ALKANE CHALCOGENOLATE - PROTECTED METAL NANOPARTICLES:
SYNTHESIS, FORMATIONS, CHARACTERIZATIONS, AND INTERFACE
INVESTIGATIONS

A Dissertation
submitted to the Faculty of the
Graduate School of Arts and Sciences
of Georgetown University
in partial fulfillment of the requirements for the
degree of
Doctor of Philosophy
in Chemistry

By

Oksana Zaluzhna, M.S.

Washington, DC
April 25, 2012
Copyright 2012 by Oksana Zaluzhna
All Rights Reserved
ABSTRACT

Organo selenolate - protected gold (Au) nanoparticles (NPs) have shown high potential for nanoelectronic applications, where electrochemical studies are crucial for understanding the charge transfer mechanism between the metal core and ligand, specifically the anchoring element (Se). Complete interfacial characterization of the NPs is essential prior to electrochemical studies to confirm uniform composition. This dissertation focuses on the successful synthesis of such homogenous NPs and interfacial characterizations between the Au core and the ligand.

Previous mechanistic studies into the renowned Brust - Schiffrin method (BSM), i.e., one- and two-phase syntheses, performed on thiolate-stabilized Au NPs identified that NP homogeneity was dependent on the precursor species prior to the formation of NPs. The research herein produced a number of key findings: the effect of encapsulated water and the amount of phase-transfer agent in the two-phase BSM were significant factors for producing higher quality NPs when comparing dialkyl disulfides and dialkyl diselenides as ligands precursors; the one-phase BSM was found to be a better route than the two-phase BSM for the production of homogenous NPs, since it produced only one intermediary species. Moreover, the effects of the ligand and alkyl chain lengths with
different chalcogen anchoring elements, *i.e.*, S, Se, and Te, on the resultant NPs were characterized by a variety of analytical techniques.

Additionally, the prospective utilization of alkyl selenocyanates as the ligand precursors for synthesis of alkane selenolate - protected Au NPs is demonstrated in this dissertation. Although the successful formation of Au NPs was achieved, the existence of cyano species on the surface of the metal core was experimentally challenging to determine.

The main conclusions drawn from this research are the ability to synthesize homogenous alkane selenolate - protected Au NPs by having a deeper understanding of the chemical structures of the precursor species in the NPs synthesis. In brief summary, this research includes fundamental investigations on the interfacial behavior between the Au core and alkane selenolate ligand that are essential for electrochemical and charge transfer studies that further the potential for application in the nanoelectronics field.
I would like to express my huge gratitude to all those who has supported me during the last six years of my journey at Georgetown University.

First I would like to thank my Ph.D. advisor and mentor, Dr. YuYe Tong. I was very fortunate to work under his guidance and support. Dr. Tong created a productive, encouraging, and also fun environment to work in. He organized numerous conference trips, skiing, fishing outings, and BBQs, which made this experience even more enjoyable.

I would also like to thank all the lab members that I have met along the way: Augusta Hofstead-Duffy, Ying Li, Ceren Susut, Bingchen Du, Dianne Atienza, Dejun Chen, Bolian Xu, Yangwei Liu, Thomas Hsu-Yao, Kevin Browne, Steven Ryckbosch, Ashley Zacca, Latoya Silverton, Lindsey Brightful, and Yuan Gao, all of whom were great co-workers and some become life-long friends.

I am very grateful to the entire chemistry department of Georgetown University. Specifically, I would like to thank my committee members, Dr. Moasser, Dr. Rubinson, Dr. Jorabchi, and Dr. Allison for continued guidance during my doctoral studies. I would also like to thank Travis Hall, Inez Traylor, Kathleen Bayne, Dr. Mohammad Itani, and Yen Miller for helping with all financial and departmental processes.

I am tremendously grateful to Ying Li, who has been incredible lab partner. Her knowledge, guidance, and support with research, papers, and presentations have been invaluable. I would also like to thank Dr. Li, Dr. Craig, Mr. Goldey, and Dr. Davis for
help with instrumentation; Dr. Allison at National Institute of Standards and Technology (NIST) for all theoretical calculations; Dr. Zangmeister from NIST for all the XPS measurements and support; Dr. Chiou and Dr. Lai at UMD NISP for TEM facility assistance and help; and Georgetown Graduate School and NSF (CHEM 04-56848 and CHEM 07-02859) for the financial support.

In addition to the people from Georgetown University, I would also like to show my appreciation to many friends, Ewa Topor, Augusta Hofstead-Duffy, Stacey Wood, Rachel Rhoney, Karina Yudharto, Bithiah Lafontant, Brian Elderbroom, Jamie and Terra Roberts, Adriana Pavlysh, Sean McLeod, Brian Muldoon, and yoga studio Serenity. All have given me great deal of support through these years.

I am eternally grateful to my little family, Tim Love and Jazz. Thank you for your love, support, listening, hugs, laughs, happiness, and never ending confidence. Thank you for keeping me positive, and giving me the energy to continue on. I love you both.

And most importantly, thank you to the most important and so-deeply loved women in my life, my mother and grandmother. You have always been my strength and my motivation. Your confidence and pride in me, your support and your unending love have made me who I am today. I dedicate this thesis to you.
TO MY MOTHER AND GRANDMOTHER
# Table of Contents

Chapter I Introduction

1.1 Background ........................................................................................................... 1

1.2 Motivational Aspects ......................................................................................... 3

1.3 Self - Assembled Monolayers ............................................................................. 6

1.4 Brust - Schiffrin Method (BSM) .......................................................................... 8

1.5 Alkane Chalcogenolate - Protected Nanoparticles (NPs) ................................. 10

1.6 Research Outline ................................................................................................ 11

1.7 References ............................................................................................................ 25

Chapter II Synthesis and Characterization Methods

2.1 Chemicals ............................................................................................................. 27

2.2 Synthesis of Ligands .......................................................................................... 28

  2.2.1 Synthesis of Dialkyl Disulfides .................................................................... 28

  2.2.2 Synthesis of Dialkyl Diselenides .................................................................. 28

  2.2.3 Synthesis of Dialkyl Ditellurides .................................................................. 29

  2.2.4 Synthesis of Alkyl Selenocyanates ............................................................... 29

2.3 Synthesis of Alkane Chalcogenolate - Protected Au NPs ................................. 29

  2.3.1 Synthesis of Alkane Thiolate - Protected Au NPs ........................................ 29

  2.3.2 Synthesis of Alkane Selenolate - Protected Au NPs ................................. 30

  2.3.3. Synthesis of Alkane Telluroxide - Protected Au NPs .............................. 31

2.4 Chemical Methods .............................................................................................. 32
2.4.1 Nuclear Magnetic Resonance (NMR) ................................................. 32
2.4.2 Raman Spectroscopy ........................................................................ 32
2.4.3 Infrared (IR) Spectroscopy ................................................................. 33
2.4.4 Transmission Electron Microscopy (TEM) ........................................... 33
2.4.5 Energy Dispersive X-Ray Spectroscopy (EDS) ................................... 34
2.4.6 UV-Vis Spectroscopy ........................................................................ 34
2.4.7 Thermogravimetric Analysis (TGA) .................................................... 34
2.4.8 X-Ray Photoelectron Spectroscopy (XPS) ........................................... 34
2.4.9 Density Functional Theory (DFT) Calculations Methodology ............ 35
2.5 References ............................................................................................ 37

Chapter III Synthesis and Characterization of Dialkyl Diselenides

3.1 Introduction ........................................................................................... 38
3.2 Synthesis of Ligands ............................................................................ 39
3.3 Characterization of Ligands ................................................................. 40
3.4 Conclusion ........................................................................................... 42
3.5 References ........................................................................................... 49


4.1 Introduction ........................................................................................... 50
4.2 Experimental Section ............................................................................ 52
4.3 Results and Discussions ...................................................................... 53
4.4 Conclusion ........................................................................................... 59
Chapter V Mechanistic Insights on One - Phase vs. Two - Phase Brust - Schiffrin Method
Synthesis of Au Nanoparticles with Dioctyl - Diselenides

5.1 Background ........................................................................................................ 73
5.2 Experimental Section ....................................................................................... 75
5.3 Results and Discussions .................................................................................. 76
5.4 Conclusion ......................................................................................................... 80
5.5 References ........................................................................................................ 95

Chapter VI Effect of Anchoring Elements and Alkyl Chain Length on Formed Gold Nanoparticles

6.1 Introduction ...................................................................................................... 97
6.2 Experimental Section ..................................................................................... 99
6.3 Results and Discussions ................................................................................... 100
   6.3.1 Dialkyl Dichalcogenides ........................................................................... 100
   6.3.2 Alkane Chalcogenolate - Protected Gold Nanoparticles ....................... 102
6.4 Conclusion ....................................................................................................... 106
6.5 References ....................................................................................................... 122

Chapter VII Synthesis and Characterization of Alkyl Selenocyanates

7.1 Introduction ..................................................................................................... 124
7.2 Synthesis of Ligands ....................................................................................... 125
7.3 Characterization of Ligands ........................................................................... 126
7.4 References ...................................................................................................... 134
Chapter VIII Synthesis of Gold and Silver Nanoparticles with Alkyl Selenocyanates

8.1 Introduction.................................................................................................................... 135
8.2 Experimental Section..................................................................................................... 137
8.3 Results and Discussions................................................................................................. 139
8.4 Conclusion ...................................................................................................................... 142
8.5 References...................................................................................................................... 155

Concluding Remarks............................................................................................................. 157

Appendix Spectroscopic Evidence of a Bidentate - Binding of Meso - 2, 3 - Dimercaptosuccinic Acid on Silver Nanoclusters

A.1 Introduction..................................................................................................................... 163
A.2 Synthesis of DMSA - Protected Ag NCs ................................................................. 165
A.3 Characterization of the DMSA - Protected Ag NCs ................................................ 165
A.4 Conclusion ...................................................................................................................... 170
A.5 References ...................................................................................................................... 179
LIST OF ILLUSTRATIONS

Figure 1.1  14
Surface science evolution toward nanoscience in terms of materials studied over a period of about 50 years.

Figure 1.2  15
Comparison of known surface structures determined in different fields by only orders of magnitude.

Figure 1.3  16
Faraday’s colloidal suspension of gold with a red laser beam clearly visible by the Tyndall effect (a), and high-resolution transmission electron microscope images of individual colloidal gold particles (b).

Figure 1.4  17
The time evolution of citations from Faraday’s 1857 NPs discovery.

Figure 1.5  18
Schematic drawing representing the changes on optical behavior of nanoparticles associated with their size (a) and corresponding colors of the NPs solutions (b).

Figure 1.6  19
Metal nanoclusters in the range from 1-100 nm.

Figure 1.7  20
Donor - Bridge - Acceptor systems.

Figure 1.8  21
Schematic view of bare electrodes (a), schematic view of total system (sample plus electrodes) (b), and schematic view of system/molecules investigated (c).

Figure 1.9  22
Difference in between the density of states of the semi - infinite electrodes with and without the molecules in Figure 1.8 in between.

Figure 1.10  23
Scheme of two - phase and one - phase Brust - Schiffrin method for synthesis of thiolate - protected Au NPs.

Figure 1.11  24
Scheme of two - phase mechanism for chalcogenolate - protected metal NPs.
Figure 3.1
$^1$H NMR spectra of (a) (C$_{12}$H$_{25}$Se)$_2$, (b) (C$_8$H$_{17}$Se)$_2$, and (c) (C$_6$H$_{13}$Se)$_2$.

Figure 3.2
$^{13}$C NMR spectra with assigned number of carbons in (a) (C$_{12}$H$_{25}$Se)$_2$, (b) (C$_8$H$_{17}$Se)$_2$, and (c) (C$_6$H$_{13}$Se)$_2$.

Figure 3.3
HMOC NMR spectrum of (C$_8$H$_{17}$Se)$_2$ in C$_6$D$_6$.

Figure 3.4
$^{77}$Se NMR spectra of (a) (C$_{12}$H$_{25}$Se)$_2$, (b) (C$_8$H$_{17}$Se)$_2$, and (c) (C$_6$H$_{13}$Se)$_2$.

Figure 3.5
IR spectra of (a) (C$_{12}$H$_{25}$Se)$_2$, (b) (C$_8$H$_{17}$Se)$_2$, and (c) (C$_6$H$_{13}$Se)$_2$.

Figure 3.6
Raman spectra of (a) (C$_{12}$H$_{25}$Se)$_2$, (b) (C$_8$H$_{17}$Se)$_2$, and (c) (C$_6$H$_{13}$Se)$_2$.

Figure 4.1
$^1$H NMR spectra of the intermediate solutions with the same Au:Se ratio = 1:1 but different TOAB:Au ratios: (a) 3:1 (TAuSe-311), (b) 2:1 (TAuSe-211), and (c) 1:1 (TAuSe-111); (d) 3:1 but with [TOA][AuBr$_4$] : 2TOAB : 0.5(C$_{12}$H$_{25}$Se)$_2$ (TAuSe-311C), and of reference materials: (e) 3TOAB : 0.5(C$_{12}$H$_{25}$Se)$_2$ (TAuSe-301), (f) (C$_{12}$H$_{25}$Se)$_2$ (TAuSe-001), and (g) 3TOAB : 1HAuCl$_4$ (TAuSe-310); all in C$_6$D$_6$.

Figure 4.2
Raman spectra of the intermediate solutions with the same Au:Se ratio = 1:1 but different TOAB:Au ratios: (a) 3:1 (TAuSe-311), (b) 2:1 (TAuSe-211), and (c) 1:1 (TAuSe-111); (d) 3:1 but with [TOA][AuBr$_4$] : 2TOAB : 0.5(C$_{12}$H$_{25}$Se)$_2$ (TAuSe-311C), and of reference materials: (e) 3TOAB : 0.5(C$_{12}$H$_{25}$Se)$_2$ (TAuSe-301), (f) (C$_{12}$H$_{25}$Se)$_2$ (TAuSe-001), and (g) 3TOAB : 1HAuCl$_4$ (TAuSe-310). The dashed vertical lines are used to identify similar bands. See Figure 4.3 for corresponding full Raman spectra.

Figure 4.3
Full Raman spectra of the intermediate solutions with the same Au:Se ratio = 1:1 but different TOAB:Au ratios: (a) 3:1 (TAuSe-311), (b) 2:1 (TAuSe-211), and (c) 1:1 (TAuSe-111); (d) 3:1 but with [TOA][AuBr$_4$] : 2TOAB : 0.5(C$_{12}$H$_{25}$Se)$_2$ (TAuSe-311C), and of reference materials: (e) 3TOAB : 0.5(C$_{12}$H$_{25}$Se)$_2$ (TAuSe-301), (f) (C$_{12}$H$_{25}$Se)$_2$ (TAuSe-001), and (g) 3TOAB : 1HAuCl$_4$ (TAuSe-310)$_6$.
Figure 4.4
Geometrically optimized molecular structures by the DFT calculations: (a) [HAu(III)Br₄]{SeC₄H₉}₂ and (b) Au(III) {SeC₄H₉}₂. Se is depicted in yellow, Au in the reddish color, and Br in the bluish color; the alkyl chains are bonded to the Se atoms and are clearly distinguishable.

Table 4.1
Cartesian coordinates [Å] of [Au(III)Br₄]⁻{SeC₄H₉}₂ and Au(III) {SeC₄H₉}₂.

Figure 4.5
¹H NMR spectra of the intermediate solutions with the same Au:S ratio = 1:1 but different TOAB:Au ratios: (a) 3:1 (TAuS-311), (b) 2:1 (TAuS-211), and (c) 1:1 (TAuS-111), (d) 3:1 but with [TOA][AuBr₄] : 2TOAB : 0.5 (C₁₂H₂₅S)₂ (TAuS-311C); and of reference materials: (e) 3TOAB : 0.5 (C₁₂H₂₅S)₂ (TAuS-301), (f) (C₁₂H₂₅S)₂ (TAuS-001), and (g) 3TOAB : 1HAuCl₄ (TAuS-310), all in C₆D₆.

Figure 4.6
Raman spectra of the intermediate solutions with the same Au:S ratio = 1:1 but different TOAB:Au ratios: (a) 3:1 (TAuS-311), (b) 2:1 (TAuS-211), and (c) 1:1 (TAuS-111), (d) 3:1 but with [TOA][AuBr₄] : 2TOAB : 0.5 (C₁₂H₂₅S)₂ (TAuS-311C); and of reference materials: (e) 3TOAB : 0.5 (C₁₂H₂₅S)₂ (TAuS-301), (f) (C₁₂H₂₅S)₂ (TAuS-001), and (g) 3TOAB : 1HAuCl₄ (TAuS-310). See Figure 4.7 for corresponding full Raman spectra.

Figure 4.7
Full Raman spectra of the intermediate solutions with the same Au:S ratio = 1:1 but different TOAB:Au ratios: (a) 3:1 (TAuS-311), (b) 2:1 (TAuS-211), and (c) 1:1 (TAuS-111), (d) 3:1 but with [TOA][AuBr₄] : 2TOAB : 0.5 (C₁₂H₂₅S)₂ (TAuS-311C), and of reference materials: (e) 3TOAB : 0.5 (C₁₂H₂₅S)₂ (TAuS-301), (f) (C₁₂H₂₅S)₂ (TAuS-001), and (g) 3TOAB : 1HAuCl₄ (TAuS-310).

Figure 4.8
EPR spectra of TAuS-311 as a representative.

Figure 4.9
TEM images and corresponding size distribution histograms of Au NPs by adding aqueous solution of 10 equiv. NaBH₄ to (a) TAuS-311, (b) TAuS-311C, (c) TAuSe-311, and (d) TAuSe-311C. The respective average sizes are (a) 1.9 ± 0.3 nm, (b) 3.64 ± 1.6nm, (c) 2.43 ± 0.8nm, and (d) 5.77 ± 2.1 nm, respectively.

Figure 4.10
Summary of Chapter IV.
Figure 5.1
TEM images of octaneselenoate-stabilized Au NPs synthesized by (a) one-phase and (b) two-phase BSM syntheses. The insets are: (i) UV-vis spectra and (ii) the respective size distributions that give the average size of 2.0 nm ± 0.5 nm for the former (a) and 4.2 nm ± 1.6 nm for the latter (b) (Note: both after centrifugation).

Figure 5.2
1H (a and b) and 13C NMR (c and d) spectra of the one-phase intermediate (black) and the pure (C8Se)2 (red) respectively. The arrows indicate the assignments of the respective peaks.

Figure 5.3
Raman spectra of (a) dioctyl diselenide, (b) the concentrated one-phase intermediate after removing THF, i.e., 1 equiv. of HAuCl4 and 0.5 equiv. of dioctyl diselenide, and (c) aqueous HAuCl4 solution.

Figure 5.4
1H NMR spectra of (a) 3TOAB + 0.5(C8Se)2, (b) 1TOAB + 1HAuCl4 + 0.5(C8Se)2, (c) 1.25TOAB + 1HAuCl4 + 0.5(C8Se)2, (d) 2TOAB + 1HAuCl4 + 0.5(C8Se)2, and (e) 3TOAB + 1HAuCl4 + 0.5(C8Se)2 in C6D6.

Figure 5.5
Enlarged zone of 1H NMR spectra of (a) 3TOAB + 0.5(C8Se)2, (b) 1TOAB + 1HAuCl4 + 0.5(C8Se)2, (c) 1.25TOAB + 1HAuCl4 + 0.5(C8Se)2, (d) 2TOAB + 1HAuCl4 + 0.5(C8Se)2, and (e) 3TOAB + 1HAuCl4 + 0.5(C8Se)2 in C6D6.

Table 5.1
Proton Numbers of the (C8Se)2 per [TOA]+ for ratios (a) 3 TOAB + 0.5 (C8Se)2, (b) 1 TOAB + 1 HAuCl4 + 0.5 (C8Se)2, (c) 1.25 TOAB + 1 HAuCl4 + 0.5 (C8Se)2, (d) 2 TOAB + 1 HAuCl4 + 0.5 (C8Se)2, and (e) 3 TOAB + 1 HAuCl4 + 0.5 (C8Se)2 in C6D6. (Note: the numbers of protons for all sample in α-CH2-N+ from TOA+ was assigned as 8). Raman spectra of (a) (C12H25Se)2, (b) (C8H17Se)2, and (c) (C6H13Se)2.

Table 5.2
DFT calculated vibrational frequencies for reference molecules.

Table 5.3
Partial DFT calculated vibrational frequencies for Cl2AuSe(C8H17)Cl2 complex.
Table 5.4
Some representative DFT calculated vibrational frequencies for X2AuSe(C8H17)X-OH complexes.

Table 5.5
Cartesian coordinates (XMol format, Angstroms) for optimized structures of 19 species calculated at the B3LYP/cc-pVDZ level of theory.

Table 5.6
XPS binding energies of (a) solid (C12Se)2, (b) one-phase intermediate with 1Au : 0.5(C8Se)2, (c) two-phase intermediate with 3TOAB : 1Au : 0.5(C8Se)2, and (d) two-phase intermediate with 2TOAB : 1Au : 0.5(C8Se)2.

Scheme 5.1
Summary of Chapter V.

Figure 6.1
1H NMR spectra of: (A) dialkyl disulfide (R2S)2 with (a) C12, (b) C8, and (c) C6 alkyl chains; (B) dialkyl diselenide (R2Se)2 with (d) C12, (e) C8, and (f) C6 alkyl chains; and (C) dialkyl ditellurides (R2Te)2 with (g) C12, (h) C8, and (j) C6 alkyl chains.

Figure 6.2
13C NMR spectra of: (A) dialkyl disulfide (R2S)2 with (a) C12, (b) C8, and (c) C6 alkyl chains; (B) dialkyl diselenide (R2Se)2 with (d) C12, (e) C8, and (f) C6 alkyl chains; and (C) dialkyl ditellurides (R2Te)2 with (g) C12, (h) C8, and (j) C6 alkyl chains.

Figure 6.3
77Se NMR of (a) (C6H13Se)2 - black, (C8H17Se)2 - red, and (C12H25Se)2 - blue, (b) 125Te NMR spectra of (C6H13Te)2 - black, (C8H17Te)2 - red, and (C12H25Te)2 - blue.

Figure 6.4
Raman spectra of (a) (C6H13S)2, (b) (C8H13Se)2, (c) (C8H17Se)2, (d) (C12H25Se)2, (e) (C6H13Te)2, (f) (C8H17Te)2, and (g) (C12H25Te)2.

Figure 6.5
Raman spectra of (a) (C12S)2, (b) (C12Se)2, and (c) (C12Te)2 ligands.

Figure 6.6
TEM images and size distribution graphs of (a) C6S - Au NPs, (b) C8S - Au NPs, (c) C12S - Au NPs, (d) C6Se - Au NPs, (e) C8Se - Au NPs, (f) C12Se - Au NPs, (g) C6Te - Au NPs, (h) C8Te - Au NPs, and (j) C12Te - Au NPs.
Figure 6.7  
UV - Vis spectra of (a) C6S - Au NPs, (b) C8S - Au NPs, (c) C12S - Au NPs, (d) C6Se - Au NPs, (e) C8Se - Au NPs, (f) C12Se - Au NPs, (g) C6Te - Au NPs, (h) C8Te - Au NPs, and (j) C12Te - Au NPs.

Figure 6.8  
$^1$H spectra of (A) RSe - Au NPs, where R = C6 (black), C8 (red), and C12 (blue); and (B) RTe - Au NPs, where R = C6 (black), C8 (red), and C12 (blue).

Figure 6.9  
$^{13}$C spectra of (A) RSe - Au NPs, where R = C6 (black), C8 (red), and C12 (blue); and (B) RTe - Au NPs, where R = C6 (black), C8 (red), and C12 (blue).

Figure 6.10  
XPS spectra of Au 4f$_{7/2}$ : (a) C12S - Au NPs, (b) C12Se - Au NPs, and (c) C12Te - Au NPs.

Figure 6.11  
XPS spectra of (a) S 2p in C12S - Au NPs, (b) Se 3d in C12Se - Au NPs, and (c) Te 3d in C12Te - Au NPs.

Figure 6.12  
TGA results for (a) C12S - Au NPs, (b) C12Se - Au NPs, and (c) C12Te - Au NPs.

Figure 6.13  
IR results for (a) (C$_{12}$H$_{25}$S)$_2$, (b) C12S - Au NPs, (c) (C$_{12}$H$_{25}$Se)$_2$, (d) C12Se - Au NPs, (e) (C$_{12}$H$_{25}$Te)$_2$, and (f) C12Te - Au NPs.

Figure 6.14  
Summary of Chapter VI.

Figure 7.1  
$^1$H NMR spectra of (a) C$_6$H$_{13}$SeCN, (b) C$_8$H$_{17}$SeCN, and (c) C$_{12}$H$_{25}$SeCN.

Figure 7.2  
$^{13}$C NMR spectra of (a) C$_6$H$_{13}$SeCN, (b) C$_8$H$_{17}$SeCN, and (c) C$_{12}$H$_{25}$SeCN in A) 95 - 104 ppm and B) 10 - 40 ppm range.

Figure 7.3  
HSQCAD NMR of C$_6$H$_{13}$SeCN in C$_6$D$_6$.

Figure 7.4  
$^{77}$Se NMR of (a) C$_6$H$_{13}$SeCN, (b) C$_8$H$_{17}$SeCN, and (c) C$_{12}$H$_{25}$SeCN.
Figure 7.5
IR spectra of (a) C₆H₁₃SeCN, (b) C₈H₁₇SeCN, and (c) C₁₂H₂₅SeCN.

Figure 7.6
Raman spectra of (a) C₆H₁₃SeCN, (b) C₈H₁₇SeCN, and (c) C₁₂H₂₅SeCN.

Figure 8.1
TEM image (a), size distribution histogram (b), and UV - Vis spectrum (c) of the 2.0 ± 0.3 nm C₁₂Se(CN) - Au NPs.

Figure 8.2
TEM and average sizes of Au NPs synthesized by 2p BSM with (a) C₆H₁₃SeCN, (b) C₈H₁₇SeCN, and (c) C₁₂H₂₅SeCN as precursor ligands.

Figure 8.3
TEM and average sizes of Au NPs synthesized by 1p BSM with (a) C₆H₁₃SeCN with average sizes of 2.8 ± 0.81 nm, (b) C₈H₁₇SeCN with average sizes of 2.4 ± 0.60 nm, and (c) C₁₂H₂₅SeCN with average sizes of 2.0 ± 0.32 nm as precursor ligands.

Figure 8.4
¹H NMR spectra of (a) C₁₂Se(CN) - Au NPs, and (b) pure C₁₂H₂₅SeCN ligand.

Figure 8.5
IR spectra of (a) C₁₂Se(CN) - Au NPs, and (b) pure C₁₂H₂₅SeCN ligand.

Figure 8.6
XPS of (a) Se d₅/₂, and (b) N 1s region in C₁₂Se(CN) - Au NPs.

Figure 8.7
XPS spectra of C₁₂Se(CN) - Au NPs of (a) Au f₇/₂ and (b) C 1s XPS region.

Figure 8.8
TGA spectra of C₁₂Se(CN) - Au NPs.

Figure 8.9
TEM image (a), size distribution histogram (b), and UV - Vis spectrum (c) of the 2.9 ± 0.3 nm C₁₂Se(CN) - Ag NPs.

Figure 8.10
IR spectra of (a) C₁₂H₂₅SeCN and (b) C₁₂Se (CN) - Ag NPs.

Figure 8.11
TGA curve of the C₁₂Se (CN) - Ag NPs.
Figure A.1
TEM images of low (a) and high (b) magnification, the corresponding size distribution histogram (c, 340 counts), and the UV - Vis spectrum of the Ag\textsubscript{7}(DMSA)\textsubscript{4} NCs.

Figure A.2
EDS spectra and analysis of Ag\textsubscript{7}(DMSA)\textsubscript{4} nanoclusters.

Figure A.3
\textsuperscript{13}C NMR spectra of the free DMSA molecules (top) and Ag\textsubscript{7}(DMSA)\textsubscript{4} NCs (bottom) recorded in D\textsubscript{2}O with DDS as internal reference.

Figure A.4
Raman spectra of the DMSA molecule (bottom) and the Ag\textsubscript{7}(DMSA)\textsubscript{4} NCs (top).

Figure A.5
Raman Spectra of Ag\textsubscript{7}(DMSA)\textsubscript{4} NCs. In this spectrum, the same area of the sample is taken 3 times: green - 1\textsuperscript{st}, blue - 2\textsuperscript{nd} and red - 3\textsuperscript{rd} (black - glass spectrum for comparison). It is noted that with decomposition of the sample, the formation of S-S bond (\(~ 500 \text{ cm}\textsuperscript{-1}\)) is possible.

Figure A.6
IR spectra of the free DMSA molecules (top) and the Ag\textsubscript{7}(DMSA)\textsubscript{4} NCs (bottom).

Figure A.7
The optimized 3D structure of Ag\textsubscript{7}(DMSA)\textsubscript{4} with the color scheme: Ag - brown, Sulfur - yellow, Carbon - blue, Oxygen - red, and Hydrogen – white.

Figure A.8
Summary of Appendix.
CHAPTER I
INTRODUCTION

1.1 Background

Surface science is considered to be the foundation for nanoscience and nanotechnology, which has developed significantly since 1950 (Figure 1.1). Surface chemistry is incredibly important for a complete structural understanding of chemical materials. Due to the increasing interest in utilizing the unique properties of nanomaterials for many practical applications, the need to understand the interface and surface chemistry at the nanoscale is of the utmost importance. According to Van Hove, the number of known structures of inorganic solids and molecules is over 100,000. However, a striking difference is seen for nanoscience materials, where the number of structures known with comparable detail is only 1000 (Figure 1.2). The disparity between nanostructures and other materials stems from the inability to fully characterize nanosurfaces largely due to complications in experimental and theoretical techniques. Fortunately, more and more of these limitations are overcome every year fueling the excitement on the future of nanoscale interfacial chemistry.

The term nanomaterial refers to a material with dimensions in the regime of $1 \times 10^{-9}$ m. Nanoparticles (NPs) typically exist in the 1 - 100 nm range and have been around for many decades. Michael Faraday was one of the first scientists who reported the synthesis of gold (Au) NPs in 1857 (Figure 1.3a). Faraday concluded that the gold was dispersed in the ruby - red solution as a “very finely divided form”. He argued that “the state of
division of these particles must be extreme; they have not as yet been seen by any power of the microscope". It took almost a century for instrumental techniques to achieve the sensitivity to characterize these NPs and to be capable to observe them via electron microscopy (Figure 1.3b). Nonetheless, the citations related to Faraday’s discovery indicate the huge development, especially in recent decades, of research in colloidal chemistry (Figure 1.4).

Since Faraday’s NPs synthesis, a multitude of synthetic methods have been reported for NPs synthesis with a diversity of metal cores, e.g., Au, Ag, Cu, Pt, Pd. In most NP syntheses, ligands are incorporated to protect the particles from agglomerating and prevent core atoms from undesirable reactions. Capping agents are usually organic in nature, and thereby provide colloidal stability of NPs in solution. Their many unique optical, thermal, magnetic, electrical, and chemical properties are greatly influenced by the size of nanoparticles and cannot be achieved by their bulk counterparts. For instance, particular sizes of NPs are expected to exhibit different optical properties dependent on their sizes as clearly depicted in Figure 1.5. Therefore, size control and homogeneity of NPs during synthesis and their ultimate characterization are very important parameters to consider. Interestingly, NPs with a core diameter of less than 3 nm experience novel electronic properties. They located in the so-called metal-to-molecule transition region where nanoparticles size and quantum size effect significantly influence the electrochemical properties (Figure 1.6). This relationship is of particular interest in our group; however, in order to observe and control the size-dependent electrochemical properties of NPs, it requires basic investigations, such as synthesis,
mechanistic understanding, and physical characterizations of the desired homogenous nanostructures.

1.2 Motivational Aspects

The nanotechnology revolution is making a ground-breaking impact on diverse fields of science and consequently many important applications. Companies continue to commercialize novel applications of nanometer scale materials ranging from the fields of biotechnology, drug-delivery systems, and biomedical applications to those of engineering, construction industry, energy and the environment.\textsuperscript{5, 6, 10} The unique properties of nanomaterials, specifically their physical and chemical characteristics, are promising properties for future capability in catalysis, conductivity, mechanical strength, energy storage devices, sensors, and particularly in electronics.\textsuperscript{10}

Charge transfer at the nanometer scale and its understanding is crucial to both fundamental science and applications.\textsuperscript{11, 12} Since nanomaterials occupy a relatively small area, this can help to produce smaller electronic devices, while leaving space for other useful functions. Thus far, Moore’s law has been reached by the semiconductor industry, where the number of transistors per chip has doubled every 1 - 2 years.\textsuperscript{11-13} However, more research and discoveries lie ahead for Moore’s law to thrive and continue to succeed in the future, and molecular and nanoelectronics have become first candidates to do just that.
Molecular electronics has become one of the most promising and the most interesting field over the last decade. Molecule-based electronics has a considerable future in the scientific world due to the wide range of applications. The general goal is to replace current electronic devices, such as wires and transistors, with one or a few molecules. A major step is to replace bulk silicon, because it does not provide the same bulk properties on the nanometer scale. Furthermore, the objective of the nanoelectronics field in the continued realization of the Moore’s law is to use nanomaterials in transistors to help to decrease chip size. The proposed use of molecules and nanomaterials in electronic systems remains promising, though it continues to be a very challenging process. Research in this area is necessary to develop, consequently it would bring great benefits for the future of electronic devices, such as improved operations speed, power consumption, and most importantly, cost.

The transfer of electrical charge has been deeply widely studied at the bulk and molecular level; however, investigations at the nanoscale are still minimal. Electron transfer, as suggested by Bjørnholm’s group, depends on the type of the chemical bond between the ligand and the metal. Ratner et al. provided the most widely accepted representative model for nanoscale charge-transfer processes, the so-called “donor-bridge-acceptor model”, where the electron can flow through a bridge or a wire between the donor (D) and acceptor (A) (Figure 1.7). A metal or semiconductor NP can serve as a donor/acceptor or even bridge. Furthermore, for example Murray et al. found that alkanethiolate-protected Au NPs can be considered as nanoelectrodes, which
make organochalcogen - protected NPs perfect models to study the electronic interactions between the metal core and the ligands, especially anchoring elements.

Diverse selections of different techniques are used to determine the electronic transparency of a single molecule. The tunnel transparency, also known as the conductance, $G$, of metal - molecular wire between two metallic electrodes is determined by the following formula: $G = G_0 e^{-\gamma L}$, where $L$ is the interelectrode separation, $\gamma$ is the inverse damping length, and $G_0$ is the contact conductance, which depends on the electrode - wire end interactions.$^{21, 23}$ Thereby we are interested in the value of $G_0$ between the metal NPs and ligands, where the metal NPs serve as electrodes, different chalcogens as the anchoring group, and altered alkane chains as the molecular wires.

Chalcogenide groups were found to be the simplest anchoring elements by many groups, since they are able to connect to the metal with covalent bonds.$^{18, 24}$ Understanding the interface between metal and chalcogen is extremely important, especially when considering how each of its components contribute to the conductance.$^{25}$

In order to determine the conductance of a metal with a chalcogen group, it is crucial to unravel how such contact results from a mixing of the end part of the wire’s molecular orbitals (HOMO and LUMO) with the surface metallic orbitals.$^2$ The charge transport between electrodes and the circuit elements is strongly affected by the location of Fermi levels of the electrodes and by the broadening of the energy levels of the molecular circuit elements.$^{26}$ The theoretical calculations presented by Di Ventra and Lang stated that using chalcogen groups, i.e., S, Se, and Te (Figure 1.8), could lead to practical applications as molecular components.$^{27}$ They concluded that conductance increases with
increasing atomic numbers.\textsuperscript{27} For example, Se- contacts provide a threefold increase in conductance over S- contacts, and the conductance of Te- reaches a value closer to quantum conductance. For S- and Se-, the Fermi levels fall in the HOMO - LUMO gap, whereas for Te- the Fermi level is almost exactly at the HOMO level (Figure 1.9).\textsuperscript{27} The authors also concluded that n-doping shifts to p-doping from S- to Te-, with the conductance increasing in the same direction.\textsuperscript{27} Although, this theoretical work was very promising for understanding the conductance of different anchoring elements at the interface of wire and electrode, whether the experimental efforts would be successful remains unknown. Thus, our motivation for this work was to experimentally observe and study the interface and conductance by varying different chalcogens, \textit{i.e.}, S, Se and Te, as anchoring elements, to the metal surface in NPs.

1.3 Self-Assembled Monolayers (SAMs)

There has been a great deal of research performed with chalcogen groups on SAMs that provide us with a vast amount of information, especially on the interaction of organo chalcogen based ligands and metal surfaces. The majority of research on SAMs was performed with thiol groups, since they chemisorb to gold surfaces, spontaneously form well - ordered monolayers, and are commercially accessible chemicals in most, if not all, cases. Thus, thiolate - Au SAMs have become a commonly used reference system for many experiments.\textsuperscript{28, 29-31}
Several groups have started research on organic selenides for use in SAMs, since the chemistry of selenium is often compared to the chemistry of sulfur. Nakamura et al. observed that dioctyl dichalcogenide molecules were dissociatively adsorbed on Au (111) to form octanechalcogenolate - gold species. Interestingly, the heavy chalcogens of selenium and tellurium with different alkyl chains formed monolayers on the gold surface, but the lower tilt angles lead to more disordered coverage than that of thiols. Using in situ SEIRAS (in situ surface - enhanced IR absorption spectroscopy) and electrochemical techniques, it was found that even though benzeneselenol took a longer time to adsorb on a gold surface than benzenethiol, it still formed a benzeselenolate - Au bond. Furthermore, it was shown that the diselenide bond chemisorbs on gold forming a Se-Au bond, and that the covalent Se-Se bonds are cleaved, through an oxidative addition mechanism.

SAMs research with organo chalcogens ligands is growing with more studies performed each year. Accordingly, the general understanding of the interface between chalcogens and metal surface of SAMs is fairly well understood, but the information on NPs remains minimal. Nonetheless, the effort performed on SAMs provides us with helpful information of interfacial interactions at the metal surface with chalcogen based ligands, and gives us some insight into future expectations for interfacial interactions in NPs.
1.4 Brust - Schiffrin Method (BSM)

The Brust - Schiffrin method has become one of the most common and popular routes to synthesize organo chalcogenolate - protected metal NPs, in particular thiolate - protected Au NPs.\(^{42}\) In general, there are two types of BSM: two - phase \(^{42}\) and one - phase \(^{43}\) (Figure 1.10). For the two - phase BSM, the exact mechanism was unknown for more than a decade and it was generally assumed to have the following reaction steps (reactions are not balanced).\(^{2,9,42}\)

(i) Phase transfer of a gold salt from aqueous into organic layer with tetraoctylammonium bromide (TOAB) acting as a phase - transfer agent:

\[
\text{HAuCl}_4\text{aq} + \text{TOAB (toluene)} \rightarrow [\text{AuCl}_4^-][\text{TOA}]^+\text{(toluene)} + \text{HCl(Br)}\text{aq}
\]

(ii) Reduction of Au (III) to Au (I) by thiol addition:

\[
[\text{AuCl}_4^-][\text{TOA}]^+\text{(toluene)} + \text{HSR} \rightarrow \text{polymeric } [\text{AuSR}]_n \text{ complexes}
\]

(iii) Reduction of Au (I) to Au (0) by the NaBH\(_4\) addition:

\[
[\text{AuSR}]_n\text{(toluene)} + \text{NaBH}_4\text{aq} \rightarrow \text{thiolate - protected NPs}
\]

Recently, the long - held assumption, that the addition of thiol reduced Au (III) to Au (I) and formed polymeric [AuSR]\(_n\) species (ii), was altered by the work of Goulet and Lennox.\(^{44}\) They showed that the metal precursor species prior to addition of reducing agent, \(i.e., \text{NaBH}_4,\) was a [TOA][AuX\(_2\)] complex instead of the assumed [AuSR]\(_n\) polymeric complexes.\(^{44}\) Our recent studies not only confirm their findings, but also delve into the mechanistic understanding of the BSM (Figure 1.11).
Our group found that the metal precursors in the two-phase BSM first formed inverse micelle structures with TOAB and a minuscule amount of encapsulated water. Furthermore, the addition of thiol lowered the oxidation state of the metal precursor, but it did not break the inverse-micelle structure. Subsequently, encapsulated metal ions with the lower oxidation state (+1 for Au, Cu, and Ag) were reduced by NaBH₄ to form the nucleation centers for NPs growth (Figure 1.11).⁴⁵

In addition, we discovered the critical role of water encapsulated in the inverse micelles in the two-phase BSM.⁴⁶ It has been observed that existence of the encapsulated water made the as-prepared Au NPs smaller with narrower distribution size when thiols were used as ligands. More importantly, the encapsulated water provided a hydrophilic microenvironment as a proton-accepting medium for the thiol proton, RS-H, which enabled the reduction of Au(III) to Au(I) by thiol to occur.⁴⁶ The amount of water in the reaction medium was found to have a profound effect on the Au(I) precursor species, thus the existence of water made the synthesized Au NPs smaller and more monodisperse.⁴⁶

In contrast, the one-phase BSM has only one phase for the reaction, which is usually performed in ethanol as a solvent medium (Figure 1.10).⁴³ Since there is no phase transfer agent involved in the reaction, the only possible reaction would be between HAuCl₄ and thiols (i), which is followed by reduction of NaBH₄_{aq} (ii).⁴³ According to the assumption, the one-phase BSM also formed polymeric complexes when Au (III) was reduced to Au (I) by thiols; however, no studies were performed to disprove this statement and the mechanism remains elusive.
1.5 Alkane Chalcogenolate - Protected Nanoparticles (NPs)

As previously mentioned, the thiolate-protected metal NPs have become the reference system of choice for many studies. Although the BSM is a facile procedure to produce NPs that can be easily collected, stored, and redisolved, occasionally the resulted NPs sizes are not homogenous and can vary from 2 - 5nm depending on the metal and ligand. Many modified procedures have been used to control the size of NPs, such as heat treatments, varying the gold to thiol ratio, and manipulating other reaction conditions.

While intensive research has been performed with thiolate-protected NPs, the studies with other alkane chalcogenolate (i.e., Se and Te) - protected NPs have been extremely rare. Brust and co-workers attempted to prepare such Au NPs by the two-phase BSM, yet they did not provide any characterization results other than Langmuir isotherms. Furthermore, the stability of their NPs was a major issue for further applications. Although this was the first publication in the field related to synthesizing metal NPs with didodecyl dichalcogens as precursor ligands, it did neither clearly stated nor described their structure and chemical properties. Later, Ulman’s group synthesized and characterized Au NPs with didodecyl diselenide, denoted here as (C12Se)$_2$, as a ligand precursor by the one-phase BSM in THF, since the two-phase BSM synthesis produced heterogeneous Au NPs. Yee et. al. concluded that no reaction occurred between the Au(III) and the (C12Se)$_2$, because they observed no noticeable color change prior to the
addition of the NaBH$_4$. They speculated that the THF replaced Cl$^-$ to coordinate with Au(III), which stabilized the formed Au NPs before being replaced by the selenolate.$^{49}$

In a study by our group, octaneselenolate - protected Au NPs of an average particle size of 2.5 nm were reported to be synthesized via the two - phase BSM using dioctyl diselenides as precursor ligands.$^{50}$ The first observation of $^{77}$Se nuclear magnetic resonance (NMR) of octaneselenolate - protected Au NPs strongly suggested that Se becomes metallic upon binding to the Au NPs surfaces. In 2011, the first synthesis of octaneselenolate - protected Au$_{25}$ clusters by an inverse synthetic two - phase BSM route was published by Negishi et al.$^{51}$ The group also used dioctyl diselenides as initial ligands and reported isolation and structural characterization of Au$_{25}$ clusters protected by octaneselenolates. They argued that charge transfer between the metal atoms and ligands in [Au$_{25}$(SeC$_8$H$_{17}$)$_{18}$] was lower than that of the thiol, [Au$_{25}$(SC$_8$H$_{17}$)$_{18}$].$^{51}$ These studies are very promising for the alkane selenolate - protected Au NPs synthesis; however, they did not provide reproducibility, long - term stability, or insights into mechanisms for the NPs formations.

1.6 Research Outline

The research presented in this dissertation focuses on the nanomaterial synthesis, in particular organo chalcogenolate - protected gold (Au) NPs, the formation mechanism of NPs, and their subsequent characterization. First, the synthesis of dialkyl diselenides, i.e.,
(C₆H₁₃Se)₂, (C₈H₁₇Se)₂, and (C₁₂H₂₅Se)₂, as precursor ligands and their full characterization is reported in Chapter III.

Water is a part of the BSM and its role in the synthesis is crucial to understand, especially in the two-phase BSM. In Chapter IV, we investigate if water encapsulated in the inverse micelles formed in the BSM has an effect on the intermediate species. Furthermore, we show the water effect in a comparative study of Au nanoparticle formation using dialkyl diselenides and dialkyl disulfides as ligand sources in the two-phase BSM.

It has been noticed that the two-phase BSM does not consistently work for preparation of homogenous NPs when dialkyl diselenides are used as precursor ligands, therefore we performed the studies focused on the mechanistic insights of one-phase and two-phase BSM for octaneselenolate-protected Au NPs. In Chapter V we investigated metal precursors in the one-phase and two-phase BSM and identified the key reason why the former is better than the latter.

Moreover, the NPs were synthesized by using dialkyl dichalcogens, i.e., RS-SR, RSe-SeR, and RTe-TeR, as precursor ligands, and variety of analytical techniques were used to characterize them. The effect of different chalcogens as anchoring elements, i.e., S, Se, and Te, and different alkyl chain lengths, i.e., C₆, C₈, and C₁₂, effects on Au NPs are discussed in Chapter VI.

So far, the likelihood to synthesize alkane selenolate-protected NPs only was demonstrated with dialkyl diselenides as precursor ligands. Therefore, in Chapter VII, the synthesis and characterization of alkyl selenocyanates are presented, i.e., C₆H₁₃SeCN,
C$_8$H$_{17}$SeCN, and C$_{12}$H$_{25}$SeCN, while in Chapter VIII the possibility to use these alkyl selenocyanates as ligands precursors for synthesis of Au NPs is discussed. Although the successful formation of Au and Ag NPs was achieved, the experimental determination for the existence of cyano species on the surface of the metal core remains a challenging task.

In the Appendix section, we look into the interaction between meso - 2, 3 - dimercaptosuccinic acid and silver nanoclusters, specifically at the sulfur - silver bond. The spectroscopic evidence of a bidentate - binding of the interface is described.
Figure 1.1 Surface science evolution toward nanoscience in terms of materials studied over a period of about 50 years. Adapted from Hove, M. A. V., Surf. Scie. 2009, 603, (10-12), 1301-1305.¹
Figure 1.2 Comparison of known surface structures determined in different fields by only orders of magnitude. Adapted from Hove, M. A. V., Surf. Scie. 2009, 603, (10-12), 1301-1305.
Figure 1.3 Faraday’s colloidal suspension of gold with a red laser beam clearly visible by the Tyndall effect (a), and high-resolution transmission electron microscope images of individual colloidal gold particles (b). Adapted from Edwards, P. P.; Thomas, J. M., Angew. Chem. Int. Ed. 2007, 46, 5480-5486.
Figure 1.4 The time evolution of citations from Faraday’s 1857 NPs discovery. Adapted from Edwards, P. P.; Thomas, J. M., Angew. Chem. Int. Ed. 2007, 46, 5480-5486. 4
Figure 1.5 Schematic drawing representing the changes on optical behavior of nanoparticles associated with their size (a) and corresponding colors of the NPs solutions (b). Adapted from Mansur, H. S., *Wiley Interdisciplinary Reviews: Nanomedicine and Nanobiotechnology* 2, (2), 113-129.
Figure 1.6 Metal nanoclusters in the range of 1-100 nm. Adapted from Jin, R., *Nanoscale* 2, (3), 343-362.
Figure 1.8 Schematic view of bare electrodes (a), schematic view of total system (sample plus electrodes) (b), and schematic view of system/molecules investigated (c). Adapted from Di Ventra, M.; Lang, N. D., Phys. Rev. B 2001, 65, (4), 045402.27
Figure 1.9 Difference in between the density of states of the semi - infinite electrodes with the molecules in Figure 1.8 in between. Adapted from Di Ventra, M.; Lang, N. D., *Phys. Rev. B* **2001**, *65*, (4), 045402.²⁷
Figure 1.10 Scheme of two-phase and one-phase Brust-Schiffrin method for synthesis of thiolate-protected Au NPs.
Figure 1.11 Scheme of two-phase mechanism for chalcogenolate-protected metal NPs.
1.7 References

CHAPTER II
SYNTHESIS AND CHARACTERIZATION METHODS

2.1 Chemicals

Selenium (100mesh, 99.5%), tellurium (200mesh, 99.85%), sodium borohydride (NaBH₄ powder, 98%), potassium selenocyanate, silver nitrate (AgNO₃), 1 - bromohexane (98%), 1 - bromooctane (99%), 1 - bromododecane (97%), 1 - hexanethiol (C₆SH, 98%), 1 - octanethiol (C₈SH, 98%), 1 - dodecanethiol (C₁₂SH, 98%), meso -2, 3 - dimercaptosuccinic acid (DMSA), tetrahydrofuran (THF, >99.0%), dichloromethane (99.8%), methanol (MeOH, >99.9%), hexanes (>98.5%), and diethyl ether (>99.0%), were purchased from Sigma - Aldrich and used as received. Acetonitrile (ACN) and toluene were bought from Fisher Chemicals, while ethanol (EtOH) was from Graham Company, dimethyl formamide (DMF) from Mallinckrodt Chemicals, sodium sulfite (Na₂SO₃) from EM Science, hydrogen tetrachloroaurate hydrate (HAuCl₄, 49 wt % Au) from Stem Chemicals, tetra-n-octylammonium bromide (TOAB, 98%) from Alfa Aesar, silica from Silicycle, and potassium tetrabromoaurate (III) dehydrate (KAuBr₄ · 2H₂O) were from Alfa Aesar. All the glassware was cleaned in sulfuric acid that contained Nochromix, then washed with water and acetone and dried in the oven. All the stirring bars and small containers/dishes were additionally cleaned in aqua regia (3 HCl : 3 HNO₃) mixture. Milli-Q water was used in all the experiments (18.2 MΩ·cm).
2.2 Synthesis of Ligands

2.2.1 Synthesis of Dialkyl Disulfides

Dialkyl Disulfides, *i.e.*, (C\textsubscript{6}H\textsubscript{13}S)\textsubscript{2}, (C\textsubscript{8}H\textsubscript{17}S)\textsubscript{2}, (C\textsubscript{12}H\textsubscript{25}S)\textsubscript{2}, were synthesized via a modified literature procedure\textsuperscript{52} where the same process was followed for all alkyl chain lengths (C6, C8, and C12). In general, 15 mg NaI was added to a solution of 2.4 mL RSH and 30 mL ethyl acetate. After the addition of 1.1 mL H\textsubscript{2}O\textsubscript{2} (30 wt%), the mixture was stirred at room temperature for 30 min. To the clear yellow solution, 15 mL of Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} (3.13 g) aqueous solution was then poured in. The two-phase mixture was transferred to a separatory funnel. The upper layer was removed and the solvent evaporated to yield a clear liquid for C6 and C8, and as a white crystal powder for the C12 alkyl chain.

2.2.2 Synthesis of Dialkyl Diselenides

Dialkyl Diselenides, *i.e.*, (C\textsubscript{6}H\textsubscript{13}Se)\textsubscript{2}, (C\textsubscript{8}H\textsubscript{17}Se)\textsubscript{2}, (C\textsubscript{12}H\textsubscript{25}Se)\textsubscript{2}, were synthesized according to our group’s previous procedure\textsuperscript{53} with an additional final purification step, where silica/hexanes column (60 cm in length and 6 cm in diameter) was used. The yellow band in the column was collected and rotary evaporated to obtain a yellow oily liquid product for C6 and C8, and yellow solid product for C12 alkyl chain. Further details about the synthesis and characterization of the ligands are provided in Chapter III.
2.2.3 Synthesis of Dialkyl Ditellurides

Dialkyl Ditellurides, *i.e.*, \((\text{C}_6\text{H}_{13}\text{Te})_2\), \((\text{C}_8\text{H}_{17}\text{Te})_2\), \((\text{C}_{12}\text{H}_{25}\text{Te})_2\), were synthesized as described in our previous paper.\(^{54}\) The same procedure was followed for C6 and C8; however, since C12 was a solid product the purification step at the end was not necessary.

2.2.4 Synthesis of Alkyl Selenocyanates

Alkane Selenocyanates, *i.e.*, \((\text{C}_6\text{H}_{13}\text{SeCN})\), \((\text{C}_8\text{H}_{17}\text{SeCN})\), \((\text{C}_{12}\text{H}_{25}\text{SeCN})\), were synthesized directly from a literature procedure.\(^{55}\) In brief, the solution of potassium selenocyanate (2.16 g) and DMF (7.5 ml) were mixed under nitrogen. Alkyl halides were slowly added to the solution and stirred for about 12 - 14 hours at 90°C. The solution was hydrolyzed with 30 ml of water, extracted twice with 50 ml of ether, then washed again with water and dried with \(\text{MgSO}_4\). The solvent was evaporated, and remaining solution was run through the hexane column. A detailed discussion about synthesis and characterization of the alkyl selenocyanate ligands will be discussed in Chapter VII.

2.3 Synthesis of Alkane Chalcogenolate - Protected Au NPs

2.3.1 Synthesis of Alkane Thiolate - Protected Au NPs

In general for alkane thiolate - protected Au NPs, *i.e.*, RS - Au NPs, a modified two-phase BSM\(^{42}\) was used, where 1 mmol of \(\text{HAuCl}_4\) aq solution was poured in to 50 mL of toluene with 3 mmol TOAB (tetraoctylammonium bromide). The solution was stirred until all Au ions were transferred into the organic layer that can be observed with change
of aqueous color from yellow to clear. Subsequently, 0.5 mmol of \( \text{R}_2\text{S}_2 \) was added and stirred in the organic layer after separation from aqueous media, and followed by the addition of 10 mmol of \( \text{NaBH}_4 \text{aq} \) solution. After overnight stirring, the organic layer was separated and centrifuged for 1h at 10,000 rpm. The top solution was collected, rotary evaporated, and then a large amount of ethanol (EtOH) (~250 mL) was added before being stored overnight in a refrigerator. The next day the NPs were collected by filtering through the micropore filter and washed with EtOH. The collected NPs were then re-dissolved in toluene and centrifuged for 2 hours at 14,500 rpm. The supernatant was collected and usually used for the characterizations.

Note, when ACN was used as a crashing solvent, the final NPs were insoluble in toluene after the aforementioned step, while when EtOH was used, the NPs were easily re-dissolved in organic solvents.

2.3.2 Synthesis of Alkane Selenolate - Protected Au NPs

Initially, modified two-phase \( \text{BSM}^{42} \) was used for synthesis of alkane selenolate-protected Au NPs, \( i.e. \), \( \text{RSe} - \text{Au NPs} \), with the ratio of \( 1\text{Au} : 3\text{TOAB} : 0.5(\text{C}_8\text{Se})_2 : 10\text{NaBH}_4 \). First 0.15 mmol of TOAB was dissolved in 20 ml of toluene, then 0.05 mmol (0.35 ml, 0.1329 M) of \( \text{HAuCl}_4\text{aq} \) was added to the solution. The solution changed color from dark red color to clear. When all Au ions where transferred into organic layer, 0.025 mmol of \( (\text{C}_8\text{H}_{13}\text{Se})_2, (\text{C}_8\text{H}_{17}\text{Se})_2, (\text{C}_{12}\text{H}_{25}\text{Se})_2 \) was added and stirred for 1 - 2 hours, while the solution turned to dark yellow color. Later, aqueous 5 mmol \( \text{NaBH}_4\text{aq} \) in 5 ml of \( \text{H}_2\text{O} \) was added and stirred for 3 hours, while the color of the solution turned to black immediately. The aqueous layer was removed and organic layer was rotary-evaporated.
Large amount of ACN (~ 250 mL) was added and stored in the refrigerator overnight. Next day, the NPs were filtered through micropore paper, re-dissolved in toluene, and centrifuged for 2 hours at 14.5K rpm.

The procedure did not produce homogenous NPs, therefore, modified one-phase BSM synthesis was used to produce RSe - Au NPs. A mixture of 75mL THF was mixed with 1 mmoles of HAuCl₄. After stirring for 30 min in ice bath, 0.5 mmol of (C₆H₁₃Se)₂, (C₈H₁₇Se)₂, (C₁₂H₂₅Se)₂ was added to the solution and stirred for another 2 hours. While keeping the stirring solution in ice bath, 10 mmol of NaBH₄aq solution was added and stirred for 2 hours for C6, 3 hours for C8, and 4 hours for C12, respectively. Subsequently, the solution was rotary evaporated at room temperature and a large amount of ACN (~250 mL) was added and the resulting solution was stored overnight in a refrigerator. The next day the NPs were collected through the micropore filter, and washed with ACN. The collected NPs were then re-dissolved in toluene, and centrifuged twice for 1 hour at 14,500 rpm. The supernatant was collected after centrifugation and analyzed.

Note, that for the Se system the crashing solvent effect was opposite to the S system. When EtOH was used as a crashing solvent, the NPs were insoluble in toluene, while when ACN was used, no solubility issues were noticed.

2.3.3 Synthesis of Alkane Telluroxide - Protected Au NPs

For alkane telluroxide - protected Au NPs, i.e., RTe - Au NPs, an adapted two-phase BSM procedure was followed. The stirring time after addition of NaBH₄aq solution was
30 min for C6, 3 hours for C8, and overnight for the C12 alkyl chain. In addition, ACN, instead of EtOH, was used to crash out NPs.

2.4 Chemical Methods

2.4.1 Nuclear Magnetic Resonance (NMR)

$^1$H and $^{13}$C NMR spectra were obtained using a Bruker AM 300 MHz spectrometer that was coupled with a Tecmag DSpect acquisition system. $^{77}$Se and $^{125}$Te NMR were performed on a 400 MHz Varian Unity spectrometer. For references, $^1$H (7.16ppm) and $^{13}$C (128.39ppm) peaks were used in the deuterated benzene ($C_6D_6$) solution, for deuterated chloroform ($CDCl_3$) TMS was used as a locking agent and peaks at $^1$H (0 ppm) and $CDCl_3$ $^{13}$C (77.23 ppm) were used as references. For deuterated water ($D_2O$) solvent, DSS (3-trimethylsilyl-1-propanesulfonic acid sodium salt) acted as soluble TMS, and it was used as an internal reference with the first peak set at $^1$H and $^{13}$C (0 ppm). The dimethyl selenide peak (0ppm) in deuterated benzene and the peak of tellurium hexahydroxide (707ppm) in deuterated oxide served as references for $^{77}$Se and $^{125}$Te NMR.

2.4.2 Raman Spectroscopy

Raman spectra were collected using a confocal microprobe Raman system (Renishaw RM1000) equipped with a deep depletion CCD peltier cooled down to -70°C. The microscope attachment was based on an Olympus BH2-UMA system and a 50x-long working-length objective (8 mm) was used. A holographic notch filter was used to filter
the exciting line and selective holographic gratings (1200 g/mm). The excitation wavelength was 785 nm from diode laser with a max power of 27 mW and a spot of ca. 3 μm on the surface. The slit and pinhole in experiment were 100 and 400 μm, respectively. The spectroscopy was calibrated with the peak at 520 cm⁻¹ of clean Si wafer. Liquid sample spectra were measured in a 5 - mm NMR tube. Solid or slurry sample spectra were measured on a clean microscope slide.

2.4.3 Infrared (IR) Spectroscopy

IR spectra were obtained by using a Bruker Vector - 22 infrared spectrometer. For the liquid ligands, the liquid of interest was dropped onto a KBr pellet and covered with another KBr pellet. For the solid samples, i.e., NPs in solid form, were mixed with KBr powder as a solid support and ground to an even mixture with a pestle. For the NPs samples in a liquid form, a couple of drops of the solution was dropped into the small dish, the solvent was evaporated, and then KBr was added to the dried solid and mixed well with the pestle. The mixture was pressed into a wafer for IR measurement. All measurements were performed in transmittance mode with a 2 cm⁻¹ resolution and the spectra were background subtracted with respect to KBr.

2.4.4 Transmission Electron Microscopy (TEM)

The TEM characterization was performed on JEOL JEM - 2100 LaB₆ transmission electron microscope. The NPs samples were first dissolved in toluene, then depending on the concentration, one to three drops of the solution was applied on carbon - coated copper grids (200 mesh, Electron Microscopy Science), and then air dried. The sizes of
the NPs were measured by hand with minimum of 200 counts and by the ImageJ program.

2.4.5 Energy Dispersive X - Ray Spectroscopy (EDS)

EDS analysis was conducted using the EDS detector attached to the JEOL JEM - 2100 LaB₆ TEM for quantitative analysis of the composition of NPs. For each sample, various areas were selected for analysis and the results were averaged.

2.4.6 UV - Vis Spectroscopy

A UV - Vis spectrometer equipped with HP 8453 diode array was used for measurements. NPs were dissolved in toluene, and then the solution was placed into a 1 cm path length quartz cuvette. The samples were scanned in the range from 300 - 800nm, where the blank sample was toluene.

2.4.7 Thermogravimetric Analysis (TGA)

The measurements were carried out on a TA Instruments TGA Q50. About 2 - 5 mg of NPs was placed into a ceramic pan, and then the temperature was ramped from 25°C to 1000°C with the heating rate of 10°C/min.

2.4.8 X - Ray Photoelectron Spectroscopy (XPS)

The XPS spectral data were acquired at NIST on a Kratos Axis Ultra DLD using an Al Kα (1486.7 eV) source. A sonicated NPs toluene solution was drop - cast onto a clean Si substrate. Each sample was measured three times at different locations and the results were averaged. The spectra were calibrated with the binding energy of C 1s at 285 eV.
2.4.9 Density Functional Theory (DFT) Calculations Methodology

All DFT calculations were performed at NIST. For Chapter IV, calculations were carried out at the B3LYP/cc-pVDZ level of theory (the cc-pVDZ-PP pseudopotential basis set was used on Au) using the GAMESS quantum chemistry program.\(^9\) All structures were fully optimized at the stated level of theory. Vibrational frequencies were computed using two-sided numerical differencing of the analytical gradient and a scaling factor of 0.97 was used.\(^10\)

For Chapter V, calculations were carried out for HAuCl\(_4\), AuCl\(_4^-\), X\(_2\)Au-Se(C\(_8\)H\(_{17}\))(OH)X (X=Cl, Br), XYAu-Se(C\(_8\)H\(_{17}\))XY (X,Y=Cl, Br), and (C\(_8\)H\(_{17}\)Se)\(_2\) at the B3LYP/cc - pVDZ level of theory (the cc - pVDZ - PP pseudopotential basis set was used on Au) using the GAMESS quantum chemistry program. All structures were fully optimized at the stated level of theory. Vibrational frequencies were computed using two-sided numerical differencing of the analytic gradient.

In the Appendix section of this dissertation, specifically dimecaptosuccinic acid (DMSA) protected Ag clusters project, the structure was fully optimized using the B3LYP density functional as implemented in the NWChem computational chemistry program.\(^56\) The cc - pVDZ - PP basis set\(^57\) was used for the Ag atoms and the cc - pVDZ basis set was used for the remaining atoms. Vibrational frequencies were computed analytically by NWChem. The structures reported did not correspond to minima on the potential energy surface - there were a number of imaginary vibrational frequencies. However, inspection of the vibrational modes (mainly small rotations) associated with the imaginary frequencies lead us to believe that they would have a significant effect on the
stretching frequencies that were of interest in this study. This supposition was supported by calculations performed on several related molecules (CO, H₂CO, HCOOH, MSA = mercaptosuccinic acid, DMSA = dimercaptosuccinic acid and AgMSA), which yielded frequencies in good agreement with those observed in Ag₇DMSA₄⁻. We were concerned mainly with three types of stretching frequencies for the molecule, namely Ag-S, C=O and C-OH.
2.5 References

CHAPTER III
SYNTHESIS AND CHARACTERIZATION OF DIALKYL DISELENIDES

3.1 Introduction

The chemistry of selenium has attracted a lot of attention in the past decades due to its interesting functionalities and properties for variety of applications.\textsuperscript{58, 59} The well-known thiols are widely used as ligands for synthesis of thiolate-protected nanoparticles. Compared to them, selenols cannot be used as ligand precursors for alkane selenolate-protected Au NPs synthesis due to their instability in air.\textsuperscript{60, 61, 62} Therefore, to achieve this goal of the project, dialkyl diselenides were chosen, since it has been shown that diselenides can adsorb to the Au surface and form alkane selenolate-gold species in SAMs.\textsuperscript{24} Many of the published syntheses of diselenides in the literature involve long and tedious procedures that were not suitable for our purpose.\textsuperscript{24, 63-66} Therefore, we choose a simpler, although still challenging method, previously reported by our group, to synthesize dialkyl diselenides.\textsuperscript{53} In the previous work it was stated that dioctyl diselenides were easily prepared via one-pot synthesis; however, later it was found that the final product was contaminated with unreacted initial materials. Consequently, the goal was to purify the resultant solution, to separate impurities from the desired dialkyl diselenides, and provide a reproducible method for further preparation of diselenides for our project.
3.2 Synthesis of Ligands

Three ligands, ((C$_6$H$_{13}$Se)$_2$, referred here as C6), ((C$_8$H$_{17}$Se)$_2$ - C8), and ((C$_{12}$H$_{25}$Se)$_2$ - C12) were synthesized through the same modified procedure published by our lab previously.$^{53}$ Dialkyl diselenides were prepared by dispersing 2 g of Se (selenium powder) in 300 mL of dichloromethane (CH$_2$Cl$_2$). This solution was then combined with 1 g of sodium borohydride (NaBH$_4$) in 50 mL of methanol, which reduced the elemental Se in the reaction.$^{66, 67}$ The black solution turned dark red color, an indication of the disodium diselenide formation.$^{66, 68}$ After 2 - 3 hours of stirring, 4 mL of the appropriate bromoalkane, i.e., C$_6$H$_{13}$Br, C$_8$H$_{17}$Br, and C$_{12}$H$_{25}$Br, was added and after an hour, one more equivalent of NaBH$_4$ was added. The solution was stirred overnight, whereupon the dark red solution changed to a pale yellow thick suspension. Subsequently, it was filtered by vacuum filtration (Whatman filter paper 50) to remove all precipitate, which left a bright yellow solution behind. (Note, in some cases multiple filtration was performed to decrease the amount of precipitate for future steps in the procedure). This solution was processed through the rotary evaporation to remove the solvent. The orange oily product, usually mixed with residual precipitate from previous step, was run through a silica gel/hexane column (40 cm in length and 2 - 3 cm in diameter) to remove the lingering solid impurities. The column produced two distinct yellow bands and a precipitate layer on top of the column. The first band was collected, and the solvent was then removed via rotary evaporation. The resultant yellow solution was run through the second silica gel/hexane column (60 cm in length and 6 cm in diameter) to separate the unreacted
bromoalkane and the dialkyl diselenide. Since bromoalkane elutes from the column first, the yellow band was carefully collected. Note, that for longer alkyl chain length initial yellow solution was not collected for about 20 mL, to assure purity of the product at the end. Subsequently, the solution was rotary evaporated leaving a clean product, dialkyl diselenide in percent yield of 45%-50%. The final product is a yellow oil for C6 and C8, and a yellow solid for C12 with a very low melting point (slightly higher than the room temperature).

3.3 Characterization of Ligands

After the modifications noted above to the published procedure, ultimately pure C6, C8 and C12 were successfully synthesized based on the spectroscopic results described below. $^{1}$H, $^{13}$C, $^{77}$Se NMR, IR and Raman spectroscopies were performed on the synthesized ligands to ensure the purity. Since there are multiple reaction pathways in the synthesis, the final product could contain other undesirable products, such as unreacted bromoalkanes, and multiple selenide products, i.e., dialkyl selenides (RSeR) and dialkyl triselenides (RSeSeSeR).

$^{1}$H NMR spectra for all three ligands are presented in Figure 3.1. The peak positions of C6, C8 and C12 are in an agreement with the peaks previously reported.$^{24,64,66}$ The triplet peaks at ~ 2.8 ppm in C$_6$D$_6$ (~ 2.9 ppm in CDCl$_3$) clarity to the presence of dialkyl diselenide, since it corresponds to the methyl group directly bound to the Se atom. In more details, a slight alkyl chain length effect was noticed. For example, the peak of
interest, such as $\text{H}_2\text{C-Se-}$ protons shifted from 2.75 ppm for C6 (Figure 3.1c) to 2.77 ppm for C8 (Figure 3.1b) to 2.79 ppm for C12 (Figure 3.1a). Furthermore, peaks corresponding to bromoalkanes at $\sim$ 2.9 ppm in C$_6$D$_6$ ($\sim$ 3.4 ppm in CDCl$_3$) and RSeR at $\sim$ 2.5 ppm$^{63}$ were not present in the spectra, indicating purity of the ligands.

$^{13}$C NMR spectra are presented in Figure 3.2. Figure 3.2c clearly shows 6 well-resolved peaks for C6. The peak assignments were achieved by HMQC (heteronuclear multiple quantum coherence) data experiments, where C8 is presented in Figure 3.3 for reference. All the carbon peaks for three ligands were assigned and no alkyl chain length dependence was observed. For C6, C8, and C12, C-1 that was directly bound to Se was located at $\sim$ 31 ppm.

To make sure that the ligands contained only one type of selenium, $^{77}$Se NMR was performed and is presented in Figure 3.4 (the internal reference was dimethylselenide set at 0 ppm). Only one peak at 310.3 ppm in all ligands was present, indicating one type of the selenium in the samples and demonstrating the presence of dialkyl diselenides.$^{53}$

Further, IR characterization was performed on the ligands and the data is presented in Figure 3.5. There are three main areas of interest in the spectrum: 2800 - 3000 cm$^{-1}$, 1100 - 1500 cm$^{-1}$, and 550 - 800 cm$^{-1}$. The high frequency region exhibits three well-resolved peaks in the $\sim$ 2850 - 2854 cm$^{-1}$, $\sim$ 2917 - 2922 cm$^{-1}$, and 2956 - 2964 cm$^{-1}$ regions which have been previously assigned to methylene (C-H$_{\text{sym}}$), methylene (C-H$_{\text{antisym}}$), and methyl (CH$_3$-$\text{sym}$) vibrational absorption bands.$^{66,68}$ The peaks found between 1100 cm$^{-1}$ and 1500 cm$^{-1}$ correspond to the twisting and wagging frequencies of methyl/methylene
and are typical behavior for chain alkanes.\textsuperscript{53} Finally, the peaks in the area of 550 cm\textsuperscript{-1} and 800 cm\textsuperscript{-1} correspond to $\nu_{\text{rocking}}$ (CH\textsubscript{2}) at 721 cm\textsuperscript{-1} and $\nu_{\text{stretch}}$ (Se-C)\textsubscript{trans} at 630 cm\textsuperscript{-1}.\textsuperscript{53}

Raman spectra are presented in Figure 3.6, where all samples were analyzed as liquids. No alkyl chain length dependence was noticed and all three ligands showed similar frequencies. The peaks of interest were assigned as follows: peak at 632 cm\textsuperscript{-1} that corresponds to $\nu_{\text{stretch}}$ (Se-C)\textsubscript{trans} and peak at 543 cm\textsuperscript{-1} to $\nu_{\text{stretch}}$ (Se-C)\textsubscript{gauche}, respectively. The strongest peak at 290 cm\textsuperscript{-1} was assigned to Se-Se, which provides clear evidence of the Se-Se stretching frequency.\textsuperscript{38, 69, 70}

3.4 Conclusion

A previously reported synthetic method was optimized to produce pure ligands, (C\textsubscript{6}H\textsubscript{13}Se)$_2$, (C\textsubscript{8}H\textsubscript{17}Se)$_2$, and (C\textsubscript{12}H\textsubscript{25}Se)$_2$. Final products were verified via $^1$H, $^{13}$C, $^{77}$Se NMR, IR and Raman spectroscopies. $^1$H NMR showed the existence of pure products and likely nonexistence of impurities, such as bromooctanes and other selenide by-products. With the help of HMQC NMR, the peaks in $^{13}$C NMR were assigned, indicating the peak location of C-1 in the molecules. $^{77}$Se NMR once again proved the existence of only one kind of selenium present, while IR and Raman confirmed the purity of the ligands.
Figure 3.1 $^1$H NMR spectra of (a) (C$_{12}$H$_{25}$Se)$_2$, (b) (C$_8$H$_{17}$Se)$_2$, and (c) (C$_6$H$_{13}$Se)$_2$. 
Figure 3.2 $^{13}$C NMR spectra with assigned number of carbons in (a) $(\text{C}_{12}\text{H}_{25}\text{Se})_2$, (b) $(\text{C}_{8}\text{H}_{17}\text{Se})_2$, and (c) $(\text{C}_{6}\text{H}_{13}\text{Se})_2$. 
Figure 3.3 HMQC NMR spectrum of \((C_8H_{17}Se)_2\) in C_6D_6.
Figure 3.4 $^{77}$Se NMR spectra of (a) $(\text{C}_{12}\text{H}_{25}\text{Se})_2$, (b) $(\text{C}_8\text{H}_{17}\text{Se})_2$, and (c) $(\text{C}_6\text{H}_{13}\text{Se})_2$. 

46
Figure 3.5 IR spectra of (a) \((\text{C}_{12}\text{H}_{25}\text{Se})_2\), (b) \((\text{C}_{8}\text{H}_{17}\text{Se})_2\), and (c) \((\text{C}_{6}\text{H}_{13}\text{Se})_2\).
Figure 3.6 Raman spectra of (a) $\text{(C}_{12}\text{H}_{25}\text{Se})_2$, (b) $\text{(C}_8\text{H}_{17}\text{Se})_2$, and (c) $\text{(C}_6\text{H}_{13}\text{Se})_2$. 
3.5 References

CHAPTER IV

INVERSE-MICELLE-ENCAPSULATED WATER-ENABLED BOND BREAKING OF DIALKYL-DISELENIDE/DISULFIDE: A CRITICAL STEP FOR SYNTHESIZING HIGH-QUALITY Au NANO PARTICLES

Reproduced with permission from Zaluzhna, O.; Li, Y.; Tong, Y. J., Allison, T. C.: Inverse - micelle - encapsulated water - enabled bond breaking of dialkyl – diselenide/disulfide: a critical step for synthesizing high - quality Au nanoparticles, J. A. Chem. Soc., 2012, to be submitted. This work was a combined effort of Zaluzhna, O. and Tong Y. J. Additionally, Dr. Ying Li aided in data discussions and revisions of the paper. Dr. Allison has performed all the computational studies.

4.1 Introduction

The popular BSM procedure has been widely used to synthesize thiolate - protected Au NPs. Its profound impact on making modern metal NPs in general, and on inspiring their many promising novel applications, can hardly be overstated. Moreover, several recent studies have also made great strides in our mechanistic understanding of the chemistry of metal NP formation in terms of identifying the Au precursors and the reaction micro - environment. These include the discoveries of the formation of a stoichiometric Au complex involving cations of the Au - ion - transferring surfactant (i.e., TOA+, tetra - octylammonium cation) and of inverse micelles in which the Au complex [TOA][Au(III)X₄] is hosted and subsequently reduced to [TOA][Au(I)X₂]. The latter must involve a reaction like Au(III) + 2RSH → Au(I) + RSSR + 2H⁺ in which...
inverse - micelle - encapsulated water provides a favourable hydrophilic micro -
environment as a proton - accepting medium for the cleaved thiol protons.\textsuperscript{46} In other
words, the presence and quantitative control of inverse - micelle - encapsulated water is
absolutely essential for achieving high - quality thiolate - protected metal NPs.

However, despite its prevailing use, sulfur is far from being the best chemical
linker for optimal electrical conductance between the metal and the carbon backbone of
potential molecular wires. Consequently, it is highly desirable to investigate other
alternatives among which Se is a promising candidate. However, the instability of
alkylselenol in air\textsuperscript{49,74} dictates the use of the more stable dialkyl diselenide as the ligand
source for self - assembled monolayer and metal NP stabilizer in which the diselenide Se-
Se bond is expected to be broken. Therefore, unraveling the detailed chemistry of Se-Se
(or dichalcogenide in general) bond breaking in the formation of metal NPs and its
relationship with encapsulated water in the context of the BSM two - phase synthesis of
selenolate - protected Au NPs is an important and timely subject and the focus herein. To
illustrate further the bond - breaking chemistry, we also carried out a comparative study
of dialkyl disulfide as the source of protecting ligand. We discovered that it is the inverse
- micelle - encapsulated water that enables uniquely the bond breaking of the diselenide
or disulfide bond and the formation of paramagnetic Au(II) complex, a step that is
essential in forming high - quality Au NPs.

The steps of a BSM two - phase synthesis of Au NPs used here are as follows: (1)
phase transfer of Au(III) from the aqueous solution of HAuCl\textsubscript{4} to the organic (benzene)
phase by the surfactant tetraoctylammonium bromide (TOAB), (2) separation of the
organic phase after complete Au(III) transfer in order to better control the amount therefore delineate the effect of water, (3) addition of the ligand (dialkyl disulfide or dialkyl diselenide) to the separated organic phase, and (4) mixture of the NaBH₄ aqueous solution with the organic solution of (3) to reduce Au cations to Au(0) through which Au NPs are formed. We’ll first focus on identifying chemical species involved in Steps (2) and (3) by ¹H NMR and Raman spectroscopies, aided by ab initio density functional theory (DFT) calculations for the assignments of vibrational bands observed by Raman.

4.2 Experimental Section

For the ¹H NMR study, the following intermediate solutions were prepared: 0.0164 g of TOAB was dissolved in 0.5 mL of C₆D₆ to which 0.189 mL, 0.0949 mL, or 0.0649 mL of HAuCl₄ aqueous solution (0.158 M) was added to form solutions of TOAB:Au ratio = 1:1, 2:1, and 3:1, respectively. After the aqueous layer turned colorless indicating that all Au(III) ions were transferred into the organic phase, the wine - red top organic layer was collected, and 0.5 equiv of (C₁₂H₂₅S)₂ or (C₁₂H₂₅Se)₂ (i.e., Au:S or Se = 1:1) was added. (Notice that the separation of organic layer was done after the addition of ligands and a subsequent overnight stirring in ref. 14 in which the color change was observed.) The reference intermediate solution was made by dissolving the [TOA][AuBr₄] complex directly in C₆D₆ with addition of 2 equiv of TOAB and 0.5 equiv of dichalcogenides. This ensured that no water was present and the organic solution had a final ratio of TOAB:Au = 3:1. All the (separated) organic solutions were stirred for 2 hours and then
analyzed by $^1$H NMR. For the Raman studies, the corresponding concentrated solutions were obtained by evaporating the solvent from the given organic solution, dropping a sample on a clean glass slide, and drying it in air overnight. Notice that no obvious color change was observed for both dichalcogenides after 2 hours of stirring. However, both the NMR and Raman data suggest that certain reactions between the ligands and Au ions did take place. It was discovered that no obvious color change was due to the formation of an unusual Au(II) complex (vide infra).

Synthesis of ligands, complex, and NPs are reported in Chapter II and III.

4.3 Results and Discussions

We begin by describing the didodecyl diselenide, $(C_{12}H_{25}Se)_2$, system. The $^1$H NMR spectra of the intermediate solutions obtained after the addition of diselenide, together with spectra of some reference materials, are shown in Figure 4.1. Figure 4.1a to 4.1c are the spectra of the intermediate solutions after adding diselenide to the separated organic phase - transferred layer with Au:Se = 1:1, but with TOAB:Au = 3:1, 2:1, and 1:1, respectively. Figure 4.1d is the spectrum obtained by adding $(C_{12}H_{25}Se)_2$ to a $C_6D_6$ solution of pre-formed [TOA][AuBr$_4$] complex plus 2 equivalents of TOAB yielding TOA:Au = 3:1. Figure 4.1e to 4.1g are references: those of the simple mixture of TOAB:$(C_{12}H_{25}Se)_2$ = 3:1, pure $(C_{12}H_{25}Se)_2$, and the organic solution after the complete Au(III) phase transfer with TOAB:Au = 3:1. All these solutions were prepared using $C_6D_6$ as solvent. Since about a dozen samples will be discussed, we will name the
samples as TAU[Se/S]-nnn(C) to simplify their description and facilitate discussion. Here T represents the surfactant, C represents the [TOA][AuBr₄] complex, and nnn represents a number that gives the atomic ratio of the sample. For instance, TAUSe-311C stands for a sample prepared with [TOA][AuBr₄] and TOAB:Au:Se=3:1:1.

In Figure 4.1, the triplet peaks at 2.78 ppm (orange) belong to the α-CH₂Se- protons of (C₁₂H₂₅Se)₂ (Figure 4.1f, TAUSe-001), those indicated by the blue numbers arise from the α-CH₂N⁺ protons of TOAB, and those indicated by red numbers come from encapsulated water with acidic protons (3.72 ppm in Figure 4.1a, TAUSe-311, and 3.10 ppm in Figure 4.1b, TAUSe-211). Figure 4.1g (TAUSe-310) reproduces exactly what was observed previously⁴⁶ and the 2.63 ppm peak came from the inverse-micelle-encapsulated water. It was also observed previously⁴⁶, ⁷⁵ that TAUSe(S)-210 encapsulate water, but not TASe(S)-110.

As expected, no reaction occurred by simply mixing TOAB with the ligand (TAUSe-301), Figure 4.1e. Neither reaction occurred in TAUSe-311C (Figure 4.1d) in which no water was present, although the presence of the Au(III) complex did shift the peak at 2.78 ppm to 2.97 ppm without changing its triplet lineshape. This suggests the possible formation of a Lewis adduct between diselenide and Au ions without the Se-Se bond being broken. However, if the ligand was added to the post-Au(III)-transferred organic solution where inverse-micelle-encapsulated water existed, i.e., TAUSe-310 (Figure 4.1g) and TAUSe-210⁴⁶, ⁷⁵, the reaction took place as evidenced by the appearance of the acidic proton peaks at 3.72 ppm and 3.1 ppm and the complete disappearance of the peaks at 2.78 ppm in Figure 4.1a (TAUSe-311) and 4.1b (TAUSe-211), respectively.
latter indicates that all Se-Se bonds were broken. What is striking is that no evidence of reaction was observed in Figure 4.1c (TAuSe-111) where no encapsulated but free-like water (0.7 ppm peak) was observed.

The corresponding Raman spectra of Figure 4.1 are shown in Figure 4.2. Figure 4.2g (TAuSe-310) is a simple addition of the spectra of individual components: TOAB and HAuCl₄. Clearly no reaction occurred between them. As observed previously, the diselenide stretching band in the presence of TOAB showed a 6 cm⁻¹ (TAuSe-301, Figure 4.2e) positive shift as compared to that (290 cm⁻¹) in Figure 4.2f (TAuSe-001), although no shift was observed in the α-CH₂Se-proton peak (Figure 4.1e). The latter observation convinced us that no reaction took place between diselenide and TOAB in TAUSe-301. That is, the Se-Se bond was intact.

Interestingly, when diselenide was added to the Au complex solution without water (TAuSe-311C), the Raman spectrum changed dramatically: an intense band at 254 cm⁻¹ was observed in addition to two much weaker bands at 195 cm⁻¹ and 212 cm⁻¹ that can be assigned to the [AuBr₄]⁻ moiety. In order to identify the intense band at 254 cm⁻¹, since NMR (Figure 4.1d) strongly suggests that the Se-Se bond was most likely not broken, DFT (density functional theory) calculations were carried out on two candidate molecular structures whose optimized molecular structures are shown in Figure 4.4 and Table 4.1. (The candidate structures listed gave the best agreement with the experimental measurements out of many possible structures that were considered.) For the [HAu(III)Br₄] (SeC₄H₉)₂ structure, the calculated (scaled) Se-Se stretching frequency is 281 cm⁻¹, but is 260 cm⁻¹ for the Au(III)(SeC₄H₉)₂ structure. Therefore, we assigned the
band at 254 cm$^{-1}$ to Au(III)(SeC$_4$H$_9$)$_2$ - like species, which is consistent with the positive $^1$H NMR peak shift (Figure 4.1d) that can be rationalized by the interaction with electron withdrawing Au(III). Equally interesting is that Figure 4.2c (TAuSe-111) appears to also be a simple addition of Figure 4.2g (TAuSe-310) and 4.2f (TAuSe-001), suggesting strongly that no reaction between diselenide and the Au complex took place despite the presence of non - encapsulated water (0.7 ppm peak in Figure 4.1c), in agreement with the NMR observation. Moreover, no obvious change in the bands from [AuCl$_4$]$^-$ (325 cm$^{-1}$ and 341 cm$^{-1}$) and no bands from [AuBr$_4$]$^-$ (195 cm$^{-1}$ and 212 cm$^{-1}$) were observed in Figure 4.2c (TAuSe-111), which suggests that no major replacement of Cl$^-$ by Br$^-$ in the [AuX$_4$]$^-$ moiety took place with TOAB:Au = 1:1.

On the other hand, a reaction did occur once the inverse - micelle - encapsulated water was present (TAuSe-311 and -211), as evidenced by the complete disappearance of the Se-Se bonds i.e., the complete disappearance of the Se-Se stretching band in Figure 4.2a and 4.2b and $\alpha$-CH$_2$Se- proton peak in Figure 4.1a and 4.1b. Also, significant displacement of Br$^-$ by Cl$^-$ occurred as evidenced by the appearance of the 213 cm$^{-1}$ band from [AuBr$_4$]$^-$ and the substantial decrease of the bands (325 cm$^{-1}$ and 341 cm$^{-1}$) from [AuCl$_4$]$^-$. Therefore, per the above observations, we conclude that the presence of inverse - micelle - encapsulated water enabled the bond - breaking reaction between diselenide and the Au(III) complex.

We also investigated the dialkyl disulfide for purposes of comparison. The $^1$H NMR spectra of the intermediate solutions under the same conditions as those in Figure 4.1 replacing dialkyl diselenide with dialkyl disulfide are shown in Figure 4.5. As in Figure
4.1, the peaks at 2.57 ppm (orange) in Figure 4.5 belong to the protons of α-CH$_2$S- of TAuS-001 (Figure 4.5f), those indicated by the blue numbers arise from the protons of α-CH$_2$N$^+$ of TOAB, and those by red numbers come from the encapsulated water with (Figure 4.5a, TAuS-311, and 4.5b, TAuS-211) or without (Figure 4.5g, TAuS-310) acidic protons. Figure 4.5g is the same spectrum as Figure 4.1g, reproduced here for reference.

As in the case of diselenide, no reaction occurred by simply mixing TOAB with the ligand (TAuS-301), Figure 4.5e. Neither reaction occurred in TAuS-311C with no water present (Figure 4.5d). No shift of the 2.57 ppm peak was observed in this case, indicating that little interaction - if any - between disulfide and the Au complex existed, unlike the case of diselenide (TAuSe-301) where the formation of a Lewis adduct was inferred (Figure 4.1d, Figure 4.2d, and the DFT calculations). As observed for the Se case, the presence of inverse - micelle - encapsulated water in the post - Au(III) - transferred organic solution immediately enabled the reaction between disulfide and Au complex in TAuS-311 and -211, as implied by the appearance of the acidic proton peaks at 5.26 ppm and 4.21 ppm in Figure 4.5a and 4.5b, respectively. However, in contrast to the case of diselenide, the reaction did not consume all the starting disulfide as the peak at 2.57 ppm still remained, although with substantially decreased amplitude.

The corresponding Raman spectra of the solutions in Figure 4.5 are presented in Figure 4.6. Figure 4.6g is a reproduction of Figure 4.2g for reference. Figure 4.6d shows a simple addition of disulfide to the C$_6$D$_6$ solution of [TAO][AuBr$_4$] (TAuS-311C), though the S-S band at 525 cm$^{-1}$ is tiny compared to the intense peaks at 197 cm$^{-1}$ and 215 cm$^{-1}$ from the [AuBr$_4$]$^-$ moiety. This suggests that the disulfide did not interact
strongly (if at all) with the Au complex, consistent with the conclusion reached based on
the $^1$H NMR, Figure 4.5d. This is in great contrast to the case of diselenide where the
possible formation of a Lewis adduct was inferred, Figure 4.1d and 4.2d. As in Figure
4.2c (TAuSe-111), Figure 4.6c (TAuS-111) appears to be a simple addition of the spectra
of the individual components, TAuS-310 (Figure 4.6g) and TAuS-001 (Figure 4.6f), with
no evidence of reaction between the disulfide and the Au complex, but with evidence
(vide supra) indicating that no major displacement of Br$^-$ by Cl$^-$ took place. On the other
hand, Figure 4.6a (TAuS-311) and 4.6b (TAuS-211) show that significant change
occurred once inverse - micelle - encapsulated water was present. That is, a reaction took
place as in the case of diselenide (Figure 4.2a and 4.2b), although the remaining S-S
vibrational band at 525 cm$^{-1}$ in Figure 4.6a and 4.6b (also the 2.57 ppm peak in Figure
4.5a and 4.5b) indicates that not all original ligands were consumed.

As in the cases of diselenide (vide supra), results obtained on disulfide show again that
inverse - micelle - encapsulated water was indispensable for the reaction of disulfide with
the Au complex. What was intriguing in both cases is that no obvious color change was
observed, suggesting that the Au(III) was not reduced to Au(I) because the latter would
be colorless, but rather to the rarely observed Au(II) which is paramagnetic and whose
color was observed to be reddish$^{76}$. ERS measurements indeed confirmed the existence
of the paramagnetic species in the samples that produced Figure 4.1a and 4.1b and Figure
4.5a and 4.5b (see representative ESR spectrum in Figure 4.8). Since no viable proton
sources other than water existed in the reaction solutions and no vibrational evidence of
Au-S ($\sim$327 cm$^{-1}$) and Au-Se ($\sim$230 cm$^{-1}$) bond formation was observed, the appearance
of acidic protons in TAuSe-311 (Figure 4.1a), TAuSe-211 (Figure 4.1b), TAuS-311 (Figure 4.5a), and TAuS-211 (Figure 4.5b) strongly implies that the overall reaction may also involve hydrolysis, most likely in the form:

\[
[\text{TOA}][\text{Au(III)Br}_3] + \frac{1}{2}\text{RX} - \text{XR} + \text{H}_2\text{O} \\
\rightarrow [\text{TOA}][\text{Au(II)Br}_3]^\text{−} + \text{RXOH} + \text{Br}^\text{−} + \text{H}^\text{+} \ (1)
\]

where X=Se or S. However, the Se-Se bond was more reactive than the S-S bond.

The last step in the BSM two-phase synthesis of NPs is the reduction of Au ions by aqueous solution of NaBH₄. The TEM images of the Au NPs obtained by adding 10 equiv. NaBH₄ to TAuS-311/-311C and TAuSe-311/-311C are presented in Figure 4.9. The difference between the two samples for a given pair is that one of them had encapsulated water and the other did not. As can be seen clearly in Figure 4.9, the intermediates formed via Reaction (1) in the presence of encapsulated water led to the formation of Au NPs of much higher quality in terms of size distribution.

4.4 Conclusion

In summary, we have identified unambiguously that it was the inverse-micelle-encapsulated water that enabled *uniquely* the bond breaking reaction of diselenide/disulfide with Au cations, leading to the formation of unusual paramagnetic Au(II) complex (Figure 4.8) and the production of higher-quality Au NPs (Figure 4.10). We have also unraveled some subtle differences in chemistry involving dialkyl diselenide vs. disulfide in interaction with Au cations. For instance, the former could form
Au(III)(SeC₄H₉)₂ - like Lewis adduct species but not the latter and the bond-breaking was complete for the form but only partially for the latter. These findings should have important practical ramifications in terms of synthesizing organochalcogen-containing (particularly Se- or Te-containing) ligand-stabilized homogeneous Au metal NPs. Moreover, the inverse-micelle-encapsulated water-enabled bond-breaking chemistry in dialkyl-diselenide and dialkyl-disulfide may also have implications in biochemical processes involving like species.
Figure 4.1 $^1$H NMR spectra of the intermediate solutions with the same Au:Se ratio = 1:1 but different TOAB:Au ratios: (a) 3:1 (TAuSe-311), (b) 2:1 (TAuSe-211), and (c) 1:1 (TAuSe-111); (d) 3:1 but with [TOA][AuBr$_4$] : 2TOAB : 0.5(C$_{12}$H$_{25}$Se)$_2$ (TAuSe-311C), and of reference materials: (e) 3TOAB : 0.5(C$_{12}$H$_{25}$Se)$_2$ (TAuSe-301), (f) (C$_{12}$H$_{25}$Se)$_2$ (TAuSe-001), and (g) 3TOAB : 1HAuCl$_4$ (TAuSe-310); all in C$_6$D$_6$. 
Figure 4.2 Raman spectra spectra of the intermediate solutions with the same Au:Se ratio = 1:1 but different TOAB:Au ratios: (a) 3:1 (TAuSe-311), (b) 2:1 (TAuSe-211), and (c) 1:1 (TAuSe-111); (d) 3:1 but with [TOA][AuBr₄] : 2TOAB : 0.5(C₁₂H₂₅Se)₂ (TAuSe-311C), and of reference materials: (e) 3TOAB : 0.5(C₁₂H₂₅Se)₂ (TAuSe-301), (f) (C₁₂H₂₅Se)₂ (TAuSe-001), and (g) 3TOAB : 1HAuCl₄ (TAuSe-310). The dashed vertical lines are used to identify similar bands. See Figure 4.3 for corresponding full Raman spectra.
Figure 4.3 Full Raman spectra spectra of the intermediate solutions with the same Au:Se ratio = 1:1 but different TOAB:Au ratios: (a) 3:1 (TAuSe-311), (b) 2:1 (TAuSe-211), and (c) 1:1 (TAuSe-111); (d) 3:1 but with [TOA][AuBr₄] : 2TOAB : 0.5(C₁₂H₂₅Se)₂ (TAuSe-311C), and of reference materials: (e) 3TOAB : 0.5(C₁₂H₂₅Se)₂ (TAuSe-301), (f) (C₁₂H₂₅Se)₂ (TAuSe-001), and (g) 3TOAB : 1HAuCl₄ (TAuSe-310)₆.
Figure 4.4 Geometrically optimized molecular structures by the DFT calculations: (a) [HAu(III)Br₄](SeC₄H₉)₂ and (b) Au(III) (SeC₄H₉)₂. Se is depicted in yellow, Au in the reddish color, and Br in the bluish color; the alkyl chains are bonded to the Se atoms and are clearly distinguishable.
Table 4.1 Cartesian coordinates [Å] of \([\text{Au(III)}\text{Br}_4]^–(\text{SeC}_4\text{H}_9)_2\) and \(\text{Au(III)} (\text{SeC}_4\text{H}_9)_2\).

<table>
<thead>
<tr>
<th></th>
<th>(\text{Au(III)}\text{Br}_4]^–(\text{SeC}_4\text{H}_9)_2)</th>
<th>(\text{Au(III)} (\text{SeC}_4\text{H}_9)_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{Au}</td>
<td>-2.1575475297 2.755832098 1.694676955</td>
<td>-1.1304697915 -0.015577063 6.152730617</td>
</tr>
<tr>
<td>\text{Br}</td>
<td>-0.5668112454 3.472031552 3.746323478</td>
<td>-2.890764314 -1.520674487 8.485970859</td>
</tr>
<tr>
<td>\text{Br}</td>
<td>-0.0973183832 3.189751955 0.386171740</td>
<td>-0.502386881 -0.848004543 3.939178294</td>
</tr>
<tr>
<td>\text{Br}</td>
<td>-3.426370269 2.346273881 -0.392771815</td>
<td>-2.547589619 -3.526336514 5.225500355</td>
</tr>
<tr>
<td>\text{Br}</td>
<td>-2.5944424206 2.613504247 2.983605633</td>
<td>-2.952163536 -3.626252951 6.244108205</td>
</tr>
<tr>
<td>\text{Se}</td>
<td>-3.1091017614 -0.994856463 2.857951755</td>
<td>-1.501749034 -3.827725787 5.176715454</td>
</tr>
<tr>
<td>\text{Se}</td>
<td>-1.262254676 0.280270365 2.093651536</td>
<td>-3.475026987 -4.096762707 4.145422971</td>
</tr>
<tr>
<td>\text{Se}</td>
<td>-2.0631951532 -2.402987464 3.820763796</td>
<td>-3.075028367 -3.961235053 3.130096918</td>
</tr>
<tr>
<td>\text{H}</td>
<td>-1.4944653233 -1.903427420 4.610836533</td>
<td>-4.494212300 -3.558872670 2.468176905</td>
</tr>
<tr>
<td>\text{H}</td>
<td>-1.3774154647 -2.808237108 3.107159609</td>
<td>-3.509657028 -5.676614254 4.077526487</td>
</tr>
<tr>
<td>\text{C}</td>
<td>-3.0482976643 -3.428458630 2.989075956</td>
<td>-3.973767144 -5.796135545 5.503580770</td>
</tr>
<tr>
<td>\text{C}</td>
<td>-5.925093588 -3.918671797 3.851250172</td>
<td>-2.575038444 -6.685742094 4.193848933</td>
</tr>
<tr>
<td>\text{C}</td>
<td>-3.7989798069 -2.906382775 5.921583987</td>
<td>5.526948189 -6.274052706 3.455999210</td>
</tr>
<tr>
<td>\text{C}</td>
<td>-2.337016602 -4.483222557 2.526709554</td>
<td>-5.660048661 -5.905424465 3.520697186</td>
</tr>
<tr>
<td>\text{H}</td>
<td>-1.804384445 -3.983232756 6.082026748</td>
<td>-4.536349866 -7.361298664 3.736395129</td>
</tr>
<tr>
<td>\text{H}</td>
<td>-1.583841766 -4.987441279 4.649768261</td>
<td>-4.157888907 -6.245591214 2.423401561</td>
</tr>
<tr>
<td>\text{C}</td>
<td>-3.3055802348 -5.523525209 5.927014447</td>
<td>-0.801711974 0.362607361 3.235053338</td>
</tr>
<tr>
<td>\text{C}</td>
<td>-0.664219746 -5.049763166 6.649447875</td>
<td>-0.112168689 1.192174697 2.525800040</td>
</tr>
<tr>
<td>\text{C}</td>
<td>-0.774281375 -6.267822988 4.683512538</td>
<td>-1.845520982 0.694204783 2.305512642</td>
</tr>
<tr>
<td>\text{C}</td>
<td>-3.826918125 -6.061264150 5.022391287</td>
<td>-0.3539304251 -0.541625197 1.170972168</td>
</tr>
<tr>
<td>\text{C}</td>
<td>-0.0256268957 -0.376482929 2.246513113</td>
<td>-1.052336295 -3.305707730 0.978712872</td>
</tr>
<tr>
<td>\text{H}</td>
<td>-1.2352587287 0.489367046 -5.187895145</td>
<td>-0.667968081 -0.910800928 1.286083608</td>
</tr>
<tr>
<td>\text{H}</td>
<td>-0.6164990476 -1.129995617 0.069697358</td>
<td>-0.356788009 0.447152055 -0.139231996</td>
</tr>
<tr>
<td>\text{C}</td>
<td>0.3799739084 -0.327102028 -0.015761134</td>
<td>0.3403541305 1.262406726 0.092796348</td>
</tr>
<tr>
<td>\text{H}</td>
<td>0.587547390 -1.769215523 0.684241320</td>
<td>-1.374840358 0.839969690 -0.251708186</td>
</tr>
<tr>
<td>\text{C}</td>
<td>1.118213883 -0.148286354 0.240167104</td>
<td>0.684824305 -0.381544553 -1.324027389</td>
</tr>
<tr>
<td>\text{C}</td>
<td>0.580713086 -1.287421786 -1.453910959</td>
<td>-0.616856619 -1.176122647 -1.690412048</td>
</tr>
<tr>
<td>\text{H}</td>
<td>0.831870776 -0.541672704 -2.129855615</td>
<td>1.1099452589 -0.767243868 -2.403292209</td>
</tr>
<tr>
<td>\text{H}</td>
<td>-0.1648369571 -2.169959343 -1.697480374</td>
<td>0.0807730357 0.3481236046 -2.178094633</td>
</tr>
<tr>
<td>\text{H}</td>
<td>1.9887440926 -1.392670577 -1.711224904</td>
<td>2.021359224 -2.802053990 1.071528059</td>
</tr>
<tr>
<td>\text{H}</td>
<td>2.7534573338 -1.169146924 -1.508890846</td>
<td>2.104297398 -2.249764272 2.765917406</td>
</tr>
<tr>
<td>\text{H}</td>
<td>-2.5400592928 4.155473038 1.510593035</td>
<td></td>
</tr>
</tbody>
</table>
4.5 $^1$H NMR spectra of the intermediate solutions with the same Au:S ratio = 1:1 but different TOAB:Au ratios: (a) 3:1 (TAuS-311), (b) 2:1 (TAuS-211), and (c) 1:1 (TAuS-111), (d) 3:1 but with [TOA][AuBr$_4$] : 2TOAB : 0.5 (C$_{12}$H$_{25}$S)$_2$ (TAuS-311C): and of reference materials: (e) 3TOAB : 0.5 (C$_{12}$H$_{25}$S)$_2$ (TAuS-301), (f) (C$_{12}$H$_{25}$S)$_2$ (TAuS-001), and (g) 3TOAB : 1HAuCl$_4$ (TAuS-310), all in C$_6$D$_6$. 
Figure 4.6 Raman spectra of the intermediate solutions with the same Au:S ratio = 1:1 but different TOAB:Au ratios: (a) 3:1 (TAuS-311), (b) 2:1 (TAuS-211), and (c) 1:1 (TAuS-111), (d) 3:1 but with [TOA][AuBr₄] : 2TOAB : 0.5 (C₁₂H₂₅S)₂ (TAuS-311C): and of reference materials: (e) 3TOAB : 0.5 (C₁₂H₂₅S)₂ (TAuS-301), (f) (C₁₂H₂₅S)₂ (TAuS-001), and (g) 3TOAB : 1HAuCl₄ (TAuS-310). See Figure 4.7 for corresponding full Raman spectra.
Figure 4.7 Full Raman spectra of the intermediate solutions with the same Au:S ratio = 1:1 but different TOAB:Au ratios: (a) 3:1 (TAuS-311), (b) 2:1 (TAuS-211), and (c) 1:1 (TAuS-111), (d) 3:1 but with [TOA][AuBr₄] : 2TOAB : 0.5 (C₁₂H₂₅S)₂ (TAuS-311C), and of reference materials: (e) 3TOAB : 0.5 (C₁₂H₂₅S)₂ (TAuS-301), (f) (C₁₂H₂₅S)₂ (TAuS-001), and (g) 3TOAB : 1HAuCl₄ (TAuS-310).
Figure 4.8 EPR spectra of TAuS-311 as a representative.
Figure 4.9 TEM images and corresponding size distribution histograms of Au NPs by adding aqueous solution of 10 equiv. NaBH₄ to (a) TAuS-311, (b) TAuS-311C, (c) TAuSe-311, and (d) TAuSe-311C. The respective average sizes are (a) 1.9 ± 0.3 nm, (b) 3.64 ± 1.6nm, (c) 2.43 ± 0.8nm, and (d) 5.77 ± 2.1 nm, respectively.
Figure 4.10 Summary of Chapter IV.
4.5 References

CHAPTER V
MECHANISTIC INSIGHTS ON ONE - PHASE VS. TWO - PHASE BRUST - SCHIFFRIN METHOD SYNTHESIS OF AU NANOPARTICLES WITH DIOCTYL - DISELENIDES

Reproduced with permission from Zaluzhna, O.; Li, Y.; Zangmeister, C.; Allison, T.C.; Tong, Y.J., Mechanistic insights on one - phase vs. two - phase Brust - Schiffrin method synthesis of Au nanoparticles with dioctyl - diselenides, Chemical Communication, 2012, 48, 362 - 364. This work was a combined effort of Zaluzhna, O. and Tong Y. J. Additionally, Dr. Ying Li aided in data discussions, revisions of the paper, and preparation of XPS spectra pictures. Dr. Allison has performed all the computational studies and Dr. Zangmeister has done all the XPS experiments.

5.1 Background

Since Brust and Schiffrin discovered the one - phase and two - phase procedures for the synthesis of Au NPs with a thiol - containing protecting ligand, i.e., BSM, many studies have used it to prepare thiolate - protected metal NPs. The long - held assumption was that the addition of thiol reduces Au(III) to Au(I) and forms polymeric \([\text{AuSR}]_n\) species in both the one - phase and two - phase BSM. But it was shown recently that the [TOA]\([\text{AuX}_2]\) complex (tetraoctyl - ammonium gold (I) halide), which was formed from the reduction of \([\text{Au(III)X}_2]\) by thiol, was actually the Au precursor in the two - phase BSM. We recently showed further that the BSM is in principle an inverse
micelle based synthesis and water plays an important role in forming different intermediate species.\textsuperscript{89-91}

On the other hand, despite that heavy chalcogens (\textit{i.e.}, Se and Te) may be better alternatives to S as anchoring elements with better conductance,\textsuperscript{92, 93} it is surprising that only a few groups made attempts to use Se - or Te - containing organo ligands for self - assembled monolayers (SAMs) on Au or Ag substrates over the last two decades.\textsuperscript{94-99} Even fewer studies on metal NPs protected by Se - or Te - containing ligands, a 3D analogue of the 2D SAMs, are available.\textsuperscript{100-104} Mechanistic understanding of the corresponding NP formation chemistry is almost non - existent. Ulman's group synthesized and characterized Au NPs with didodecyl diselenide as a ligand precursor by the one - phase (THF) BSM since their two - phase BSM synthesis produced much larger and more widely dispersed Au NPs.\textsuperscript{102} Based on the observation of no noticeable color change prior to NaBH\textsubscript{4} addition, it was concluded that no reaction occurred between Au(III) and the ligands. It was also speculated that THF replaced Cl\textsuperscript{−} to coordinate with Au(III) and stabilized the newly formed Au NPs before being replaced by the selenolate. Here, we report the plausible chemistry responsible for the observation that one - phase is better than two - phase synthesis of alkane selenolate - stabilized Au NPs\textsuperscript{102} as exemplified by the TEM images of the respective Au NPs in Figure 5.1.
5.2 Experimental Section

Synthesis of Intermediates: For one-phase BSM, the mixture of (HAuCl₄, 0.05 mmol) aqueous solution (0.35 mL, 0.1329M) was mixed with (C₈H₁₇Se)₂ (0.025 mmol) in THF (5.0 mL). (After the addition of (C₈Se)₂ no color change was noted, the solution stayed yellow even after stirring overnight.) This mixture of HAuCl₄ and (C₈Se)₂ with the ratio of 1Au : 0.5(C₈Se)₂ was stirred in THF overnight, then rotary-evaporated, and C₆D₆ (0.8 mL) was added to run NMR experiments. The same concentrated intermediate solution was used for Raman (a couple of drops) and XPS measurements, where the experiments were run after C₆D₆ evaporated leaving solid for characterization behind.

For two-phase BSM, the mixture of hydrogen tetrachloroaurate (HAuCl₄, 0.05 mmol) aqueous solution (0.35 mL) was mixed with a TOAB (0.15 mmol for ratio of 3TOAB : 1Au, 0.10 mmol for ratio of 2TOAB : 1Au, and 0.05 mmol for ratio of 1TOAB : 1Au, respectively) in 0.8 mL of C₆D₆. The solution turned burgundy red in color. Then (C₈H₁₇Se)₂ (0.025 mmol) was added to toluene layer (note: for all solutions Au and (R₂Se)₂ volume used was constant), and after overnight stirring the solution color changed to yellow. After stirring it overnight, the aqueous layer was discarded and samples were measured via NMR, Raman and XPS.

Synthesis of ligands and alkane selenolate-protected Au NPs for one- and two-phase BSM are reported in Chapter III.
5.3 Results and Discussions

Figure 5.2 presents the $^1$H (a & b) and $^{13}$C (c & d) NMR spectra of the one-phase intermediate (black) and starting (C8Se)$_2$ (red) for comparison. The $^1$H peak of $^1$H$_2$CSe- at 2.75 ppm in the ligand (Figure 5.2b, red) disappeared in the one-phase intermediate (Figure 5.2a, black), which indicates that the Se-Se bond of the starting ligand was broken, i.e., the reaction between (C8Se)$_2$ and HAuCl$_4$ occurred, although no color change was observed. This also corroborates with the large $^{13}$C shift for C$_1$/C$_2$ in (Figure 5.2c) vs. (Figure 5.2d). Most importantly, the eight $^{13}$C peaks in Figure 5.2c imply that the one-phase intermediate consists dominantly of a single type of metal complex.

The Raman spectra of the one-phase intermediate and of the starting materials ((C8Se)$_2$ and HAuCl$_4$) are presented in Figure 5.3. The peak at 287 cm$^{-1}$ can be assigned to the RSe-SeR bond$^{105}$ of (C8Se)$_2$ (Figure 5.3a) and those at 327 cm$^{-1}$ and 351 cm$^{-1}$ (Figure 5.3c) to Au-Cl$_2$ asymmetric vibrations in the AuCl$_4^-$ anion (HAuCl$_4$ is highly water-absorbing) and the HAuCl$_4$ molecule, respectively.$^{106}$ The latter assignments were confirmed by our density functional theory (DFT) calculations (Tables 5.2 & 5.3 & 5.5). All those peaks disappeared and new peaks appeared in Figure 5.3b, confirming further that the reaction between (C8Se)$_2$ and Au(III) did occur, even though no noticeable color change was observed. Based on the available literature values,$^{107, 108}$ and our DFT calculations (Table 5.3), we assigned the 332 cm$^{-1}$ band to $\nu_{\text{as}}$(Au-Cl$_2$), the 315 cm$^{-1}$ band to $\nu_{\text{as}}$(Se-Cl$_2$), and the 142 cm$^{-1}$ band to $\nu_c$(Au-Se). Although we were unable to assign unambiguously the remaining peaks, the DFT calculations suggested that the 225 cm$^{-1}$
and 210 cm\(^{-1}\) bands involve the vibrations of \(\nu_s(Au-Cl_2)\) and the 124 cm\(^{-1}\) band involves Au-SeC8 backbone waving motions.

Additionally, the XPS results (Table 5.6b) show that the oxidation states of Au and Se in the 1p intermediate were +1 (84.25 eV\(^{109}\)) and +2 (58.4 eV\(^{110}\)), respectively. By combining the above NMR, Raman, and XPS results altogether, we concluded that the reaction between HAuCl\(_4\) and (C8Se)\(_2\) did occur and produced dominantly one type of metal complex, highly likely in the form of Cl\(_2\)AuSe(C8)Cl\(_2\).

Comparatively, we also studied the two-phase intermediates of the BSM synthesis as a function of TOAB (tetraoctylammonium bromide) : Au ratio but with a constant Au : Se ratio (1 : 1). Figure 5.4 presents the \(^1\)H NMR spectra of the samples (the corresponding \(^{13}\)C NMR spectra were dominated by TOAB therefore useless). The unchanged peak positions of \(^1\)H\(_2\)C-N\(^+\) and \(^1\)H\(_2\)C-Se in the simple mixture of TOAB and (C8Se)\(_2\) as compared to their respective pure forms (Figure 5.4a) indicate that no reaction happened. However, in the presence of HAuCl\(_4\), a large shift of the \(^1\)H\(_2\)C-N\(^+\) peak was observed (Figure 5.4(b-e)), evidencing strong interaction between them. This is consistent with the previously observed formation of TOA-Au-halide complex.\(^{88}\) But the variations in the \(^1\)H\(_2\)C-Se peak are subtle and suggest that the degree of the Se-Se bond breaking depended on the reaction conditions (Figure 5.5). At TOAB : Au = 1 : 1, the \(^1\)H\(_2\)C-Se peak was broadened and showed a very small but an observable positive shift. At TOAB : Au = 1.25 : 1, the peak splits into two, with the more positive one losing the original triplet structure while the other still maintaining it. At TOAB : Au = 2 : 1, the split peaks both lost the triplet structure with one shifted further positively. Finally at TOAB : Au = 3 : 1,
the split peaks can barely be seen. We integrated the amplitude of the $^1\text{H}_2\text{C-}\text{Se}$ peaks and normalized them by respective integral of the $^1\text{H}_2\text{C-N}^+$ peak. If we assume that these observed $^1\text{H}_2\text{C-}\text{Se}$ peaks represent the unbroken Se-Se bonds, the normalized integrals (Table 5.1) then suggest that the percentages of Se-Se bond breaking were about 0%, 27%, 33%, and 67% for (b), (c), (d), and (e) respectively.

On the other hand, the observation of the hydronium ions ($\text{H}_3\text{O}^+$) as indicated in Figure 5.4 is intriguing because a simple phase transfer of Au(III) does not generate observable hydronium ions. Although the subsequent addition of thiol does it, where the hydrogen in the -SH group acts like a reductant, $^{91}$ (C8Se)$_2$ does not have such an obvious proton source. Thus, we speculate that hydrolysis of water might have happened.

Complementary information can be gleaned from the Raman measurements as presented in Figure 5.6. As expected, the simple mixture of TOAB and (C8Se)$_2$ led to a simple addition of the respective Raman spectra of the pure forms (the RSe-SeR band was slightly blue-shifted to 292 cm$^{-1}$), in agreement with the NMR observation of no reaction between TOAB and (C8Se)$_2$. However, new vibrational bands appeared after the addition of Au salt, Figure 5.6 (b-e). Again, by relying on literature values, our DFT calculations (Table 5.4), and the fact that Br$^-$ could replace the majority of Cl$^-$ in AuCl$_4^-$ at high TOAB loadings, $^{91}$ we tentatively assigned the 660 cm$^{-1}$ band to $\nu_s$(Se-OH) $^{70}$ (vide infra), the 340 cm$^{-1}$ band to $\nu_a$(Au-Cl$_2$), the 236 cm$^{-1}$ band to $\nu_s$(Au-Cl$_2$), and the 215 cm$^{-1}$ band to $\nu_a$(Au-Br$_2$). We were unable to assign the 175 cm$^{-1}$ band but noticed that there was an observable band at the same wavenumber in Figure 5.6(c) and its disappearance at higher TOAB loading (i.e., more replacement of Cl$^-$ by Br$^-$ that also led to the gradual
decrease of the 340 cm\(^{-1}\) and 236 cm\(^{-1}\) bands). We thus speculated that it might involve vibrations of the Au-Cl bond.

The unabated C8Se-SeC8 band at 292 cm\(^{-1}\) in Figure 5.6(a) confirms that the majority of Se-Se bonds were not broken at TOAB : Au = 1 : 1. As the ratio of TOAB : Au increased, the amplitude of the C8Se-SeC8 band at 292 cm\(^{-1}\) decreased and became barely observable in Figure 5.6(e), implying that more and more Se-Se bonds were broken, consistent with the NMR observations discussed above. Since the 660 cm\(^{-1}\) band appeared in Figure 5.6(b) where majority of the Se-Se bonds were still intact, we speculate that it might actually belong to \(\nu\) (Se-OH) of a water activating process involving the majority of the (C8Se)\(_2\) molecules in which one of the two Se formed a molecular structure like Se-OH\(_2\) while still maintaining its bond with the other Se. Still, a very small amount of Se-Se bonds would break, which led to the hydrolysis such as H\(_2\)O + Se → Se–OH + H\(^+\) and the appearance of the \(^1\)H peak of hydronium ions in Figure 5.4 (b & c). As more Se-Se bonds were broken, more hydrolysis took place, more Se-OH was formed, and more hydronium ions were generated. So did the corresponding \(^1\)H NMR signals in Figure 5.4 (d & e). This would also explain the red-shift of the band to 642 cm\(^{-1}\) from the initial value of 660 cm\(^{-1}\), as can be seen in Figure 5.6.

Finally, the XPS data for the 3TOAB : 1Au and 2TOAB : 1Au samples (Table 5.6c & d) indicate that the oxidation states of Au in these two-phase samples (84.2 eV and 84.3 eV respectively) were basically the same as that of Au in the one-phase synthesis (84.25 eV) but those of the Se (57.98 eV and 58.05 eV) were different from the one-phase synthesis (58.4 eV). That is, the smaller binding energies in the former indicate that the
charge screening of Se was higher than that in the latter. This is consistent with the proposed Se-OH bonding.

Both the $^1$H NMR (Figure 5.4) and Raman (Figure 5.6) data strongly suggest that more than one species exist as the two-phase intermediates. The appearance of encapsulated H$_2$O$^-$ as shown in Figure 5.4 $^{88, 89, 91}$ suggests that hydrolysis of water had happened and likely led to species such as X$_2$AuSe(C8)(OH)X (X = Br or Cl) as one of the intermediates whose exact compositions still need to be further studied. One important difference between the one-phase and two-phase BSM syntheses, however, is that the result shown in Figure 5.3 was highly reproducible but not those in Figure 5.6 that appeared to be highly dependent on many hard-to-control factors.

The final Au NPs were formed by adding NaBH$_4$ to the one-phase and two-phase intermediate solutions. As can be clearly seen in Figure 5.1 and as was also observed previously, $^{102}$ the quality of the Au NPs synthesized via the one-phase BSM was much higher than that via the two-phase BSM. We propose that the chemical reason for this difference is that the former had only a single dominant type of metal precursor while the latter had multiple ones. $^{90, 91}$

5.4 Conclusion

In conclusion, we have shown that in both one-phase and two-phase BSM syntheses and prior to the addition of NaBH$_4$, (C8Se)$_2$ reacted with Au(III) by reducing it to Au(I). At the same time, the RSe-SeR bond was broken and Se was oxidized from the initial $-1$ to the final
+2 state in both the one-phase and two-phase syntheses but in the latter case the charge screening of Se appeared to be higher as evidenced by the lower electron binding energies. Most importantly, a single dominant intermediate metal precursor, likely Cl$_2$AuSe(C8)Cl$_2$, was formed in the former, but more than one intermediate metal precursors, some of which might be X$_2$AuSe(C8)(OH)X (X = Br or Cl), existed in the latter (Scheme 5.1). We propose that having a rather uniform metal precursor in the one-phase but not in the two-phase BSM synthesis was the underlying chemical reason for producing Au NPs of higher quality in the former synthesis.
Figure 5.1 TEM images of octaneselenoate-stabilized Au NPs synthesized by (a) one-phase and (b) two-phase BSM syntheses. The insets are: (i) UV-vis spectra and (ii) the respective size distributions that give the average size of 2.0 nm ± 0.5 nm for the former (a) and 4.2 nm ± 1.6 nm for the latter (b) (Note: both after centrifugation).
Figure 5.2 $^1$H (a and b) and $^{13}$C NMR (c and d) spectra of the one-phase intermediate (black) and the pure (C8Se)$_2$ (red) respectively. The arrows indicate the assignments of the respective peaks.
Figure 5.3  Raman spectra of (a) dioctyl diselenide, (b) the concentrated one-phase intermediate after removing THF, \textit{i.e.}, 1 equiv. of HAuCl$_4$ and 0.5 equiv. of dioctyl diselenide, and (c) aqueous HAuCl$_4$ solution.
Figure 5.4  $^1$H NMR spectra of (a) 3TOAB + 0.5(C8Se)$_2$, (b) 1TOAB + 1HAuCl$_4$ + 0.5(C8Se)$_2$, (c) 1.25TOAB + 1HAuCl$_4$ + 0.5(C8Se)$_2$, (d) 2TOAB + 1HAuCl$_4$ + 0.5(C8Se)$_2$, and (e) 3TOAB + 1HAuCl$_4$ + 0.5(C8Se)$_2$ in C$_6$D$_6$. 
Figure 5.5  Enlarged zone of $^1\text{H}$ NMR spectra of (a) 3TOAB + 0.5(C8Se)$_2$, (b) 1TOAB + 1HAuCl$_4$ + 0.5(C8Se)$_2$, (c) 1.25TOAB + 1HAuCl$_4$ + 0.5(C8Se)$_2$, (d) 2TOAB + 1HAuCl$_4$ + 0.5(C8Se)$_2$, and (e) 3TOAB + 1HAuCl$_4$ + 0.5(C8Se)$_2$ in C$_6$D$_6$. 
<table>
<thead>
<tr>
<th>Sample*</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>α-CH$_2$-N$^+$</td>
</tr>
<tr>
<td>(a) 3TOAB : 0.5(C$_8$Se)$_2$</td>
<td>8</td>
</tr>
<tr>
<td>(b) 1TOAB : 1Au : 0.5(C$_8$Se)$_2$</td>
<td>8</td>
</tr>
<tr>
<td>(c) 1.25TOAB : 1Au : 0.5(C$_8$Se)$_2$</td>
<td>8</td>
</tr>
<tr>
<td>(d) 2TOAB : 1Au : 0.5(C$_8$Se)$_2$</td>
<td>8</td>
</tr>
<tr>
<td>(e) 3TOAB : 1Au : 0.5(C$_8$Se)$_2$</td>
<td>8</td>
</tr>
</tbody>
</table>

**Table 5.1** Proton Numbers of the (C8Se)$_2$ per [TOA]$^+$ for ratios (a) 3 TOAB + 0.5 (C8Se)$_2$, (b) 1 TOAB + 1 HAuCl$_4$ + 0.5 (C8Se)$_2$, (c) 1.25 TOAB + 1 HAuCl$_4$ + 0.5 (C8Se)$_2$, (d) 2 TOAB + 1 HAuCl$_4$ + 0.5 (C8Se)$_2$, and (e) 3 TOAB + 1 HAuCl$_4$ + 0.5 (C8Se)$_2$ in C$_6$D$_6$. (Note: the numbers of protons for all sample in α-CH$_2$-N$^+$ from TOA$^+$ was assigned as 8).
Figure 5.6 Raman spectra of (a) (C8Se)$_2$, (b) 3TOAB + 0.5(C8Se)$_2$, (c) 1TOAB + 1HAuCl$_4$ + 0.5(C8Se)$_2$, (d) 1.25TOAB + 1HAuCl$_4$ + 0.5(C8Se)$_2$, (e) 2TOAB + 1HAuCl$_4$ + 0.5(C8Se)$_2$, and (e) 3TOAB + 1HAuCl$_4$ + 0.5(C8Se)$_2$. 
<table>
<thead>
<tr>
<th>Compound</th>
<th>Frequency (cm(^{-1}))</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>AuCl(_4)</td>
<td>261.6</td>
<td>Au-Cl symm. stretch (2 in, 2 out)</td>
</tr>
<tr>
<td></td>
<td>297.6</td>
<td>Au-Cl symm. stretch (all 4)</td>
</tr>
<tr>
<td></td>
<td>321.5</td>
<td>Au-Cl assym. stretch (doubly degenerate, opposite Cl stretch)</td>
</tr>
<tr>
<td>HAuCl(_4)</td>
<td>272.4</td>
<td>Au-Cl symm. stretch (2 in, 2 out)</td>
</tr>
<tr>
<td></td>
<td>309.8</td>
<td>Au-Cl symm. stretch (all 4)</td>
</tr>
<tr>
<td></td>
<td>344</td>
<td>Au-Cl assym. stretch (2 of 4, opposite)</td>
</tr>
<tr>
<td></td>
<td>348.5</td>
<td>Au-Cl assym. stretch (2 of 4, opposite)</td>
</tr>
<tr>
<td></td>
<td>351</td>
<td>Au-Cl assym. stretch (looks like 344)</td>
</tr>
<tr>
<td>(CB(_8)H(_7)Se(_2))</td>
<td>267.3</td>
<td>Se-Se stretch</td>
</tr>
<tr>
<td></td>
<td>310.6</td>
<td>Se-Se stretch (coupled)</td>
</tr>
<tr>
<td></td>
<td>346.3</td>
<td>Se-Se stretch (coupled)</td>
</tr>
</tbody>
</table>

Table 5.2 DFT calculated vibrational frequencies for reference molecules.
<table>
<thead>
<tr>
<th>Complex</th>
<th>Frequency (cm(^{-1}))</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl(_2)AuSe(C(<em>8)H(</em>{17}))Cl(_2)</td>
<td>158</td>
<td>Au-Se stretch</td>
</tr>
<tr>
<td></td>
<td>284.9</td>
<td>Se-Cl stretch</td>
</tr>
<tr>
<td></td>
<td>299.6</td>
<td>Se-Cl stretch</td>
</tr>
<tr>
<td></td>
<td>307.7</td>
<td>Au-Cl stretch</td>
</tr>
<tr>
<td></td>
<td>316.7</td>
<td>Se-Cl stretch</td>
</tr>
<tr>
<td></td>
<td>360.9</td>
<td>Au-Cl(_2) assym. stretch</td>
</tr>
</tbody>
</table>

**Table 5.3** Partial DFT calculated vibrational frequencies for Cl\(_2\)AuSe(C\(_8\)H\(_{17}\))Cl\(_2\) complex.
Table 5.4 Some representative DFT calculated vibrational frequencies for $X_2\text{AuSe(C8H17)}X$-OH complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Frequency (cm$^{-1}$)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br$_2$AuSe(C8H17)OHBr</td>
<td>102.5</td>
<td>Au-Se stretch</td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>Au-Se stretch</td>
</tr>
<tr>
<td></td>
<td>194.6</td>
<td>Au-Br symm. stretch</td>
</tr>
<tr>
<td></td>
<td>207.4</td>
<td>Au-Br symm. stretch</td>
</tr>
<tr>
<td></td>
<td>258.8</td>
<td>Au-Br asymm. stretch</td>
</tr>
<tr>
<td></td>
<td>255.9</td>
<td>Se-Br stretch</td>
</tr>
<tr>
<td></td>
<td>682.9</td>
<td>Se-OH stretch</td>
</tr>
<tr>
<td>Br$_2$AuSe(C8H17)OHCl</td>
<td>107.5</td>
<td>Au-Se stretch</td>
</tr>
<tr>
<td></td>
<td>117.3</td>
<td>Au-Se stretch</td>
</tr>
<tr>
<td></td>
<td>199.9</td>
<td>Au-Br symm. stretch</td>
</tr>
<tr>
<td></td>
<td>205.3</td>
<td>Au-Br symm. stretch</td>
</tr>
<tr>
<td></td>
<td>259.6</td>
<td>Au-Br asymm. stretch</td>
</tr>
<tr>
<td></td>
<td>284.7</td>
<td>Se-Cl stretch</td>
</tr>
<tr>
<td></td>
<td>686.6</td>
<td>Se-OH stretch</td>
</tr>
<tr>
<td>ClBrAuSe(C8H17)OHBr</td>
<td>102.7</td>
<td>Au-Se stretch</td>
</tr>
<tr>
<td></td>
<td>110.6</td>
<td>Au-Se stretch (coupled)</td>
</tr>
<tr>
<td></td>
<td>181.9</td>
<td>Se-Br stretch</td>
</tr>
<tr>
<td></td>
<td>207.2</td>
<td>Se-Br stretch</td>
</tr>
<tr>
<td></td>
<td>211.2</td>
<td>Se-Br stretch</td>
</tr>
<tr>
<td></td>
<td>233.4</td>
<td>Se-Br stretch</td>
</tr>
<tr>
<td></td>
<td>292.6</td>
<td>Au-Cl stretch</td>
</tr>
<tr>
<td></td>
<td>309.7</td>
<td>Au-Cl stretch (coupled)</td>
</tr>
<tr>
<td></td>
<td>685.9</td>
<td>Se-OH stretch</td>
</tr>
<tr>
<td>ClBrAuSe(C8H17)OHCl</td>
<td>107</td>
<td>Au-Se stretch</td>
</tr>
<tr>
<td></td>
<td>114</td>
<td>Au-Se stretch</td>
</tr>
<tr>
<td></td>
<td>234.8</td>
<td>Au-Br stretch</td>
</tr>
<tr>
<td></td>
<td>287.2</td>
<td>Se-Cl stretch</td>
</tr>
<tr>
<td></td>
<td>291.8</td>
<td>Se-Cl stretch (coupled)</td>
</tr>
<tr>
<td></td>
<td>310.2</td>
<td>Au-Cl stretch</td>
</tr>
<tr>
<td></td>
<td>341.8</td>
<td>Au-Cl stretch (coupled)</td>
</tr>
<tr>
<td></td>
<td>688</td>
<td>Se-OH stretch</td>
</tr>
<tr>
<td>Cl$_2$AuSe(C8H17)OHBr</td>
<td>115.5</td>
<td>Au-Se stretch</td>
</tr>
<tr>
<td></td>
<td>215.9</td>
<td>Se-Br stretch</td>
</tr>
<tr>
<td></td>
<td>288.8</td>
<td>Au-Cl stretch</td>
</tr>
<tr>
<td></td>
<td>324</td>
<td>Au-Cl stretch</td>
</tr>
<tr>
<td></td>
<td>350.7</td>
<td>Au-Cl$_2$ asymm. stretch</td>
</tr>
<tr>
<td></td>
<td>675.5</td>
<td>Se-OH stretch</td>
</tr>
<tr>
<td>Cl$_2$AuSe(C8H17)OHCl</td>
<td>116.5</td>
<td>Au-Se stretch</td>
</tr>
<tr>
<td></td>
<td>139</td>
<td>Au-Se stretch</td>
</tr>
<tr>
<td></td>
<td>237.1</td>
<td>Se-Cl stretch (coupled)</td>
</tr>
<tr>
<td></td>
<td>282.5</td>
<td>Au-Cl stretch</td>
</tr>
<tr>
<td></td>
<td>289</td>
<td>Se-Cl stretch</td>
</tr>
<tr>
<td></td>
<td>304.3</td>
<td>coupled Au-Cl, Au-Se, Se-Cl stretch</td>
</tr>
<tr>
<td></td>
<td>318.6</td>
<td>Au-Cl$_2$ stretch (coupled)</td>
</tr>
<tr>
<td></td>
<td>350.7</td>
<td>Au-Cl$_2$ asymm. stretch</td>
</tr>
<tr>
<td></td>
<td>681.6</td>
<td>Se-OH stretch</td>
</tr>
</tbody>
</table>
Table 5.5 Cartesian coordinates (X Mol format, Angstroms) for optimized structures of 19 species calculated at the B3LYP/cc-pVDZ level of theory.
Table 5.6 XPS binding energies of (a) solid (C12Se)\(_2\), (b) one-phase intermediate with 1Au : 0.5(C8Se)\(_2\), (c) two-phase intermediate with 3TOAB : 1Au : 0.5(C8Se)\(_2\), and (d) two-phase intermediate with 2TOAB : 1Au : 0.5(C8Se)\(_2\).
Scheme 5.1 Summary of Chapter V.

\[
\text{RS}_{\text{Se-Se}R} + \text{HAuCl}_4
\]

One-phase synthesis

\text{Single Component of Intermediate} \\
\text{Cl}_2\text{AuSe}(R)\text{Cl}_2

\text{Two-phase synthesis}

\text{Multiple Components of Intermediate} \\
\text{X}_2\text{AuSe}(R)(\text{OH})\text{X}, \text{etc}

\[
\text{10 nm}
\]

\[
\text{10 nm}
\]
5.5 References


CHAPTER VI
EFFECT OF ANCHORING ELEMENTS AND ALKYL CHAIN LENGTH ON FORMED GOLD NANOPARTICLES

Reproduced with permission from Zaluzhna, O.; Li, Y.; Liu, Y.; Zangmeister, C.; Allison, T.C.; Tong, Y.J., Effect of Anchoring Elements and Alkyl Chain Length on Formed Gold Nanoparticles, *Langmuir* 2012, to be submitted. This paper was a combined effort of Zaluzhna, O., Li, Y., and Tong Y. J. Dr. Ying Li performed all experiments with Te system, aided in the data discussions, and revisions of the paper. Yangwei Liu worked on the experimental part of the S system. Dr. Allison has performed all the computational studies and Dr. Zangmeister has done all the XPS experiments.

6.1 Introduction

Since Brust and Schiffrin discovered an effective method for synthesizing thiolate-protected gold nanoparticles (NPs), abundant exploration has been made by using one-phase and two-phase synthetic routes to produce not only just thiolate-protected Au NPs, but also other metal NPs in general. Furthermore, the quantum calculations have predicted that heavy chalcogens (*i.e.*, Se and Te) are much more promising candidates as anchoring elements to have better conductance than S. Several groups have investigated self-assembled monolayers of dialkyl dichalcogenides (*i.e.*, R₂Se₂ or R₂Te₂) being absorbed on Au or Ag substrates. Brust and coworkers first reported to use R₂Se₂ or R₂Te₂ as ligand precursors to stabilize Au NPs;
unfortunately, their obtained Au NPs were unstable and no characterizations except Langmuir - Blodgett isotherms were performed. Recently, some of our studies focusing on the mechanistic understanding of the formation of organo chalcogenolate-protected NPs have demonstrated that stable Au NPs protected by \( \text{R}_2\text{Se}_2 \) could be successfully obtained with narrow size distribution via Ulman’s group modified one-phase synthetic route, and protected by \( \text{R}_2\text{Te}_2 \) by using revised two-phase Brust-Schiff rin method. However, there are still insufficient amount of studies accomplished on characterizations of NPs and how the ligands with different alkyl chain length and anchoring elements (i.e., S, Se, and Te) affect the protected Au NPs.

The alkyl chain length effect has been observed on thiolate-protected Au NPs, where by using 1-octanethiol (C8SH), 1-decanethiol (C10SH), and 1-hexadecanethiol (C16SH) as ligands in digestive ripening, the NPs size increased with increasing the alkyl chain. Similar observations were reported by Martin et al. where they used superlattices of unfractionated Au nanoclusters made in inverse micelle solution for synthesis of thiolate-protected Au NPs and noticed, that as thiol chain length increased, i.e., from C8SH to C10SH, C12SH, and C16SH, the obtained Au NPs became larger and more polydispersed. Recently, Stellwagen et al. reported alkyl chain dependence on \( \text{Au}_{38}(\text{SR})_{24} \) clusters that were prepared by ligand exchange from \( \text{Au}_n(\text{SG})_m \), where G was gluthathione. They observed opposite trend when compared their results with aforementioned ones: the average particle size appeared to decrease with increasing carbon chain length of the ligand. Specifically, they found that for C4S-Au NPs the particles aggregated, for C6S-Au NPs the diameter was \( \sim 2.60 \text{ nm} \), for C8S
- Au NPs ~ 1.84 nm, for C12S - Au NPs ~ 1.69 nm, and for C12S - Au NPs the diameter decreased to 1.47 nm, respectively.\textsuperscript{124} Although, the results from TEM images contradicted with their UV-Vis and MALDI analysis, where the same diameter as accepted theoretical value for Au$_{38}$ cluster (~ 1.1 nm) was observed, the group argued that NPs were damaged by the electron beam during TEM measurements that destroyed organic ligands in the samples.\textsuperscript{124}

In addition to the above seemingly unsettled observations of the carbon - chain - length effect on the thiol systems, it remains even more unclear whether the similar effect of the alkyl chain length would exist when dialkyl dichalcogenides, \textit{i.e.}, R$_2$S$_2$, R$_2$Se$_2$ and R$_2$Te$_2$, are used as ligand precursors and how the heavy chalcogens, \textit{i.e.}, Se and Te, as anchoring elements affect the formed Au NPs. In this paper, we systematically compared the Au NPs synthesized with R$_2$S$_2$, R$_2$Se$_2$ and R$_2$Te$_2$ and by varying different alkyl chain lengths (C6, C8, and C12).

### 6.2 Experimental Section

For the purpose of comparison, dialkyl dichalcogenides (\textit{i.e.}, R$_2$S$_2$, R$_2$Se$_2$, R$_2$Te$_2$) were used as ligand precursors to synthesize Au NPs, although thiols are more commonly used for synthesizing thiolate - protected Au NPs. Due to commercial unavailability, the dialkyl dichalcogenides were prepared in the lab via the reported synthetic routes (see detailed procedures in Chapter II and III).\textsuperscript{52,53,54} When R$_2$S$_2$ or R$_2$Te$_2$ were used as ligand precursors, modified two - phase Brust - Schiffrin procedure \textsuperscript{42,45, 54} was used for
synthesis of NPs with the ratio of 0.5(R₂S₂) : 1HApCl₄ : 3TOAB : 10NaBH₄ or 1/3(R₂Te₂) : 1HApCl₄ : 3TOAB : 10NaBH₄. Note that EtOH was used to crash out NPs prepared with R₂S₂, while ACN for R₂Te₂ as ligand precursors. In addition, when R₂Te₂ was used, the stir time after the addition of NaBH₄ aqueous solution was changed with the different alkyl chain lengths of R₂Te₂: 30 min for C6, 3 hours for C8, and overnight for C12. When R₂Se₂ was used as ligand precursors, a modified one - phase synthetic route¹²⁵ rather than the two - phase Brust - Schiffrin method was followed with the ratio of 0.5(R₂Se₂) : 1HApCl₄ : 10NaBH₄, since it has been shown that the one - phase synthesis produces more homogenous NPs.¹²⁰ The stir time after the addition of NaBH₄ aqueous solution was also changed with the different alkyl chain lengths of R₂Se₂: 2 hours for C6, 3 hour for C8, and 4 hours for C12. Like the NPs prepared with R₂Te₂, ACN was found to be a better solvent to crush out the NPs synthesized with R₂Se₂ than EtOH. The detailed synthetic procedure of NPs with dialkyl dichalcogenides are described in Chapter II.

6.3 Results and Discussions

6.3.1 Dialkyl Dichalcogenides

All ligands were correspondingly characterized via NMR and Raman spectroscopies. Figure 6.1 and Figure 6.2 represents the ¹H and ¹³C NMR spectra for R₂S₂, R₂Se₂, and R₂Te₂, respectively. The ¹H NMR peak positions of dialkyl dichalcogenides are all in agreement with those reported previously.³⁴, ⁵⁴, ¹²⁰, ¹²¹ No matter which kind of chalcogen
element was incorporated, there is a similar trend with the increase of alkyl chain lengths. That is, the chemical shift of α - protons was slightly shifted downfield as the alkyl chain length increased from C6 to C8 to C12. In details the peak of α - protons in disulfides, i.e., H₂C-S-, are 2.54 ppm for C6 (Figure 6.1c), 2.57 ppm for C8 (Figure 6.1b), and 2.58 ppm for C12 (Figure 6.1a), respectively; for Se system H₂C-Se- protons shifted from 2.75 ppm for C6 (Figure 6.1f), 2.77 ppm for C8 (Figure 6.1e), to 2.79 ppm for C12 (Figure 6.1d); and for Te system from 2.94 ppm for C6 and C8 (Figure 6.1j & h), and 2.95 ppm for C12 (Figure 6.1g), respectively. In addition, heavier chalcogen leads to more downfield shift of α – protons. For C8 alkyl chains, this varies from ~ 2.57 ppm for R₂S₂, to ~ 2.77 ppm for R₂Se₂, and to ~ 2.94 ppm for R₂Te₂, respectively. Figure 6.2 also show the 13C NMR spectra for of all dialkyl dichalcogenides, where all peaks were assigned accordingly. The effect of alkyl chain length on the chemical shift of C - 1 is too small to be noticed for a given chalcogen element. But interestingly, it is upfield shifted dramatically when the chalcogen element becomes heavier: the peak of C - 1 is at 40 ppm for R₂S₂ (Figure 6.2A), but at ~ 31ppm for R₂Se₂ (Figure 6.2B), and at ~ 5 ppm for R₂Te₂ (Figure 6.3C). To further evaluate the purity of the prepared dialkyl dichalcogenides, i.e., whether or not only one type of chalcogen exist, the 77Se and 125Te NMR measurements were performed respectively. Though with different alkyl chains, the 77Se NMR spectra of diselenides (Figure 6.3a) all show a single peak at ~ 310 ppm, which is in good agreement with previously reported data53 and corresponds to the exclusive existence of a single type of Se-Se bond. In Figure 6.3b, the single 125Te peak also indicates the existence of only one kind of Te-Te bond.54 However, for R2Te2, it was observed that
with the increase of alkyl chain, $^{125}\text{Te}$ peak is upfield shifted: 111.7 ppm for C6, 110.8 ppm for C8, and 105.8 ppm for C12, respectively. We believe that these NMR data with different shift values imply different electron donating/accepting ability among chalcogens/alkyl chain.

Since no obvious effect of alkyl chain length was noticed on the vibrations bands of dialkyl dichalcogenides (Figure 6.4), the Raman spectra of dialkyl dichalcogenides with C12 are compared in Figure 6.5. The vibration band of RS-SR is at ~ 525 cm$^{-1}$, RSe-SeR is at ~ 287 cm$^{-1}$, and RTe-TeR is at ~ 193 cm$^{-1}$. Not surprisingly, it is clearly observed that with heavier chalcogens, the vibration band of dichalcogenides is red-shifted to lower frequencies. Moreover, there is an almost perfect linear relationship between the stretching frequency of chalcogen - chalcogen bond and the corresponding $1/(\text{chalcogen mass})^{1/2}$, which implies very similar, of not the same, chalcogen - chalcogen bonding strength.

6.3.2 Alkane Chalcogenolate - Protected Gold Nanoparticles

The TEM images of the Au NPs (Figure 6.6) synthesized with different chalcogens as anchoring elements and with different alkyl chain length were compared together with the corresponding UV spectra (Figure 6.7). When $R_2S_2$ was used as ligand precursors, the average size of the obtained NPs was 2.6 ± 0.53 nm for C6S - Au NPs (Figure 6.6a), 2.38 ± 0.46 nm for C8S - Au NPs (Figure 6.6b), and 1.95 ± 0.35 nm for C12S - Au NPs (Figure 6.6c). All of these NPs dissolved in toluene showed a surface plasmon resonance (SPR) bump in the corresponding UV - Vis spectra around ~ 518 nm (Figure 6.7a & b & c). When using $R_2Se_2$, the average of NPs was 2.60 ± 0.72 nm for C6Se - Au NPs.
(Figure 6.6d), 2.00 ± 0.56 nm for C8Se-Au NPs (Figure 6.6e), and 1.54 ± 0.33 nm for C12Se-Au NPs (Figure 6.6f). In their UV-Vis spectra, C6Se-Au NPs (Figure 6.7d) showed a small SPR bump at ~ 510 nm, but no noticeable SPR was observed for C8Se-Au NPs and C12Se-Au NPs (Figure 6.7e & f), due to the predominant presence of small NPs. When R2Te2 was used, the average size was 3.92 ± 0.50 nm for C6Te-Au NPs (Figure 6.6g), 3.76 ± 0.69 nm for C8Se-Au NPs (Figure 6.6h), and 3.44 ± 0.51 nm for C12Se-Au NPs (Figure 6.6f). All of these NPs showed a SPR band at ~ 508 nm (Figure 6.7g & h & j). Therefore, no matter which kind of chalcogen was used as anchoring element, the NPs average size decreased with the increase of alkyl chain length. Also interesting is that there is a clear blue shift in SPR as the anchoring chalcogen becomes heavier, indicating an electron richer environment on the Au NPs, which is consistent with the XPS results (vide infra).

To help understand the interface between metal surface and the ligand and how the protected ligands bind to the Au NPs, in other words, whether chalcogens indeed work as anchoring elements to connect alkyl chain with Au core, some NMR characterizations were performed on the obtained NPs. Compared to the spectra of R2S2, the 1H peaks of \( \text{H}_2\text{C-S-} \) (at ~ 2.56 ppm) disappeared in the spectra of the obtained RS-Au NPs, and the peaks of CH3 at ~ 0.95 ppm and \((\text{CH}_2)_{n=2}\) in the range of ~ 1.1 to ~ 2.0 ppm significantly broadened (Figure is not presented in this dissertation), indicating that the organic moiety was bound to the Au surface. The same observation was noticed for the 1H NMR spectra of both RSe-Au NPs and RTe-Au NPs, where \( \text{H}_2\text{C-Se-} \) protons at ~ 2.77 ppm and the \( \text{H}_2\text{C-Te-} \) protons at ~ 2.95 ppm disappeared and the proton peak of CH3 at ~ 0.95
ppm and \((\text{CH}_2)_{n-2}\) in the range of \(~1.1\) to \(~2.0\) ppm broadened dramatically (Figure 6.8). Similar changes were observed in the \(^{13}\text{C}\) NMR spectra of the obtained NPs (Figure 6.9), where the C - 1 peak of dialkyl dichalcogenides at 40 ppm for \(\text{R}_2\text{S}_2\), at \(~31\)ppm for \(\text{R}_2\text{Se}_2\), and at \(~5\) ppm for \(\text{R}_2\text{Te}_2\) vanished and other carbon peaks far from chalcogen widened. Considering that C - 1 in all ligands locates the closest to the metal surface, its disappearance due to the chemical heterogeneity suggested the metal - chalcogen bonding.\(^{129}\)

To understand the interfacial interaction between chalcogens and Au core in NPs, the binding energies (BE) of chalcogens (S 2p, Se 3d, and Te 3d) and Au 4f in the formed NPs were investigated. The Au 4f XPS spectra of the NPs with different chalcogens as anchoring elements are shown in Figure 6.10. In the Au 4f spectrum of \(\text{C}_{12}\text{S} - \text{Au}\) NPs, the two BE bands at 87.85 eV and 84.15 eV (Figure 6.10a) suggest that alkanethiolate bonded to gold surface.\(^{48,49}\) The Au 4f bands of both \(\text{C}_{12}\text{Se} - \text{Au}\) NPs and \(\text{C}_{12}\text{Te} - \text{Au}\) NPs were slightly shifted to lower binding energy at 87.75 eV and 84.05 eV (Figure 10b & c). With the caveat that Te in the \(\text{C}_{12}\text{Te} - \text{Au}\) NPs might be likely in a form of Te-O, the BE of Au 4f in NPs is overall more positive as compared to the BE of the bulk Au 4f at 84.0 eV, which indicates a charge transfer from Au to chalcogen.\(^{130}\) Moreover, the smaller Au 4f BE for heavier chalcogens is consistent with it being less electrophilic as compared to sulfur, which is also in agreement with what was implied by the SPR results discussed above. The band of S 2p in \(\text{RS} - \text{Au}\) NPs experience two split peaks at 163.5 eV and 162.5 eV (Figure 6.11a), and it is in good agreement with previously reported data where thiolate bound to Au surface and with no oxidized sulfur was present.\(^{35,49}\) This
also confirmed the breakage of the RS-SR bond during the formation of RS - Au NPs. For C12Se - Au NPs, the BE of Se 3d peak at 55.4 eV (Figure 6.11b) compared to the BE of Se 3d peak in free diselenide at 55.3 eV, was in good agreement with the data for C12Se - Au NPs observed by Ulman et al.49 The Te 3d bands in C12Te - Au NPs at 586.55 eV and 576.15 eV (Figure 6.11c), are similar to the literature values of SAMs formed when R2Te2 was adsorbed on the Au substrate, and are consistent with Te(IV) species, showing that Te oxides were formed.34, 35, 54, 118, 131 From the XPS spectra of Au NPs, it is concluded that chalcogen - chalcogen bonds of dialkyl dichalcogenides were broken during the formation of NPs and the alkyl chain were bound to the Au NPs surface via chalcogens, although Te species were oxidized.

In addition, the thermal stability of the Au NPs with different chalcogen as anchoring elements was evaluated by TGA (Figure 6.12). The C12S - Au NPs (Figure 6.12a) and C12Se - Au NPs (Figure 6.12b), showed similar patterns, in which one - step weight loss was observed. The dominant weight loss (~ 23% for C12S - Au NPs and ~ 47% for C12Se - Au NPs) occurred at ~ 200°C and stopped before the temperature reached 500°C, which attributed to the loss of the ligand from the NPs surface.49 Interestingly, C12Te - Au NPs showed two - step weight loss, with 16.4% from 100 to 400°C and 14.4% from 720 to 930°C, respectively (Figure 6.12c). The second step weight loss, is due to the Te oxidized species in the NPs as reported in our previous work.54 The complete loss of the ligand containing heavier chalcogen at higher temperature (280°C for S - containing ligand vs. 360°C for Se - ligand vs. 930°C Te - containing ligands ) suggest that the bond between heavier chalcogen and Au is stronger.
IR spectroscopy was also used to provide the information about the conformation and packing characteristics of the ligands on the Au NPs. In the high-frequency region from 2800 - to 3000 cm\(^{-1}\) the C12S - Au NPs (Figure 6.13) spectra showed the three well resolved bands at the same positions as those of R\(_2\)S\(_2\). Three bands in C12Se - Au NPs were slightly red-shifted compared to R\(_2\)Se\(_2\), indicating more ordered conformational state in NPs; however, these bands in C12Te - Au NPs were slightly blue-shifted compared to R\(_2\)Te\(_2\), indicating less ordered conformation.

6.4 Conclusion

In summary, our investigation has revealed the effect of the alkyl chain length of ligand precursors on size of the formed Au NPs: longer alkyl length chain of the dialkyl dichalcogenides ligands is apt to the formation of smaller Au NPs, no matter how heavy the chalcogen is (Figure 6.14). It is important to point out, that the final yield of NPs, especially with shorter alkyl chains was very low. In addition, all the NPs were not easy to synthesize and the process required many purification steps. For all dialkyl dichalcogenides, \textit{i.e.}, R\(_2\)S\(_2\), R\(_2\)Se\(_2\), and R\(_2\)Te\(_2\), the NMR and XPS results indicated that chalcogen - chalcogen bonds were broken and alkyl chains were bounded to the Au surface via chalcogens, although the Te system was oxidized as it was also confirmed by TGA. Moreover, the SPR and XPS results indicate that Au NPs with heavier chalcogens are more electron rich. We believe that the data in here can be beneficial for future
investigations of the metal NPs protected by heavy chalcogen-containing ligands, and provide significant amount of useful information.
Figure 6.1 $^1$H NMR spectra of: (A) dialkyl disulfide $(R_2S)_2$ with (a) C12, (b) C8, and (c) C6 alkyl chains; (B) dialkyl diselenide $(R_2Se)_2$ with (d) C12, (e) C8, and (f) C6 alkyl chains; and (C) dialkyl ditellurides $(R_2Te)_2$ with (g) C12, (h) C8, and (j) C6 alkyl chains.
Figure 6.2 $^{13}$C NMR spectra of: (A) dialkyl disulfide ($R_2S)_2$ with (a) C12, (b) C8, and (c) C6 alkyl chains; (B) dialkyl diselenide ($R_2Se)_2$ with (d) C12, (e) C8, and (f) C6 alkyl chains; and (C) dialkyl ditellurides ($R_2Te)_2$ with (g) C12, (h) C8, and (j) C6 alkyl chains.
Figure 6.3 $^{77}\text{Se}$ NMR of (a) ($\text{C}_6\text{H}_{13}\text{Se})_2$ - black, ($\text{C}_8\text{H}_{17}\text{Se})_2$ - red, and ($\text{C}_{12}\text{H}_{25}\text{Se})_2$ - blue; (b) $^{125}\text{Te}$ NMR spectra of ($\text{C}_6\text{H}_{13}\text{Te})_2$ - black, ($\text{C}_8\text{H}_{17}\text{Te})_2$ - red, and ($\text{C}_{12}\text{H}_{25}\text{Te})_2$ - blue.
Figure 6.4 Raman spectra of (a) (C₆H₁₃S)₂, (b) (C₆H₁₃Se)₂, (c) (C₈H₁₇Se)₂, (d) (C₁₂H₂₅Se)₂, (e) (C₆H₁₅Te)₂, (f) (C₈H₁₇Te)₂, and (g) (C₁₂H₂₅Te)₂.
Figure 6.5 Raman spectra of (a) (C12S)$_2$, (b) (C12Se)$_2$, and (c) (C12Te)$_2$ ligands.
Figure 6.6 TEM images and size distribution graphs of (a) C6S-Au NPs, (b) C8S-Au NPs, (c) C12S-Au NPs, (d) C6Se-Au NPs, (e) C8Se-Au NPs, (f) C12Se-Au NPs, (g) C6Te-Au NPs, (h) C8Te-Au NPs, and (j) C12Te-Au NPs.
Figure 6.7 UV - Vis spectra of (a) C6S - Au NPs, (b) C8S - Au NPs, (c) C12S - Au NPs, (d) C6Se - Au NPs, (e) C8Se - Au NPs, (f) C12Se - Au NPs, (g) C6Te - Au NPs, (h) C8Te - Au NPs, and (j) C12Te - Au NPs.
Figure 6.8 $^1$H spectra of (A) RSe - Au NPs, where R = C6 (black), C8 (red), and C12 (blue); and (B) RTe - Au NPs, where R = C6 (black), C8 (red), and C12 (blue).
Figure 6.9 $^{13}$C spectra of (A) RSe - Au NPs, where R = C6 (black), C8 (red), and C12 (blue); and (B) RTe - Au NPs, where R = C6 (black), C8 (red), and C12 (blue).
Figure 6.10 XPS spectra of Au 4f<sub>7/2</sub> : (a) C12S - Au NPs, (b) C12Se - Au NPs, and (c) C12Te - Au NPs.
Figure 6.11 XPS spectra of (a) S 2p in C12S - Au NPs, (b) Se 3d in C12Se - Au NPs, and (c) Te 3d in C12Te - Au NPs.
Figure 6.12 TGA results for (a) C12S - Au NPs, (b) C12Se - Au NPs, and (c) C12Te - Au NPs.
Figure 6.13 IR results for (a) (C$_{12}$H$_{25}$S)$_2$, (b) C12S - Au NPs, (c) (C$_{12}$H$_{25}$Se)$_2$, (d) C12Se - Au NPs, (e) (C$_{12}$H$_{25}$Te)$_2$, and (f) C12Te - Au NPs.
Figure 6.14 Summary of Chapter VI.
6.5 References

7.1 Introduction

In the previous sections, the synthesis and characterization of alkyl selenolate-protected Au NPs were reported, where dialkyl diselenides were used as precursor ligands. Since the final yield of the resultant NPs was smaller than required for characterizations, such as TGA and extensive NMR studies, another method for producing alkyl selenolate-protected Au NPs was pursued and investigated.

Work with SAMs by Tour et al., showed that although diselenides are synthetically beneficial, there are some drawbacks, i.e., the frequent usage of strong reducing agents to cleave the Se-Se bond. An alternatively proposed approach, was to use potassium selenocyanate (KSeCN), that is toxic, strongly nucleophilic, and readily reacts with alkyl halides. In a subsequent paper, Tour’s group used a thiolcyanate to form SAMs on Au surface. It was stated that thiocyanate assembly on Au gives the same thiolate bonding structure as thiol assemblies. Unfortunately, the presence of cyanide, which occurred on average as one cyanide per four atoms of sulfur, was a notable contamination issue. In addition, the monolayers of thiolcyanate were lower in quality on Au surface when compared to thiols. In an effort to alleviate this problem, nonpolar solvents were proposed to be used. Although this would lead to less packed SAMs, but to an easier method to achieve a state of free of cyanide impurities. Therefore, by using this
method with thiocyanates proposed by Tour et al., on 2D SAMs, we decided to examine if the selenocyanates derivatives could be used as precursor ligands for synthesis of alkyl selenolate - protected Au NPs.

7.2 Synthesis of Ligands

Many groups used thiocyanates\textsuperscript{136, 137} and selenocyanates\textsuperscript{138, 139} molecules in their studies; therefore, there are a variety of options for synthesis of selenocyanates.\textsuperscript{140, 141} The synthesis of C\textsubscript{6}SeCN, C\textsubscript{8}SeCN, and C\textsubscript{12}SeCN was followed directly from the literature.\textsuperscript{141}

The solution of potassium selenocyanate (KSeCN, 2.16 g) and dimethylformamide (DMF, 7.5 mL) were mixed under nitrogen in a 100 mL three - neck round bottom flask. Appropriate alkyl halides, \textit{i.e.}, C\textsubscript{6}H\textsubscript{13}Br, C\textsubscript{8}H\textsubscript{17}Br, and/or C\textsubscript{12}H\textsubscript{25}Br, in 10 mL DMF were slowly added to the solution and stirred for about 12 - 14 hours at 90°C. The solution was hydrolyzed with 30 mL of water, extracted twice with 50 mL of ether, then washed again with water a couple of times and dried with MgSO\textsubscript{4}. Subsequently, DMF was rotary - evaporated, and the remaining solution was run through the silica gel hexane column (40 cm in length and 2 - 3 cm in diameter). The first yellow band that eluted from the column was dialkyl diselenide. As soon as the dialkyl diselenide eluted from the column, the solvent was changed to 8/2 mixture of hexane/ether. This would force alkyl selenocyanates to elute from the column. Then the second band was collected and rotary - evaporated, leaving a yellow and malodorous oily liquid for all alkyl chain lengths.
7.3 Characterization of Ligands

Following the synthesis of the aforementioned selenocyanates, \textit{i.e.}, \(C_6\text{SeCN},\) \(C_8\text{SeCN},\) and \(C_{12}\text{SeCN},\) characterizations using several analytical techniques, such as \(^1\text{H},\) \(^{13}\text{C},\) HSQCAD, \(^{77}\text{Se}\) NMR, IR, and Raman spectroscopies were performed. Prior to record \(^1\text{H}\) and \(^{13}\text{C}\) NMR in \(C_6\text{D}_6\) solvent to verify the purity of the samples, corresponding NMR in CDCl\(_3\) were taken to ensure that the observed peak positions were identical with literature values.\(^{133,141}\) Figure 7.1 represents \(^1\text{H}\) NMR spectra of all three ligands in \(C_6\text{D}_6\) solvent. The triplet peaks at \(\sim 2.1\) ppm indicate the presence of alkyl selenocyanates, since it corresponds to the methyl group directly bound to the Se atom, \textit{i.e.}, \(\text{H}_2\text{C}-\text{Se}\)-protons. The peak position was the same for all three ligands.

The \(^{13}\text{C}\) NMR spectra are presented in Figure 7.2. Panel A in the Figure 7.2 show the peaks in the range of \(95 - 104\) ppm that are in agreement with expected \(\text{C}≡\text{N}\) peak at \(\sim 101\) ppm in the alkyl selenocyanates. Note that due to long relaxation time for this peak was difficult to observe and large numbers of scans were needed to observe this peak (taking about 3 days). Panel B in the Figure 7.2 shows the peaks in the range of \(10 - 40\) ppm, which are attributed to the carbon chain in the alkane selenocyanates. For example, Figure 7.2a clearly demonstrates six well - resolved peaks for \(C_6\text{H}_{13}\text{SeCN}\.\) The peak assignments were achieved by 2 – dimensional HSQCAD NMR, where the correlation spectrum of \(C_6\text{H}_{13}\text{SeCN}\) is presented in Figure 7.3 as reference. For \(C_6\text{SeCN},\) \(C_8\text{SeCN},\) and \(C_{12}\text{SeCN},\) C-1 that was directly bound to Se appeared at \(\sim 29.2\) ppm.
To insure that the alkyl selenocyanates contained only one type of selenium species, $^{77}\text{Se}$ NMR was performed and is presented in Figure 7.4. (The reference was $\text{Se(CH}_3)_2$ in C$_6$D$_6$, which was set at 0 ppm). Only one peak was observed in all three ligands, corresponding to one type of selenium present. The peak position in all selenocyanates is about 208 ppm, which is very close to the published values, again indicating purity of the samples.

Further characterization was performed on the ligands using IR spectroscopy and the data are presented in Figure 7.5. There are three main areas of interest in the spectrum. First, the high frequency region that exhibits three well-resolved peaks in the $\sim$ 2850 - 2854 cm$^{-1}$, $\sim$ 2917 - 2922 cm$^{-1}$, and 2956 - 2964 cm$^{-1}$ regions, which have been previously assigned to methylene (C-H$_{sym}$), methylene (C-H$_{antisym}$), and methyl (CH$_3$-$_{asym}$) vibrational absorption bands, respectively. The second area of interest is the sharp peak in all ligands at $\sim$ 2150 cm$^{-1}$, corresponding to the C≡N frequency. Thirdly, the peaks in the low frequency area at 721 cm$^{-1}$ and 630 cm$^{-1}$ correspond to the (CH$_2$)$_{rocking}$ and (Se-C)$_{trans}$ vibrations, respectively.

Raman spectra are presented in Figure 7.6. The peaks corresponding to the sp$^3$ carbons, C≡N, and CH$_2$ rocking vibrations, were nearly identical to the IR spectra, around 2800 cm$^{-1}$, 2144 cm$^{-1}$, and 630 cm$^{-1}$ respectively. Additional peaks at $\sim$ 548 cm$^{-1}$ and 520 cm$^{-1}$ were assigned as Se-CN stretching vibrations.
Figure 7.1 $^1$H NMR spectra of (a) C$_6$H$_{13}$SeCN, (b) C$_8$H$_{17}$SeCN, and (c) C$_{12}$H$_{25}$SeCN.
Figure 7.2 $^{13}$C NMR spectra of (a) C$_6$H$_{13}$SeCN, (b) C$_8$H$_{17}$SeCN, and (c) C$_{12}$H$_{25}$SeCN in A) 95 - 104 ppm and B) 10 - 40 ppm range.
Figure 7.3 HSQCAD NMR of C₆H₃SeCN in C₆D₆.
Figure 7.4 $^{77}$Se NMR of (a) C$_6$H$_{13}$SeCN, (b) C$_8$H$_{17}$SeCN, and (c) C$_{12}$H$_{25}$SeCN.
Figure 7.5 IR spectra of (a) C$_6$H$_{13}$SeCN, (b) C$_8$H$_{17}$SeCN, and (c) C$_{12}$H$_{25}$SeCN.
Figure 7.6 Raman spectra of (a) $C_6H_{13}SeCN$, (b) $C_8H_{17}SeCN$, and (c) $C_{12}H_{25}SeCN$. 
7.4 References

CHAPTER VIII
SYNTHESIS OF GOLD AND SILVER NANO PARTICLES WITH ALKYL SELENOCYANATES

Reproduced with permission from Zaluzhna, O.; Zangmeister, C.; Tong, Y. J., Synthesis of gold and silver nanoparticles with alkane selenocyanates, Chemical Communication 2012, submitted. This paper was a combined effort of Zaluzhna, O., and Dr. Tong Y. J. Dr. Zangmeister has done all the XPS experiments.

8.1 Introduction

The discovery of the thiolate - protected Au NPs synthesis by Brust and Schiffrin method (BSM) \(^{42,43}\) opened the door for extensive research in this field with a variety of ligands and metals. \(^3,48,54,65,72,84,128,143\) Although the mechanism for formation of thiolate - protected metal NPs is better understood; \(^{44,46,73,144}\) similar investigations on other heavy chalcogen protected NPs are rare. \(^{121,145}\) According to quantum calculations, heavy chalcogens (i.e., Se and Te) have showed to have promising electronic properties, such as better conductance than the prevalent anchoring element S. \(^{27}\) While a few groups have investigated self - assembled monolayers (SAMs) with dichalcogenides (i.e., \(R_2Se_2\) and \(R_2Te_2\)) adsorbed on Au and Ag substrates, \(^{34,35,41,146,147}\) studies on the corresponding Au and Ag NPs are scarce, \(^{49,51,54,148}\) and the majority has been performed with dialkyl dichalcogenides as initial ligands, since heavy chalcogenols are more air-sensitive \(^{149}\) than
their light chalcogen cousin, thiol. To open further this important and promising field of research, developing good alternatives is highly desirable.

Ciszek et al. have recently used organic thiocyanates as alternative precursors for forming SAMs primarily on Au, but also on other metals (Ag and Pt), and determined that thiocyanates assemblies resembled thiolate SAMs.\(^{150, 151}\) It was demonstrated that the surface coverage remains higher for the traditional thiols than for thiocyanates, yet thiocyanate SAMs showed superiority in stability on the surfaces and were not as prone to undesired polymerization processes.\(^{150, 152, 153}\) The main challenge in characterizing the SAMs was to identify and quantify the presence of (CN) species. The authors argued morphology played a significant role in the expulsion of (CN)\(_{ads}\) from metal surfaces, such as evaporated (ragged) Au SAMs had less residual nitrogen than stripped (smooth) template.\(^{151, 152}\)

Inspired by the work discussed in the previous paragraph, we explored using the similar ligands to synthesize metal (Au and Ag) NPs via the BSM and report the successful outcome in this paper. To the best of our knowledge, the only work that has dealt with NPs and organo selenocyanates as potential ligands was the work by Lim et al. However, their investigations were performed in a very different context.\(^ {154}\) They investigated the adsorption of nitrophenyl selenocyanate on the surface of pre-formed Au NPs stabilized by citrate via ligand exchange and compared it with benzeneselenol.\(^ {154}\) Despite the lack of TEM images evidence, the authors assumed that their colloidal ensemble remained unchanged following the ligand exchange, \textit{i.e.}, 15 nm spherical NPs.\(^ {154}\) In this paper, we focus on using the general BSM to synthesize metal (Au and
Ag) NPs with alkyl selenocyanates as the starting ligands and to compare and contrast the formation chemistry of the 3D SAMs analogues to that of the corresponding 2D SAMs.

8.2 Experimental Section

Several alkyl selenocyanates ligands, such as C₆H₁₃SeCN, C₈H₁₇SeCN, and C₁₂H₂₅SeCN were synthesized⁵⁵ and characterized in Chapter 7. Herein, only dodecaneselenocyanate, i.e., C₁₂H₂₅SeCN or C₁₂Se(CN) in brief, as the starting ligand will be discussed as a representative case. Both one-phase (1p) and two-phase (2p) BSM were employed to synthesize the Au NPs. While the 2p BSM was successful in producing Au NPs (Figure 8.2), the 1p BSM produced more homogenous NPs with C₁₂Se(CN) (Figure 8.3). Therefore, the latter will be the focus of study and discussion here.

Synthesis of the Au NPs: For two-phase BSM synthesis modified Brust - Schiffrin procedure was used,⁴² with the ratio of 1Au : 3TOAB : 1 (C₆-,C₈-, C₁₂- SeCN) : 10 NaBH₄. First 0.15 mmol of TOAB was dissolved in 20 ml of toluene, the 0.05 mmol (0.3 ml 0.1463M) of HAuCl₄aq was added to the solution. The solution turned to dark red in color from clear. When all Au ions were transferred into organic layer, the 0.05 mmol (C₆-, C₈-, C₁₂- SeCN), were added and stirred 1 - 2 hours. The solution turned lighter in color, and then 10 mmol 10NaBH₄aq (in 5ml H₂O) was added to it and stirred overnight. Next day, it was washed with H₂O, rotary - evaporated, and large amount of ACN (~ 250 mL) was added and left overnight in the refrigerator. The next day, NPs were micropore
filtered, re- dissolved in toluene, and centrifuged for 1 hour at 14, 500 rpm. See Figure 8.2 for all the TEM images with different alkyl chain length.

For one-phase BSM, modified literature procedure was used. $^{43, 49, 145}$ 1 mmol (0.1 ml 0.1643M) HAuCl$_4$aq was dissolved in 50ml THF. After stirring for 30 min, 1 mmol of (C6-, C8-, C12-SeCN) was added and stirred for 1-2 hours. The 10 mmol NaBH$_4$aq (in 5ml of H$_2$O) was added to the solutions and stirred for 2-3 hours. The solution was rotary-evaporated, washed with toluene/water, toluene layer was collected and centrifuged for 1 hour at 14, 500 rpm. The supernatant was collected and rotary-evaporated. The final NPs were washed and centrifuged in ethanol. See Figure 8.3 for all the TEM images with different alkyl chain length.

Synthesis of the Ag NPs: To date, only C$_{12}$H$_{25}$SeCN was used in the synthesis of Ag NPs. For 2-phase BSM, the ratio of 1Au : 3TOAB : 1C$_{12}$H$_{25}$SeCN : 10 NaBH$_4$ was used under N$_2$ gas blanket and covered with Al foil. First 0.15 mmol of TOAB was dissolved in 50 mL of toluene, then 0.05 mmol of AgNO$_3$aq was added to the solution. When all Ag ions were transferred into organic layer, 0.05 mmol C$_{12}$H$_{25}$SeCN were added and stirred for 1-2 hours. Subsequently, 10 mmol NaBH$_4$aq (in 5 mL H$_2$O) was added and stirred for 4 hours. It is important to point out, that for the following sample, the N$_2$ gas evaporated all of the solvent, therefore additional toluene and water was added and stirred. After 4 hours, the solution was washed with H$_2$O, the toluene layer was collected and then rotary-evaporated, and large amount of ACN was added before being stored overnight in the refrigerator. The next day, the NPs were micropore filtered, washed with a large amount
of EtOH, re-dissolved in toluene, and centrifuged for 1 hour at 14,500 rpm. The precipitate was collected and dispersed after sonication in toluene.

8.3 Results and Discussions

TEM, UV - Vis, and size distribution data are presented in Figure 8.1 for the C12Se(CN) - Au protected NPs synthesized by the 1p BSM. The resultant NPs were homogenous, with average particle size of 2.0 ± 0.3nm (Figure 8.1a), and exhibited a narrow size distribution (Figure 8.1b). The UV - Vis did not display any surface enhance resonance peaks around 500 - 520 nm due to small sizes of NPs (Figure 8.1c).  

The obtained NPs were characterized via $^1$H NMR, IR, and XPS. Figure 8.4 displays $^1$H NMR results for the NPs (Figure 8.4a) and the free ligand (Figure 8.4b). The triple peak corresponding to the protons in -H$_2$C-SeCN at 2.09 ppm in the free ligand (Figure 8.4b) disappeared in the NPs spectra (Figure 8.4a), indicating that the organic moiety is bound to the metal surface via Se. Also, note that the broadening of the alkyl chain peaks at 1.0 to 1.5 ppm is indicative of the ligand bound to the NPs. Unfortunately, $^{13}$C NMR lacked the sensitivity to determine the presence of C≡N species within the NPs sample, as illustrated by difficulty to observe the C≡N peak in the free RSe-C≡N ligand (Chapter 7, Figure 7.2A). The IR characterization was performed to observe the CN species presence on the Au NPs surface. As shown in Figure 8.5, the cyanide peak at 2150 cm$^{-1}$ (Figure 8.5b) that was present in the free ligand disappeared in the NPs sample (Figure 8.5a). That is,
within the detection limit of IR, no residual CN was observed after the formation of Au NPs. Moreover, the disappearance of the gauche conformation vibrational band of Se-C at 630 cm\(^{-1}\) in the Au NPs sample indicates that the alkyl selenoate formed a ligand monolayer of trans conformation.

In their work on 2D SAMs, Ciszek et al. have used IR to detect the presence of very small amount of residual CN and proposed the existence of two kinds of cyanides within samples: the adsorbed cyanide (\(\text{CN}_{\text{ads}}\)) and an intermediate form absorbed on the surface during the etching of the metal (Au(CN)) intermediate species with vibration in IR at \(\sim 2160 \text{ cm}^{-1}\),\(^{151}\) although their respective quantifications proved to be challenging. Choi et al., also had challenges to identify and quantify the presence of cyano species in their octylthiocyanate - generated SAMs on Au(111).\(^{152}\) They predicted that the CN bands could be more readily observed on the surface of Au via SERS, though the amount of CN was impossible to determine.\(^{152,154}\) Our results clearly suggest that there is little to no cyanide species present in NPs sample, since no observable C≡N vibrational peaks were present in the spectra.

XPS analysis, as a more sensitive tool of elemental analysis, was used to determine the ligand - metal characteristics (Figure 8.6 & 8.7). Figure 8.6a displays the XPS spectra of Se 3d\(_{5/2}\) with a binding energy value of 55.3 eV, which has been observed for the C12Se - Au NPs synthesized with dialkyl diselenides as the starting ligand.\(^{49,145}\) The same binding energies for Au 4f\(_{7/2}\) doublet (Figure 8.7a) were also observed. These binding energies lead to the conclusion that the organic moiety is indeed bound to the Au
surface via the chalcogen and the Au NPs synthesized with alkyl selenocyanate and
dialkyl-disselenide are essentially the same.

Furthermore, XPS was used to investigate the existence of (CN) species within the Au
NPs. As mentioned previously, Ciszek et al., proposed the existence of two types of
cyanides within the SAMs samples, i.e., CN$_{ads}$ on Au (with XPS binding energy of N 1s
electron = 397.9 eV) and Au(CN) intermediate species (with XPS binding energy of N 1s
= 399.5 eV).\textsuperscript{151} A weak and noisy N 1s XPS signal was observed
in our samples at ~ 399 eV (Figure 8.6b) as one broad peak in the spectra. Unfortunately, the contribution of low
sensitivity and peak broadening (Figure 8.6b) on C12Se(CN) - Au NPs sample make the
differentiations of the two possible cyano species impossible. Based on these results, we
can ascertain that the Au NPs synthesized with alkyl selenocyanate are predominantly
protected by alkyl selenolate, while (CN) species exist in a trace amount that cannot be
used quantitatively.

Additionally, TGA was performed on the NPs and showed a two-step weight loss
(Figure 8.8). First step occurred ~180°C of about 30% of weight loss, and the second ~
350°C of about 13%. The first weight loss temperature corresponded closely to the loss
of the organic alkyl chain with Se as an anchoring element as previously reported in
literature.\textsuperscript{49} The second weight loss, on the other hand, warrants more investigation, since
this weight loss is too large to correspond to cyanide species.

We also carried out similar but less extensive synthesis of Ag NPs with C12Se(CN)
using 2p BSM. This synthesis proved to be much more challenging than synthesizing Au
NPs in terms of reproducibility, Figure 8.9 presents the TEM image, size distribution
histogram, and UV - Vis spectrum of our best sample. While the size of the synthesized Ag NPs (2.9 ± 0.3 nm) is larger than that of the corresponding Au NPs (2.0 ± 0.3 nm), very similar IR (disappearance of the CN stretching band and the Se-C gauche conformation band in the Ag NPs, Figure 8.10) and TGA (the two - step desorption, Figure 8.11) were observed. All these indicate that the ligand monolayer on the Ag NPs shares more structural and chemical similarity than difference with its counterpart on the Au NPs.

8.4 Conclusion

In conclusion, alkyl selenocyanates were successfully used as starting ligands for the synthesis of homogenous, ca. 2 to 3 nm sized, Au and Ag NPs by using the BSM, which opens a promising general alternative to synthesizing organo - heavier - chalcogen - ligand protected metal NPs. The $^1$H NMR data clearly showed that the organic moiety was bound to the Au surface of NPs, and the XPS demonstrated that the bonding was via chalcogen. Strong evidence indicate that the ligand monolayer is most likely of alkyl selenoate, the same as that on the Au NPs synthesized with dialkyl - diselenide, and the Au and Ag NPs most likely share very similar monolayer structure. However, the determination of C≡N species in the NPs samples was proved to be a challenging task due largely to low sensitivity of instruments, as have been discussed by previous work on 2D SAMs. While IR analysis clearly showed no presence of C≡N species, XPS showed a broad weak and noisy peak that most likely corresponded to the trace amount of cyanide.
present in the synthesized NPs. Further analytical techniques with high sensitivity are needed to fully characterize the residual CN.
Figure 8.1 TEM image (a), size distribution histogram (b), and UV - Vis spectrum (c) of the 2.0 ± 0.3 nm C12Se(CN) - Au NPs.
Figure 8.2 TEM and average sizes of Au NPs synthesized by 2p BSM with (a) C₆H₁₃SeCN, (b) C₈H₁₇SeCN, and (c) C₁₂H₂₅SeCN as precursor ligands.
Figure 8.3 TEM and average sizes of Au NPs synthesized by 1p BSM with (a) C$_6$H$_{13}$SeCN with average sizes of 2.8 $\pm$ 0.81 nm, (b) C$_8$H$_{17}$SeCN with average sizes of 2.4 $\pm$ 0.60 nm, and (c) C$_{12}$H$_{25}$SeCN with average sizes of 2.0 $\pm$ 0.32 nm as precursor ligands.
**Figure 8.4** $^1$H NMR spectra of (a) C12Se(CN) - Au NPs, and (b) pure C$_{12}$H$_{25}$SeCN ligand.
Figure 8.5 IR spectra of (a) C12Se(CN) - Au NPs, and (b) pure C_{12}H_{25}SeCN ligand.
Figure 8.6 XPS of (a) Se d$_{5/2}$, and (b) N 1s region in C12Se(CN) - Au NPs.
Figure 8.7 XPS spectra of C12Se(CN) - Au NPs of (a) Au f$_{7/2}$ and (b) C 1s XPS region.
Figure 8.8 TGA spectra of C12Se(CN) - Au NPs.
Figure 8.9 TEM image (a), size distribution histogram (b), and UV - Vis spectrum (c) of the 2.9 ± 0.3 nm C12Se(CN) - Ag NPs.
**Figure 8.10** IR spectra of (a) $\text{C}_{12}\text{H}_{25}\text{SeCN}$ and (b) $\text{C}_{12}\text{Se}$ (CN) - Ag NPs.
Figure 8.11 TGA curve of the C12Se (CN) - Ag NPs.
8.5 References

CONCLUDING REMARKS

Organo chalcogenolate-protected gold (Au) nanoparticles (NPs) have shown high potential for nanoelectronic applications, where electrochemical studies are crucial for understanding the charge transfer mechanism between the metal core and ligand. Complete interfacial characterization of the NPs is essential prior to electrochemical studies to confirm uniform composition. The main project of this dissertation focuses on the successful synthesis of such homogenous NPs and interfacial characterizations between the Au core and the ligand, where anchoring element is changed to Se instead of well-known S.

Organo chalcogenolate-protected gold Au NPs can be produced by using well-known Brust-Schiffirn method (BSM). Since previous mechanistic studies into BSM, i.e., one- and two-phase syntheses, performed on thiolate-stabilized Au NPs identified that NPs homogeneity was dependent on the precursor species prior to the formation of NPs, similar studies were performed to study intermediates formed for Se system. Furthermore, interfacial studies were performed on the alkane selenolate-protected Au NPs and compared to other chalcogenolate-protected Au NPs, where anchoring elements were S and Te. Additionally, alkyl selenocyanates were utilized as initial ligands to produce alkyl selenolate-protected Au NPs. The contributions of the research to the nanomaterial chemistry, in particular nanoparticle synthesis and nanoparticle characterizations, can be summarized as follows:

In this investigation dialkyl dichalcogenides, specifically \( R_2S_2 \) or \( R_2Se_2 \), were used as ligand precursors in the two-phase BSM, where the significant effect of encapsulated water was demonstrated. In summary, we have identified unambiguously that it was the inverse-micelle-encapsulated water that enabled uniquely the bond breaking reaction of diselenide/disulfide with Au cations, leading to the formation of unusual paramagnetic Au(II) complex and the production of higher-quality Au NPs. We have also unraveled some subtle differences in chemistry involving dialkyl diselenide vs. disulfide in interaction with Au cations. For instance, the former could form \( \text{Au(III)}(\text{SeC}_8\text{H}_9)_2 \) - like Lewis adduct species but not the latter and the bond-breaking was complete for the form but only partially for the latter. These findings should have important practical ramifications in terms of synthesizing organochalcogen (particularly Se- or Te-containing) ligand-stabilized homogeneous Au metal NPs. Moreover, the inverse-micelle-encapsulated water-enabled bond-breaking chemistry in dialkyl-diselenide and dialkyl-disulfide may also have implications in biochemical processes involving like species.

Mechanistic comparison of the one-phase and two-phase Brust-Schiffrin synthesis of gold (Au) NPs. Previous studies in our laboratory with thiolate-protected Au NPs demonstrated that NPs homogeneity is dependent on the intermediate species. In this study, dioctyl diselenide, C8Se-SeC8, was used as the precursor ligand for the synthesis
of Au NPs, where the one-phase BSM was compared to the two-phase synthesis prior to the addition of the reducing agent, NaBH₄. In the one-phase BSM, the diselenide bond in C₈Se-SeC₈ was broken and it reduced Au(III) to Au(I), which indicated an intermediate was formed upon this reaction. In the two-phase BSM, C₈Se-SeC₈ also reacted with Au (III) by breaking diselenide bond; however, the reduction rate to Au(I) was slower due to the existence of the phase transfer agent, TOAB. In summary, by combining NMR, Raman, and XPS techniques with additional DFT calculations, multiple intermediate metal precursors, one of which might be X₂AuSe(C₈)(OH)X (X=Br or Cl), was present in the two-phase BSM. In contrast, there was only single dominant intermediate metal precursor, likely in the form of Cl₂AuSe(C₈)Cl₂, formed in the one-phase producing higher quality Au NPs. It was proposed that having a rather uniform metal precursor state in the one-phase, but not in the two-phase BSM synthesis was the primary reason for producing homogenous Au NPs in the former.

*Effects of anchoring elements and alkyl chain length on formed gold (Au) NPs.* This study presents the systematic comparison of Au NPs synthesized with R₂S₂, R₂Se₂ and R₂Te₂ of different alkyl chain lengths, where R= C₆H₁₃, C₈H₁₇, and C₁₂H₂₅. First, characterizations performed on the dialkyl dichalcogenides ligands clearly displayed different chemistry with the respect to the different chalcogen based ligands. Subsequently, homogenous NPs were synthesized for all systems. In summary, our investigation has revealed the effect of the alkyl chain length of ligand precursors on size of the formed Au NPs: longer alkyl length chain of the dialkyl dichalcogenides ligands is
apt to the formation of smaller Au NPs, no matter how heavy the chalcogen is. For all
dialkyl dichalcogenides, \textit{i.e.}, \( \text{R}_2\text{S}_2 \), \( \text{R}_2\text{Se}_2 \), and \( \text{R}_2\text{Te}_2 \), the NMR and XPS results indicated
that chalcogen - chalcogen bonds were broken and alkyl chains were bounded to the Au
surface via chalcogens, although the Te system was oxidized as it was also confirmed by
TGA. Moreover, the SPR and XPS results indicated that Au NPs with heavier chalcogens
are more electron rich. These results on different chalcogenolate - protected Au NPs
clearly show alkyl chain length effect on size of NPs and illustrate the effect of anchoring
chalcogen by comparative studies of interfacial characterizations between the ligand and
metal core.

\textit{Synthesis of gold and silver nanoparticles with alkyl selenocyanates.} In this project,
BSM was used to investigate alkyl selenocyanates as the initial ligands for synthesis of
small and homogenous alkyl selenolate - protected Au NPs with attempt to determine the
existence of cyano species on the surface of NPs. In conclusion, alkyl selenocyanates
were successfully used as starting ligands for the synthesis of homogenous, \textit{ca.} 2 to 3 nm
sized, Au and Ag NPs by using the BSM, which opens a promising general alternative to
synthesizing organo - heavier - chalcogen - ligand protected metal NPs. The \(^1\)H NMR
data clearly showed that the organic moiety was bound to the Au surface of NPs, and the
XPS demonstrated that the bonding was via chalcogen. Strong evidence indicated that the
ligand monolayer is most likely of alkyl selenoate, the same as that on the Au NPs
synthesized with dialkyl - diselenide, and the Au and Ag NPs most likely share very
similar monolayer structure. However, the determination of C≡N species in the NPs
samples was proved to be a challenging task due largely to low sensitivity of instruments, as have been discussed by previous work on 2D SAMs. Further analytical techniques with high sensitivity are needed to fully characterize the residual CN.

**Future suggestions.** The next step in this research is to produce high-yield organo chalcogenolate–protected Au NPs while precisely controlling the sizes of NPs. Although the alkane selenolate-protected Au NPs were synthesized and characterized, the final yield is less than desired. This would provide more material for further interfacial characterizations and for intensive electrochemical measurements. The following studies are advised to be performed:

- Based on the alkyl selenocyanate project discussed in Chapter VIII, new ligands with better leaving groups than cyanide should be applied. Cyanide groups are nearly impossible to remove due to their rapid and strong reactivity with the metal surface; therefore, other species need to be investigated. Accordingly, the reaction would occur in a similar fashion to produce alkane selenolate–species bond to metal surface. Yet the ligands molecular fragment would be more easily removed from the metal surface as it is a more efficient leaving group. The proposed moiety could be iodine and can first be demonstrated with thiols. Thiols would react with iodine to form RSI species, and then can be applied in NPs synthesis as described in this dissertation. This would serve as a reference model for Se ligands.
An additional suggestion would be to elucidate the role of the “crashing” solvent in the precipitation and homogeneity of NPs. By increasing the alkyl chain length and steric bulk of the ligands, the “crashing” solvent would be prohibited from reacting with ligands and/or metal core, which could lead to NPs heterogeneity upon precipitation. This study would clearly show if solvent interacts with the metal surfaces. In other words, if the solvent interacts with metal surfaces during the crashing process, the NPs sizes should no longer be the same as they were prior. Moreover, this study would provide additional information on the chalcogen effect if solvent does play a role.

Furthermore, another possible area to investigate is the rare Au (II) complex species that was observed in Chapter IV. For example, neutral tetra-alkyl amines could be employed instead (or in a mixture) of TOAB, because tetra-alkyl amines have mild reducing power, which would allow the reaction to slowly progress, i.e., Au(III) to Au (II) and enable detection.

Regardless, further interfacial characterizations and intensive electrochemical measurements should be performed. In addition, this research should be expanded to other metal centers for organo chalcogenolate protected NPs, e.g., Ag, Cu, Pd.

The research presented in this dissertation demonstrates new insights into synthesis and characterizations of organo chalcogenolate - protected Au NPs. This research opens the door for potential exciting studies in nanochemistry.
APPENDIX
SPECTROSCOPIC EVIDENCE OF A BIDENTATE - BINDING OF MESO - 2, 3 - DIMERCAPTOSUCCINIC ACID ON SILVER NANOCLUSTERS

Reproduced with permission from Zaluzhna, O.; Brightful, L.; Allison, T.C.; Tong, Y.J., Spectroscopic evidence of a bidentate - binding of meso - 2, 3 - dimercaptosuccinic acid on silver nanoclusters, *Chemical Physics Letters* **2011**, *509*, 148-151. This work was a combined effort of Zaluzhna, O. and Dr. Tong. Lyndsey Brightful was a summer NSF REU student who worked under my supervision. Thomas Allison has performed all the computational studies and picture models (Figures A.7 and A.8) in this work.

A.1 Introduction

An enormous amount of interest in the past decades has been focused on noble metal nanoclusters (NCs) due to their anticipated novel electronic and optical properties.\textsuperscript{100, 101, 155} It is therefore fundamentally important to understand these properties in terms of structure and chemical binding. Characteristics of metal NCs depend on their size and on the ligands that stabilize them. Consequently, understanding interfacial binding between ligands and metal cores is of great fundamental importance.\textsuperscript{100, 101, 155} This work focuses on such a binding interaction, specifically in a meso - 2, 3 - dimercaptosuccinic acid (DMSA) -protected Ag NC, Ag\textsubscript{3}DMSA\textsubscript{4}, whose synthesis has recently been developed.\textsuperscript{156}
DMSA itself is a very well-known organic molecule that is widely used as a chelating agent for treating lead poisoning.\textsuperscript{157} It is also one of the most promising chelating agents in the pharmaceutical industry.\textsuperscript{158} Studies of DMSA in the context of nanoscience are also growing significantly because of its versatility in terms of binding to the surfaces of nanoparticles (NPs). For instance, it has been shown that in DMSA-protected iron oxide NPs the carboxylate groups interact directly with the NP surface with the remainder of the DMSA molecule cross-linked with each other via S-S bonds away from the metal center.\textsuperscript{159} On the other hand, it was also demonstrated, that in Au\textsubscript{12}(DMSA)\textsubscript{7} clusters the sulfur, instead of the carboxylate groups, interacts directly with the Au core.\textsuperscript{160, 161} Consequently, it is both fundamental and practical importance to obtain precise information on how DMSA binds on NPs surface when the former is used as the stabilizing ligand.

Most recently the synthesis of thiolate-protected Ag\textsubscript{7} NCs, specifically Ag\textsubscript{7}(DMSA)\textsubscript{4}, has been reported and monodentate-binding to the Ag NCs with one of the two sulfur atoms has been proposed in which the other sulfur atom forms a disulfide bond with the neighboring DMSA.\textsuperscript{156} On the other hand, computational studies show that the most favorable energy structure is the one in which all eight sulfur atoms of the four DMSA molecules bind to the Ag\textsubscript{7} surface, \textit{i.e.}, a bidentate binding.\textsuperscript{162} Here we present the spectroscopic evidence that supports the latter.
A.2 Synthesis of DMSA - Protected Ag NCs

The synthesis of the DMSA - protected Ag NCs directly followed the procedure published in the literature.\textsuperscript{156} In brief, a silver salt (AgNO\(_3\)) was first dissolved in ethanol. The solution was kept in an ice bath and under a nitrogen blanket to prevent, to the extent possible, the reaction product from being oxidized. The flask was also fully covered by Al foil to avoid potential interference from light. The DMSA was then slowly added to the solution under mild stirring for about 4 hours, after which the color of the reaction solution turned from clear to yellowish green. NaBH\(_4\) was then added to the solution, causing an immediate color change to black that indicated the formation of the Ag NCs. The reaction solution was left for 12 hours under vigorous stirring. After that, the solution was centrifuged in methanol and the final black precipitate was collected. After multiple re-crystallization steps, the final product was collected and characterized by UV - Vis, TEM, and EDS to confirm that the product obtained was indeed Ag\(_7\)(DMSA)\(_4\).

A.3 Characterization of the DMSA - Protected Ag NCs

As in the original synthesis, we observed a UV - Vis absorption peak at around 500 nm (Figure A.1d), indicating the presence of the Ag\(_7\)(DMSA)\(_4\) NCs.\textsuperscript{156} A representative TEM images of low (a) and high (b) magnification of the Ag\(_7\)(DMSA)\(_4\) is presented in Figure A.1, together with its size distribution histogram (c). The Ag\(_7\)(DMSA)\(_4\) NCs were clearly
too small to be discerned on the TEM image of low magnification but were clearly distinguished on high magnification image. The average particle size is 0.7±0.1 nm, which is in agreement with the expected size of the Ag$_7$(DMSA)$_4$ NCs. Additionally, the energy dispersive spectroscopy (EDS) analysis of the sample (Figure A.2) gave a sulfur to Ag ratio of 1.22 which, within the uncertainty of the method, is in good agreement with 1.14, the stoichiometric ratio of Ag$_7$(DMSA)$_4$. Altogether, the results of these characterizations confirm that the NCs are in fact Ag$_7$(DMSA)$_4$ NCs.

In Figure A.3, we compare the $^{13}$C solution NMR spectrum (top) of the Ag$_7$(DMSA)$_4$ NCs with that (bottom) of the free DMSA molecules, both dissolved in D$_2$O. DDS (3-trimethylsilyl-1-propanesulfonic acid sodium salt solution) was used as the internal reference with peaks at 56.9 ppm and 21.7 ppm respectively appearing in the spectrum. It is well known that the $^{13}$C NMR signal of the carboxylate group -COO$^-$ at the natural abundance is very difficult to observe because of its very long spin-lattice relaxation times. However, the carbon bound to sulfur was observed at 47.8 ppm in the free DMSA molecules as indicated by the arrow in Figure A.3. This peak, however, disappeared once the DMSA was bound to the Ag NCs as shown by the top spectrum in the figure, which is a phenomenon often observed when a ligand binds to metal NCs due to intrinsic heterogeneity of the surfaces, such as local structural variations. No other $^{13}$C NMR peaks were observed over the entire spectral region except for the DDS. Had the DMSA formed a monodentate binding with the Ag NC surface with the other sulfur forming disulfide bond as proposed previously, one would expect to see the half of the signal at 47.8 ppm. Molecular disulfide bonding would still give a narrow peak in
solution, which is not the case experimentally. Therefore, the complete disappearance of the $^{13}$C peak at 47.8 ppm indicated strongly that both sulfur atoms of the DMSA were bound to the Ag NCs, i.e., the DMSA formed a bidentate binding on the Ag NC surface.

The absence of the disulfide bonds in the synthesized Ag$_7$(DMSA)$_4$ was further confirmed by the Raman spectra taken from the solid samples of the free DMSA molecules (bottom) and the Ag$_7$(DMSA)$_4$ (top) respectively, as shown in Figure A.4. For the free DMSA molecules, the C-H stretching at 2950 cm$^{-1}$, the S-H stretching at ~2557 cm$^{-1}$, the asymmetric and symmetric stretching of the carboxylate groups at ~1636 cm$^{-1}$ and 1446 cm$^{-1}$, the several C-C stretching-related vibrations around 1000 cm$^{-1}$, and some other unassigned peaks below 1500 cm$^{-1}$ were demonstrated. The observed spectrum is in excellent agreement with results published previously.$^{165}$ For the Ag$_7$(DMSA)$_4$, a strong fluorescence effect was observed that caused the broad (from 600 cm$^{-1}$ to 2800 cm$^{-1}$) hump which made it impossible to observe most vibrational bands. However, the appearance of this hump confirms the formation of the Ag NCs.$^{166}$ The band at 390 cm$^{-1}$ may be assigned to Ag-S related vibrations (vide infra). Two additional observations are noteworthy. First, the disappearance of the S-H stretching peaks indicates that the DMSA-Ag binding involves the sulfur atoms. Second, no S-S stretching vibration was observed which normally appears at ~500 cm$^{-1}$ and is usually very strong and easily detected,$^{159}$ even when there is strong fluorescence.$^{167}$ On the other hand, as shown in Figure A.5, a band appeared at the frequency of disulfide as the sample disintegrated under the laser beam which is evidenced by the gradual disappearance of the fluorescence effect. Altogether, these observations strongly imply that not disulfide,
but bidentate Ag-S bonds were formed in the Ag$_7$(DMSA)$_4$ NCs, which is consistent with the $^{13}$C NMR observations discussed above.

In Figure A.6, we compare further the IR spectrum of the Ag$_7$(DMSA)$_4$ (bottom) with that of the free DMSA molecules (top). The spectrum of free DMSA is also in excellent agreement with the previously published results.$^{165}$ Again, the S-H stretching peaks disappeared completely in the Ag$_7$(DMSA)$_4$, indicating that all sulfur atoms were involved in binding that was qualitatively different from that in the free DMSA molecules. On the other hand, the strong peak at ~ 1700 cm$^{-1}$ observed in the free DMSA molecules clearly indicates that the molecule exists in the form of a symmetric carboxylic diacid.$^{159}$ In Ag$_7$(DMSA)$_4$, the bidentate binding of the DMSA to the Ag NCs breaks the original symmetry and splits the peak into two different, red-shifted vibrations at 1580 cm$^{-1}$ and 1377 cm$^{-1}$, respectively. Overall, the observed IR spectral changes from the free DMSA to the Ag$_7$(DMSA)$_4$ are very similar to those observed in the MSA-protected Ag$_9$ NCs$^{166}$ and MSA- and DMSA-protected Au NPs previously reported in the literature.$^{160,165}$

In order to gain further insight into the structure of the Ag$_7$(DMSA)$_4$ NCs, we carried out density functional theory (DFT) calculations of normal vibrational frequencies of the Ag-S, C=O and C-OH bonds in Ag$_7$(DMSA)$_4$ NCs using the 3D Ag$_7$DMSA$_4^-$ molecular structure obtained by Xiang et al.$^{162}$ as a starting point. Figure A.7 demonstrates the optimized NC structure. (Note that calculated vibrational frequencies have been scaled by a factor of 0.97 as recommended elsewhere.$^{168}$) The C=O vibrational frequencies are closely spaced and clearly separated from other frequencies in the Ag$_7$DMSA$_4^-$ molecule.
Eight C=O vibrational frequencies lie in the range 1772 cm$^{-1}$ to 1787 cm$^{-1}$. The C-OH stretching frequencies are more difficult to discern as they are coupled to other molecular motions. We observe significant C-OH stretching motion associated with frequencies ranging from 1110 cm$^{-1}$ to 1179 cm$^{-1}$ in the molecule. Though the calculated C=O and C-OH normal mode frequencies agree well with previous experimental and theoretical work on COOH vibrations, they do not reproduce the experimentally observed two bands at 1580 cm$^{-1}$ and 1377 cm$^{-1}$ respectively. We consider two possible sources for this discrepancy. First, it has been shown that bonding between carboxylic acid groups will raise C-OH frequencies and lower C=O frequencies.$^{169,170}$ Second, if the COOH groups exist as COO$^-$, one should expect to see a strong asymmetric stretch near 1550 cm$^{-1}$ - 1650 cm$^{-1}$ and a weaker symmetric stretch near 1400 cm$^{-1}$. We have tested this second possibility by performing vibrational frequency calculations on the Ag$_7$DMSA$_4$ structure with the hydroxyl hydrogen atoms removed. We observe eight vibrational frequencies corresponding to asymmetric stretching of the COO$^-$ in the range 1611 cm$^{-1}$ - 1635 cm$^{-1}$ and eight vibrational frequencies corresponding to symmetric stretching of COO$^-$ in the range 1291 cm$^{-1}$ - 1313 cm$^{-1}$. Though the assumption of the anionic structure does not completely resolve the discrepancy between experiment and theory; however, it significantly increases the agreement and strengthens the validity of our assignment.

In the structure shown in Figure A.7, each S atom is bonded to two Ag atoms and an Ag atom is bonded to two or three S atoms. Consequently, the Ag-S frequencies do not emerge in clearly identifiable pairs. We observe an Ag-S stretching motion associated with numerous frequencies from $\sim$ 250 cm$^{-1}$ to $\sim$ 350 cm$^{-1}$. While the spread of
frequencies is in good agreement with the experimental observation, the calculated values seem to underestimate the Ag-S frequency in Ag$_7$(DMSA)$_4$ NCs. However, the calculations also show torsional frequencies involving Ag-S around 390 cm$^{-1}$.

A.4 Conclusion

In conclusion, we have synthesized the DMSA - protected Ag NCs by following the published procedure.$^{156}$ TEM, UV - Vis, and EDS characterizations showed that the synthesized Ag NCs were indeed Ag$_7$(DMSA)$_4$ as proposed in the original synthesis. Combined $^{13}$C NMR, Raman and IR spectroscopic study, which has been further aided by DFT calculations has provided the strongest experimental evidence to date showing that DMSA forms a bidentate, rather than the originally proposed monodentate, binding with the underlying Ag NC (Figure A.8). This conclusion is in full agreement with the most stable Ag$_7$DMSA$_4$ structure predicted in recent ab initio DFT calculations. Given the increasing usage of DMSA as stabilizing ligand for metal NPs, the findings presented in the paper should have important fundamental ramifications.
Figure A.1 TEM images of low (a) and high (b) magnification, the corresponding size distribution histogram (c, 340 counts), and the UV - Vis spectrum of the Ag$_7$(DMSA)$_4$ NCs.
Figure A.2 EDS spectra and analysis of Ag₇(DMSA)₄ nanoclusters.
Figure A.3 $^{13}$C NMR spectra of the free DMSA molecules (top) and Ag$_7$(DMSA)$_4$ NCs (bottom) recorded in D$_2$O with DDS as internal reference.
**Figure A.4** Raman spectra of the DMSA molecule (bottom) and the Ag$_7$(DMSA)$_4$ NCs (top).
Figure A.5 Raman Spectra of Ag$_7$(DMSA)$_4$ NCs. In this spectrum, the same area of the sample is taken 3 times: green - 1$^{st}$, blue - 2$^{nd}$ and red - 3$^{nd}$ (black - glass spectrum for comparison). It is noted that with decomposition of the sample, the formation of S-S bond (~ 500 cm$^{-1}$) is possible.
Figure A.6 IR spectra of the free DMSA molecules (top) and the Ag$_7$(DMSA)$_4$ NCs (bottom).
Figure A.7 The optimized 3D structure of Ag$_7$(DMSA)$_4^-$ with the color scheme: Ag - brown, Sulfur - yellow, Carbon - blue, Oxygen - red, and Hydrogen - white.
Figure A.8 Summary of Appendix.
A.5 References

Oksana Zaluzhna

Education

Ph.D, Analytical Chemistry, Georgetown University, Washington, DC 2012


Advisor: Dr. YuYe J. Tong

B.S, Chemistry, University of North Carolina - Asheville, NC 2002-2006

Thesis title: Elimination and Interchange Reactions of CF₃CFCICH₂Cl, CF₂ClCFCICH₂F and CF₂ClCF₂CH₂Cl

Advisor: Dr. Bert E. Holmes

Published works at Georgetown University:


