exchanged with ethyl thiol and hexane thiol to produce the Au$_{25}$(SR)$_{18}$ NM.

6.3 Experimental

6.3.1 Materials. Hydrogen tetrachloroaurate (III) (HAuCl$_4$. 3H$_2$O), sodium borohydride (Acros, 99%), tertiary butylthiol (Acros, 99%), 2-propene-1-thiol (TCI, 99%), n-butane thiol (TCI, 98%), 2-methyl-1-propane thiol (TCI, 99%), 2-butane thiol (Acros, 99%), and 3-methyl-2-butane thiol (Acros, 99%), and trans-2-[3[(4-tertbutyl-phenyl)-2-methyl-2-propenylidene] malononitrile (DCTB matrix) (Fluka≥99%) were purchased and used as received. HPLC grade solvents such as
tetrahydrofuran, toluene, methanol, butylated hydroxytoluene stabilized tetrahydrofuran and acetonitrile were obtained from Fisher Scientific.

6.3.2 Synthesis. Au$_{25}$(SCH$_2$CH$_2$Ph)$_{18}$ and Au$_{30}$(S-tBu)$_{18}$ are synthesized and purified according to the literature. Once purified 1mg of Au$_{25}$(SCH$_2$CH$_2$Ph)$_{18}$ was etched in excess amounts of each incoming thiol. The reaction was monitored between 24-48 hours to observe the effects taking place on the NMs. The incoming ligands used include: 2-propene-1-thiol, n-butane thiol, 2-methyl-1-propane thiol, 2 butane thiol, and 3-methyl-2-butane thiol. This same protocol was carried out on Au$_{30}$(S-tBu)$_{18}$ with each incoming thiol.

6.3.3 Instrumentation. Matrix assisted laser desorption time-of-flight (MALDI-TOF) mass spectra was acquired using DCTB matrix$^{30}$ on a Voyager DE PRO mass spectrometer. Compositional analysis was performed with electrospray ionization mass spectra (ESI-MS) collected from Waters Synapt HDMS using THF:CH$_3$CN as the solvent.

6.3.4 Optical Spectroscopy. UV-vis-NIR absorption response of NMs was performed in toluene using a UV-vis-NIR Cary 5000.

6.4 Results & Discussion

6.4.1 Exchanges on Au$_{25}$(SCH$_2$CH$_2$Ph)$_{18}$

6.4.1.1 Mass Spectrometry. ESI-MS and MALDI spectra were collected 24-48 hours after etching the starting NM in excess incoming thiol at 60°C. Figure 6.2 ESI-MS (a) and MALDI-MS (b) of the starting material, Au$_{25}$(SCH$_2$CH$_2$Ph)$_{18}$ (black). When Au$_{25}$(SCH$_2$CH$_2$Ph)$_{18}$ is exchanged with 2-propene-1-thiol (red), MALDI-MS shows that a many species form, smaller than Au$_{25}$(S-2-propene)$_{18}$. The ESI-MS spectra (red, a) shows a broad peak around 4000Da. The ESI-MS spectrum indicates that the Au$_{25}$(SCH$_2$CH$_2$Ph)$_{18}$ core has converted and that several smaller nanomolecules have formed during the reaction. Figure 6.2b shows that when
Au$_{25}$(SCH$_2$CH$_2$Ph)$_{18}$ is exchanged with n-butane thiol (green) the nanomolecule converts to Au$_{25}$(S-n-butane)$_{18}$, as seen in the complete exchange in MALDI-MS. MALDI-MS spectra (Figure 6.2 green, b) shows both the +1 peak for Au$_{25}$(S-n-butane)$_{18}$ at 6520Da and the -Au$_4$(SR)$_4$ fragment at 5320Da. However, the ESI-MS (a) indicates the presence of Au$_{25}$(SCH$_2$CH$_2$Ph)$_{15}$(SC$_4$H$_9$)$_3$. The MALDI (b) data however does not indicate the presence of Au$_{25}$(SCH$_2$CH$_2$Ph)$_{15}$(SC$_4$H$_9$)$_3$. The

**Figure 6.2.** (a) ESI-MS (left) and (b) MALDI-MS (right) of exchange on the starting material Au$_{25}$(SCH$_2$CH$_2$Ph)$_{18}$ (black) with 2-propene-1-thiol (red), n-butane thiol (green), 2-methyl-1-propane thiol (blue), 2 butane thiol (purple), and 3-methyl-2-butane thiol (orange). (c) UV-Vis spectra of starting material Au$_{25}$(SCH$_2$CH$_2$Ph)$_{18}$ (black) with 2-propene-1-thiol (red), n-butane thiol (green), 2-methyl-1-propane thiol (blue), 2 butane thiol (purple), and 3-methyl-2-butane thiol (orange).

**Figure 6.3.** (a) ESI-MS (left) and (b) MALDI-MS (right) of exchange on the starting material Au$_{30}$(S-rBu)$_{18}$ (black) with 2-propene-1-thiol (red), n-butane thiol (green), 2-methyl-1-propane thiol (blue), 2 butane thiol (purple), and 3-methyl-2-butane thiol (orange). (c) UV-Vis spectra of starting material Au$_{30}$(S-rBu)$_{18}$ (black) with 2-propene-1-thiol (red), n-butane thiol (green), 2-methyl-1-propane thiol (blue), 2 butane thiol (purple), and 3-methyl-2-butane thiol (orange).
ionization efficiency of \( \text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{15}(\text{SC}_4\text{H}_9)_3 \) is likely higher than \( \text{Au}_{25}(\text{S-n-butane})_{18} \) which is why a negligible portion is ionizing with the ESI source. The presence of the \( \text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18} \) species in ESI-MS provide indication that the \( \text{Au}_{25} \) core is not destabilized by the HS-n-butane ligand. When \( \text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18} \) is exchanged with 2-methyl-1-propane thiol (blue) the MALDI-MS (Figure 6.2b) and ESI-MS (Figure 6.2a) indicate that \( \text{Au}_{25}(\text{S-2-methyl-1-propane})_{18} \) forms after exchange. In MALDI-MS the \( \text{Au}_{25}(\text{S-2-methyl-1-propane})_{18} \) +1 peak is observed at 6520Da and the -\( \text{Au}_4(\text{SR})_4 \) fragment at 5330. The ESI spectra also shows the +1 peak \( \text{Au}_{25}(\text{S-2-methyl-1-propane})_{18} \) at 6527Da. There is also at 8192Da, however there are no species above the 6520Da peak at high laser MALDI-MS indicating that the 8192Da peak is negligible in the sample. When \( \text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18} \) is exchanged with 2-butane thiol (Figure 6.2b, purple) the core destabilizes and multiple species form which are small than \( \text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18} \), as observed in the several peaks shown in the MALDI-MS spectra in the 5000-6500Da range. The ESI-MS also indicates the presence of small clusters and several peaks in the 5500-6000Da range with AuSR isotopic shapes are observed. When \( \text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18} \) is etched with 3-methyl-2-butane thiol (Figure 6.2a, orange), smaller sized nanomolecules are formed as seen in both ESI-MS as +2 charge states with AuSR isotopic shaped species in the 2500Da range as well as peaks observe in MALDI-MS spectra at the 5500Da range.

6.4.1.2 Optical Spectroscopy. UV-Vis spectra were collected 24-48 hours after etching in excess incoming thiol at 60°. Figure 6.2c shows UV-Vis spectra of the starting material \( \text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18} \) (black) and \( \text{Au}_{30}(\text{S-rBu})_{18} \) (black) respectively. When exchanged with 2-propene-1-thiol (red) both nanomolecules, \( \text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18} \) and \( \text{Au}_{30}(\text{S-rBu})_{18} \), convert to several NM species within the sample as indicated by the monotonous UV-Vis spectra. When \( \text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18} \) is exchanged with n-butane thiol (green) the nanomolecule converts to
Au$_{25}$(S-n-butane)$_{18}$ as seen in reduced Au$_{25}$ features in the spectra. When Au$_{25}$(SCH$_2$CH$_2$Ph)$_{18}$ is exchanged with 2-methyl-1-propane thiol (blue) UV-Vis spectra indicates Au$_{25}$(S-2-methyl-1-propane)$_{18}$ forms and the presence of the Au$_{25}$ core from the presence of the 450 and 625nm peaks. The UV of Au$_{25}$(SCH$_2$CH$_2$Ph)$_{18}$ when exchanged with 2-butane thiol (purple), shows loss of Au$_{25}$ features indicating core conversion and the lack of features indicate one or more NM species are present. When Au$_{25}$(SCH$_2$CH$_2$Ph)$_{18}$ is etched with 3-methyl-2-butane thiol (orange), smaller sized nanomolecules are formed as indicated by loss of UV features.

6.4.2 Exchanges on Au$_{30}$(S-tBu)$_{18}$

6.4.2.1 Mass Spectrometry.

Figure 6.3 shows the ESI-MS (a) and MALDI-MS (b) of the ligand exchanges on Au$_{30}$(S-tBu)$_{18}$ (black), which is shown on the top spectra. When Au$_{30}$(S-tBu)$_{18}$ is etched with HS-2-propene the MALDI-MS shows several peaks larger than Au$_{30}$(S-tBu)$_{18}$ and Au$_{30}$(S-2-propene)$_{18}$. This indicates that the HS-2-propene ligand has induced core conversion on the Au$_{30}$(S-tBu)$_{18}$ to larger NM species. ESI-MS did not yield a signal after several attempts at ionizing the sample and addition of cesium acetate to induce adduct formation in the ionization process to yield a signal. Attempts were unsuccessful and failed attempts may be indicative of a mixture of NM species however conclusions are drawn from MALDI-MS and UV data. MALDI-MS shows that when the Au$_{30}$(S-tBu)$_{18}$ is etched with n-butane thiol (Figure 6.3b, green), the NM converts to larger NM species, as indicated in MALDI-MS with the 8362 Da species dominating in the sample. ESI-MS shows only small clusters in the 3000Da range. Au$_{30}$(S-tBu)$_{18}$ when etched with 2-methyl-1-propane thiol (Figure 6.3b,blue) shows an increase in core size with an 8068 species as well as the presence of Au$_{30}$(S-2-methyl-1-propane)$_{18}$ as indicated by MALDI-MS. ESI-MS spectra also indicates the formation of Au$_{30}$(S-2-methyl-1-propane)$_{18}$, a +1 charge state at 7523Da is observed.

79
in the ESI-MS spectra. When \( \text{Au}_{30}(S\text{-tBu})_{18} \) is exchanged with 2-butane thiol (Figure 6.3b, purple), both \( \text{Au}_{30}(S\text{-2-butane})_{18} \) and multiple NM species form which are smaller than \( \text{Au}_{30}(S\text{-2-butane})_{18} \) as indicated in MALDI. When \( \text{Au}_{30}(S\text{-tBu})_{18} \) is etched with 3-methyl-2-butane thiol (Figure 6.3b, orange), \( \text{Au}_{30}(S\text{-3-methyl-2-butane})_{18} \) is observed in the MALDI-MS along with smaller sized nanomolecules are formed. ESI-MS only shows several small species in the 3500Da range.

6.4.2.2 Optical Spectroscopy. Figure 6.3c shows the UV spectra of \( \text{Au}_{30}(S\text{-tBu})_{18} \). When \( \text{Au}_{30}(S\text{-tBu})_{18} \) etched with n-butane thiol (green), the NM converts another species as indicated by red shifted absorbance peaks in spectra. \( \text{Au}_{30}(S\text{-tBu})_{18} \) when etched with 2-methyl-1-propane thiol (blue) indicates the presence of \( \text{Au}_{30}(S\text{-2-methyl-1-propane})_{18} \). UV-Vis spectra of \( \text{Au}_{30}(S\text{-tBu})_{18} \) exchanged with 2-butane thiol (purple) the \( \text{Au}_{30} \) features diminish indicating other products are present with \( \text{Au}_{30}(S\text{R})_{18} \). UV-Vis spectra indicate \( \text{Au}_{30}(S\text{-tBu})_{18} \) when etched with 3-methyl-2-butane thiol (orange) the NM’s core converts, as indicated by the loss of \( \text{Au}_{30} \) UV features.

6.5 Conclusions and Future Work

The results obtained from ESI-MS, MALDI-MS, and UV-Vis spectra were used to draw final conclusions regarding the exchanges of \( \text{Au}_{25}(S\text{CH}_{2}\text{CH}_{2}\text{Ph})_{18} \) and \( \text{Au}_{30}(S\text{-tBu})_{18} \). Table 6.2 summarizes these conclusions. However, MALDI-MS data is more reliable for quantitation of these NMs, this is because of the nature of the laser ionization source in that all products with in a sample will be ionized and intensity is reliably proportional to the portion of a species in the sample. Whereas, in ESI spectral intensity is based on ionization efficiency of the sample.

When both \( \text{Au}_{25}(S\text{CH}_{2}\text{CH}_{2}\text{Ph})_{18} \) and \( \text{Au}_{30}(S\text{-tBu})_{18} \) are exchanged with 2-propene-1-thiol (red) both nanomolecules convert to several NM species. In the case of \( \text{Au}_{25}(S\text{CH}_{2}\text{CH}_{2}\text{Ph})_{18} \) the core destabilizes and forms smaller NMs, while the \( \text{Au}_{30}(S\text{-tBu})_{18} \) core destabilizes and forms
larger NMs species. When \( \text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18} \) is exchanged with \( n \)-butane thiol (green) it converts to \( \text{Au}_{25}(\text{S}-n\text{-butane})_{18} \). When \( \text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18} \) was exchanged with 2-methyl-1-propane thiol (blue) MALDI-MS and ESI-MS indicate that \( \text{Au}_{25}(\text{S}-2\text{-methyl-1-propane})_{18} \) forms after exchange. When \( \text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18} \) was exchanged with \( 2 \)-butane thiol (purple), multiple species form which are small than \( \text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18} \) with smaller core sizes.

When \( \text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18} \) was etched with 3-methyl-2-butane thiol (orange), smaller sized nanomolecules are formed as well. \( \text{Au}_{30}(\text{S}-t\text{Bu})_{18} \) when etched with \( n \)-butane thiol (green), the NM converts to larger NM species as indicated by MALDI-MS (right) and ESI-MS (left). \( \text{Au}_{30}(\text{S}-t\text{Bu})_{18} \) when etched with 2-methyl-1-propane thiol (blue) shows and increase in core size as well as conversion to \( \text{Au}_{30}(\text{S}-2\text{-methyl-1-propane})_{18} \). When \( \text{Au}_{30}(\text{S}-t\text{Bu})_{18} \) is exchanged with 2-butane thiol (purple) several NM species form, which are smaller than \( \text{Au}_{30}(\text{S}-t\text{Bu})_{18} \) and well as \( \text{Au}_{30}(\text{S}-2\text{-butane})_{18} \). When \( \text{Au}_{30}(\text{S}-t\text{Bu})_{18} \) is etched with 3-methyl-2-butane thiol (orange), smaller sized nanomolecules and \( \text{Au}_{30}(\text{S}-3\text{-methyl-2-butane})_{18} \) are formed. Future work involves crystallization of these NMs for sc-XRD and optimization of the synthesis protocols. These ligand exchanges have also brought about changes in their electronic structure as revealed by the UV-Vis, therefore future structural and computation studies will provide insights into the role of different ligands on the properties of the different AuNMs. As well as investigation of other the ligand effects on other systems to study the effect of the ligand on the overall nanostructure.
Table 6.2 Results summary of exchanges on \( \text{Au}_{25}(\text{SCH}_2\text{CH}_3\text{Ph})_{18} \) (black) and \( \text{Au}_{30}(\text{S-tBu})_{18} \) (black) with 2-propene-1-thiol (red), n-butane thiol (green), 2-methyl-1-propane thiol (blue), 2 butane thiol (purple), and 3-methyl-2-butane thiol (orange).

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<tr>
<th>Starting Product</th>
<th>Incoming Ligand</th>
<th>Thiol (m/z)</th>
<th>( \Delta ) Thiol (m/z)</th>
<th>Final Product</th>
<th>Summary</th>
</tr>
</thead>
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<td>( \text{Au}_{25}(\text{SCH}_2\text{H}<em>4\text{Ph})</em>{18} )</td>
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<td>HS-1-Bu</td>
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<td>( \text{Au}<em>{25}(\text{S-2-Me-1-Prop})</em>{18} )</td>
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</tr>
<tr>
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<td>HS-2-Bu</td>
<td>90.2</td>
<td>-48</td>
<td>( &lt; \text{Au}<em>{25}(\text{S-2-Bu})</em>{18} )</td>
<td>( \triangledown ) Core size</td>
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<td></td>
<td>HS-3-Me-2Bu</td>
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<td>( &lt; \text{Au}<em>{25}(\text{S-3-Me-2-Bu})</em>{18} )</td>
<td>( \triangledown ) Core size</td>
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<td>( \text{Au}<em>{30}(\text{S-tBu})</em>{18} )</td>
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<td>-16.1</td>
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<td>( \triangledown ) Core size</td>
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<td></td>
<td>HS-1-Bu</td>
<td>90.2</td>
<td>0</td>
<td>( &gt; \text{Au}<em>{30}(\text{S-n-butane})</em>{18} )</td>
<td>( \triangledown ) Core size</td>
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<tr>
<td></td>
<td>HS-2-Me-1-Prop</td>
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<td>( \text{Au}<em>{30}(\text{S-2Me-1Prop})</em>{18} ) and NMs ( &gt; \text{Au}<em>{30}(\text{S-2Me-1Prop})</em>{18} )</td>
<td>( \triangledown ) Core size and Exchange</td>
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<td>90.2</td>
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<td>( \text{Au}<em>{30}(\text{S-2-Bu})</em>{18} ) and NMs ( &lt; \text{Au}<em>{30}(\text{S-3Me-2Bu})</em>{18} )</td>
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REFERENCES


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100. Nimmala, P. R.; Dass, A., Au$_{99}$(SPh)$_{12}$ Nanomolecules: Aromatic Thiolate Ligand Induced Conversion of Au$_{144}$(SCH$_2$CH$_2$Ph)$_{60}$. *J Am Chem Soc* 2014, 136 (49), 17016-23.
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104. Rambukwella, M.; Sementa, L.; Fortunelli, A.; Dass, A., Core-Size Conversion of Au$_{36}$(SCH$_2$CH$_2$Ph)$_{24}$ to Au$_{36}$(S-tBu)$_{18}$ Nanomolecules. *J. Phys. Chem. C* 2017, 121 (27), 14929-14935.


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LIST OF APPENDICES
APPENDIX A: SUPPLEMENTARY INFORMATION FOR CHAPTER 2
Table S2.1. Crystallographic data for Au$_{21}$S(SAdm)$_{15}$

<table>
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<td>Space Group</td>
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**Table S2.2.** Reproducibility table for the successful synthesis of Au$_{21}$(SAdm)$_{15}$ this reaction was repeated 6 times.

![Au$_{21}$S$_{16}$ thermal ellipsoid model](image)

**Figure S2.1.** Au$_{21}$S$_{16}$ thermal ellipsoid model of the crystal structure this depicts the quality of anisotropic refinements.
Figure S2.2. Photograph of Au$_{21}$S(SAdm)$_{15}$ crystal

LB94 TZP Au$_{21}$S(SAdm)$_{15}$

Figure S2.3. Comparison of the TDDFT spectra of Au$_{21}$S(SAdm)$_{15}$ and Au$_{21}$S(SCH$_3$)$_{15}$ simulated using the LB94 xc-functional and TZP basis set showing that no qualitative differences are brought about in the optical response by the replacement of adamantyl with methyl residues.
Figure S2.4. TDDFT spectrum of Au$_{21}$S(SCH$_3$)$_{15}$ distinguished into Cartesian components, showing that the cluster exhibits a significant anisotropy. The spectrum is simulated using the B3LYP xc-functional.

Au$_{21}$S(SCH)$_{15}$ TDDFT Y component

Figure S2.5. Comparison of TDDFT spectra of Au$_{21}$S(SCH$_3$)$_{15}$ simulated using the SAOP and B3LYP xc-functionals limited to the most interesting y-Cartesian component Cartesian component, demonstrating an overall similarity between the two approaches, despite some quantitative differences especially in the ratio of intensities of the main peaks below 400 nm.
Figure S6. Energy plot of photon energy of Au$_2$S(SCH$_3$)$_{15}$: experimental spectrum at 78K compared with theoretical TDDFT-PBE spectrum.
APPENDIX B: SUPPLEMENTARY INFORMATION FOR CHAPTER 3
### Table S3.1. Crystallographic data for Au$_{30}$(S-rtBu)$_{18}$

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**Figure S3.1.** Detailed explanation of synthesis $\text{Au}_{30}(\text{S-}t\text{Bu})_{18}$
**Figure S3.2.** Pictorial representation of SEC preformed on final etch product to purify Au$_{30}$(S-tBu)$_{18}$

**Figure S3.3.** ESI-MS of crude, etched, and final SEC product, Au$_{30}$(S-tBu)$_{18}$
Figure S3.4. ESI mass spectra (black) and MALDI mass spectra (red) of Au$_{30}$(S-tBu)$_{18}$. ESI mass spectra shows the presence of +1 and +2 charge states.

Figure S3.5. Theoretical photo-absorption spectra of Au$_{30}$(S-tBu)$_{18}$ calculated at the TDDFT level of theory with TZP basis set and SAOP exchange-correlation potential.
Figure S3.6. Experimental temperature-dependent UV-vis-NIR Au$_{30}$(S-tBu)$_{18}$ nanomolecules plotted as photon energy where peaks marked by asterisk depicts an instrumental artifact.
APPENDIX C: SUPPLEMENTARY INFORMATION FOR CHAPTER 4
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**Table S4.1.** Replication table of the syntheses done to make Au_{46}(S-tBu)_{24} and Au_{65}(S-tBu)_{29}.
Fig. S4.2. Pictures and details of synthesis and etching of Au₀₉(S-tBu)₉ mixed species
Fig S4.3. Zoom-in of MALDI-MS of $\text{Au}_{46}(\text{S-tBu})_{24}$ and $\text{Au}_{65}(\text{S-tBu})_{29}$, with peaks assigned.

Fig. S4.4. (A) Optical absorption measurements carried out on samples with CARY and dissolving the samples in Carbon tetrachloride. (B) Plot of absorbance intensity ($A \times 10^4$) as a function of energy in eV and it was used to determine the HOMO-LUMO gap.
Figure S4.5. (A) Excited state absorption at different time delays for Au$_{23}$(S-$t$Bu)$_{16}$ after excitation at 370 nm. (B) Species-associated spectra obtained from global fit analysis and (C) Kinetic decay trace monitored at 620 nm.
Figure S4.6. (A) Excited state absorption at short time delays of Au30(S-tBu)18 from 200 fs to 1.6 ps, (B) Excited state absorption from 1.6 ps to 480 ps time delays, (C) Species-associated spectra obtained from global fit analysis for Au30 after excitation at 370 nm. (D) Kinetic decay trace monitored at 550 nm.
Figure S4.7. (A) Excited state absorption at different time delays for $\text{Au}_{46}(\text{S-tBu})_{24}$ after excitation at 370 nm. (B) Species-associated spectra obtained from global fit analysis. (C) Kinetic decay trace monitored at 530 nm.
Figure S4.8. (A) Excited state absorption at different time delays for Au_{65}(S-tBu)_{29} after excitation at 370 nm. (B) Species-associated spectra obtained from global fit analysis and (C) Kinetic decay traces monitored at 550 nm.

Table S4.2. Lifetimes obtained from femtosecond and nanosecond transient absorption measurements.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Intra core-state relaxation</th>
<th>Exciton decay</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au_{23}</td>
<td>1.9 ± 0.2 ps</td>
<td>0.75 ± 0.05 ns (40.9%), 43 ± 2 ns (16.5%), 1920 ± 50 ns (42.6%) □_{avg} = 830 ns</td>
</tr>
<tr>
<td>Au_{30}</td>
<td>0.32 ± 0.05 ps, 1.1 ± 0.1 ps</td>
<td>1.5 ± 0.1 ns (64.5%), 59 ± 2 ns (35.5%) □_{avg} = 22 ns</td>
</tr>
<tr>
<td>Au_{46}</td>
<td>1.2 ± 0.2 ps</td>
<td>4.4 ± 0.2 ns (44.3%), 68 ± 2 ns (65.7%) □_{avg} = 47 ns</td>
</tr>
<tr>
<td>Au_{65}</td>
<td>--</td>
<td>1.6 ± 0.1 ps (75%), 2.5 ± 0.1 ns (25%) □_{avg} = 0.63 ns</td>
</tr>
</tbody>
</table>
Figure S4.9. UV-Vis spectra and photographs of HS-tBu NMs before and after catalysis.

Figure S4.10. The standard error associated with the slope and intercept, reduced chi-square and Adj. R-square of the allometric power fit. $\text{Au}_{n}(\text{S-tBu})_m$ - Red – solid, squares; $\text{Au}_{n}(\text{SCH}\text{CH}_2\text{Ph})_m$ - olive – dash, spheres.
APPENDIX D: SUPPLEMENTARY INFORMATION FOR CHAPTER 5
es at 75 °C.

The resulting product is washed with excess methanol twice. The product from first etch is re-dissolved in 100µL toluene and 100 µL of t-butyl mercaptan and etched again for another 40 minutes at 75 °C. Then, the final product is washed with methanol twice to obtain the pure final product, of Au\textsubscript{36}(S\texttextsubscript{t}Bu)\textsubscript{34}.

Table S5.1. Reproducibility table for the exchange conditions used in the conversion of Au\textsubscript{36}(S\texttextsubscript{t}Bu)\textsubscript{18} to Au\textsubscript{36}(SPhX)\textsubscript{24} including: date, sample code, amount of Au\textsubscript{36}(S\texttextsubscript{t}Bu)\textsubscript{18} the amount of solvent used, the amount of thiol used, temperature, time, and final amount of Au\textsubscript{36}(SPhX)\textsubscript{24} collected.

<table>
<thead>
<tr>
<th>No.</th>
<th>Date</th>
<th>Sample Code</th>
<th>Au\textsubscript{36}(SPhX)\textsubscript{24} x=H or tBu</th>
<th>Au\textsubscript{36}(SPhX)\textsubscript{24} (mg)</th>
<th>Solvent (µL)</th>
<th>HSPhX (µL)</th>
<th>Temp (°C)</th>
<th>Time (h)</th>
<th>Au\textsubscript{36}(SPhX)\textsubscript{24} (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>04-11-2016</td>
<td>TJ2_14_C</td>
<td>H</td>
<td>1</td>
<td>600</td>
<td>54</td>
<td>80</td>
<td>16</td>
<td>0.7</td>
</tr>
<tr>
<td>2</td>
<td>04-21-2016</td>
<td>TJ2_21_1_A</td>
<td>H</td>
<td>1</td>
<td>600</td>
<td>54</td>
<td>80</td>
<td>16</td>
<td>0.8</td>
</tr>
<tr>
<td>3</td>
<td>04-21-2016</td>
<td>TJ2_21_1_B</td>
<td>H</td>
<td>1</td>
<td>600</td>
<td>54</td>
<td>80</td>
<td>16</td>
<td>0.8</td>
</tr>
<tr>
<td>4</td>
<td>05-05-2016</td>
<td>TJ2_29_A</td>
<td>H</td>
<td>5</td>
<td>3000</td>
<td>270</td>
<td>80</td>
<td>14</td>
<td>4.2</td>
</tr>
<tr>
<td>5</td>
<td>05-10-2016</td>
<td>TJ2_31_B</td>
<td>H</td>
<td>1</td>
<td>0</td>
<td>185</td>
<td>80</td>
<td>16</td>
<td>0.5</td>
</tr>
<tr>
<td>6</td>
<td>11-25-2016</td>
<td>TJ2_73</td>
<td>tBu</td>
<td>1</td>
<td>600</td>
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<td>48</td>
<td>80</td>
<td>0.6</td>
</tr>
<tr>
<td>7</td>
<td>01-24-2017</td>
<td>TJ2_86_A</td>
<td>H</td>
<td>1</td>
<td>600</td>
<td>54</td>
<td>80</td>
<td>16</td>
<td>0.8</td>
</tr>
<tr>
<td>8</td>
<td>01-24-2017</td>
<td>TJ2_86_B</td>
<td>tBu</td>
<td>1</td>
<td>600</td>
<td>50</td>
<td>80</td>
<td>16</td>
<td>0.8</td>
</tr>
</tbody>
</table>

*ST’s method involved, starting material Au\textsubscript{36}(Sph\texttextsubscript{t}Bu)\textsubscript{24} for the synthesis of Au\textsubscript{36}(S\texttextsubscript{t}Bu)\textsubscript{18} is prepared following the reported procedure\textsuperscript{11} and then purified using size-exclusion chromatography. 1mg of Au\textsubscript{36}(Sph\texttextsubscript{t}Bu)\textsubscript{24} is dissolved in 100µL toluene and 100 µL of t-butyl mercaptan. The mixture is stirred in an oil bath maintained at 75 °C for 30-40 mins. The resulting product is washed with excess methanol twice. The product from first etch is re-dissolved in 100µL toluene and 100µL of t-butyl mercaptan and etched again for another 40 minutes at 75 °C. Then, the final product is washed with methanol twice to obtain the pure final product, of Au\textsubscript{36}(S\texttextsubscript{t}Bu)\textsubscript{18}.

Table S5.2. Reproducibility table for exchange conditions used in the conversion of Au\textsubscript{36}(SPh-X)\textsubscript{24} to Au\textsubscript{36}(S\texttextsubscript{t}Bu)\textsubscript{18} including: date, sample code, amount starting material Au\textsubscript{36}(SPh-X)\textsubscript{24}, the amount of solvent used, the amount of thiol used, temperature, time, and final amount of Au\textsubscript{36}(S\texttextsubscript{t}Bu)\textsubscript{18} collected.
Table S5.3. Energy values for the \( \text{Au}_n(\text{SR})_M \) systems here considered. The nomenclature is the following: \( \text{Au}_n(\text{SR})_M \) = full nanomolecule; \( \text{Au}_n \) = gold cluster in the interacting configuration; \( (\text{SR})_M \) = crown or shell of ligands in the interacting configuration; \( \text{SR}_{\text{relaxed}} \) = fully relaxed SR thiol; \( \text{HSR}_{\text{relaxed}} \) = fully relaxed HSR thiol; \( \text{Au}_\text{atom} \) = isolated Au atom; \( \text{Au}_n(\text{SR})_M \, \text{anion-adiab} \) = total energy of \( \text{Au}_n(\text{SR})_M \) anion in the geometry of the neutral species; \( \text{Au}_n(\text{SR})_M \, \text{cation-adiab} \) = total energy of \( \text{Au}_n(\text{SR})_M \) anion in the geometry of the neutral species. All energies are in atomic units.

Fig. S5.1. MALDI-MS from manuscript Fig 1 b (blue). This a zoom-in of the spectra showing the corresponding peaks and their assignments.
Fig. S5.2. High laser fluence [left] and low laser fluence [right] MALDI-MS, and UV-Vis spectra of the starting material and the 5mins etched product, from the photographs it can be seen that a green color change occurred indicating that Au$_{36}$(SPh-tBu)$_{24}$ had began to core convert to Au$_{30}$(S-tBu)$_{18}$. The Au$_{30}$ core is observed in the MALDI-MS as indicated by the arrow and the 620nm peak in observed which is characteristic of Au$_{30}$(S-tBu)$_{18}$.

MALDI-MS

Fig. S5.3. MALDI-MS spectra of Au$_{30}$(S-tBu)$_{18}$ at high laser fluence (blue) and low laser fluence (green) (Final product from Au$_{36}$(SPh-tBu)$_{24}$ to Au$_{30}$(S-tBu)$_{18}$ conversion) to show that Au$_{30}$(S-tBu)$_{18}$ is the major product and there are no significant amount of Au$_{21}$(S-tBu)$_{15}$ or larger species present. The inset shows the full spectra in the mass range from 3000Da to 30000Da.
THE FOLLOWING IS A REPEAT OF THE INTERCONVERSION USING HSPh-tBu TO SHOW REPRODUCIBILITY

Fig. S5.4. Conversion of Au₃₀(S-tBu)₁₈ to Au₃₆(SPh-tBu)₂₄. (a) ESI-MS (b) MALDI-MS (c) UV-Vis and picture of the starting, intermediate and final products. Note that the peak marked by the asterisk corresponds to Au₂₈(TBBT)₂₀, which could be arising due to impurities in the starting materials or small amounts of Au₂₈ could be formed during the conversion.

Fig. S5.5. Conversion of Au₃₀(SPh-tBu)₂₄ to Au₃₀(S-tBu)₁₈. ESI-MS data shown (left) and MALDI-MS (middle). UV-Vis (right) and picture of the starting and final products
THE FOLLOWING IS ANOTHER TRIAL OF INTERCONVERSION USING HSPh-H TO SHOW REPRODUCIBILITY

Fig. S5.6. Conversion of Au_{36}(S-tBu)_{18} to Au_{30}(SPhH)_{24}. (a) ESI-MS data (b) MALDI-MS (c) UV-Vis and pictures of the starting, intermediate and final products

Fig. S5.7. Conversion of Au_{36}(SPh)_{24} to Au_{30}(S-tBu)_{18}. (a) ESI-MS data (b) MALDI-MS and (c) UV-Vis and picture of the starting and final products
VITA

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Education

Bachelor of Science Degree in Chemistry & Biology Dec 2013
University of South Carolina, Columbia, SC
Research Advisor: Dr. Stephen Morgan

Professional Experience

• Research Assistant July 2014-Present
  - University of Mississippi, Oxford, MS; Supervisor Dr. Amala Dass
    • 6 peer reviewed publications
    • Synthesis and publication of new nanomolecular structures
    • Crystal growth, atomic structure determination, and publication of new structures
    • Collaborated on 5 research projects
    • 1 National Level Oral Presentation at American Chemical Society meeting
    • 3 Oral presentations at American Chemical Society SERMACS meetings
    • 1 Poster presentation at American Chemical Society SERMACS meetings
    • Experienced in several analytical techniques including: nESI-Q-TOF-MS, MALDI-TOF-MS, UV-Vis spectroscopy, low temperature UV-Vis spectroscopy, x-ray crystallography (sc-XRD), ICP-MS, HPLC-MS, SEC, chromatography, and electrochemical methods (CV and DPV)
    • Fabrication of in-house emitters for the nano-ESI source
    • Maintenance and general upkeep of analytical instruments
    • 3D-printing and modeling of molecular structures

• Teaching Assistant Jan 2016-May 2018
  - University of Mississippi, Oxford, MS; Supervisor Dr. John Wiginton
    • Prepared General Chemistry laboratory materials, graded exams/assignments, and gave lectures
    • 5 semesters; 250+ students

  - University of Mississippi, Oxford, MS; Supervisor Dr. Amala Dass
    • Analysis using ESI and MALDI mass spectrometry for publication quality determination of a wide variety of compounds for the Department of Chemistry & Biochemistry and Department of Pharmacy

• Research Assistant Jan 2013-Jun 2014
University of South Carolina, Columbia, SC; Supervisor Dr. Stephen Morgan

- Methodology development and analysis for determination of age and degradation of magnetic tape by attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) microscopy, and titration
- Development of sample preparation techniques for quantitative analysis of bloodstain age using ATR-FTIR with an emphasis on method development

Publications


Graduate Presentations

- “Core Size Interconversions of Nanomolecules Au₃₀(S-tBu)₁₈ & Au₃₆(SPhX)₂₄” Oral Presentation, 255th American Chemical Society National Meeting, New Orleans, LA, Mar 2018

- “Core Size Interconversions of Nanomolecules Au₃₀(S-tBu)₁₈ & Au₃₆(SPhX)₂₄” Oral Presentation, 2017 Southeastern Regional American Chemical Society meeting, Charlotte, NC, Nov 2017
• “Crystal Structure and Theoretical Analysis of Green Gold \( \text{Au}_{30}(\text{S-}t\text{-Bu})_{18} \) Nanomolecules and Their Relation to \( \text{Au}_{30}\text{S(}t\text{-Bu})_{18} \)” Oral Presentation; 2016 Southeastern Regional American Chemical Society meeting, \textit{Columbia, SC, Oct 2016}


• “Synthesis and Characterization of Bulky-Thiolated Nanomolecules.” Oral Presentation at 2015 Southeastern Regional American Chemical Society meeting, \textit{Memphis, TN, Oct 2015}

• “Synthesis and Characterization of Aromatic-Thiolated Nanoparticles from \( \text{Au}_{25}(\text{SR})_{18} \).” Poster presentation at 2014 Southeastern Regional American Chemical Society meeting, \textit{Nashville, TN, Nov 2014}

Undergraduate Presentations

• “Observation of Natural and Artificial Magnetic Tape Aging Using Acid Titration and Infrared Spectroscopy” 1st place poster presentation at 4th Annual Andrews Graduate Symposium, \textit{Starkville, MS, May 2014}

• Dr. Morgan, Stephen; Jones, Tanya; Bensussen, Alena; Bringley, Eric, "Undergraduate Research at USC: Real world Applications of Chemistry” Board of Trustees Meeting, \textit{University of South Carolina, Columbia, SC, Dec 2013}

• Jones, Tanya; Bensussen, Alena, "Fourier Transform Infrared Spectroscopy and its Application in Determining Bloodstain Age: Preliminary Study with Emphasis on Method Development” 1st place abstract, Discovery Day, \textit{University of South Carolina, Columbia, SC, Apr 2013}

Honors, Fellowships, & Organizations

• Cover art submitted to Journal of Physical Chemistry C with manuscript “Bulky \( t \)-Butyl Thiolated Nanomolecular Series: Synthesis, Characterization, Optical Properties and Electrocatalysis” selected for publication

• Graduate Assistant in Areas of National Need (GAANN) fellow \textit{Jan-May 2016}  
  Supervisor: Dr. Susan Pedigo

• Member of the American Chemical Society \textit{Induction 2014}

Collaboration Experience

• Dr. Ramki Guda, University of Michigan, Collaboration for transient absorption measurements of gold thiolated nanomolecules and publication of three manuscripts together

• Dr. Alessandro Fortunelli, University of Geneva for collaboration in DFT calculations from crystallographic data on gold thiolated nanomolecules and publication of four manuscripts

• Dr. James Cizdziel and Dr. Carolyn Freiwald, University of Mississippi collaboration for heavy metal trace analysis of soils samples from a historical cemetery using ICP-MS
• Dr. Jared Delcamp University of Mississippi collaboration for sc-XRD analysis of organic molecules and publication of a manuscript
• Dr. Samuen Chakraborty & Ms. Leigh Sumner, University of Mississippi for collaboration for electrocatalysis experimentation of gold thiolated nanomolecules and publication of a manuscript

Graduate Mentoring Experience
• Trained 3 new graduate peers, 3 undergraduate students, and 1 high school student in analytical laboratory techniques, research, gold nanomolecule synthesis, chromatography, UV-Vis spectroscopy, x-ray crystallography, mass spectroscopy, related software, and presentation of research

Undergraduate Mentoring Experience
• Trained 2 incoming undergraduates to take over aforementioned undergraduate research projects